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Digitalization of the thermoplastic beryllium oxide slurry forming process using ultrasonic activation

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ABSTRACT

This paper presents the results of the digitalization of the thermoplastic beryllium oxide slurry forming process using ultrasonic activation. Ceramics made from beryllium oxide (BeO) using ultrasound-assisted forming exhibit more intense sintering and, in comparison to ceramics formed without ultrasound, have reduced shrinkage (by 2.4-4.3%) and sintering temperature (by 50-180°C). The forming processes occurring during ultrasonic treatment resulted in the homogenization of the thermoplastic suspension and dense packing of BeO powders in the casting. Ultrasound activation alters the rheology of the thermoplastic slurries. These changes are attributed to processes of slurry mass dispersion and mass exchange at the phase boundary of the suspension. Ultrasound activation also enhances casting properties. During the cooling-solidification process under the influence of ultrasound, the density and strength of the castings increase due to the effective compensation of shrinkage. Shrinkage compensation is carried out according to the classical scheme by supplying a liquid suspension. For hot casting with ultrasound of thermoplastic beryllium oxide slurries, it is advisable to use compositions with a binder content of 11.0-11.7% by weight since these compositions provide better shrinkage compensation and, consequently, a denser casting.

Keywords: forming process, thermoplastic slurry, beryllium oxide, viscoplastic state, casting solidification.

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Introduction

High thermal conductivity beryllium oxide slurries within the technological temperature and solid phase concentration range exhibit thixotropic properties and a high dependence on viscosity and yield stress on temperature [[1], [2], [3], [4], [5]]. The nature of the changes in structural-mechanical properties is determined by the ratios of the solid phase (BeO) and binders and occurs in all stages of the forming process [[1], [5]].

The analysis of volume-phase relationships revealed that the density increase during the cooling process of the liquid state for casting systems amounts to 5-6% [1,6]. The interval of the solid-plastic state accounts for 70-80% of the temperature shrinkage. This highlights the need for special attention to shrinkage compensation at this stage. Varying the ratio of solid phase and binders does not provide an approximation of the rheological properties of beryllium oxide - thermoplastic binder to traditionally hot molding technologies [[1], [5]].

Ultrasound activation leads to a significant change in the rheology of thermoplastic casting systems [[1], [3], [4], [5]]. Varying the intensity and temperature-time parameters of ultrasound

treatment enhances the effectiveness of its impact on the rheology of thermoplastic slurries. The mechanism of such influence is related to the control of the solid-liquid phase interface and the parameters of absorption layers [[1], [3], [4], [5]]. The most favorable conditions in terms of deformational behavior of casting systems are achieved in the temperature range of 63-68°C and an ultrasound treatment time of 7-10 minutes [[1], [3], [4], [5]].

The change in the properties of the slurry mass under the influence of ultrasound affects the microstructure and properties of ceramics. The samples obtained with ultrasound have a more homogeneous structure and higher structural-mechanical and electrophysical parameters [[1], [3], [4], [5]].

The method of hot casting of beryllium oxide ceramics has been developed mainly empirically [[1], [6], [8]]. Conducting a detailed analysis of this method will allow a more reasonable approach to the ceramic molding process. This work presents some results of modeling the process of beryllium oxide ceramic forming using the hot casting method.

Problem Statement

The forming process of a thermoplastic slurry takes place in a die (Fig. 1). The flat cavity has a thickness of 2h = 0.0015 m, a width of B = 0.03 m, and a length of L = 0.071 m. The cooling circuit of the die, illustrated in Figure 1, comprises three segments. The cooling contour of the die, illustrated in Figure 1, comprises three segments. Liquid slurry with an initial temperature of t_0 = 80°C flows into the cavity.

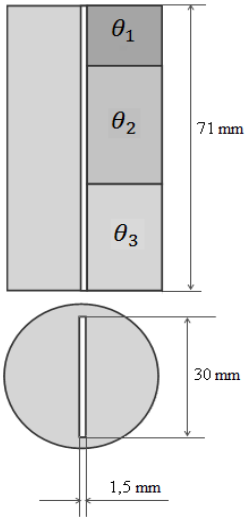

Figure 1 - Diagram of a flat cavity die

Rheological Model of the Thermoplastic Slurry

The composition of the thermoplastic slurry comprises a solid phase (beryllium oxide powder) and a liquid phase (organic binder) [[1], [3], [4], [5]]. The liquid phase is composed of paraffin, beeswax, and oleic acid in a ratio of 0.82:0.15:0.03. The particle size distribution of the beryllium oxide powder is provided in Table 1. The organic binder has a mass fraction ω within the range of 0.095 to 0.117.

Table 1 - Characteristics of Beryllium Oxide Powder [1]

Bulk Density, ρ_0 ·10³ kg/m³		**0.75**
Specific surface area, S·10⁻³ m²/kg		**1.72**
Particle size distribution by fractions of BeO particles	Particle Size Fraction, μm	%
	Up to 1.4	35.2
	1.4-4.2	52.7
	4.2-7.0	9.6
	7.0-9.8	1.7
	9.3-12.6	0.4
	12.6-15.4	0.3
	15.4-18.2	0.1

This composition of BeO powder (see Table 1) demonstrates satisfactory casting properties of the slurry with a variation in the mass fraction of the binder from ω = 0.095 to ω = 0.117. In the case of increasing the finer fractions of BeO powder in the composition, there is a higher demand for binder content ω. On the other hand, an increase in the coarser fractions of BeO powder leads to the discoloration of ceramics, indicating the presence of micro-pores and cracks [1].

Within the range of shear rate variation from 0.005 to 1200 1/s, the thermoplastic slurry can be classified as viscoplastic liquids according to Schwedoff-Bingham [[1], [5]]. The effective molecular viscosity μ_{eff} of this fluid takes the following form [[7], [8], [9], [10], [11], [12]]:

$$\mu_{\text{eff}} = \begin{cases} \mu_p + \tau_0 |\dot{\gamma}|^{-1}, & \text{if } |\tau| > \tau_0 \\ \infty, & \text{if } |\tau| \le \tau_0 \end{cases} \quad (1)$$

Here τ_0 is the yield shear stress, μ_P is the plastic viscosity, $\boldsymbol{\tau} = \mu_{\text{eff}}\boldsymbol{S}$ is the shear stress tensor, $\boldsymbol{S} \equiv \sqrt{2S_{ij}S_{ij}}$ is the strain rate tensor, $S_{ij} = \frac{1}{2}\left(\frac{\partial U_i}{\partial x_j} + \frac{\partial U_j}{\partial x_i}\right)$ is the second invariant of the strain rate tensor. The Schwedoff-Bingham model is a simple viscoplastic fluid model that linearly relates

the yield shear stress to the viscosity [[7], [8], [9], [10], [11], [12]].

Ultrasonic treatment influences the rheological properties of the slurry. The plastic viscosity (μ_p) and the yield stress (τ_0) of the slurry are dependent on the temperature (t) and the binder mass fraction (ω). Experimental data for the binder mass fraction ω = 0.117 after ultrasonic treatment are expressed by empirical relationships [[1], [3], [4], [5]]:

$$\mu_p(t) = 293.626 \cdot \exp(-0.058 \cdot t), \text{ Pa·s} \quad (2)$$

$$\tau_0(t) = 11.4 + 11.41 \cdot \exp\left(-\frac{t-70.05}{5.47}\right), \text{ Pa} \quad (3)$$

The density of the thermoplastic slurry can be expressed in standard form as:

$$\rho = \frac{\rho_{mb} \cdot \rho_{cb}}{(1-\omega)\rho_{cb} + \omega \cdot \rho_{mb}} \text{ kg/m}^3 \quad (4)$$

where ρ_{mb} and ρ_{cb} are the densities of beryllium oxide and binder, respectively; ω is the relative mass fraction of the binder.

The temperature dependence of the binder density at ω = 0.117 is as follows:

$$\rho_{cb}(t) = 0.852 + 0.073 \cdot \cos(0.056 \cdot t - 1.44), \text{ kg/m}^{3`} \quad (5)$$

The density of beryllium oxide is ρ_{mb}=3020 kg/m³. In the temperature range from 80 to 40 °C, the density of the binder increases from 779.7 to 901.0 kg/m³, and the density of the slurry also increases from 2245.7 to 2355.3 kg/m³.

During the molding process, the slurry mass cools and solidifies within the mold cavity. The change in the aggregate state initiates in the near-wall area of the cavity and gradually encompasses the entire cavity.

According to experimental data, the phase transition occurs within a temperature range of 54 to 40°C. The binder remains in an amorphous state. Within the range of aggregate state change, the slurry transitions from an amorphous viscous-plastic state to an amorphous solid-plastic state [[1], [3]]. The heat of phase transition, released per unit mass of the slurry, is determined by the enthalpy change ΔH.

The apparent heat capacity method [[13], [14], [15], [16], [17],[18], [19], [20], [21]] determines changes in the heat capacity and enthalpy of the slurry during the phase transition. The heat capacity of the slurry increases due to the latent heat associated with the phase transition within the temperature range [[14], [15], [21]]:

$$c_p = c_s \cdot \left(1 - \alpha(\bar{t})\right) + c_l \cdot \alpha(\bar{t}) + H_{1\to 2}\frac{d\alpha}{dt} \quad (6)$$

where c_s and c_l are the heat capacities of the slurry in solid and liquid states, respectively; $\alpha(\bar{t}) = 0$, $\alpha(\bar{t}) = 1$ for the slurry in solid and liquid states, respectively; $\bar{t}$ is the dimensionless temperature of the slurry. For the binder mass fraction ω=0.117 the function $\alpha(\bar{t})$ takes the following form:

$$\alpha(\bar{t}) = 5.714 \cdot \bar{t} - 2.857$$

The apparent heat capacity method is advantageous in that the phase transition zone's location is not known beforehand and is determined by the calculation of the thermoplastic slurry's temperature [[19], [20], [21]].

The dependency of the thermal conductivity of the slurry on temperature for ω = 0.117 is given by [[1], [5]]:

$$\lambda = 1.6 + 4.8 \cdot \exp(-0.017 \cdot t), \text{ W/(m·}^0\text{C)} \quad (7)$$

Formulas (2)-(7) express the properties of the thermoplastic slurry during the hot casting process.

Mathematical Model

The OZ axis of the Cartesian coordinate system is directed along the axis of the flat mold cavity, while the OY axis is perpendicular to it (Fig. 1). The casting process occurs along the OZ axis. Intensive water circulation takes place in the cooling contours. The temperature of the slurry at the wall of each part of the cavity is considered equal to the temperature of the cooling liquid.

The molding process occurs with a change in the aggregate state and rheological properties of the slurry.

The system of equations for the motion of the thermoplastic slurry using the Schwedoff-Bingham rheological model (1) can be written in the following form:

$$\rho u\frac{\partial u}{\partial z} + \rho v\frac{\partial u}{\partial y} = -\frac{dp}{dz} + \frac{\partial}{\partial y}\left(\mu_{eff}\frac{\partial u}{\partial y}\right) + \rho g \quad (8)$$

$$\frac{\partial \rho u}{\partial z} \quad \frac{\partial \rho v}{\partial z} = 0 \quad (9)$$

The energy equation, considering the enthalpy of the phase transition by the apparent heat capacity method, can be expressed as follows:

$$\rho u c_p \frac{\partial t}{\partial z} + \rho v c \frac{\partial t}{\partial y} = \frac{\partial}{\partial y}\left(\lambda \frac{\partial t}{\partial y}\right) + \mu\left(\frac{\partial u}{\partial y}\right)^2 \quad (10)$$

Here, z and y are the longitudinal and transverse coordinates, u and v are the components of the velocity, $p, \rho, t, c_p, \mu_p, \lambda$ are the pressure, density, temperature, heat capacity, viscosity, and thermal conductivity of the slurry, respectively.

The system of equations (8)-(10) describes the slurry molding process in a flat mold cavity. The rheological properties of the slurry are expressed by formulas (1)-(7).

The pressure gradient in the motion equation is determined from the conservation of mass flow rate within the mold cavity [22]:

$$\int_S \rho u dS = \rho_o u_o S \quad (11)$$

where S_0 is the cross-sectional area of the cavity.

The problem is solved with boundary conditions as follows:

at z = 0, at the inlet: $u = u_0,\ v = 0,\ t = \theta$ (12)

at z > 0, on the axis: $\frac{\partial u}{\partial y} = — = v = 0$ (13)

at z>0, y=y$_1$, on the wall: $v = 0,\ \frac{\partial u}{\partial y}$ 0 (14)

The water temperature in the first, second, and third cooling zones is denoted as θ_1, θ_2, θ_3, respectively. The boundary conditions for temperature on the wall are as follows:

$$\begin{aligned} &\text{at } 0 \le z < l_1,\ y = y_1,\ t = \theta_1; \\ &\quad \text{at } l_1 \le z < l_2,\ y = y_1,\ t = \theta_2; \\ &\text{at } l_2 \le z < l_3,\ y = y_1,\ t = \theta_3 \end{aligned} \quad (15)$$

The numerical method [22] is used to solve the system of equations (1)–(11) with boundary conditions (12)–(15). The discretization grid consists of cells with sides Δz_i, and Δy_j. The second-order accuracy Crank-Nicholson scheme is applied to solve the momentum equation (8) and the energy equation (10). A two-layer second-order scheme is used to solve the equation (9). The method of splitting is used to determine the pressure gradient from the mass flow conservation condition (11).

Discussion of Computational Data

Fig. 2 illustrates the temperature and density distributions within three thermal contours of a flat mold cavity with a thickness of $2h$ = 0.0015 m, a casting speed u_0=0.05 m/min, and an initial slurry temperature of 80 °C. In the first cooling contour, the wall temperature is θ_1 = 80 °C. The temperature field demonstrates a decrease from 80 to 78 °C (Fig. 2a), and the density increases from 2245 kg/m³ to 2260 kg/m³ (Fig. 2b).

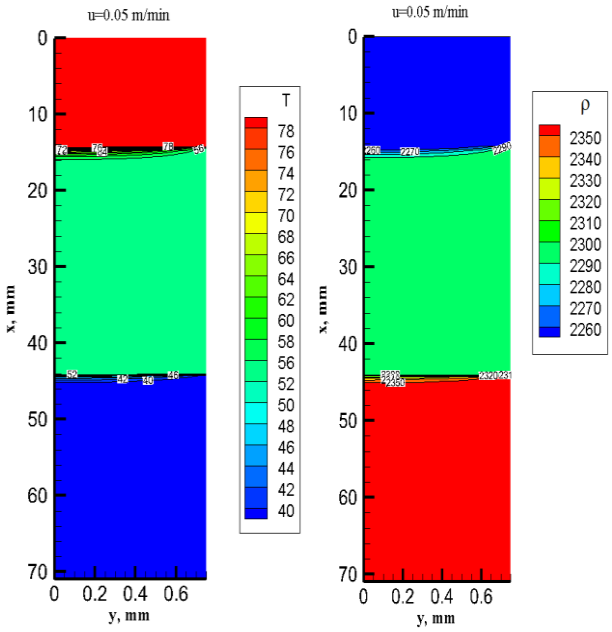

Figure 2 – Temperature and density distribution of the thermoplastic slurry in the flat mold cavity at u_0 = 0.05 m/min, ω=0.117

In the second cooling contour, the wall temperature is θ_2=56 °C. With decreasing temperature, the dynamic viscosity, $\mu_p(t)$, density $\rho(t)$, and yield stress, $\tau_0(t)$ all experience an increase. The temperature of the slurry drops from 78 to 52 °C (Fig. 2a), leading to an elevation in the slurry density from 2250 to 2300 kg/m³ (Fig. 2b).

At the beginning of the second cooling contour, there exists a transitional region where the temperature sharply drops from 78 to 56 °C, while the density increases from 2250 to 2290 kg/m³. Subsequently, the rate of temperature reduction slows down from 56 to 52 °C due to the heat release from the phase transition (Fig. 2a). An observable density increase of the thermoplastic slurry can be noted, from 2290 to 2300 kg/m³ (Fig. 2b).

In the third cooling contour, the wall temperature reaches θ_3=40 ^{0}C, leading to further cooling of the slurry mass and a decrease in

temperature within the region transitioning from 52 to 40 °C (Fig. 2a). This causes a rise in density from 2290 to 2350 kg/m³ (Fig. 2b).

In this area, the transition from a viscous-plastic state to a solid-plastic state occurs, resulting in the solidification of the thermoplastic slurry (Fig. 2).

Doubling the casting speed to 0.1 m/min under otherwise identical conditions has a negligible impact on the structural transformation of the slurry (Fig. 3). This is attributed to the rapid cooling rate within the flat mold cavity.

Experimental data [[1], [5]] indicate that an increase in the transition region between different states can lead to slurry shrinkage and the formation of cracks and voids, subsequently reducing the casting's strength. The smaller the transition area between aggregate states, the less the slurry will shrink. Ultrasonic treatment, by improving rheological properties, leads to a reduction in the transition area and consequently decreases the shrinkage of the beryllium oxide casting.

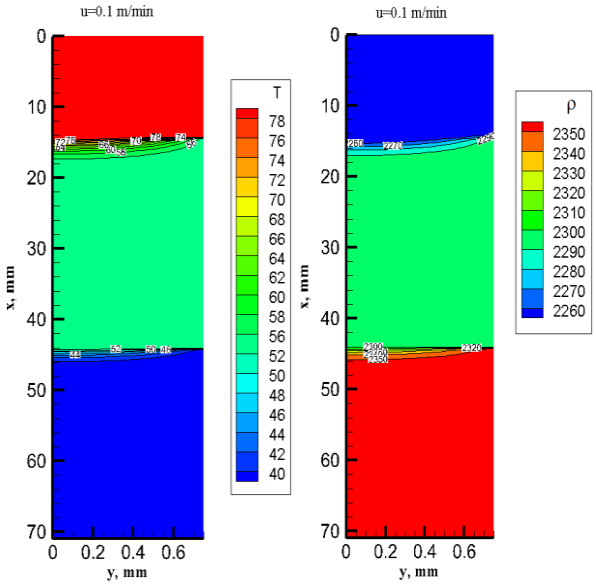

Figure 3 - Temperature and density distribution of the thermoplastic slurry in the flat mold cavity at u_0 = 0.1 m/min, ω=0.117

Comparison of Calculation with Experiment

Table 2 shows the experimental data of casting ability and mechanical strength of the casting as a function of binder content and casting speed [1].

The calculated data (Fig. 4) were obtained at two experimental casting speeds in the flat mold cavity: u_0=0.185 m/min and u_0=0.165 m/min for the binder mass fraction ω=0.117.

Table 2 - Dependency of Ceramic Strength on Casting Speed in the Flat Mold Cavity

Binder content in the slurry, mass fraction	The viscosity of slurry at T_0=75 °C, Pa·s	Casting ability of slurry, mm	Casting speed, mm/min	Mechanical strength of casting in bending, MPa
0.117	4.17	89	165	8.17

In the first cooling contour, the cooling water temperature is θ_1=75 °C, in the second it's θ_2=59 °C, and in the third, it's θ_3=45 °C. The liquid slurry flows into the flat mold cavity at an initial temperature of t_0=75 °C (Fig. 1).

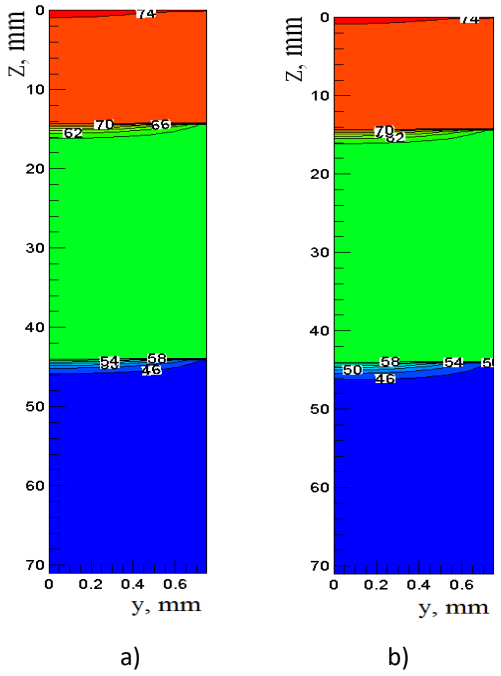

Figure 4 - Temperature field distributions depending on casting speed: a) u_0= 0.185 m/min; b) u_0= 0.165 m/min

As can be observed from Fig. 4, the transition regions between different cooling contours occupy minor intervals. The casting speed ensures a nearly uniform temperature distribution across the cavity's cross-section. Such temperature distribution leads to the homogeneity of rheological and thermophysical properties of the slurry over the cavity cross-section. In this case, the shrinkage of the thermoplastic slurry will be uniform. Consequently, cracks and voids, which could lead to a reduction in the strength of the beryllium oxide casting, do not form.

The slurry mass solidifies within the mold cavity.

This indicates that the beryllium oxide ceramic product has taken a structural shape.

Conclusion

Ultrasonic treatment improves the rheological properties and increases the flowability of thermoplastic beryllium oxide slurry in the molding cavity. Empirical formulas for plastic viscosity and shear stress of the slurry as a function of temperature were obtained. The phase transition of thermoplastic beryllium oxide slurry occurs within a certain temperature range. The latent heat is accounted for by an increase in heat capacity within the temperature range of the phase transition.

Calculation results show the entire molding stage of thermoplastic beryllium oxide slurry. Comparative calculations with experimental data established the conditions for molding thermoplastic slurry with ultrasonic activation, allowing to obtain solidified castings of beryllium oxide. The speed and temperature conditions of the molding slurry are important for determining the internal shrinkage of the casting during the cooling-hardening process of beryllium oxide and are a topic for future research.

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

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ТҮЙІНДЕМЕ

Жұмыста ультрадыбысты қолдану арқылы бериллий оксидінің термопластикалық шликерін қалыптау процесін цифрландыру нәтижелері берілген. Ультрадыбысты қолдану арқылы алынған бериллий оксиді BeO керамикасы қарқынды күйежентектелумен сипатталады және ультрадыбыссыз қалыпталған керамикамен салыстырғанда шөгуі (2,4÷4,3%) және күйежентектелу температурасы (50÷180 °C) төмен. Ультрадыбыстық өңдеу кезіндегі қалыптау процестері термопластикалық шликердің гомогенизациялануына және құймадағы BeO ұнтақтарының тығыз орналасуына әкеледі. Ультрадыбыстық белсендіру термопластикалық шликердің реологиясын өзгертеді. Бұл өзгерістер шликер массасының ұсақталу процестеріне, сондай-ақ суспензияның фазалар бөліну шекарасындағы масса алмасуына байланысты. Ультрадыбыстық белсендіру құймалардың қасиеттерін де жақсартады. Ультрадыбыс әсерінен салқындау–қату процесі кезінде шөгуді тиімді компенсациялау есебінен құймалардың тығыздығы мен беріктігі артады. Шөгудің өтемі (компенсациясы) сұйық суспензияны жңберу арқылы классикалық схемаға сәйкес жүзеге асырылады. Бериллий оксидінің термопластикалық шликерін ультрадыбыс арқылы ыстық құю үшін байланыстырғыш салмағы бойынша 11,0-11,7% құрамда болған жөн. Өйткені бұл құрам шөгудің жақсы компенсациясы болуға және тиісінше тығызырақ құйма алуға қол жеткізеді.

Түйін сөздер: қалыптау процесі, термопластикалық шликер, бериллий тотығы, тұтқыр-пластикалық күй, құйманың қатаюы.

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Цифровизация процесса формования термопластического шликера оксида бериллия с ультразвуковой активизацией

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АННОТАЦИЯ

В работе представлены результаты цифровизации процесса формования термопластичного шликера оксида бериллия с использованием ультразвуковой активации. Керамика из оксида бериллия BeO, формованная с применением ультразвука, отличается более интенсивным спеканием и имеет по сравнению с керамикой, формованной без ультразвука, меньшую усадку (на 2,4÷4,3%) и температуру спекания (на 50÷180 °C). Процессы формования, протекающие при ультразвуковой обработке, приводят к гомогенизации термопластичного шликера и плотной упаковке порошков BeO в отливке. Ультразвуковая активация изменяет реологию термопластичных шликеров. Эти изменения обусловлены процессами диспергации шликерной массы, а также массообменном на границе раздела фаз суспензии. Ультразвуковая активация улучшает также свойства отливок. В процессе охлаждения-затвердевания под действием ультразвука происходит увеличение плотности и прочности отливок за счет эффективной компенсацией усадки. Компенсация усадки идет по классической схеме за счет подпитки жидким шликером. Для горячего литья с ультразвуком термопластичного шликера оксида бериллия целесообразно использовать составы с содержанием связки 11,0-11,7% вес. Поскольку на этих составах достигается лучшая компенсация усадки и соответственно более плотная отливка.

Ключевые слова: процесс формования, термопластичный шликер, оксид бериллия, вязкопластичное состояние, затвердевание отливки.

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Metallurgy

Thermodynamics of antimony—selenium alloys formation and evaporation

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ABSTRACT

The thermodynamic functions of alloy formation and evaporation were considered for two particular systems — Sb – Sb_2Se_3 and Sb_2Se_3 – Se in connection with the presence of congruently melting compound Sb_2Se_3 in the antimony—selenium system. The calculations are based on the partial vapor pressure values of the components forming the particular systems. The thermodynamic activity of antimony selenide and selenium as the most volatile components in the systems was calculated based on the saturated vapor pressure values of antimony selenide over the Sb – Sb_2Se_3 and selenium melts over Sb_2Se_3 – Se liquid alloys determined by the boiling point method (isothermal variant). Similar functions of the low volatile components in the above systems: Sb in the first system and Sb_2Se_3 in the latter one was calculated by numerical integration of the Gibbs—Duhem equation using the substitution proposed by Darken. The partial pressures of antimony selenide and antimony over Sb – Sb_2Se_3 and Sb_2Se_3 – Se melts were approximated by temperature—concentration relationships. The system is distinguished with a positive deviation from ideality due to the presence of a delamination region in the first system. The partial and integral entropies and enthalpies of the formation of liquid alloys were calculated based on the values of component activities found as the ratio of the partial vapor pressure of an element or compound above the solution to the saturated vapor pressure of a pure element or compound. The partial and integral functions of alloy formation are presented in the form of graphical dependences on the selenium amount in the melt. The obtained thermodynamic constants will replenish the physical and chemical data base and will be used to calculate the boundaries of the vapor— liquid equilibrium fields on the diagram of state, allowing to determine the possibility and completeness of distillation separation of molten systems.

Keywords: Lead, tin, alloy, vapor pressure, thermodynamics, formation, mixing, evaporation, partial and integral quantities, entropy, enthalpy.

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Introduction

The development of vacuum — the thermal method intended to process polymetallic matte from lead and antimony smelters where this matte is based on copper (Cu_2S) and iron (FeS) sulfides and contains rare elements — cadmium, antimony, arsenic, indium, as well as selenium and tellurium isomorphous substituting sulfur in sulfides, contributed to the emergence of a sufficiently large number of thermodynamic studies devoted to the study of chalcogenides, including those of rare metals. One of them is antimony with the content that varies within 1% in lead production matte, and reaches several percent in antimony production matte.

Polymetallic matte — chalcogenide alloys as an intermediate product are produced during pyrometallurgical processing of sulfide concentrates at copper, lead, and antimony smelters. Copper (Cu_2S) and iron (FeS) sulfides form the basis of polymetallic matte from copper and lead smelters. Rare elements — cadmium, antimony, arsenic, indium, and others in the form of sulfides as well as selenium and tellurium, isomorphically replacing sulfur in sulfides are present in the matte besides the main components. Production and processing technologies for polymetallic matte are well enough studied and developed. However, works on their improvement are still underway due to the involvement in processing of new types of raw materials, including those poor in the main component [[1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11]].

Physical and chemical studies of liquid alloys of the antimony—selenium system were performed by a number of researchers. The authors [12] measured the kinematic viscosity and density of melts in the range of compositions 40 mol. % Sb_2Se_3 + 60 atm. % Se —20 mol. % Sb_2Se_3 + 80 atm. % Sb from melting temperature to 1100 — 1200 °C.

In [13], the crystallization kinetics for glassy alloys of $Se_{100-x}Sb_x$ ($2 \le x \le 10$), was studied by differential scanning calorimetry at different heating rates, the activation energy of the crystallization process, order parameter, rate constant, frequency factor was determined, and it was found that chalcogenide glasses had lower thermal stability while having a higher crystallization rate.

The antimony sesquiselenide behavior during vacuum sublimation was studied by the authors of [14] where the congruent nature of evaporation was noted.

The predominant presence of Sb, Se molecules, half the amount of Sb_2Se_2, three times the amount of Sb_2Se_3 and further, on a downward spiral Sb_3Se, Sb_4Se_4, Sb_4Se_3, Sb_3Se_3, Sb_3Se_2, Se_2, Sb_2Se_4 and very low amount of Sb_2Se_4 were found with mass spectrometric determination of the vapor composition over Sb_2Se_3 [[15], [16]].

The antimony sesquiselenide vapor pressure was determined using radioisotopes within 491—687 K (218— 414 °C) in studies [[17], and [18]]. The temperature dependence of the vapor pressure corresponded to the expression:

$\lg p$ [mmHg] = 8,7906 — 6432,3$\cdot T^{-1}$.

The vapor pressure over liquid antimony selenide within 550—868 °C (823—1201 K) was determined with the static method with the use of a quartz membrane manometer in the study [19]. The results of the determinations are described with the equation:

$\lg p$ [mmHg] = (8.4130±0.0328) – (7,220.4 ± 250) T^{-1}.

Later, the authors determined vapor pressures and activities of selenium and antimony at 994 K (721 °C) within 60—100 at. % Selenium and hypothetically propagated it to the whole concentration interval [[20], [21]].

Some researchers performed thermodynamic studies to determine the heat capacity and mixing functions of liquid alloys in the antimony—salenium system [[22], [23], [24]].

The thermodynamics of Sb_2Se_3 was modeled and used in calculations of the antimony—selenium phase diagram together with the thermodynamic properties of the liquid phase obtained based on the associative model [25]. The calculated phase equilibrium lines coincided well with the experimental data.

It should be emphasized in the publications analyzed that the data on evaporation thermodynamics are insufficient, and the results of experimental determinations and calculations are inconsistent despite the presence of a sufficiently large number of works devoted to the study of antimony and selenium melts. So, in [[20], [21], and [25]] thermodynamic activity of selenium was found and calculated for a temperature of 994 K (721 °C) which is higher than the boiling point of solutions of this composition. Thermodynamic constants were not calculated.

Therefore, the authors performed studies aimed to obtain thermodynamic functions for the formation and evaporation of antimony—selenium alloys based on partial pressure values of the components constituting the system.

Experimental part

Antimony and selenium alloys with the contents of 14.82, 26.35, 35.27, 47.51, 60.00, 68.96, 75.37, 83.38, 91.30 at. % (10.14, 18.83, 26.11, 36.99, 49.31, 59.03, 66.49, 76.49, 87.19 %) Se, and the rest — antimony, was taken as the study object. The alloys were prepared by alloying the metals in evacuated quartz ampoules with

heating at 100 °C above the liquidus temperature, holding for 12 hours at this temperature with shaking stirring, followed by quenching in water. Selenium with content of 99.99 wt. % and antimony — 99.99 wt. % of the main elements were used for the preparation of alloys.

The activity value defined as the ratio of the partial pressure of the component above the solution to the saturated vapor pressure above the elemental metal was taken as the basis to find the partial thermodynamic mixing functions: $a_i = \overline{p}_i / p_i^o$, where a_i is thermodynamic activity; $\overline{p}_i$ is the partial vapor pressure of *i*— component; p_i^o — saturated vapor pressure of the same component over the elemental metal.

The boiling point method (isothermal variant) detailed earlier was used to determine the saturated vapor pressure value [[26], [27]]. It is based on a significant increase in the evaporation rate at the equality of the external pressure and the saturated vapor pressure of the substance under study when the pressure above the melt decreases at a given temperature. The only congruently melting compound — Sb_2S_3 is present in the antimony—selenium system [28]. In this regard, the Sb — Se system was considered as two particular ones: Sb – Sb_2Se_3 and Sb_2Se_3 — Se. Due to the fact that the vapor pressure of antimony selenide at its melting temperature of 890 K (617 °C) determined with the membrane manometer method according to [29] is 40÷60 times higher than the pressure of elemental antimony [30], and the vapor pressure of elemental selenium [30] at the specified temperature is 200÷300 times higher than the vapor pressure of antimony sesquiselenide, it was considered that the total vapor pressure determined by the boiling point method in the Sb – Sb_2Se_3 system corresponds to the saturated vapor pressure of antimony selenide in the Sb_2Se_3 — Se system. Argon was used as a volume— filler gas in the boiling point method.

The partial free energy of alloy formation was calculated as $\Delta\overline{G}_i^{mix} = -RT \ln a_i$; partial enthalpy of mixing: $\left(\partial\Delta\overline{G}_i^{mix} / \partial T\right)_P = -\Delta\overline{S}_i^{mix}$; partial enthalpy: $\Delta\overline{H}_i^{mix} = \Delta\overline{G}_i^{mix} + T \cdot \Delta\overline{S}_i^{mix}$. Hereinafter, $\Delta\overline{G}_i^{mix}$, $\Delta\overline{S}_i^{mix}$ $\Delta\overline{H}_i^{mix}$ — partial free energy, partial entropy, and partial enthalpy of mixing of *i*— component, respectively. Hereinafter *T* is temperature, K.

Integral mixing functions are calculated as the number of fractions of partial values.

The activity of the second component in the melt (on the example of the Sb – Sb_2Se_3 system) was found from the expression $a_{Sb} = \gamma_{Sb} \cdot x_{Sb}$, the tin activity coefficient (γ_{Sb}) — by numerical integration of the Gibbs — Duhem equation with the use of the auxiliary function proposed by Darken [[31], [32]]:

$$\ln \gamma_{Sb} = -\frac{\ln \gamma_{Se} \cdot x_{Se} \cdot x_{Sb}}{x_{Sb}^2} + \int_{x_{Se}=0}^{x_{Se}} \frac{\ln \gamma_{Se}}{(1-x_{Se})^2} dx_{Se}$$

The partial free energy of evaporation was determined from the partial pressure values the for saturated vapor of the melt components $\Delta\overline{G}_i^{evp} = -RT \ln \overline{p}_i[atm]$, and entropies and enthalpies were similar to those for alloy formation.

The temperature dependences of activity and partial vapor pressure of volatile components for each of the compositions in each particular system were described by Arrhenius—type equations. Further, the temperature—concentration dependence of activity $\ln a_i = f(x_i, T)$ and vapor pressure $\ln \overline{p}_i = f(x_i, T)$ was obtained approximating the dependence of the coefficients in the equations on the concentration of volatile components in the alloy. Similarly calculated dependences were obtained for the activity and partial vapor pressure of less volatile components of the alloys.

The error in determination of the thermodynamic constants is assumed to be equal to the error in determination of lead saturated vapor pressure values as the number of errors of independent measurements, %: temperature — 1; weighing — 0.1; pressure 0.5; approximation of experimental data for the system Sb – Sb_2Se_3— 3.88, equal to 5.48; in the system — Sb_2Se_3 – Se, the approximation error is 3.12 and overall, 4.72.

Results and their discussion

The coefficients of the equations of dependence of saturated vapor pressure of antimony selenide and selenium on temperature for each of the alloy compositions are specified in Table 1.

Table 1 - Coefficients of the equation of dependence of lead partial vapor pressure on temperature

Content of selenium in the alloy:		$\ln \bar{p}_{Sb_2Se_3}[Pa] = \frac{A}{T} + B$	
atm. %	wt. %	A	B
14.82	10.14	— 14.989	21.887
26.35	18.83	— 15.883	22.926
35.27	26.11	— 16.434	23.490
47.51	36.99	— 16.868	23.972
60.00	49.31	— 17.010	24.264
		$\ln \bar{p}_{Se}[Pa] = \frac{A}{T} + B$	
68.96	59.03	— 11.771	23.051
75.37	66.49	— 11.869	23.578
83.38	76.49	— 12.063	23.949
91.30	87.19	— 12.286	24.341
100	100	— 12.509	24.763

The partial pressure of saturated vapor of antimony selenide in the Sb – Sb_2Se_3 partial system is represented by the expression:

$$\ln \bar{p}_{Sb_2Se_3}[Pa] = (-6358x^4_{Sb_2Se_3} + 16234x^3_{Sb_2Se_3} - -10839x^2_{Sb_2Se_3} - 1990_{Sb_2Se_3} - 14057)\cdot T^{-1} + + 4{,}961x^4_{Sb_2Se_3} - 11{,}959x^3_{Sb_2Se_3} + 8{,}019x^2_{Sb_2Se_3} + + 0{,}379\, x_{Sb_2Se_3} + 22{,}864 + \ln x_{Sb_2Se_3}$$

where $x_{Sb_2Se_3}$ — mole fraction of antimony selenide in the melt equal to: $0 \le x_{Sb_2Se_3} \le 1$.

The partial vapor pressure of antimony in this system corresponds to equation:

$$\ln \bar{p}_{Sb} = (-6358\, x^4_{Sb} + 17675\, x^3_{Sb} - 14082\, x^2_{Sb} + + 968\, x_{Sb} - 14958 - 398 \ln x_{Sb})\cdot T^{-1} + + 4{,}961^4_{Sb} - 14{,}5x^3_{Sb} + 13{,}735\, x^2_{Sb} - - 4{,}2x_{Sb} + 20{,}312 + 1{,}384 \ln x_{Sb},$$

Hereinafter x_{Sb} — the mole fraction of antimony.

The activities of antimony selenide and antimony are equal, respectively:

$$\ln a_{Sb_2Se_3}[Pa] = (-6358x^4_{Sb_2Se_3} + 16234x^3_{Sb_2Se_3} - -10839x^2_{Sb_2Se_3} - 1990_{Sb_2Se_3} + 2953)\cdot T^{-1} + + 4{,}961x^4_{Sb_2Se_3} - 11{,}959x^3_{Sb_2Se_3} + 8{,}019x^2_{Sb_2Se_3} + + 0{,}379\, x_{Sb_2Se_3} - 1{,}4 + \ln x_{Sb_2Se_3}$$

$$\ln a_{Sb} = (-6358\, x^4_{Sb} + 17675\, x^3_{Sb} - 14082\, x^2_{Sb} + + 968\, x_{Sb} + 1797 - 398 \ln x_{Sb})\cdot T^{-1} + + 4{,}961^4_{Sb} - 14{,}5x^3_{Sb} + 0{,}004 + 13{,}735\, x^2_{Sb}$$

The partial pressures of selenium and antimony selenide are approximated by the following relationships in the Sb_2Se_3—Se particular system:

$$\ln \bar{p}_{Se} = (1042\, x^3_{Se} - 2226\, x^2_{Se} + 446\, x_{Se} - -11771)\cdot T^{-1} - 0{,}583\, x^3_{Se} + 2{,}132\, x^2_{Se} - -1{,}589\, x_{Se} + 24{,}803 + \ln x_{Se},$$

where: x_{Se} — mole fraction of selenium in the melt equal to: $0 \le x_{Se_3} \le 1$.

$$\ln \bar{p}_{Sb_2Se_3}[Pa] = (-1042x^3_{Sb_2Se_3} + 2463x^2_{Sb_2Se_3} - - 920_{Sb_2Se_3} - 17511 - 880 \ln x_{Sb_2Se_3})\cdot T^{-1} + + 0{,}583x^3_{Sb_2Se_3} - 0{,}491x^2_{Sb_2Se_3} - 1{,}692x_{Sb_2Se_3} + + 25{,}864 + 1{,}926 \ln x_{Sb_2Se_3}.$$

In the Sb_2Se_3 – Se particular system the activities are equal to, respectively:

$$\ln a_{Se} = (1042\, x^3_{Se} - 2226\, x^2_{Se} + 446\, x_{Se} + + 738)\cdot T^{-1} - 0{,}583\, x^3_{Se} + 2{,}132\, x^2_{Se} - -1{,}589\, x_{Se} + 0{,}04 + \ln x_{Se},$$

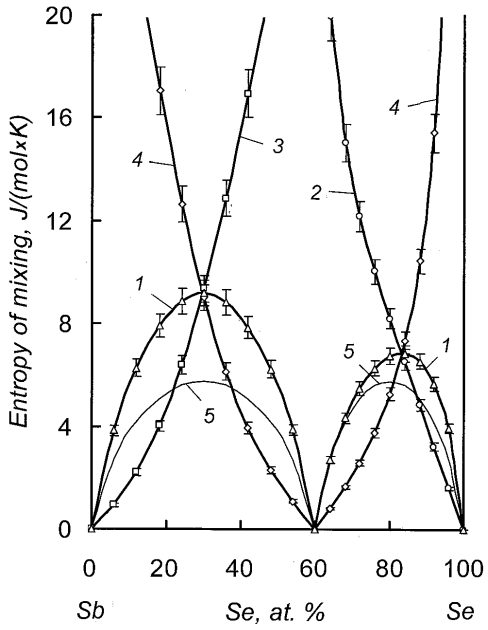
$$\ln a_{Sb_2Se_3}[Pa] = (-1042x^3_{Sb_2Se_3} + 2463x^2_{Sb_2Se_3} - - 920_{Sb_2Se_3} - 501 - 880 \ln x_{Sb_2Se_3})\cdot T^{-1} + + 0{,}583x^3_{Sb_2Se_3} - 0{,}491x^2_{Sb_2Se_3} - 1{,}692x_{Sb_2Se_3} + + 1{,}6 + 1{,}926 \ln x_{Sb_2Se_3}.$$

The integral entropy of mixing in the antimony—selenium system differs from the ideal system in magnitude in both particular systems. It indicates the positive value of excess functions.

It can be seen from the analysis of the dependencies (Figures 1, 2) that the integral mixing functions of alloys in the antimony — selenide antimony system have a positive maximum — the formation of alloys is accompanied by an increase in disorder in the system and goes with heat absorption.

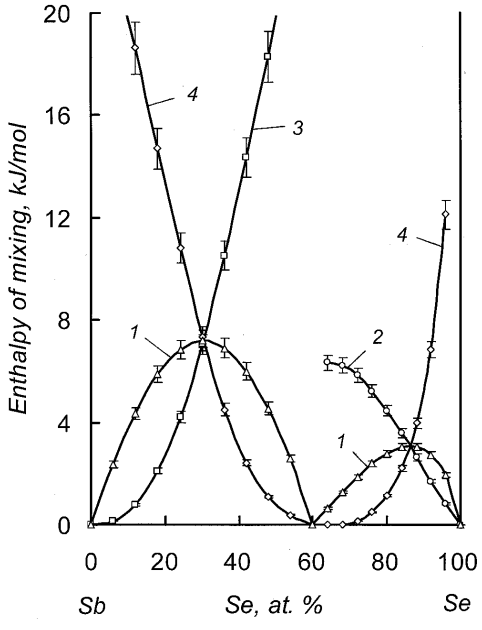
The extremum of the integral entropy of mixing reaches the value of 9.18 ± 0.50 J/ (mol·K), enthalpy of mixing — 7.19 ± 0.39 kJ/mol. The integral enthalpy of mixing of antimony and its selenide has a noticeable positive value (3.03 ± 0.14 J/mol) with a shift of the extremum to the selenium edge of the state diagram, which indicates the absence of interaction of particles in the liquid bath.

The formation of liquid alloys in the Se — Sb system is accompanied with an increase in disorder in the system.



2 - selenium; 3 - selenide of antimony;
4 - antimony; 5 - ideal system.

Figure 1 - Integral (1, 5) and partial (2— 4) entropies of mixing of the components of antimony—selenium melts.



2 — selenium; 3 — aluminum selenide;
4 — aluminum

Figure 2 - Integral (1) and partial (2— 4) enthalpies of mixing of components of antimony— selenium melts

The enthalpy of mixing is positive in the whole range of melt concentrations; hence, the formation of solutions proceeds with heat absorption — the reaction is endothermic.

The values of thermodynamic functions of evaporation of antimony— selenium system melts are summarized in Tables 2 and 3.

The integral function of the vaporization enthalpy in the antimony— selenide system has a slight minimum at 30 at. % selenium and is 133.18 ± 7.30 kJ/mol. The vaporization entropy of Sb_2Se_3 is equal to 105.93 ± 5.12 J/ (mol·K).

Thus, obtained values of saturated vapor pressure and thermodynamic constants are used to construct a complete state diagram including the fields of melt and vapor coexistence at atmospheric pressure and in vacuum.

Table 2 - Variation of partial and integral entropies of vaporization of Sb— Se system

Alloy composition, atm. %		$\Delta\overline{S}_{Se}^{evp}$, J/(mol·K)	$\Delta\overline{S}_{Sb_2Se_3}^{evp}$, J/(mol·K)	$\Delta\overline{S}_{Sb}^{evp}$, J/(mol·K)	ΔS_{Sb-Se}^{evp}, J/(mol·K)
Se	**Sb**				
0	100	—	—	73.02 ± 4.00	73.02 ± 4.00
10	90	—	81.32 ± 4.46	71.28 ± 3.91	72.95 ± 4.00
20	80	—	90.42 ± 4.95	68.28 ± 3.74	75.66 ± 4.15
30	70	—	96.90 ± 5.31	63.67 ± 3.49	80.28 ± 4.40
40	60	—	101.32 ± 5.55	57.50 ± 3.15	86.71 ± 4.75
50	50	—	104.03 ± 5.70	49.25 ± 2.70	94.90 ± 5.20
60	40	—	105.93 ± 5.12	—	105.93 ± 5.12
70	30	96.59 ± 4.56	113.02 ± 5.33	—	108.92 ± 5.14
80	20	101.85 ± 4.81	122.86 ± 5.80	—	112.36 ± 5.30
90	10	106.02 ± 5.00	137.71 ± 6.50	—	113.94 ± 5.38
100	0	110.06 ± 5.19	—	—	110.06 ± 5.19

Table 3 - Variation of partial and integral enthalpies of vaporization of Sb— Se system

Alloy composition, atm. %		$\Delta\overline{H}_{Se}^{evp}$, kJ/mol	$\Delta\overline{H}_{Sb_2Se_3}^{evp}$, kJ/mol	$\Delta\overline{H}_{Sb}^{evp}$, kJ/mol	ΔH_{Sb-Se}^{evp}, kJ/mol
Se	**Sb**				
0	100	—	—	139.31 ± 7.63	139.31 ± 7.63
10	90	—	121.52 ± 6.66	138.81 ± 7.61	135.93 ± 7.45
20	80	—	128.06 ± 7.62	136.59 ± 7.49	133.75 ± 7.33
30	70	—	134.11 ± 7.35	132.25 ± 7.23	133.18 ± 7.30
40	60	—	138.41 ± 7.58	126.26 ± 6.92	134.36 ± 7.36
50	50	—	140.63 ± 7.71	119.71 ± 6.56	137.15 ± 7.52
60	40	—	141.43 ± 6.68	—	141.42 ± 6.68
70	30	97.96 ± 4.62	141.36 ± 6.67	—	130.51 ± 6.16
80	20	99.56 ± 4.70	140.31 ± 6.62	—	119.93 ± 5.66
90	10	101.84 ± 4.81	136.22 ± 6.43	—	110.44 ± 5.21
100	0	104.00 ± 4.91	—	—	104.00 ± 4.91

Conclusions

When the studies were conducted by the boiling point method, the values of saturated vapor pressure of antimony selenide and selenium in the

Sb – Sb_2Se_3 and Sb_2Se_3 – Se partial systems were determined, and the partial pressures of antimony and antimony sulfide were found by numerical integration of the Gibbs—Duhem equation, respectively. Thermodynamic functions of formation and evaporation of alloys were calculated based on experimental values of thermodynamic activity for components and partial values of vapor pressure. It enabled to add these data to the base of physical and chemical properties of antimony—selenium system.

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Сурьма және селен қорытпаларының түзілу және булану термодинамикасы

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ТҮЙІНДЕМЕ

Екі нақты жүйе үшін – Sb-Sb_2Se_3 және Sb_2Se-Se, Сурьма-селен жүйесінде Sb_2Se_3 конгруентті балқыту қосылысының болуына байланысты қорытпаның түзілуі мен буланудың термодинамикалық функциялары қарастырылды. Есептеулер нақты жүйелерді құрайтын компоненттердің ішінара бу қысымының мәндеріне негізделген. Жүйелердегі ең ұшқыш компоненттер ретінде сурьма селениді мен селеннің термодинамикалық белсенділігі қайнау температурасы әдісімен (изотермиялық нұсқа) анықталатын Sb-Sb_2Se_3 және Sb_2Se_3 - Se сұйық қорытпалары бойынша селен балқымалары үстіндегі сурьма селенидінің қаныққан бу қысымының мәндері негізінде есептелді. Жоғарыда аталған жүйелердегі аз ұшқыш компоненттердің ұқсас функциялары: бірінші жүйеде Sb және соңғысында Sb_2Se_3 Даркен ұсынған алмастыруды пайдаланып Гиббс-Дюхем теңдеуін сандық интегралдау арқылы есептелді. Sb-Sb_2Se_3 және Sb_2Se_3-Se балқымаларындағы сурьма селениді мен сурьманың парциалды қысымдары температура-концентрация қатынасы арқылы

жуықталды. Бірінші жүйе деламинация аймағының болуына байланысты идеалдылықтан оң ауытқуымен ерекшеленеді. Сұйық қорытпалардың түзілуінің парциалды және интегралдық энтропиялары мен энтальпиялары элементтің немесе қосылыстың ерітінді үстіндегі парциалды бу қысымының таза элементтің немесе қосылыстың қаныққан бу қысымына қатынасы ретінде табылған құрамдас белсенділік мәндері негізінде есептелді. Қорытпа түзілуінің парциалды және интегралдық функциялары балқымадағы селен мөлшеріне графикалық тәуелділіктер түрінде берілген. Алынған термодинамикалық константалар физика-химиялық деректердің базасын толықтырады және балқытылған жүйелердің ректификациялық бөліну мүмкіндігін және толықтығын анықтауға мүмкіндік беретін фазалық диаграммадағы бу-сұйықтық тепе-теңдік өрістерінің шекараларын есептеу үшін пайдаланылады.

Түйін сөздер: Қорғасын, қалайы, қорытпа, бу қысымы, термодинамика, түзілу, араласу, булану, парциалды және интегралдық шамалар, энтропия, энтальпия.

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Термодинамика образования и испарения сплавов сурьмы и селена

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АННОТАЦИЯ

Рассмотрены термодинамические функции образования и испарения сплава для двух частных систем — Sb—Sb_2Se_3 и Sb_2Se_3—Se в связи с наличием конгруэнтно плавящегося соединения Sb_2Se_3 в системе сурьма—селен. Расчеты основаны на значениях парциального давления паров компонентов, образующих конкретные системы. Термодинамическую активность селенида сурьмы и селена как наиболее летучих компонентов в системах рассчитывали по значениям давления насыщенных паров селенида сурьмы над жидкими сплавами Sb–Sb_2Se_3 и селена над жидкими сплавами Sb_2Se_3–Se, определенными методом температуры кипения (изотермическая вариант). Аналогичные функции малолетучих компонентов в указанных выше системах: Sb в первой системе и Sb_2Se_3 во второй были рассчитаны численным интегрированием уравнения Гиббса—Дюгема с использованием замены, предложенной Даркеном. Парциальные давления селенида сурьмы и сурьмы над расплавами Sb—Sb_2Se_3 и Sb_2Se_3—Se аппроксимированы зависимостью температура—концентрация. Система отличается положительным отклонением от идеальности из-за наличия в первой системе области расслоения. Парциальные и интегральные энтропии и энтальпии образования жидких сплавов рассчитывали на основе значений активностей компонентов, найденных как отношение парциального давления пара элемента или соединения над раствором к давлению насыщенного пара чистого элемента или соединения. Частные и интегральные функции сплавообразования представлены в виде графических зависимостей от количества селена в расплаве. Полученные термодинамические константы пополнят базу физико-химических данных и будут использованы для расчета границ полей парожидкостного равновесия на диаграмме состояния, позволяющих определить возможность и полноту ректификационного разделения расплавленных систем.

Ключевые слова: Свинец, олово, сплав, давление паров, термодинамика, образование, смешение, испарение, парциальные и интегральные величины, энтропия, энтальпия.

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Metallurgy

Purification of wastewater from heavy metal ions using nanostructured adsorbents

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ANNOTATION

The activities of industrial enterprises in ferrous and non-ferrous metallurgy and other industries lead to environmental pollution with wastewater containing harmful substances that, even in small quantities, have a rather serious negative impact on human health and the state of the biosphere. There are a large number of natural sorbents used to solve water treatment problems. Among inorganic sorption materials, zeolites are widely used in practice. These natural materials have thermal and radiation stability and high selectivity. The purpose of this article is to study the sorption capacity of zeolites modified with nanostructured rare metals in several ways, with different options for activating the matrix to improve sorption properties with respect to ions of heavy and non-ferrous metals. Based on the experiments conducted, it was proven that zeolites modified with vanadium and titanium nanocompounds are highly effective in removing heavy metal ions from wastewater. The resulting composition on a zeolite matrix creates a highly dispersed solid phase of nanoparticles in the form of a sol-gel. Such systems have an excess of energy, which leads to increased reactivity and adsorbing properties. It is obvious that the activation of zeolites makes it possible to obtain a wider range of active centers of different nature. This determines the varied use of zeolites in the technological system for treating wastewater from heavy and non-ferrous metal ions, which will make it possible to achieve MPC standards.

Key words: zeolite, sorption technologies, heavy metals, wastewater, adsorbent.

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Introduction

Heavy metals, which have a toxic effect on aquatic organisms in even relatively low concentrations, are extremely dangerous in natural waters. The harm of heavy metals to a living organism is due to their ability to bioaccumulate and concentrate, which leads to disruption of the functioning of organ systems. The difficulty of removing heavy metal ions (HTI) from the body is due to the fact that they form strong bonds with proteins and other components of cellular structures [1].

In this regard, wastewater treatment from industrial enterprises must be carried out until heavy metals are almost completely removed. But using only traditional methods this is difficult to achieve.

One of the common methods for treating wastewater from ITM is sorption and ion exchange methods, hence the need to obtain cheaper sorbents with improved physicochemical properties increases [2]. Despite the variety of adsorbents used, many of them do not satisfy the full range of requirements for materials of this type, and therefore the search and development of new sorption materials is ongoing. The most efficient and

cost-effective treatment of water from heavy metal ions is when using materials such as aluminosilicates of various types. It is known that the high sorption properties of natural aluminosilicates, their low cost, and their large reserves in nature serve as the basis for their choice as adsorbents for metal impurities from wastewater from various industries. To expand the scope of natural zeolites and give them new additional properties (anion-exchange, adsorption, magnetic, bactericidal, etc.), zeolites are modified with both organic and inorganic modifiers.

Recently, there has been an increased interest in the use of complex zeolite-containing reagents in the treatment of wastewater of various origins [3]. It should also be noted here that an important approach to the creation of effective and environmentally safe sorbents is the modification of the structure of zeolites due to the formation of new functional groups (sorption-active centers) that strongly bind heavy metal ions. Adsorbents on a zeolite carrier, activated by rare and rare earth elements, deserve special attention, since many of them show selectivity to heavy metals. Therefore, developments devoted to the study of the sorption activity of zeolites modified with rare metals with different types of activation with respect to non-ferrous metal ions are relevant.

In English and Russian language publications, much attention is paid to the toxic effects of heavy metals on living organisms and methods of its neutralization. Works [[4, [5], [6]] provide data on the sources of heavy metals and characteristics of toxic effects.

The solubility of individual heavy metals in aqueous solutions and the extent of their removal using alkaline agents and sodium sulfides are strictly regulated by the United States Environmental Protection Agency.

Among modern methods that provide effective wastewater treatment from various pollutants, including heavy metal ions, a special role belongs to physicochemical technologies [[7], [8], [9], [10]]. One of the environmentally safe methods of surface water purification is the use of the adsorption mechanism, which is most often implemented as one of the stages of the complex technological process of water purification since other methods can lead to secondary pollution of the natural environment [9].

A distinctive feature of sorption is the ability to extract substances from multicomponent mixtures, high efficiency even at low concentrations of pollutants, as well as the quality of the sorption material used.

There are a large number of natural sorbents used to solve water treatment problems, such as quartz sand, activated carbon, chitosan, jute, cellulose, sawdust, bentonite clay, etc. The most common sorbent in domestic and foreign practice for deep purification of drinking water is activated carbons: granular and powdered [11]. But the use of such traditional sorbents in wastewater treatment, in the presence of specific contaminants in the source water, does not provide a guaranteed water quality that meets sanitary rules and regulations.

Among inorganic sorption materials, zeolites are widely used in practice. These natural materials have thermal and radiation stability, high selectivity, fairly good sorption properties, and the possibility of obtaining them in granular form make them very attractive for use in the water sector [12]. Zeolites can absorb not only ions of heavy metals, organic pollutants, oil products, pesticides, radioactive elements, but also pathogenic microorganisms, bacteria and viruses. The ability to extract heavy metals, surfactants, organic substances and other toxicants from water, including biologically stable ones that cannot be removed by other methods, as well as the absence of secondary contaminants, make zeolites especially valuable when used in systems industrial wastewater treatment [13].

An analysis of modern literature [[6], [7], [8], [9], [10], [11], [12], [13]] showed a significant increase in the rate of publications devoted to the study of numerous modifications based on zeolites with the introduction of metal nanoparticles and the scope of the corresponding sorption and catalytic systems. The high surface energy of nanosystems makes them especially attractive for use in many catalytic industries since this property makes it possible to carry out technological processes under milder conditions than traditionally accepted ones. Nanomaterials based on oxides of rare and rare earth metals have unique properties that make them promising for wide use in chemistry and technology.

A promising direction for water purification from impurities of priority environmental pollutants is the use of modified synthetic or natural zeolites, which have a high sorption capacity with respect to many organic and inorganic substances [6].

In order to improve the adsorption properties of natural zeolites, they are modified or activated by heat treatment without destroying the crystal structure [3]. This leads to the fact that their porous open microstructure is capable of regulating the structure, for example, modifying with nanosized particles of rare and rare earth metals, which

determines their unique sorption properties, increases their selectivity, and reduces the sorption time [4].

In order to use natural zeolites for the purification of wastewater from industrial and mining enterprises from salts of heavy metals, the authors of [13] studied the adsorption characteristics of natural zeolites with an exchange capacity of 95–140 meq/100 g during the exchange of sodium cations or ammonium ions for ions lead, cadmium, copper and zinc from aqueous solutions at an adsorption time of 10 - 100 minutes, and the degree of extraction of heavy metal ions from the solution is 90 - 98% and decreases in the indicated series of heavy metals: Pb > Cd > Zn > Cu > Ni.

The paper [14] proposes a method for wastewater treatment from heavy metal cations, based on the use of slag formed during the complex processing of steel, which has a complex chemical composition and is characterized by a highly developed surface and the presence of a large number of microcracks, pores, and active centers, which determine the sorption properties. slag. With an increase in the amount of added slag, the purification efficiency increases, which is explained by an increase in pH and an increase in the number of active centers. During the purification process, the efficiency of purification from $Fe^{2+}$and Fe^{3+} ions was up to 99.5%, from Zn^{2+} ions - up to 97.5% with the addition of 0.7 g/l of slag and the initial concentration of model solutions of 30 mg/l. Shungite rocks of Karelia, which exhibit sorption activity in the process of wastewater treatment from heavy metals and oil products, are also material for solving environmental problems [15].

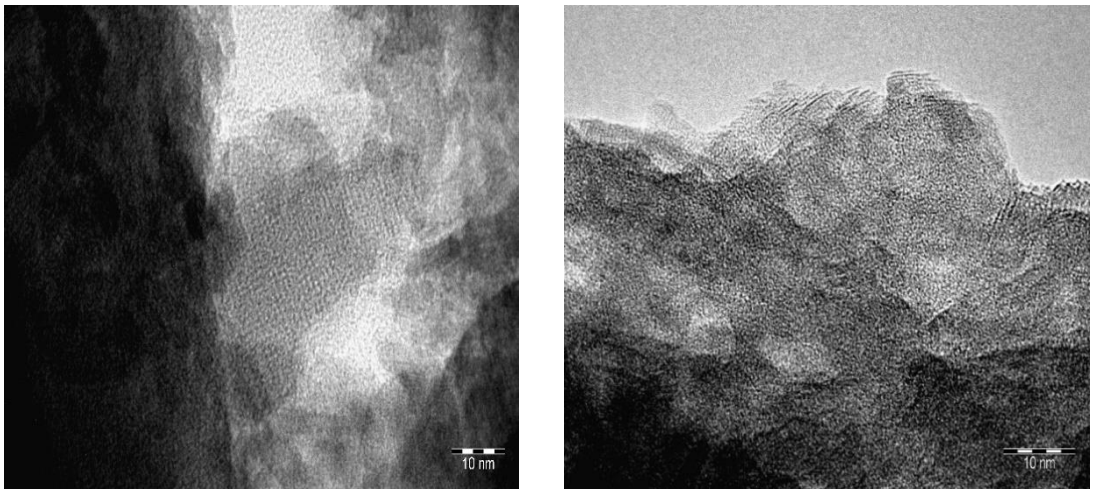
One of the possible ways to increase the efficiency of wastewater treatment technologies from heavy metals is the use of new nanodispersed sorbents that act as sorbents-coprecipitators of toxic components. Their basis is natural highly dispersed aluminosilicates, zeolites, the surface of which is modified by substances of inorganic and organic nature [[16], [17], [18], [19], [20], [21], [22]].

Thus, the information obtained from published sources is fragmentary and does not contain sufficient information about the possibilities and advantages of using modified aluminosilicates for water purification from heavy metal ions, which necessitated the present research.

Experimental part

The purpose of this work is to study the sorption capacity of zeolites modified with nanostructured rare metals in several ways, with different variants of matrix activation to improve the sorption properties with respect to ions of heavy and nonferrous metals. The results obtained will be used for further development of a hybrid technology for the treatment of process and wastewater.

In this regard, the task of our research is to create a rational method for treating industrial wastewater, which would ensure the implementation of sorption technology, taking into account the economic and environmental requirements for it. The effectiveness of the developed adsorbents in the process of removing heavy metals was assessed using model water.



a) b)

Figure 1 - Scanning electron microscopy of the original zeolite (a) and activated (b)

As adsorbents with high metal consumption, we used aluminosilicate (clinoptilolite), zeolites of the KN-30 brand in statics and dynamics, and modified with a mixture of vanadium and titanium nanopowder. Figure 1 shows SEM images of the original zeolite (A) and activated (B) by nanosized particles of a mixture of rare metals (V + Ti).

According to electron microscopy data, finely dispersed structures with d≈ 2.0 - 4.0 nm predominate on the surface of the unmodified ZSM-Al_2O_3 zeolite. The straight channels of the ZSM-5 zeolite intersect with the zigzag channels, forming a three-dimensional structure of narrow channels with sizes of 5.1–5.6 Å. Such a structure causes, on the one hand, the selectivity of the zeolite, and, on the other hand, diffusion restrictions, which lead to low exchange activity.

As can be seen from the electron microscopic image (Fig. 1, B), formations with d ≈ 3.0–5.0 nm, consisting of V_2O_5 and TiO_2, prevail on the surface of the activated zeolite. There are structures, the size of which varies within 5.0-7.0 nm, formed by $VxTi_{1-xO2}$. There is also an insertion of vanadium and titanium atoms into the structure of the zeolite and Al2O3 with the formation of $V_4Ti_2Si_3O_{10}$ and $VO_xTiO_xAlO_3$.

Nanoparticles of many substances exhibit properties that make it possible to use them as catalysts and adsorbents, and the question of the size at which the catalytic and sorption features of the nanostate of the studied materials begin to appear becomes important. In addition, it was found that at the nanolevel, the properties of the elements used for modification, for example, nanovanadium, nanocarbon, nanotitanium, etc., change significantly [[5], [19]]. This is apparently due not only to an increase in the active surface of the adsorbent, consisting of nanoparticles, but also to the fact that a significant proportion of the atoms that form its surface are in the so-called low-coordinated state, in which they exhibit maximum activity, both catalytic and sorption [20].

Results and Discussion

The zeolite sorbent used in the work was activated with nanostructured titanium-vanadium powder prepared from titanium dioxide and ammonium metavanadate. A promising raw material for obtaining a Ti-V-O hybrid composition is middlings and wastes of titanium-magnesium production, as the most accessible and cheap.

During the research, conditions were worked out that combined optimal adsorbent concentrations, mixing mode, and reagent supply rate, ensuring the precipitation and removal of heavy metals from the solution. The work studied sorption properties, and assessed the static exchange capacity (COE, mg/g) under standard conditions (initial concentration of heavy metal ions, ratio of solid to liquid phases 1:10, particle size, static sorption time). Determination of the concentrations of various ions from aqueous solutions was carried out using certified methods in accredited laboratories.

Figure 2 shows the technological scheme of wastewater treatment from ITM under static conditions using the obtained activated zeolites. The process of sorption from wastewater can be carried out under static and dynamic conditions. In the static mode, the liquid particle does not move relative to the sorbent particle; moves along with the latter in a sorption reactor with a stirrer.

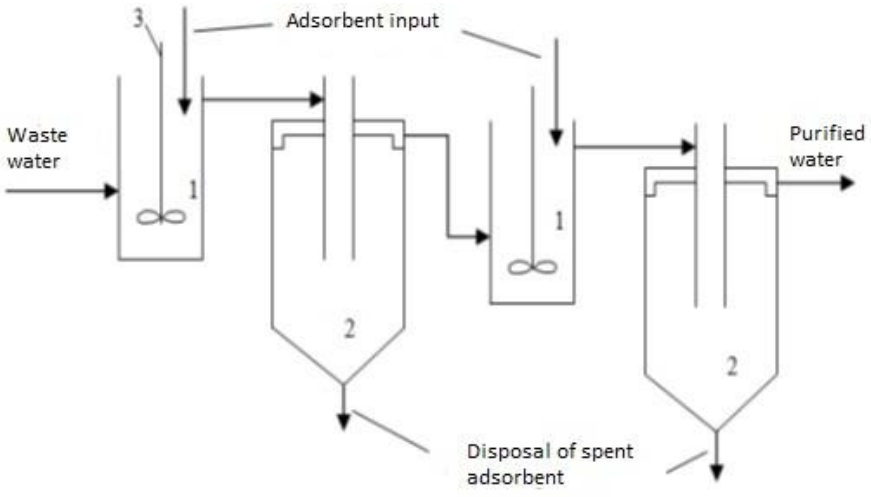


Figure 2 - Scheme of the adsorption plant in static conditions: 1 - sorption reactor; 2 - sump; 3 – stirrer

Table 1 - shows the ZOE values (mg/g) for heavy metal ions when using zeolites.

Zeolites	Cations			
	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}
Aluminosilicate	3.97	1.75	2.28	2.50
(clinoptilolite)	2.53	1.53	1.81	2.20
Zeolite KN-30	2.04	1.47	1.78	1.88
(processing in static)	1.83	1.17	1.53	1.61

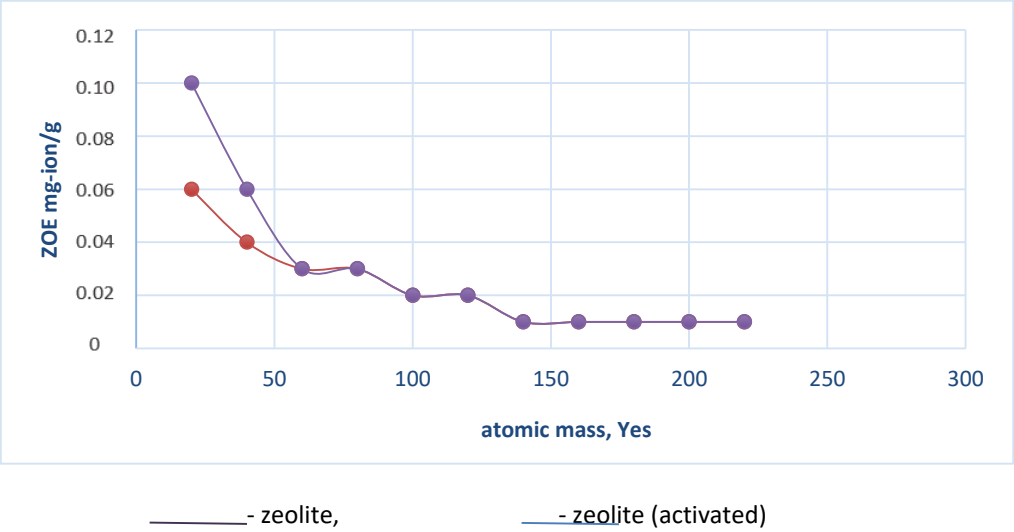


Figure 3 - Dependence of ZOE values (mg-ion/g) for heavy metal ions on atomic mass

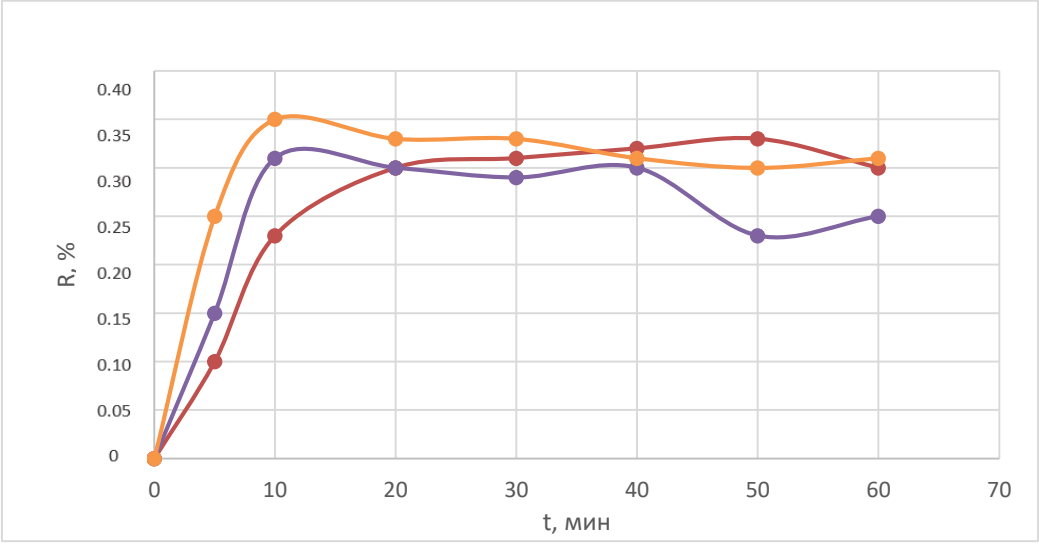


Figure 4- Determination of the sorption capacity of the zeolite from the mass of the introduced element: 1- Cu(II), 2- Ni(II) 3- Zn(II)

The table shows that the studied zeolite samples have a significant and close sorption capacity for heavy metal ions (Cu^{2+}, Ni^{2+}, Zn^{2+}), and a particularly toxic Pb^{2+} ion, which is currently very likely to be found in natural waters. At the same time, the activated zeolite sample is more selective to the Ni^{2+} and Zn^{2+} ions, and the zeolite (in dynamics) is more selective to the Ni^{2+} ion, although they also have an increased selectivity to the Cu^{2+} and Pb^{2+} ions.

It was shown [11] that the removal of lead from natural waters using natural zeolites is very effective both on pure clinoptilolite rocks and in combination with clinoptilolite with other minerals. In the conducted studies, a sample of the zeolite activated with nanocompounds shows an increased selectivity in relation to the lead ion.

Hence, it follows that the sorption capacity of activated zeolite is much higher than that of synthetic non-activated ones. For example, the dynamic sorption capacity before the breakthrough of 0.01 mg/l was at least 0.022 mg/l, and before the breakthrough of 0.1 mg/l - at least 0.034 mg/l. It should be noted that the dynamic curves of lead ion sorption on natural zeolites differ from the curves on activated samples in a flatter form, which requires the use of a sorption load height of at least 2–2.5 m to obtain effective purification. Figure 3 shows the dependences of ZOE mg-ion/g on the atomic mass of these metals.

The dependences obtained for various zeolite samples practically converge in the region of high values of atomic masses. This makes it possible to determine with high accuracy by extrapolation the limiting value of ZOE for metals, which is very difficult to determine experimentally for high concentrations due to the high contamination of wastewater with multiple impurities.

The sorption capacity of the zeolite was determined experimentally in the process of studying Cu^{2+}, Ni^{2+}, and Zn^{2+} ions.

For the studied "sorbent-metal" system, a series of solutions were prepared with the same content of the sorbent (0.1 g) and different increasing content - 60.100, 140, and 180 μg/ml of metal cations. The optimum acidity of the medium was created and mixed on magnetic stirrers for the optimum time and at the optimum temperature, which were previously selected for these systems. The amount of the adsorbed element was determined in each experiment, as described above, and a graph was plotted in the coordinates: "the degree of sorption (R, %) - the mass of the introduced element" (Fig. 4).

A specific property of zeolites is the rate of sorption of metal ions, which depends on the structure and properties of the zeolite matrix, the nature of the ion, and the degree of dispersion of the sorbent. When the temperature rises to 60°C, the sorption time is slightly reduced, by an average of 10 minutes.

Studies of the properties and structure of the substrate of various sorption materials and modified zeolite activated with a mixture of titanium and vanadium nanopowder applied powder showed that an increase in adsorption on the sorbent occurs on a highly developed substrate structure due to the formation of adsorption layers on the surface and in the pores activated by the powder. The activity of the modified zeolite depends on the rate of formation and subsequent transformation of surface intermediates, which is determined by the nature of the interaction, that is, the nature of emerging and breaking bonds, in some cases also by the spatial configuration.

Table 2 - Results of chemical analysis of wastewater treatment from heavy metals in the presence of various sorption materials

Applied sorption materials	Metal content after treatment, mg/l				Degree of removal, %			
	Cu^{2+}	Zn^{2+}	Ni^{2+}	Pb^{2+}	Cu^{2+}	Zn^{2+}	Ni^{2+}	Pb^{2+}
Clinoptilolite	0.06	0.16	0.08	0.13	89.2	74.2	86.7	59.4
Zeolite KN-30 (processing in static)	0.05	0.12	0.042	0.11	91.1	80.6	93.0	65.6
Zeolite processing in dynamics	0.05	0.09	0.024	0.08	91.2	85.5	96.0	75.4
Zeolite activated	0.02	0.02	0.012	0.04	96.4	96.8	98.0	87.5

Table 2 shows the results of processing a model solution containing heavy and non-ferrous metals with the sorption materials used. Initial concentration of metals in the model solution, mg/l: Cu^{2+}-0.56; Zn^{2+}- 0.62; Ni^{2+}- 0.60; Pb^{2+}- 0.32

An analysis of the results obtained (Table 2) allows us to draw the following conclusions: the best sorption capacity under static conditions with respect to heavy metal ions has a zeolite modified with vanadium and titanium, after activation, the degree of extraction for the studied ITMs ranged from 87.5 to 98, 0%. The chemical modification of the zeolite with the use of nanostructured vanadium and titanium compounds significantly increased the sorption capacity with respect to Cu(II), Ni(II), and Zn(II) ions; good sorption properties are also observed for Pb^{2+}, but the recovery is lower. It can be seen that the sorption capacity of zeolites activated with rare metals is much higher than that of activated carbons [5]. It is known [13] that after water treatment with technical aluminum sulfate and two-stage mechanical filtration, the zinc content in it increases significantly. Cleaning with activated zeolite allows, as can be seen from the table, not only post-treatment for zinc but also to reduce the odor, color, and ammonium ion content. To remove the ammonium ion, the sorption method using natural zeolites, including modified ones, is also the most effective, which was shown in [[20], [22]].

Based on the experiments conducted, it was proven that zeolites modified with vanadium and titanium nanocompounds are highly effective in the process of removing heavy metal ions from wastewater. The degree of metal removal was (%): Cu2+ - 96.4; Zn2+ - 96.8; Ni2+ - 98.0; Pb2+ -87.5. Particular consideration should be given to the removal of lead ions, which are widespread in industrial wastewater, using the developed nanosorbent. As has been shown [6], the removal of lead from natural waters using natural zeolites is very effective both on pure clinoptilolite rocks and in a combination of clinoptilolite with other minerals but does not ensure water quality that meets sanitary standards [11]. The significant sorption capacity of the studied samples for the lead ion Pb2+ makes it possible to use them for the purification of stormwater and detoxification of soils in adjacent areas of large highways. As a result of studies of the sorption properties of nanostructured adsorbents based on a zeolite matrix, their ability to extract heavy metal ions from water, as well as to remove ammonia nitrogen, has been proven.

Conclusion

The resulting composition on a zeolite matrix creates a highly dispersed solid phase of nanoparticles in the form of a sol-gel. Such systems have an excess of energy, which leads to increased reactivity and adsorbing properties. It is obvious that the activation of zeolites makes it possible to obtain a wider range of active centers of different natures. This determines the varied use of zeolites in the technological system for treating wastewater from heavy and non-ferrous metal ions, which will make it possible to achieve MPC standards.

Modification of zeolite-containing rocks with nanostructured compounds of rare metals changes their physical and chemical characteristics, their molecular structure is ordered and acid and adsorption properties are improved.

Thus, the study of the processes of sorption of heavy non-ferrous metals by natural materials, such as zeolites, is of practical interest to the water sector of industry. Of particular priority is the production of relatively cheap sorption materials based on industrial waste, since this waste is reused. Industrial wastes used as adsorbents do not have the main disadvantage of most used adsorbents - high cost. Taking into account the high cost of individual compounds of vanadium and titanium, samples of nanostructured adsorbents were obtained from technogenic vanadium-titanium-containing solutions of the titanium-magnesium plant (Ust-Kamenogorsk), which showed high efficiency. This advantage will reduce the amount of production waste, which will have a positive impact on capital costs. The use of waste and by-products of the metallurgical complex to activate matrix structures is promising and economically beneficial for purifying aqueous solutions of various compositions from ITM, ranging from wastewater from industrial enterprises to natural waters and food systems.

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

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Наноқұрылымды адсорбенттерді қолдану арқылы ағынды суларды ауыр металл иондарынан тазарту

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ТҮЙІНДЕМЕ

Қара және түсті металлургия және басқа да салалардағы өнеркәсіптік кәсіпорындардың қызметі қоршаған ортаның зиянды заттары бар ағынды сулармен ластануына әкеліп соғады, олар аз мөлшерде болса да адам денсаулығына және биосфера жағдайына айтарлықтай теріс әсер етеді. Суды тазарту мәселелерін шешу үшін қолданылатын көптеген табиғи сорбенттер бар. Бейорганикалық сорбциялық материалдардың ішінде тәжірибеде цеолиттер кеңінен қолданылады. Бұл табиғи материалдар термиялық және радиациялық тұрақтылыққа және жоғары селективтілікке ие. Бұл мақаланың мақсаты ауыр және түсті металдардың иондарына қатысты сорбциялық қасиеттерін жақсарту үшін матрицаны белсендірудің әртүрлі нұсқалары бар наноқұрылымды сирек металдармен модификацияланған цеолиттердің сорбциялық қабілетін бірнеше тәсілдермен зерттеу болып табылады. Жүргізілген тәжірибелер негізінде ванадий және титан наноқосылыстарымен модификацияланған цеолиттердің ағынды сулардан ауыр металл иондарын кетіруде тиімділігі жоғары екендігі дәлелденді. Цеолит матрицасында алынған композиция золь-гель түріндегі нанобөлшектердің жоғары дисперсті қатты фазасын жасайды. Мұндай жүйелерде энергияның артық мөлшері болады, бұл реакциялық және адсорбциялық қасиеттердің жоғарылауына әкеледі. Цеолиттерді белсендіру табиғаты әртүрлі белсенді орталықтардың кең спектрін алуға мүмкіндік беретіні анық. Бұл ауыр және түсті металл иондарынан ағынды суларды тазартудың технологиялық жүйесінде цеолиттердің әртүрлі қолданылуын анықтайды, бұл ШРК (шекті рұқсат етілген концентрация) стандарттарына қол жеткізуге мүмкіндік береді.

Түйін сөздер: цеолит, сорбциялық технологиялар, ауыр металдар, ағынды сулар, адсорбент.

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Очистка сточных вод от ионов тяжелых металлов с применением наноструктурных адсорбентов

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АННОТАЦИЯ

Деятельность промышленных предприятий чёрной и цветной металлургии и других отраслей приводит к загрязнению окружающей среды сточными водами, содержащие в своём составе вредные вещества, оказывающие и в небольших количествах довольно серьёзное негативное воздействие на здоровье человека и состояние биосферы. Существует большое количество природных сорбентов, используемых для решения задач водоочистки. Среди неорганических сорбционных материалов на практике широко используются

цеолиты. Эти природные материалы обладают термической и радиационной стабильностью, высокой селективностью. Цель данной статьи — изучение сорбционной способности цеолитов, модифицированных наноструктурированными редкими металлами несколькими способами, при разных вариантах активации матрицы для улучшения сорбционных свойств по отношению к ионам тяжелых и цветных металлов. На основании проведенных экспериментов было доказано, что цеолиты, модифицированные наносоединениями ванадия и титана, обладают высокой эффективностью в процессах удаления ионов тяжелых металлов из сточных вод. Полученная композиция на цеолитной матрице создает высокодисперсную твердую фазу из наночастиц в форме золя-геля. Такие системы имеют переизбыток энергии, что и приводит к повышенной реакционной способности и адсорбирующим свойствам. Очевидно, что активирование цеолитов позволяет получить более широкий набор активных центров различной природы. Это обуславливает разнообразное использование цеолитов в технологической системе очистки сточных вод от ионов тяжелых и цветных металлов, ввиду чего станет возможным достижение нормативов ПДК.

Ключевые слова: цеолит, сорбционные технологии, тяжелые металлы, сточные воды, адсорбент.

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Metallurgy

Hydrometallurgical studies on the leaching of copper from man-made mineral formations

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ABSTRACT

The article presents the study results for the processing of industrial waste from copper production at copper smelter Kazakhstan. The samples taken were analysed with the help of X-ray fluorescence and phase analyses which showed that the composition of the studied raw materials was determined as silicate, oxidized, and copper was in a mixed form with a total content of 0.481%, including some in the form of sulfates and sulfides. Mineralogical analysis showed the presence of magnetite, hematite and martite, while copper was present in various mineralogical formations - from magnetic fractions mainly with very fine dusty micron dissemination to native copper and copper minerals. Beneficiation studies performed included flotation and gravity methods. As a result, a concentrate with a copper content of 9.35% was obtained during gravity beneficiation, and a concentrate with a copper content of up to 46% was obtained during flotation. Copper was extracted from beneficiated raw materials with a sulfuric acid leaching method in agitation mode. The solid residue analysis conducted after (cake) leaching also showed the content of the noble metal - gold at the level of 0.47 g/t enabling us to consider its extraction in the future as an additional valuable component.

Keywords: copper, mineralogical analysis, technogenic raw materials, enrichment, leaching.

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Introduction

Technogenic waste from metallurgical production is a promising secondary raw material for obtaining valuable components. Effective processing of mineral raw materials and adjusted technology intended to extract valuable components will enable to involve poor, off-balance raw materials into the production cycle and increase production profitability. Slag is the main waste of copper pyrometallurgical production. Thus, 2–4 tons of slag from smelting, converting and refining processes are released at copper smelters during production of a ton of copper. And hydrometallurgical, pyrometallurgical and flotation methods are used to process it. The choice of processing method is determined by the composition of the feedstock, fluxes and the technologies used at the enterprises. However, to date scientifically based technologies intended to process slag and other copper production waste have not been developed [[1], [2], [3], [4], [5]].

An analysis of the existing technologies used for processing of waste slag from copper production shows that pyrometallurgical processing methods using reduction smelting are not always suitable for this product. This is due to the presence of various forms of oxides in the slag often impossible to be reduced with carbon during the smelting process. Hydrometallurgical processing of copper slag most often involves sulfuric acid leaching, with the practice to use additional methods to intensify metal extraction. The following slag processing designs are being studied at the moment - leaching of slag with solutions of sulfuric acid and iron sulfate; autoclave ammonia-carbonate leaching of slag in an oxidizing environment; autoclave sulfuric acid leaching. Autoclave nitrate leaching is mainly used for reverberatory and shaft melting slags [[6], [7], [8], [9], [10], [11]].

Bio-leaching studies conducted for reverberatory smelting slag and its beneficiation products showed that the copper extraction into the solution increased up to 82% when bacterial oxidation was used.

The composition and characteristics of raw materials and the use of hydrometallurgical processing methods and processes were studied to involve slag in the technological cycle, and to develop effective technological solutions [[12], [13], [14], [15], [16]].

Experimental part

Samples were taken from the dumps of man-made mineral formations (MMMF) of the Kazakhstan smelter to perform the work. The technological sample is composed of vitreous slags which are mainly black, less often brown and dark green. The detailed elemental composition of the initial MMMF sample presented in Table 1 was determined with the help of X-ray fluorescence analysis enabling to capture spectra of elements from oxygen to uranium [[17], [18], [19], [20]]. To involve slag in the technological cycle and develop effective technological solutions, studies of the composition and characteristics of raw materials and the use of methods and methods of hydrometallurgical processing were carried out.

From Table 1 it can be seen that the raw material, under study, slag, belong to complex chemical systems, where the predominant metal is iron 9.796%, significant calcium content is 6.762%, copper content is 0.481%.

Table 1 - Results of X-ray fluorescence analysis of Karsakpay slag sample

Element	Content, %	Element	Content, %	Element	Content, %	Element	Content, %
O	36.386	S	0.093	Cu	0.481	P	0.055
Na	0.926	K	0.305	Zn	0.335	Fe	9.796
Mg	0.517	Ca	6.762	Rb	0.004	Pb	0.202
Al	3.231	Ti	0.271	Zr	0.013	Co	0.020
Si	19.084	Mn	0.247	Sr	0.021	Cl	0.012
						Ba	0.107

Table 2 - Phase composition of the initial slag sample

Component name	Formula	Amount, %
Gedenbergite, sodium	$(Ca_{0,615}Na_{0,385})Fe(Si_2O_6)$	27.3%
Magnetite	Fe_3O_4	15.6%
Aluminum augite	$Ca(Mg,Fe,Al)(Si,Al)_2O_6$	14.5%
Quartz	SiO_2	11.7%
Almandine	$Fe_3(Al_2Si_3O_{12})$	9.1%
Sodium mica, dehydroxylated paragonite, Sodium aluminosilicate	$NaAl_3Si_3O_{11}$	8.2%
Calcium silicate	$CaSiO_3$	6.9%
Calcium-aluminum silicide	CaAlSi	6.8%

The phase composition of the slag was determined using a D8 Advance (Bruker), α-Cu apparatus, with a tube voltage of 40 kV and a current of 40 mA. Processing of the obtained diffraction pattern data and calculation of interplanar distances were carried out using EVA software. Sample interpretation and phase search were carried out using the Search/match program using the PDF-2 Powder Diffractometric Database. The results of X-ray phase and chemical analysis are presented in Tables 2, 3.

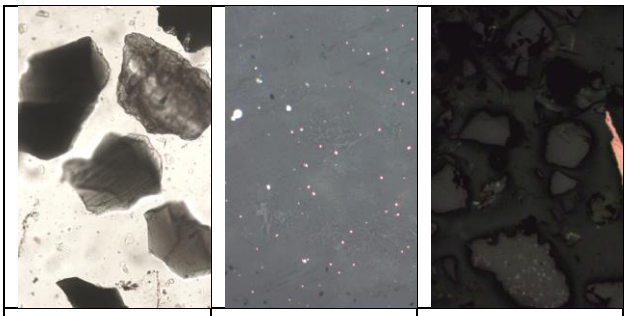
The data of Tables 1 and 2 show the MMMF specific composition, the noticeable predominance of oxidized forms of phases containing significant amounts of iron, silicon, aluminum and calcium. It has been established that the predominant phases have a silicate form, as well as in the form of oxidized iron using the example of magnetite.

Table 3 - Results of chemical phase analysis of the MMMF sample

No.	Name of components and types of compounds	Content, in %
1	Copper sulfate	0.59
	Copper of oxidized compounds (except for sulfate)	0.44
	Metallic copper	-
	Copper sulfide	0.18
	Total copper content	0.75
2	Iron (II) oxide (ferrous oxide)	3.68
	Iron (III) oxide (iron oxide)	12.08
	Iron metallic	-
	Iron sulfide	1.04
	Total iron	14.06

Mineralogical analyses. A polished thin section (∅= 25 mm, m-suspension = 10-15 grams) formed from this material was studied under the Axio Scope.A1 optical microscope. Magnetite, hematite and martite are present in the ore according to literature data. Two samples with the coarseness up to 5-7 centimeters were received for the study of slag - crushed sample up to 200 mesh and gravity concentrate with the coarseness -2,0 mm. The bulk sample material was separated into 4 fractions using a four-pole Sochnev magnet: No. 1. Strongly magnetic fraction (magnetite), No.2 Medium magnetic fraction (hematite), No.3. Weakly magnetic fraction (glassy slag fragments), iron oxides and hydroxides), No.4 Non-magnetic fraction (amorphous non-metallic glass). A polished thin section was made from the sample, and an artificial polished thin section (briquette) was made from the gravity concentrate. All products were studied under a Leica DM 2500 P microscope. The crushed material of the sample was studied in immersion liquids under a microscope.

The sample is black, with a glassy sheen on chips, fine-grained, with layers of dark gray color of a fine-grained structure. In the immersion preparation, the bulk material of the sample is represented mainly by glass fragments of a light brownish tint, isotropic in crossed nicols (amorphous) (Figure 1, a).



a	b	c
The non-magnetic fraction of the gravity concentrate. Immersion product. Magnification 100.	Dust-like inclusions of native copper and globules of ore minerals in slag. Polished thin section, magnification 200.	Native copper in slag. Polished thin section, magnification 100.

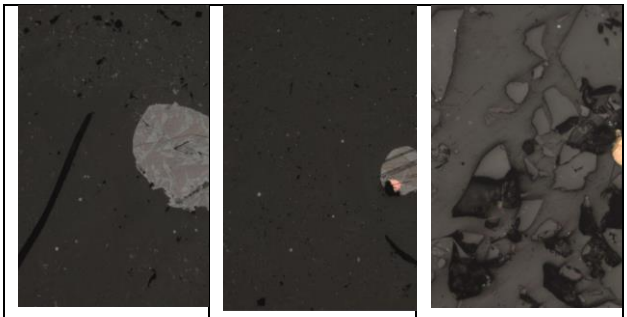
Figure 1 - Polished thin section of MMMF

The sample is represented by fragments of slag (glassy mass) with very fine dust-like micron inclusions of native copper and copper minerals with the size of hundredths and thousandths of mm and perfect rounded globular grains (chalcosine) in the polished thin section in the reflected light. These grains sometimes contain very small inclusions of native copper. The main body of the rock also contains point inclusions of globular-shaped mineral with the size of hundredth and thousandth fractions of mm (Fig. 1, b) along with copper phenocrysts. Copper crystals up to 0.2 mm in size are present in the polished thin section and briquettes of the gravity concentrate (Figure 1, c).

The gravity concentrate consists of glass fragments often with small inclusions of copper minerals and globules of white and light gray mineral. Light minerals are in the form of rounded crystals up to 0.13mm in size. Globular crystals sometimes have heterogeneous taxite coloration with fragments of light gray and beige-pink color (Figure 2, a). Inclusions of native copper are sometimes found in chalcosine crystals (Figure 2, b).

There are crystals of chalcopyrite with a tinge of orange color, characteristic of bornite in the briquette from gravity concentrate (Figure 2, c). Probably they have an intermediate composition between these two minerals (solid solution).

Determination under the microscope needs to be clarified and confirmed on the electron-probe analyzer to clarify the composition of minerals.



a	b	c
Globular mineral with taxite coloration. Polished thin section, magnification 100	Chalcosine with inclusion of native copper. Polished thin section, magnification 100.	Chalcopyrite in slag. Briquette, magnification 200

Figure 2 - Mineralogical studies of the copper mineral

Flotation beneficiation of the initial slag sample.

Initial slag was prepared for flotation beneficiation in the same way as for gravity beneficiation. Several crushing and grinding stages were envisaged followed by flotation beneficiation of the initial MMMF, including the main and control flotation.

Besides, three variants of pH of the medium were provided with flotation of initial MMMF. The main 10-minute flotation mode included the following components: butyl xanthogenate - 150 g/t, foaming agent C7 - 150 g/t, sulfidizer Na_2S - 1000 g/t. The 5-minute control flotation mode provided the following consumption of reagents - butyl xanthogenate - 100 g/t, foaming agent C7 - 50 g/t. Caustic soda was added additionally at the rate of 5 kg/t to the slag slurry for the variant with alkaline environment, and 2 kg/t of sulfuric acid was added for the variant with acidic environment.

Three products of each pH variant were also obtained as a result of flotation beneficiation - main and control concentrates, tailings of flotation beneficiation. When the samples of each product were dried and weighed, they were analyzed for elemental composition presented in Tables 4-7.

Table 4 - Elemental composition of flotation beneficiation products in the initial MMMF sample at pH = 8.4

Element	Element content, %		
	Main concentrate	Control concentrate	Flotation tailings
O	39.14	43.092	36.034
Na	1.036	1.067	0.915
Mg	0.635	0.664	0.501
Al	3.465	3.756	2.949
Si	20.095	22.15	17.565
P	0.057	0.056	0.045
S	0.189	0.122	0.055
K	0.447	0.494	0.417
Ca	8.96	9.546	8.218
Ti	0.457	0.54	0.437
Mn	0.235	0.228	0.214
Fe	11.369	11.119	10.34
Co	0.026	0.0	0.029
Cu	1.277	0.525	0.329
Zn	0.432	0.363	0.317
Sr	0.021	0.022	0.015
Zr	0.015	0.012	0.008
Pb	0.293	0.197	0.187

Table 5 - Elemental composition of flotation beneficiation products of initial slag sample at pH = 10.5

Element	Element content, %		
	Main concentrate	Control concentrate	Flotation tailings
O	41.739	41.806	35.116
Na	1.142	1.115	0.952
Mg	0.647	0.66	0.487
Al	3.653	3.634	2.748
Si	21.49	21.32	16.407
P	0.054	0.054	0.046
S	0.302	0.161	0.055
K	0.44	0.459	0.369
Ca	8.971	8.835	7.916
Ti	0.441	0.466	0.414
Mn	0.215	0.224	0.206
Fe	10.415	10.441	10.234
Co	0.019	0.0	0.02
Cu	1.937	0.769	0.37
Zn	0.393	0.36	0.332
Sr	0.018	0.022	0.017
Zr	0.011	0.011	0.01
Pb	0.274	0.207	0.224

Table 6 - Elemental composition of flotation beneficiation products of initial slag sample at pH = 6.0

Element	Element content, %		
	Main concentrate	Control concentrate	Flotation tailings
O	44.443	44.623	37.795
Na	1.147	1.075	0.986
Mg	0.634	0.609	0.535
Al	3.823	3.865	3.189
Si	22.067	22.137	18.689
P	0.068	0.057	0.047
S	0.214	0.209	0.092
K	0.492	0.454	0.404
Ca	8.922	9.228	8.47
Ti	0.491	0.47	0.453
Mn	0.243	0.216	0.216
Fe	10.535	10.732	10.457
Co	0.0	0.022	0.023
Cu	1.18	1.12	0.476
Zn	0.321	0.334	0.348
Sr	0.017	0.021	0.014
Zr	0.009	0.011	0.009
Pb	0.226	0.203	0.176

Table 7 - Results of flotation beneficiation of initial slag at different parameters of the medium pH

Experiment 1 (initial slag)					
Conditions	Product	weight, g	wt. yield, %	Cu, %	E Cu, %
Main flot. t-10 min, butyl xanth - 150 g/t, C7 -150 g/t, ; Control flot. t-5 min, b.xanth - 100 g/t, C7 - 50.; initial pH - 8,4.	Main concentrate	340.3	17.015	1.3	43.83
	Control concentrate	55	2.75	0.525	2.91
	Combined concentrate	395.3	19.765	1.2	46.75
	Tailings	1604.7	80.235	0.33	53.25
	Initial	2000.0	100.0	0.496	100.0
Experiment 2 (initial slag)					
Conditions	Product	weight, g	weight yield, %	Cu, %	E Cu, %
Main flot. t-10 min, butyl xanth - 150 g/t, C7 -150 g/t, ; Control flot. t-5 min, b.xanth - 100 g/t, C7 - 50.; pH - 10,5.	Main concentrate	128.0	6.4	1.9	26.08
	Control concentrate	24.8	1.24	0.769	2.01
	Combined concentrate	152.8	7.64	1.7	28.09
	Tailings	1847.2	92.36	0.37	71.91
	Initial	2000.0	100.0	0.475	100.0
Experiment 3 (initial slag)					
Conditions	Product	weight, g	wt. yield, %	Cu, %	E Cu, %
Main flot. t-10 min, butyl xanth - 150 g/t, C7 -150 g/t, ; Control flot. t-5 min, b.xanth - 100 g/t, C7 - 50.; pH - 6,0.	Main concentrate	79.7	3.985	1.1	8.61
	Control concentrate	50.2	2.51	1.12	5.43
	Combined concentrate	129.9	6.495	1.1	14.04
	Tailings	1870.1	93.505	0.48	85.97
	Initial	2000.0	100.0	0.518	100.0

The highest copper contents are observed in the main concentrates obtained at alkaline (10.5) and initial (8.4) pH in contrast to the gravity tailings beneficiation products. Copper content reaches 1.937 % in the main concentrate obtained by flotation beneficiation at pH = 10.5, and 0.769 % - in the control concentrate. The main concentrate with copper content of 1.277 % and control concentrate with 0.525 % were obtained at flotation in the initial medium pH = 8.4. Flotation at pH = 6.0 allowed to obtain the main concentrate with copper content of 1.18 % and control concentrate with 1.12 %. The main and control concentrates of all variants differed significantly in mass yield similarly to flotation of gravity concentration tailings. Thus, the highest mass yield (total 19.765 %) was also observed in the variant with initial pH = 8.4. Metal balance and copper recovery were calculated based on the obtained results and masses of beneficiation products as presented in Table 7.

The highest copper recovery of 46.75% was recorded in the experiment with initial pH = 8.4 in the case of beneficiation of initial slag as in the case with flotation beneficiation of gravity tailings. However, the beneficiation concentrate is inferior only to the concentrate obtained by flotation in alkaline medium in terms of quality in this case. Discrepancy of analysis (Cu 0,481 %) and balance for the initial slag sample is 3,0 % in Experiment 1; 1,25 % in Experiment 2; 7,14 % in Experiment 3. Discrepancies of the calculated balance for the beneficiation products and the analysis results are within the acceptable range for copper raw materials.

Experiments intended to leach initial slag and beneficiation products by agitation method.

Samples of initial slag, concentrate of gravity concentration, main concentrates of flotation concentration of initial slag and gravity tailings were leached with sulfuric acid leaching.

Agitation leaching was performed under the following conditions - 80 % grade - 0.074 mm; weight of the sample 100 g; pH of the solution during

leaching 1.6-2.0; concentration of HH_2SO_4 - 2.5 %; leaching duration - 10 hours.

The concentration of sulfuric acid and pH of the medium were monitored in the leaching process, and reagents were added if necessary. Experiments intended to leach initial samples were conducted with the use of agitator stirrers with a rotation speed of 150-200 rpm. Thus, there was a constant decrease in the concentration of sulfuric acid in the initial slag sample up to 0 within the first 4 hours. Initial slag was added to the variant with three times throughout the experiment. Acid addition was required only in the first two hours of leaching in the experiments with concentrate leaching, and further decrease in acidity was not observed.

The solution was separated by filtration and analyzed for copper content at the end of leaching. The cake was analyzed to consider the possible increase in gold content during the removal of impurities by sulfuric acid leaching. The copper recoveries presented in Table 8 were calculated based on the amounts of productive solutions obtained and their corresponding copper concentrations.

The results of agitation leaching experiments showed that the amount of recoverable copper from the initial slag and products of its beneficiation are at the level of 23.08 and 30.89 %. The highest recovery is observed in the flotation concentrate sample obtained after beneficiation of gravity tailings - 30.83 % but the solution quality is at the level of copper concentration of 0.503 g/l taking into account the relatively low copper content in this concentrate. The maximum concentration of copper is noted in the solution after leaching of flotation concentrate of initial slag - 1.035 g/l resulted in recovery of 27.87 %. Copper content was found at 0.508 g/l, and the recovery was 24.36 % in the solution after leaching of gravity concentrate. The lowest copper concentration was recorded in the solution after leaching of the initial slag at 0.37 g/L, with a final recovery of 23.08 %.

The variant of biochemical leaching included pretreatment of mineral raw materials with a bacterial culture of A. Ferrooxidans at pH 2.2-2.4. Subsequently, leaching was carried out with sulfuric acid in a similar mode as with the standard method. The results of leaching after bacterial treatment are presented in Table 9.

Solid sediment of each sample (cake) was analyzed for possible increase in gold content, taking into account all stages of beneficiation and removal of part of acid-soluble impurities in the leaching process. However, an increase in gold content of more than 0.47 g/t was not observed in any variants.

Table 8 - Results of agitation leaching

Sample	Initial Cu, %	Leaching solution		Weight, g	Solution amount, ml	Cu, g/l	E Cu, %
		H_2SO_4, g/l	S:L				
Initial slag	0.481	25.0	1:4	100	300	0.37	23.08
Gr. conc.slag	0.73	25.0	1:4	100	350	0.508	24.36
Con. Flot. Gr. tailings	0.57	25.0	1:4	100	350	0.503	30.89
Con. Flot. and slag	1.3	25.0	1:4	100	350	1.035	27.87

Table 9 - Results of agitation leaching after biooxidation

Sample	Initial Cu, %	Leaching solution		Weight, g	Solution amount, ml	Cu, g/l	E Cu, %
		H_2SO_4, g/l	S:L				
Initial slag	0.481	25.0	1:4	100	310	0.748	48.23
Gr. conc.slag	0.73	25.0	1:4	100	330	1.3	58.77
Con. Flot. Gr. tailings	0.57	25.0	1:4	100	335	1.15	67.59
Con. flot.	1.3	25.0	1:4	100	330	3.24	82.27

Discussion of the results

The slag sample studies included the study of the slag chemical composition and phase composition, identification of potentially valuable components and search for methods of their recovery, including flotation and gravity concentration, agitation and percolation leaching.

The study of the material composition of slag by fluorescent and X-ray phase analysis confirmed the structure characteristic of the main mass of slag in full. Thus, the analysis results showed elements and phases mainly characteristic of Si_xO_y-Fe_xO_y-Al_xO_y-Ca_xO_y- slag systems. The phase analysis found numerous silicates, aluminosilicates, iron oxides, quartz, etc.

Only copper was found in the slag sample in the analysis process for the search of potentially valuable components with the concentration of 0.4-0.5 % in the average. This copper content is acceptable for minerals involved in industrial processing (heap leaching, beneficiation). The contents of other potentially valuable elements are rather low, and it does not enable to consider their possible industrial recovery. Additional analysis for gold content also showed relatively low results at about 0.4 g/t. Gravity concentration experiments showed the possibility to recover only 9.35 % of copper in the concentrate due to the absence of clearly pronounced copper-containing fragments with high density in the slag composition relative to other components of the slag. The maximum recovery of copper in the concentrate reached the level of about 46%, while a significant part of the metal remained in the flotation tailings at flotation beneficiation of both initial samples and gravity tailings. This factor is due to the absence of an acceptable amount of flotable mineral forms of copper in the slag composition.

Agitation leaching from the initial slag sample recovered 23.08 %, while there was a significant absorption of acid and leaching solution that was also characteristic for percolation of crushed slag. The maximum copper recovery in solution during agitation leaching was observed in the variant with flotation concentrate from gravity concentration grip 30.83 %. However, the solution that was best in terms of concentration quality - 1.035 g/l with recovery of 27.87 %, was obtained by leaching of flotation concentrate from initial slag. The obtained recovery rates of beneficiation and agitation leaching processes, taking into account the necessary stages of raw material preparation (crushing, grinding) and reagent regimes (xanthogenate, foaming agent, sulfidizer, etc.) indicate the technical and economic inexpediency to process this slag by the above methods. Thus, methods involving costly grinding and beneficiation operations are excluded for effective and expedient processing of this MMMF to obtain finished copper cathode.

The use of the preliminary method of oxidation of mineral samples of enrichment products, as well as the initial slag, allows to significantly increase the degree of copper extraction into the solution in the future. Thus, the concentration of copper during biochemical leaching of the initial slag increases from 0.37 g/l to 0.748 g /l, which gives a final extraction of 48.23%. An increase in the concentration and extraction of copper was more than doubled during the leaching of gravity concentrate – from 24.36 to 58.77%, as well as the concentrate of flotation enrichment of gravity tails – from 30.89 to 67.59%. The maximum increase in the concentration of copper – 3.24 g/l, was detected during biochemical leaching of the flotation concentrate of the initial slag, and the increase in extraction showed a threefold increase from 27.87% to 82.27%.

Conclusions

High efficiency of preliminary bacterial treatment of samples with A. Ferrooxidans culture was established during agitation leaching experiments with initial slag samples and products of its beneficiation by standard and biochemical method. Thus, preliminary oxidative treatment of the initial slag sample with bacteria allows increasing the final recovery rate from 23.08 to 48.23 %. Similar bioleaching efficiency was also observed for the leaching of gravity beneficiation slag sample, where the recovery rate was 58.77 % at copper concentration of 1.3 g/L. The use of bacterial oxidation factor for flotation concentrates of slag gravity tailings increased the total recovery from 30.89 % to 67.59 %. Application of bio-oxidation with A. Ferrooxidans bacterial culture on initial slag flotoconcentrate contributed to a threefold increase in copper concentration and final recovery in solution that amounted to 82.27 %.

Thus, it has been established that the chemical and mineralogical composition of this slag makes it possible to effectively apply the biochemical method

of leaching both on the initial slag and on its enrichment products. In particular, during the leaching of the flotation concentrate, a sufficiently rich solution is observed, which can subsequently be used both for cementation deposition of copper and for extraction extraction by the organic phase. From an economic point of view, a less energy-consuming method of heap leaching with preliminary bacterial treatment may be acceptable for this type of slag, since this technology eliminates the need for preliminary crushing and grinding of mineral raw materials. However, if it is possible to implement effective enrichment methods and the prospect of extracting additional valuable components, a combined processing technology can be used for these slags of the Karsakpai deposit, including the stages of enrichment, bio-oxidation and leaching.

Conflict of interest. Если Вы (корреспондент автор) согласны, Вы не должны удалять это предложение: On behalf of all the authors, the correspondent author declares that there is no conflict of interest.

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Техногендік минералды түзілімдерден мыс алу бойынша жүргізілген гидрометаллургиялық зерттеулер

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ТҮЙІНДЕМЕ

Мақалада Қарсақпай кен орнының қазақстандық мыс балқыту зауытындағы мыс өндірісінің техногендік қалдықтарын қайта өңдеу бойынша зерттеулердің нәтижелері келтірілген. Сынама үлгілері рентгенофлуресцентті және фазалық талдаумен талданды. Зерттелетін шикізаттың құрамы силикатты, тотыққан, мыс сульфаттар, сульфидтер түрінде, жалпы мөлшері 0,481% болатындығы анықталды. Минералогиялық талдау магнетит, гематит және мартиттің болатынын көрсетті. Мыс магниттік фракцияларда, негізінен табиғи және мыс минералдарының өте жұқа шаң тәрізді микрондық сеппелілікте болады. Флотация және гравитация әдістерімен байыту бойынша зерттеулер жүргізілді, гравитациялық байыту кезінде құрамында 9,35% мыс бар концентрат, флотация кезінде құрамында 46% дейін мыс бар концентрат алынды. Байытылған шикізаттан мыс алу күкірт қышқылын шаймалау әдісімен, агитациялық режимінде, 30,83% дейін шығарылды. Қоқымның құрамындағы алтынға жүргізілген талдау оның мөлшері 0,47 г/т-дан аспайтынын көрсетті.

Түйін сөздер: мыс, минералогиялық талдау, техногендік шикізат, байыту, шаймалау.

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Гидрометаллургические исследования по извлечению меди из техногенных минеральных образований

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АННОТАЦИЯ

В статье представлены результаты исследований по переработке техногенных отходов медного производства Казахстанского медиплавильного завода, месторождения Карсакпай. Образцы проб были проанализированы рентгенофлуресцентным, и фазовым анализом, выявлено, что состав исследуемого сырья определяется как силикатный, окисленный, медь находится в форме сульфатов, сульфидов, с общим содержанием 0,481%. Минералогический анализ показал присутствие магнетита, гематита и мартита, медь присутствует в различных магнитных фракциях, преимущественно в очень тонкой пылевидной микронной вкрапленностью меди самородной и медных минералов. Проведены исследования по обогащению методами флотации и гравитации. При гравитационном обогащении получен концентрат с содержанием меди 9,35 %, при флотации получен концентрат с содержанием меди до 46 %. Извлечение меди из обогощенного сырья проводили методом сернокислотного выщелачивания, в агитационном режиме, с извлечением до 30,83 %. Проведенный анализ кека на содержание золота показал содержание не более 0,47 г/т.

Ключевые слова: медь, минералогический анализ, техногенное сырье, обогащение, выщелачивание.

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Metallurgy

The State of Affairs of 'Rare Metal Industry' in Korea

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ABSTRACT

This paper offers a thorough examination of South Korea's rare metal industry, delving into its definition, classification, supply and demand dynamics, international trade conflicts, and the government's strategic endeavors in this domain. It underscores the global significance of rare metals, spotlighting the challenges arising from their uneven distribution across the world. The paper emphasizes the pressing need for countries, including South Korea, to address these challenges through well-planned strategies. Additionally, the paper explores the legal and policy frameworks recently adopted in South Korea concerning rare metals. It places particular emphasis on the pivotal role played by the Korea Institute of Industrial Technology (KITECH) in fostering the growth and development of the rare metal industry within the nation. Furthermore, the paper provides insights into the current state of South Korea's rare metal industry, focusing on key sectors such as the utilization of rare earth metals in electric vehicles, refractory metals for semiconductors and displays, and cathode materials essential for secondary batteries. These areas of specialization illustrate the integral role that rare metals play in cutting-edge technologies, positioning South Korea as a leader in innovation. In its conclusion, the paper underscores the urgency of advancing technological capabilities, promoting recycling practices, and enhancing refining processes to establish a circular rare metal industrial economy. This approach not only guarantees a sustainable supply of rare metals but also aligns with global efforts for eco-friendly and resource-conserving industrial practices.

Keywords: Rare metals, South Korea, Global significance, Recycling and refining, International trade conflicts, Rare metal Industry

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1. Introduction

1.1 Background

The Ministry of Trade, Industry, and Energy (MOTIE), responsible for overseeing Korea's industry and trade, has unveiled the national policy on rare metals, first in 2009 and subsequently in 2021. This policy delineates the classification of rare metals, distinct from commonly mass-produced metals such as iron, copper, and aluminum.

Within the Korean context, rare metal elements encompass 35 out of 56 elements [[1], [2]]. These elements are characterized by both high industrial demand and the challenge of extraction due to their limited abundance in the earth's crust. The dictionary definition of rare metals signifies metals with a low concentration of ore. From an economic standpoint, rare metals exhibit traits such as high price volatility and substantial demand. Additionally, a resource-security perspective underscores that these resources are not uniformly distributed and are concentrated in a select few countries [[1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11]].

1.2 Global Perspective

The United States designates fifty minerals as 'Critical Minerals,' while nineteen essential energy-related elements are classified as 'Critical Materials for Energy.' In Europe, 66 elements are identified as 'Critical Law Materials,' and in Japan, 55 elements fall under the designation of 'Rare Metals.' These

classifications reflect international recognition of the strategic importance and unique characteristics of rare metals across different regions [[12], [13], [14], [15]].

2. Results and Discussion

2.1. Supply and Demand Dynamics

2.1.1 Industrial Trends

Let's examine the current landscape of the rare metal industry, focusing on the dynamics of supply and demand. Over the past decade, the demand for rare metals has exhibited consistent growth, primarily driven by the expansion of the electric vehicle, secondary battery, and emerging new and renewable energy sectors. This surge is further intensified by the imperative of carbon-neutral initiatives, which, in addition to replacing fossil energy sources, are contributing to a heightened reliance on rare metals.

A notable illustration of this trend is the increased utilization of lithium nickel manganese cobalt in secondary batteries and rare earths in electric vehicle motors compared to a decade ago. This growth underscores the pivotal role rare metals play in advancing technologies aligned with environmental and sustainability goals.

2.1.2 Market Stability and Resource Distribution

However, a potential concern arises from the concentration of rare metal production in specific regions, leading to a monopolistic resource distribution that can foster market instability and impede the development of robust global supply chains. Noteworthy instances include China producing 63% of the world's rare earth metals, and an even more substantial 83% of tungsten. Additionally, Congo accounts for 70% of global cobalt production, while South Africa produces 55% of the platinum group [1].

This concentration of production in specific geographical locations raises critical questions about the resilience and sustainability of the rare metal supply chain, necessitating a careful examination of strategies to mitigate risks associated with monopolistic resource distribution.

2.2.National Policies and Strategies

Table 1 outlines the trends in the rare metals industry across major countries.

Due to the impact of rare metal resource challenges, countries across the globe are developing tailored policies to tackle industry-specific issues and strengthen their security measures. Remarkably, although China boasts the largest production of rare earths, they are limiting their mining and smelting capabilities.

Australia currently holds the leading position in global lithium production, whereas Indonesia is the top nickel producer and the second-largest tin producer worldwide. Myanmar has recently established a rare earth smelting industry that can produce up to 22,000 tons annually. This resource imbalance has prompted resource-dependent nations to draft special policies for rare metals that align with their unique industrial landscapes and geopolitical settings.

Table 1 - The trends in the rare metals industry across major countries

Category	Country	Contents
Supply	CHINA	The world’s largest producer countries of rare metals
	AU	Lithium No. 1 producer countries
	ID	Nickel, the world’s No. 1 and Tin No. 2 producer countries
	MY	Possession of rare earth processing industry
Demand	US	Reducing excessive dependence on supply chains and facilitating the expansion of alliance-centered cooperation
	EU	Announced of a plan to stabilize the supply and demand of key raw materials
	JPN	The promotion of a new International Resources Strategy with an Energy Strategy that Includes Rare Metals

For example, the United States is actively reducing its dependence on China for rare earths through initiatives such as REEshore, which was implemented in 2022. Efforts are underway to enhance collaboration with allied nations. Europe has revealed detailed schemes to guarantee a steady supply and demand of primary rare metal raw materials. The proposals consist of four overarching goals and ten actionable initiatives. Japan has also commenced a fresh international resource strategy for 2022 in conjunction with a material strategy aimed at backing its energy industry objectives. These efforts highlight the worldwide acknowledgment of the vital significance of uncommon metals and the need for bespoke policies to navigate the intricate terrain of their production and use.

2.3. International Trade Conflict

Presently, the global scenario surrounding rare metals is entangled in international trade conflicts, where disputes between nations impede the free flow of resources in accordance with their respective interests. This has been exacerbated by the recent global upheaval caused by the COVID-19 pandemic, which has disrupted the intricacies of the global supply chain, leading to adverse consequences for industries in each affected country due to decreased production at importers.

During the era of the COVID-19 pandemic, South Korea encountered substantial challenges in securing a stable raw materials supply. The pandemic-induced reduction in production in China significantly impacted the productivity of major industries in Korea, a reality underscored by the memorable urea water crisis experienced by the nation. Given this intricate backdrop, it becomes imperative for South Korea to formulate strategic countermeasures for establishing a virtuous cycle within the rare metals' industrial ecosystem. Additionally, proactive measures need to be taken to mitigate the risks associated with the supply of rare metals, ensuring resilience in the face of unforeseen challenges in the global supply chain.

2.4.Korea’s Rare Metal Industry Development

2.4.1 'Strategy of Rare Metal Industry Development 2.0'

Against the backdrop of the current international landscape, the Korean government introduced the 'Strategy of Rare Metal Industry Development 2.0' in 2021, signifying a pivotal initiative. This strategic framework is underpinned by three overarching policy objectives: 'Nurturing Core Companies,' 'Establishment of a Stable Rare Metal Supply Chain,' and 'Securing Resources.' To effectively realize these goals, the Korean government has embarked on a multifaceted approach encompassing the establishment of a resilient resource supply system, active support for rare metal companies, and the creation of a robust industrial development promotion system at the governmental level.

Fig. 1 shows the detailed strategy for 'Strategy of Rare Metal Industry Development 2.0' The strategic imperative of nurturing core companies underscores the government's commitment to fostering the growth and sustainability of key enterprises within the rare metal sector. Simultaneously, the focus on the establishment of a stable rare metal supply chain reflects a strategic orientation toward mitigating risks associated with global disruptions and ensuring a reliable and consistent flow of rare metals critical to various industries.

In addition, the prioritization of resource security highlights an acknowledgment of the geopolitical obstacles and potential vulnerabilities in the supply of valuable minerals. The government's plan involves taking proactive measures to secure and broaden channels of resources, guaranteeing resilience against any external disruptions.

In the pursuit of these objectives, the Korean government is actively implementing a suite of strategies that collectively contribute to the realization of a dynamic and self-sustaining rare metal industry. These encompass the establishment of a robust resource supply system, targeted support mechanisms for rare metal enterprises, and the creation of a conducive environment for industrial development through comprehensive governmental initiatives.

2.4.2. Legal Framework

In 2023, a landmark legislative initiative was introduced by the Korean government in collaboration with the Korea Institute of Industrial Technology, marking the inaugural legislation aimed at fostering the rare metal industry in Korea. This legislative endeavor aligns with the overarching goal of advancing the competitiveness of the Materials·Parts·Equipment system and fortifying the stability of the rare metal supply chain.

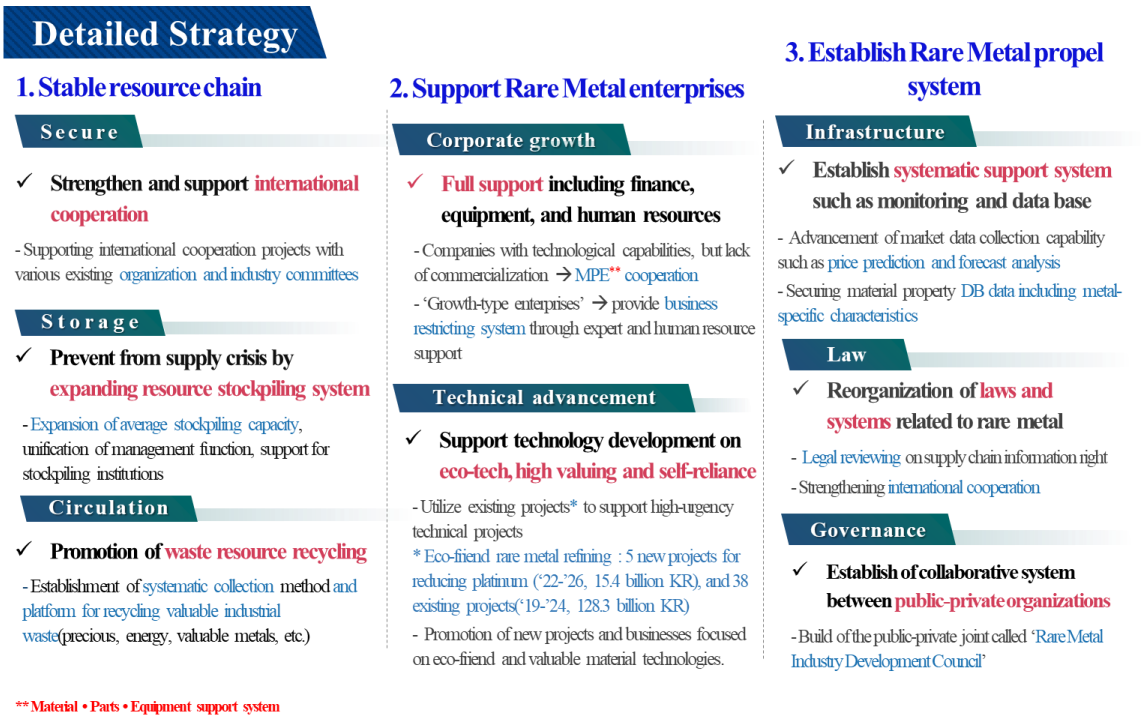

Figure 1 - Strategy of Rare Metal Industry Development 2.0

Recently instituted Actionable Commitments (ACTs) underpin efforts to propel the development of the rare metal industry, focusing on strategic measures to elevate the competitiveness of the Materials·Parts·Equipment system and ensure resilience in the rare metal supply chain. Specific details, including promulgation dates and identification numbers, elucidate the nuances of these commitments.

The legislative landscape witnessed a notable expansion with the introduction of new articles, namely Articles 37-2 and 37-3, complemented by their associated Enforcement Decree and Enforcement Rule. The motivation behind this legislative enactment is rooted in the commitment to periodically formulate policies every five years, fostering an environment conducive to nurturing and supporting companies integral to the rare metal industry.

Article 37-2 specifically addresses the formulation of policies designed to bolster the competitiveness of the rare metal industry, while Article 37-3 focuses on the establishment and operation of the National Rare Metal Center. Designated as the most fitting national research institute, the Korea Institute of Industrial Technology (KITECH) assumes the pivotal role in these legislative provisions. The Ministry of Trade, Industry, and Energy (MOTIE) officially designates KITECH as the National Rare Metal Center, reflecting its strategic significance.

In conformity with this legislative development announced last June, plans are underway for a signboard ceremony at the Korea Institute of Industrial Technology in December of the same year, formally designating it as the National Rare Metal Center. This legislative framework serves as a comprehensive strategy to cultivate and sustain the rare metal industry, addressing the evolving needs of both domestic and global industrial landscapes.

2.5.Overview of Korea's Rare Metal Industry

Figure 2 provides an overview of Korea's rare metal industry, focusing on three key categories that have recently garnered attention due to supply and demand dynamics in the country. This exposition delves into three critical categories of rare metals that have recently gained prominence due to evolving supply and demand dynamics in Korea. The focal areas include rare earth metals pivotal for electric vehicles, refractory metals crucial for semiconductors/displays, and cathode materials essential for secondary batteries.

Commencing with the rare earth category, noteworthy Korean enterprises such as Hyundai and Kia have successfully commercialized motor parts for electric vehicles. Despite these accomplishments, a prevailing challenge lies in the lack of localized production for rare earth alloys and magnetic materials, integral components for electric vehicle motors [[16], [17], [18], [19], [20]]. Consequently, Korea has initiated research endeavors to produce

rare earth metals and their alloys, either sourced from imported rare earth oxides or domestically generated scraps.

Transitioning to the domain of high-melting-point metals, conventionally employed as structural alloys or additives for steel materials, these metals have found extensive application in the semiconductor industry. Korea currently relies entirely on imports of ultra-high-purity metals, sourcing from companies like Mitsui in Japan, Honeywell in the US, and KFMI in China. To enhance self-sufficiency, collaborative efforts between KITECH and industry partners are underway to develop technology for the commercialization of ultra-high-purity metal manufacturing. Recent achievements include the successful production of commercial-grade ultra-high-purity metal, with subsequent technology transfer to domestic companies.

The third category concerns secondary batteries, with LG Energy Solutions and Samsung SDI being prominent contributors to 35% of the world's annual manufacturing capacity. Nevertheless, Korea only possesses a paltry 0.5% of corresponding precursor manufacturing capacity. Despite domestic lithium, cobalt, or nickel deposits being absent, Korea has a substantial amount of scraps and process by-products, presenting a feasible opportunity for recycling. Sungil Hitech, based in Korea, is acknowledged for its world-leading technology in the recycling of secondary batteries, and is actively expanding its production. However, the current recycling capacity amounts to only a fraction - approximately 1/10 - of the imported raw materials necessary for secondary batteries in Korea, highlighting the need for more recycling companies to meet demand.

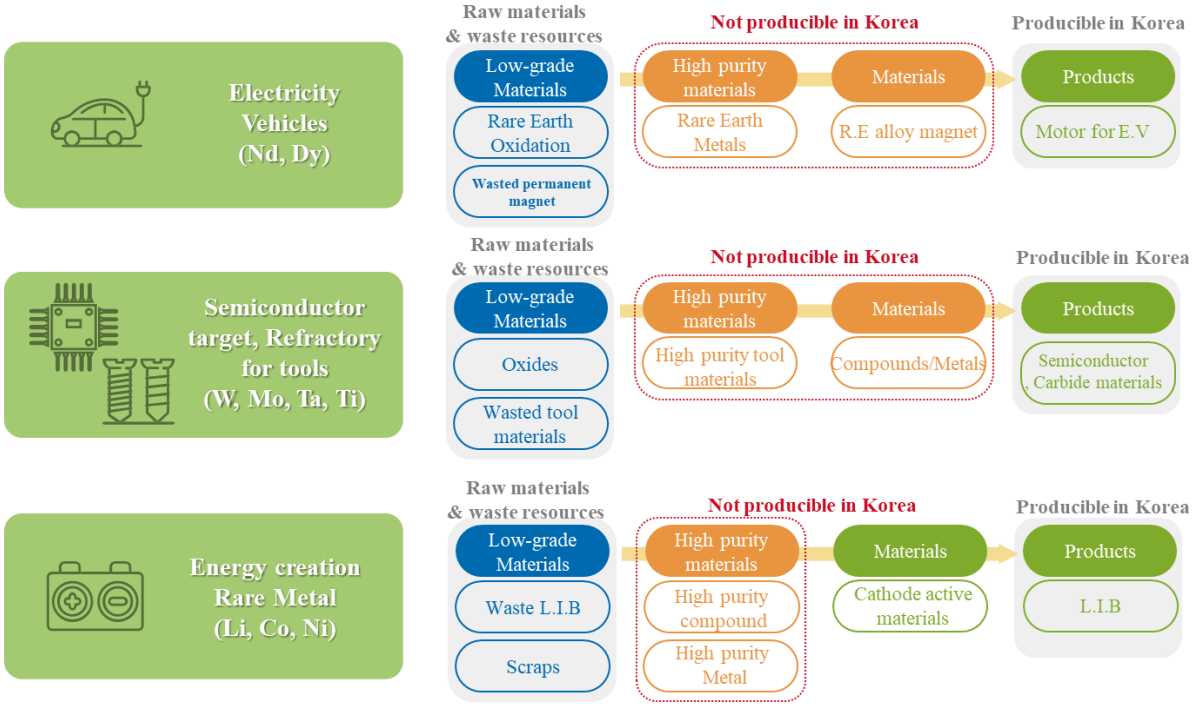

Figure 2 - Overview of Korea's rare metal industry

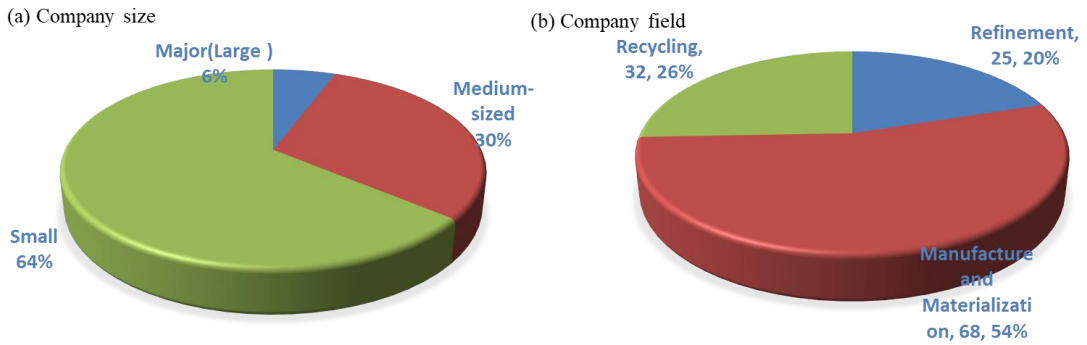

Figure 3 - Current survey results of 125 companies related to rare metal

Figure 3 illustrates a graph that surveys the size and fields of Korean companies in the rare metal industry. The study, which focuses on the rare metal sector, provides valuable insights into 125 companies operating in Korea. These entities are actively involved in rare metal-related activities, either by directly producing rare metals or by developing intermediate goods in this field. It is essential to highlight the significance of rare metals in the Korean economy, as these metals are critical components in various high-tech products.

Notably, of the 125 surveyed companies, 64% are small enterprises that may have difficulty meeting the demands of larger entities such as Samsung and LG. In light of this situation, the government has formulated policies with the objective of advancing and bolstering small-scale businesses. It is significant to note that KITECH assumes a critical position in directing its backing towards these smaller firms, conforming to state initiatives.

Building on existing policies and legislative frameworks, KITECH seeks to enhance the presence of recycling and refining firms in the rare metal industry. The primary aim is to promote the development of technologies that are essential for these companies, promoting sustainable growth and innovation within the rare metal sector in Korea.

In recent times, the international landscape has undergone significant transformations marked by events like Japan's export restrictions, the US-China trade war, and the global impact of COVID-19. Within this dynamic environment, South Korea encountered fluctuations in supply and demand, underscoring the critical importance of securing raw materials for the nation.

Recognizing the imperative of a stable resource supply foundation and the expansion of technological capacities in the Rare Metal industry, there is a pressing need to enhance recycling and refining technologies. This strategic endeavor aims not only to fortify the resilience of the industry but also to contribute to the establishment of a circular rare metal industrial economy. By fostering a circular structure, Korea seeks to ensure the sustainable utilization and circulation of rare metals, mitigating supply chain vulnerabilities and enhancing its position in the global rare metal landscape.

3. Conclusions

This paper sheds light on the current state of Korea's rare metal industry, highlighting its global context, supply and demand dynamics, and government strategies. It emphasizes the importance of international cooperation, policy adjustments, and technological advancements to ensure a sustainable and secure rare metal supply chain.

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Кореядағы «Сирек металдар өнеркәсібінің» жағдайы

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ТҮЙІНДЕМЕ

Бұл жұмыс Кореядағы сирек металдар өнеркәсібін терең зерттеп, оның сипаттамасын, жіктелуін, сұраныс пен ұсыныс динамикасын, халықаралық сауда мәселелерін және үкіметтің стратегиялық бастамаларын қарастырады. Зерттеу сирек металдардың жаһандық маңыздылығын, олардың біркелкі емес таралуынан туындайтын қиындықтарды және елдердің, соның ішінде Кореяның осы проблемаларды стратегиялық тұрғыдан шешуге міндетті екенін көрсетеді. Сондай-ақ мақалада Кореяның соңғы заңнамалық және саяси негіздері зерттеліп, Кореяның өнеркәсіптік технологиялар институтының (KITECH) сирек металл өнеркәсібін дамытудағы рөлі атап өтіледі. Сонымен қатар, мақалада электр көліктеріне арналған сирек жер металдары, жартылай өткізгіштер/дисплейлер үшін отқа төзімді металдар және екінші реттік батареяларға арналған катодты материалдар сияқты негізгі салаларға тоқталып, Кореяның сирек металдар өнеркәсібінің қазіргі жағдайы талқыланады. Қорытынды бөлімде сирек металдардың қалдықсыз өнеркәсіптік экономикасын құру үшін қажетті технологиялық жетістіктерге, қайта өңдеуге баса назар аударылады.

Түйін сөздер: сирек металдар, отқа төзімді металдар, жартылай өткізгіш/дисплей және катодты материалдар, экономика, өнеркәсіп.

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Состояние дел в «индустрии редких металлов» в Корее

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АННОТАЦИЯ

В этой статье представлено углубленное исследование индустрии редких металлов в Корее, рассматривается ее определение, классификация, динамика спроса и предложения, международные торговые проблемы и стратегические инициативы правительства. Исследование подчеркивает глобальное значение редких металлов, проблемы, связанные с их неравномерным распределением, а также необходимость для стран, включая Корею, решать эти проблемы стратегически. В документе также подробно рассматривается недавняя правовая и политическая база Кореи, подчеркивающаяся роль Корейского института промышленных технологий (KITECH) в развитии промышленности редких металлов. Кроме того, в нем обсуждается текущее состояние индустрии редких металлов в Корее, освещаются такие ключевые области, как редкоземельные металлы для электромобилей, тугоплавкие металлы для полупроводников/дисплеев и катодные материалы для аккумуляторных батарей. В заключительном разделе подчеркивается необходимость технологических достижений, переработки и переработки для создания безотходной промышленной экономики редких металлов.

Ключевые слова: металлы, тугоплавкие металлы, полупроводниковые/дисплейные и катодные материалы, экономика, промышленность.

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Earth Sciences

Experience of coalbed methane extraction in the Karaganda coal basin

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ABSTRACT

This article discusses the issues of ensuring the safe conduct of mining operations in coal mines. Ensuring the safety of coal industry workers is an urgent problem today. The gas content of the layers increases with the depth of their occurrence and is a deterrent factor in the extraction of minerals. Sudden methane emissions can provoke a large number of human casualties, financial losses, and other consequences. In recent years alone, such accidents have claimed more than 157 human lives in the mines of the Karaganda coal basin. However, by solving this important problem, you can get associated gas. It is not easy to reduce the gas content using existing degassing technologies. The formations have almost zero gas permeability and low gas output at the current depths of their development. That is why it is necessary to have an impact on the coal seam as early as possible in order to ensure the release of methane. This process will make it possible to obtain associated gas, which can be used for the needs of industry or the national economy. As a result, reducing the gas content of coal seams will reduce the risks of mining operations and increase labor safety.

Keywords: safety, coal mines, coal seams, methane, sudden emissions.

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Introduction

Investigating the issue of methane production, it can be concluded that the Karaganda coal basin is essentially a coal and gas deposit. Estimating methane reserves from various sources, it can be seen that they are comparable to natural gas reserves. From 1 to 4 trillion is concentrated in the Karaganda coal basin alone, m^3 of gas at a depth of up to 1800 m. At local enterprises, approximately 500 million m^3 of gas is extracted from the ground annually by means of degassing. At the same time, only 15% of this volume is used as fuel, the rest replenishes the emission indicators into the environment. Meanwhile, methane is 20-40 times more efficient than other gases. It destroys the ozone layer and absorbs infrared solar radiation. Comparing the anthropogenic increase in the concentration of greenhouse gases, it can be seen that the annual accumulation of methane in the atmosphere is 1-2% [1]. This indicator exceeds the intensity of the accumulation of other gases. However, methane is a good unconventional energy carrier. It can also be considered as a component of the fuel and energy raw material base of the country. For example, for the chemical industry, methane of coal genesis will serve as a valuable raw material in the production of ammonia, methanol, acetylene, protein mass, etc. [2].

Experimental part

Methane in coal seams is not in a free state. This is the main feature that must be considered when developing methane coal deposits. The mining technology is influenced by the heterogeneity of deposits, the complexity of geological conditions of the formation, stress state of coal rocks. Meanwhile, only a part of methane is in the free state in coal seams. A large proportion of it, up to 90%, is still in a sorbed state. In order to release at least part of it due to the pressure gradient, the formation is dried before the start of gas production [[3], [4]]. This allows you to change the pressure and promotes the flow of methane gas to the well. The efficiency of the development of methane-coal deposits depends on the filtration properties, density of coal rock, and gas content in the formation, because gas is contained even in a low-permeable coal matrix, and its movement is carried out through a system of microcracks Figure 1.

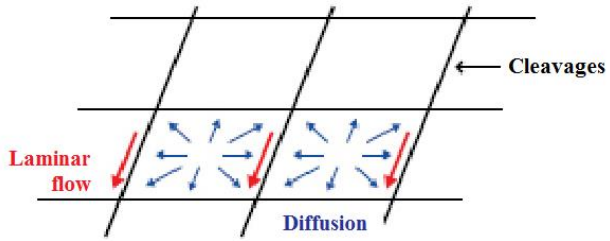

Figure 1 - Gas flow in the coal column

The amount of gas contained in the formation depends on the type of coal, reservoir pressure, and host rocks. Methane desorption is described by the Langmuir isotherm, which demonstrates the ability to contain gas with a coal matrix in accordance with reservoir pressure at a constant temperature:

$$V = V_L \frac{P}{P + P_L}, \quad (1.1)$$

where V is the volume of the adsorbed gas at normal temperature;

Tn = 0 °C and pressure, per ton of coal;

V_L is Langmuir's volumetric constant (the limiting amount of gas that can be in an adsorbed state on a unit surface of coal at infinite pressure);

P_L is the Langmuir pressure constant (corresponds to the pressure at which half of the volume of VL is in the adsorbed state);

P is the reservoir pressure [[5], [6]].

Coal methane reserves in reservoirs are often calculated by multiplying the mass of coal by the average methane content in the counting block [7].

$$Q_m = M_{av} \cdot m, \quad (1.2)$$

where Q_m is the initial methane reserves in the counting block, m^3;

M_{av} - average methane content per block, m^3/t of coal;

m is the mass of coal in the counting block, t [8].

When assessing and calculating methane gas reserves, certain blocks are first identified that have a stable consistency of reservoir capacity, approximately homogeneous tectonic disturbance, ash content, methane content, and permeability. The average methane content for the counting block is determined taking into account the volume of coal within the boundaries of the allocated block. In general, the calculation of coal methane reserves is a symbiosis of the method of geological blocks, which is used to calculate coal reserves and the volumetric method of calculating gas reserves. It is worth noting that the natural methane content depends on a large number of parameters. It is necessary to take into account the depth of the formation, the power of gas weathering, the degree of coal metamorphism, temperature, pressure, and many other parameters. As a result, it turns out that the natural methane content is an arithmetic mean value with its uniform increase in depth and a weighted average value with its uneven increase in the area of the calculation block [[9], [10]].

The extraction coefficient often depends on the technology of gas recovery intensification, filtration characteristics of coal seams, the grid of production wells, the cost of produced gas, and other factors. The recovery coefficient can also be a fixed value if the experience of developing this type of deposit is not great and it is not possible to determine this indicator by other methods. In this case, based on experimental studies, the value is taken from experience and by analogy with other deposits.

The calculation of methane reserves should begin with the justification of the boundaries and the definition of the objects of the calculation of reserves, to assess the quality of coal and geological and commercial characteristics of productive layers, to determine changes in methane content in depth and area, to identify the forecast of mining opportunities [[11], [12], [13]].

The counting block schematically shown in Figure 2. should have the same degree of exploration and study of parameters, a homogeneous geological structure or approximately the same degree of complexity of the structure, consistency of the conditions of occurrence of the studied block, similarity of mining and technological conditions of its development.

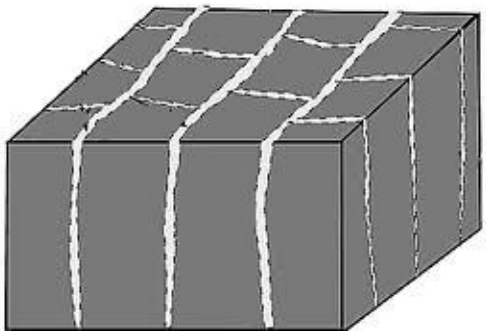

Figure 2 - Graphical model of the counting block

With the use of interpolation and extrapolation algorithms, a geometrically correct network is constructed using data from horizon plans, the points of intersection of formations with wells, and the coordinates of the points of formation exits to the surface.

The size of the cells or equilateral rectangles depends on the degree of study of the object, the heterogeneity of its structure, and the distance between the wells.

Methane production is carried out from a group of layers, which is why the calculation of the main parameters can be carried out in total for all layers within the counting block.

The distribution of properties, such as power, ash content, density, humidity, and methane content, is also an important step in building a digital model.

The depth of occurrence and the degree of metamorphism affect the indicators of methane content. That is why traditional methods of interpolation and extrapolation do not always give a positive result. According to the curvilinear law, the methane content of coal seams increases with increasing depth. Up to 300-400 m, the most intense increase in the indicator occurs. Then its growth slows down to a depth of 800-1000 m. As a result, the methane content reaches the limit values characteristic of each stage of metamorphism.

The main regularities of the natural methane content of coals in the methane gas zone can be described by the following equation:

$$M = A - \frac{B}{(C - H)}, \qquad (1.3)$$

where M is the methane content, m^3/t; A is the maximum methane capacity of coal at the maximum depths of the explored area m^3/t; B and C are empirical coefficients; H is the depth of the formation, m.

The geological process of coal formation occurs together with the formation of methane. Some part of it just remains in the thickness of the coal seam until the moment of its extraction. The development of alternative energy sources allows us to consider this gas as a new mineral. If earlier it was a source of increased danger, now it has also become an energy carrier that can change the prospects for the development of the Karaganda region.

There are at least three boilers operating at the mines of the ArcelorMittal Temirtau Coal Department that produce energy by burning coal mine methane. One installation is located at the Abayskaya mine and two are at the IM mine. Lenin. About 20 years ago, gas equipment with a capacity of 10 Gcal for each boiler unit was developed and installed by the management of "Spets shakhto montazh degazatsiya". This made it possible to significantly reduce the cost of heating the premises. In addition, it has reduced harmful methane emissions into the atmosphere. When gorenje this gas practically does not form by-products. The beginning of degassing works in the Karaganda coal basin was laid back in the mid-1950s. Pilot tests took place at one of the mines in 1961 [14].

The risk of accidents increases with the development of overlying horizons and the transition to lower horizons. For more than half a century of degassing operations at the mines of the Karaganda region, a huge positive experience has been accumulated. It was possible to test more than 10 different technological methods for extracting coalbed methane. Tested: cyclic hydraulic fracturing of formations using gaseous and liquid nitrogen; hydraulic fracturing using hydrochloric acid; hydraulic pulse action using powder pressure generators; hydro-action without well development; pneumohydro-separation of formations; pneumatic action on a water-gas-saturated formation; thermal effect; impact on the formation with chemically active gases; impact on the formation in cavitation mode [15].

155 vertical wells were drilled for research and development work. This made it possible to extract more than 100 million, m^3 of methane. In general, in the basin, the average flow rate was 2045 m^3/day. The accumulated experience in advanced degassing from 1961 to 2017 showed the prospects of this method of reducing the gas content of coal seams. The gas content of the workings was then reduced from 30 to 80% [16].

Another three-stage project for the extraction of coalbed methane was implemented by KazTransGas. During the VI International Mining and Metallurgical Congress, Deputy Director of the Coal Industry Development Department of the Ministry of Energy of Kazakhstan, Council Dambarbayev, said that a methodology for methane reserves and resources in coal seams has already been developed. KSTU has even approved a professional development program for specialists in the field of geological exploration and production of coalbed methane. The work was carried out with the involvement of the companies "Zhumysstroyservice", "Taldykudukgaz", SEC "Sary-Arka" and "Kazgeologiya". Also, the joint venture "Satbayev University" and "ArcelorMittal Gas Production" was established on July 9, 2018. Its goal is the production of methane gas in the Karaganda coal basin, as part of the project on Kazakhstan's transition to a "green" economy and the development of a new energy sector for the extraction of coal methane in the Karaganda region. "Building a full–fledged methane production cluster is not a one-day task," says Chingiz Cherniyazdanov, Managing Director for Innovation at Satbayev University, a member of the Supervisory Board of the joint venture Satbayev University & ArcelorMittal Gas Production. Coal methane degassing and extraction systems are analyzed for their subsequent improvement. The world's highest gas content of coal seams in the Karaganda basin is from 15 to 35 m^3/t. According to preliminary estimates, it contains about 490 billion. m3 of methane at a depth of 1,500 m and about 500-550 billion, m^3 at a depth of 2,000 m [17].

1.4 MW gas generating plant at the mine named after Lenin covers up to 20% of the mine's electricity needs. In addition, it reduces emissions of harmful substances into the atmospheric air compared to coal-fired boilers. According to the company's official website, in 2013, the production of electricity by the methane gas generator of the mine. Lenin was 5,541 MW of methane used 4,029,609 m3. According to the data of the Ministry of Energy of Kazakhstan published in 2015, more than 290 million tons were disposed of from 1996 to 2013, m^3 of methane. This ensured a reduction in CO_2 emissions into the atmosphere by 4 million tons.

Methane is the main greenhouse gas in the activities of mines. Currently, boilers running on this gas are used to heat the air supplied to the mine. Such installations operate at the Shakhtinskaya, Abayskaya, Kostenko, Lenin mines (Figure 3.).

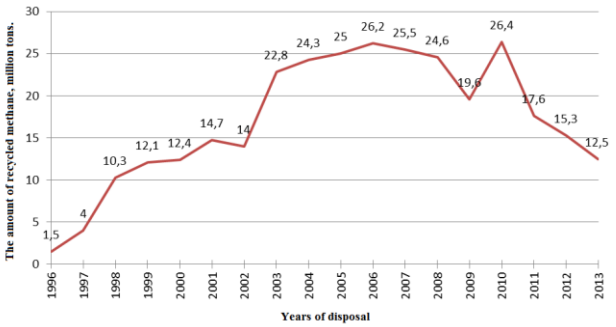

Figure 3 - Utilization of mine methane by gas-generating plants at the Shakhtinskaya, Abayskaya, Kostenko, Lenin mines

The cost of a conventional unit of methane extracted from coal seams is several times higher than natural gas. However, the leaders-gas producers are interested in the development of this industry. That is why representatives of companies from China, Germany, the USA and Poland periodically hold talks on the development of mining technologies and regularly demonstrate equipment for the extraction and processing of mine methane.

Research results and discussion

The geological and economic essence of methane as a mineral can be assessed from two fundamentally different sides. Methane extraction can be carried out by gas fishing, as an independent mineral, without coal mining. Here, the profitability of this production and the availability of a possible consumer of this gas are prioritized. By the way, the technology for controlling gas emission, according to the analysis of statistical indicators, accounts for up to 25% of the costs associated with the extraction of solid fuel.

The need to degass the layers of the Karaganda coal basin is a good factor in the profitability of methane extraction. Reducing the emission hazard and ensuring the gas safety of mining operations are an important criterion of the production process. When considering independent commercial production of methane, the

profitability of this process becomes paramount, which depends on the depth of the formation, gas content, filtration properties and extraction technology.

Methane extraction can be carried out by onshore wells in areas where coal mining does not occur or in areas adjacent to existing mines. It is also possible to organize production on the explored and exploration and evaluation areas, on gas-bearing coal deposits that are not planned for production in the near future, as well as lower horizons inaccessible for coal mining [[18], [19]].

Only a comprehensive study and consideration of all geological factors, as well as the properties of coal, will allow us to determine the efficiency of extraction technology and the profitability of methane gas production as an independent mineral.

Comparing the geological characteristics of the Karaganda basin with foreign ones, it can be concluded that the development of methane extraction projects in the basin areas is promising. Analyzing the data of the geological study of the basin, the Taldykuduk site, located in the southwestern part of the Karaganda syncline, appears to be the primary object for the implementation of the pilot project.

The geological parameters of the Black Warrior basin, one of the largest in the USA, are significantly inferior to the parameters of the Karaganda coal basin. The methane gas content in the Karaganda basin is almost 2 times or higher than the average gas content in the world's largest deposits.

This choice is based on the following indicators:

- the site has the maximum coal content in the Karaganda basin — 9.5%, the total capacity of the coal seams of the Karaganda formation is about 60m;

- the main part of the coal seams is sustained in area and capacity, they have a distribution outside the selected area within the entire basin, and the maximum capacity of a separate coal seam reaches 12.4 m;

- the site has a large number of consonant surges with displacement amplitudes up to 400 meters and regional folded structures of syncline and anticline type with amplitudes up to 200 m and a length of up to 4-5 km, which can be structural traps of methane. In this regard, it can be assumed, in addition to cleavage cracks, the development of tectonic fracturing and wide crushing zones in the locks of folds and at the displacers of discontinuous faults, as well as in general in the coal-containing massif, which will serve as additional channels for methane drainage.;

- coals of the brand from QL to OS assume a high sorption and gas-generating capacity. The vitrinite content in the range of 40-91% provides intense microcracking and gas permeability of the coal pack;

- the adjacent areas of the coal basin, which do not differ much in geological structure, represent a prospect for expanding a possible large-scale project to extract coalbed methane, increasing the resource base several times. The total area possible for the development of a promising large-scale project exceeds 120 km^2 with a projected volume of coalbed methane of about 100 billion m^3.

Brown coals are characterized by low gas content and high permeability. High gas content and low permeability - anthracites. For the extraction of methane, the most promising are the coals of the middle stages of metamorphism, which have moderate gas content, are intensely fractured, and as a result, are more permeable.

As in an unconventional reservoir, fluid filtration occurs mainly through cracks in the coal seam. The capacity for methane is macro-, meso- and micropores, although their indicator is usually insignificant in the total reservoir capacity. The change in the capacitance and filtration characteristics occurs in the process of coal metamorphism from brown to anthracite. As a result, brown coals are characterized by the lowest marginal gas capacity – 5-8 m3/t. Anthracites have the opposite situation, where the maximum gas capacity can reach 45-47 m3/t. Meanwhile, the size of pores and voids varies widely in coals.

The pore indices in anthracites are not large, meanwhile, they increase in the process of metamorphism. So hard coals have average numbers, and brown coals have the greatest value. Fracturing and geomechanical conditions characterize the filtration characteristics of coal seams.

The morphology of the formation, its hypsometry, as well as the qualitative indicators of coal, methane content, and permeability, are determined at the prospecting, evaluation, and exploration stages of the preparation of a methane coal deposit. These data are obtained by drilling structural and parametric wells, as well as by laboratory examination of the coal core.

Methane content is associated with porosity. Under the same pressure conditions, a coal seam can hold much more gas than the same volume of

sandstones. When water is removed, the formation matrix shrinks, which contributes to the formation of a system of orthogonal cracks – cleavage. The free pore volume is often filled with water. Its pumping leads to a decrease in reservoir pressure. As a result, methane trapped in micropores is released. This gas spreads in all directions spontaneously through the existing cleavage cracks. The basis of the mechanism of gas movement is a system of natural fracturing.

Hydraulic fracturing is used to intensify methane release. As a result, it is possible to open existing cracks and form new ones. This leads to an increase in the productivity of the well. In addition, the use of a wedging agent allows them to fill cracks and does not allow them to close. All this leads to an improvement in the permeability conditions, which allows methane to be released and penetrate the well [20]. This is clearly shown in Figure 4.

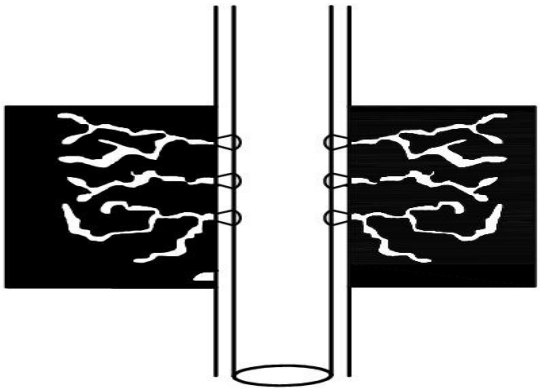

Figure 4 - Schematic representation of the process of crack formation around the borehole after applying the method of hydraulic fracturing of the coal seam

Horizontal drilling can also be a way to intensify gas recovery. The method is effective in conditions of a highly anisotropic reservoir. In this case, the hydraulic fracturing technology will be less successful. Meanwhile, cluster horizontal drilling can contribute to an increase in the flow rate of methane from the well. Important factors in this case are the direction and stability of the well. This is confirmed by the long-term experience of Australian drillers.

The intensity of gas recovery can also be enhanced by the method of pneumatic-hydrodynamic action on the formation. In this case, cavities form in the thickness around the borehole and cracks near them. This is clearly shown in Figure 5.

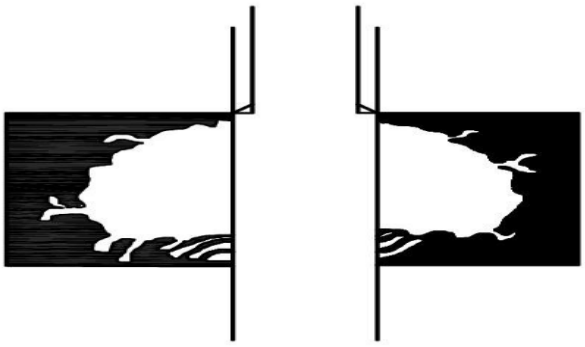

Figure 5 - Schematic representation of the process of formation of cavities and cracks after the application of the method of pneumatic-hydrodynamic action

This method consists of cyclic pulsation due to pressure when a water-air mixture is introduced into the borehole. This leads to the collapse of coal around the borehole, and the formation of cracks and cavities.

Conclusions

Kazakhstan has significant potential for the extraction and exploration of methane coal deposits. Up to a depth of 1500 meters, methane resources in the Karaganda coal basin amount to 490.47 billion m^3. This makes it possible to consider methane gas as a good alternative to traditional natural gas because its content in the Karaganda basin varies from 80 to 98%. Meanwhile, the Ekibastuz coal basin has been less studied for methane reserves, and there is no information at all on the remaining deposits, which indicates that they are poorly studied. There are deposits in Kazakhstan that occupy significant areas and concentrate coals with a high gas density. That is why it is worth carrying out a number of research works to clarify the available volumes of methane. Its extraction from coal seams is considered a more expensive process than the extraction of traditional gas. The need to create channels effects in the coal seam for the movement of methane, through hydraulic fracturing. For example, the gas contained in sandstone independently comes to the surface due to reservoir pressure.

Having analyzed the conditions of geological occurrence of methane in various countries of the world, we can conclude about the economic efficiency of extracting this gas in the Karaganda coal basin. The experience of other countries demonstrates the extraction of methane under similar conditions of occurrence of coal seams.

The prospects of the sites can be determined by the following geological and technological factors:

- the gas capacity should be more than 8-10 m3/t and grow with the deepening of the formation.

- total reservoir capacity - 8-10 m or more;

-petrographic composition of coals - vitrinite;

- the depth of assessment is limited by methods and technologies of methane extraction. At the present time, it is 300 - 1800 m. Meanwhile, 500 - 1200 m is considered the most favorable;

- the scale of resources affects the determination of the period of operation of the field for gas production. Promising can be considered with deposits of more than 50-75 MW. m^3 at a mining site or site.

- resource density evaluates the productivity of reservoir groups. A concentration of more than 150-200 million m^3/km^2 is considered favorable;

- ash content of coals up to 25-30 %;

-the degree of metamorphism – coals from the group G, W, K, OS, T.

-fracturing and fragility. Coals of the middle stage of metamorphism.

-in the tectonic plan of occurrence, the best option would be flat layers, with the angles of incidence of folds in the range of 30-40 degrees.

The fields of mines operating in the Karaganda region can be considered a source of cheap gas, which allows for the reduction of the gas content of formations and improves the safety of mining operations, provided that methane is extracted in advance.

The flow rate of wells after the application of gas recovery intensification technologies should be more than 5-10 thousand m^3/day, with an increase in this indicator in the active phase of development to 20-40 thousand m^3/day.

Industrial methane production, in areas with appropriate indicators, should be based on the desorption of gas from the surface of coal. A sharp pressure relief contributes to the flow of methane into the well through the system of cracks formed after the intensification methods.

Government support and subsidies for this process have an important impact on the development of methane production on an industrial scale, as evidenced by the experience of countries successfully producing coal methane.

The existing infrastructure has a restrictive impact on methane production in a number of countries – low throughput of gas pipelines and export terminals, technologically complex and expensive drilling, and lack of qualified personnel. [[21], [22]].

Conflict of interest. On behalf of all authors, the corresponding author states that there is no conflict of interest regarding others.

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Қарағанды көмір бассейніндегі көмір қабаттарынан метанды өндіру тәжірибесі

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ТҮЙІНДЕМЕ

Бұл мақалада көмір шахталарында тау-кен жұмыстарын қауіпсіз жүргізуді қамтамасыз ету мәселелері қарастырылған. Көмір өнеркәсібі жұмысшыларының қауіпсіздігін қамтамасыз ету бүгінгі таңда өзекті мәселе болып табылады. Қабаттардағы газ мөлшері тереңдеген сайын артады және бұл тау-кен өндірісінде тежегіш болып табылады. Метанның оқыс шығарындылары адамдардың құрбан болуына, қаржылық шығындарға және басқа жағымсыз әсерлерге әкелуі мүмкін. Тек соңғы жылдары мұндай апаттар Қарағанды көмір бассейнінің шахталарында 157-тан астам адамның өмірін қиды. Осы маңызды проблеманы шешу арқылы ілеспе газ алуға болады. Қолданыстағы газсыздандыру технологияларының көмегімен газдың мөлшерін азайту оңай емес. Қабаттар іс жүзінде нөлдік газ өткізгіштікке

ие және олардың мөлшері қазіргі тереңдіктерде аз болуы мүмкін. Сондықтан метанның бөлінуін қамтамасыз ету үшін көмір қабатына мүмкіндігінше ертерек әсер ету қажет. Бұл процесс өнеркәсіптің немесе халық шаруашылығының қажеттіліктері үшін пайдаланылатын ілеспе газды алуға мүмкіндік береді. Көмір қабаттарындағы газдың мөлшерін төмендету арқылы тау-кен жұмыстарын жүргізу тәуекелділіктері азаяды және еңбек қауіпсіздігі артады.

Түйін сөздер: қауіпсіздік, көмір шахталар, көмір қабаттары, метан, оқыс шығарындылар.

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Опыт добычи метана угольных пластов Карагандинского угольного бассейна

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АННОТАЦИЯ

В данной статье рассмотрены вопросы обеспечения безопасного ведения горных работ на угольных шахтах. Обеспечение безопасности работников угольной промышленности на сегодняшний день является актуальной проблемой. Газосодержание пластов увеличивается с глубиной их залегания и является сдерживающим фактором при добыче полезных ископаемых. Внезапные выбросы метана могут спровоцировать большое количество человеческих жертв, финансовых потерь и других последствий. Только за последние годы подобные аварии унесли более 157 человеческих жизней на шахтах Карагандинского угольного бассейна. Однако, решив эту важную проблему, можно получить попутный газ. Снизить показатель газосодержания с помощью существующих технологий дегазации непросто. Пласты имеют практически нулевую газопроницаемость и низкую газоотдачу на текущих глубинах их разработки. Вот почему необходимо как можно раньше оказать воздействие на угленосный пласт, чтобы обеспечить выброс метана. Этот процесс позволит получать попутный газ, который может быть использован для нужд промышленности или народного хозяйства. В результате снижение газосодержания угольных пластов снизит риски ведения горных работ и повысит безопасность труда.

Ключевые слова: безопасность, угольные шахты, угольные пласты, метан, внезапные выбросы.

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Earth sciences

Thermal maturity of organic matter and type of kerogen of Mesozoic sediments, Aryskum depression

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Annotation
This work is devoted to the study of the oil and gas source potential of the Mesozoic deposits of the Aryskum depression of the South Turgay oil and gas basin and aims to study the features of the geological structure, determine the facial-genetic type and degree of maturity of organic matter. Geochemical methods play an important role in assessing oil and gas source potential, one of which is pyrolytic core analysis to determine the type of organic matter and thermal maturity of the studied rock material samples. To achieve this goal, the results of pyrolytic analysis of stone material from Neocomian and Jurassic deposits were used. Analysis of geological and geophysical materials made it possible to trace the pattern of distribution over the area of oil and gas-bearing sandy layers and the underlying clay layers with high insulating properties in the Aryskum horizon. The results obtained show that the total organic carbon content ranges from 0.47 to 1.41 wt%. To establish the type of kerogen and its position relative to the zones of oil and gas formation, the Van Krevelen diagram was used in the coordinates of atomic ratios of the elemental composition of kerogen and its modification for pyrolytic data, indicating that the kerogen of the studied samples is a mixture of types I, II and III, facies-genetic the type of organic matter of which belongs to humic, humic-sapropelic, and the sedimentation conditions are coastal-marine environment in moderately reducing conditions.

Keywords: Aryskum depression, South Turgay oil and gas basin, oil and gas content, organic matter, hydrocarbons, type of kerogen

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Introduction

The question of the source of hydrocarbons finds wide practical application in predicting the oil and gas potential of the subsurface, in solving which it is difficult to overestimate the role of modern methods of geochemical research [1]. The pyrolytic method is a widely used and highly valued tool used by petroleum geochemists, the purpose of which is to assess the oil and gas generation potential of rocks, the type of kerogen, and the thermal maturity of organic matter, where stepwise heating modes of core samples are used. The samples are initially pyrolyzed in an inert atmosphere and then oxidized in an oxidizing medium. The method of rock assessment in one full cycle of analysis allows us to obtain several important indicators related to the formation of oil, such as the amount of free hydrocarbons present in the sample, the residual content of hydrocarbons, the TOC content, the level of thermal maturity of the sample, the amount of chemically active

organic matter, the presence of carbonate minerals and the quality/type of organic matter present in the samples [[2], [3]].

It is known that the characteristics of the parent rocks are evaluated according to the level of thermal maturity and the amount of organic matter and the type of kerogen [[4], [5], [6], [7], [8]]. Thus, the total organic matter content (TOC) is estimated by the amount of organic matter in a rock sample. Geochemical parameters such as hydrogen, oxygen indices (HI, OI), temperature (T_{max}) and productivity index (PI) obtained as a result of Rock-Eval pyrolysis allow us to evaluate the type of kerogen and determine the thermal maturity of organic matter [[6], [7], [8], [9], [10], [11]].

The purpose of this work is to determine the facies-genetic type and degree of maturity of organic matter, to achieve which the following tasks were solved (1) to study the history of the formation of the tectonic structure of the South Turgay oil and gas basin, the regularities of the distribution of hydrocarbons; (2) assessment of the oil-generation potential of Jurassic and Neocomian deposits, the type of kerogen and thermal maturity by pyrolytic method of core samples.

Geological settings. The South Turgay oil and gas basin, with a total area of about 60 thousand square kilometers, is a large linear structure of the northwestern strike and represents the southeastern margin of the Turgay depression (Figure 1). According to the thickness of the sedimentary cover, the peculiarities of tectonic and lithological-stratigraphic characteristics, the basin belongs to the intracontinental. The oil and gas potential of the basin was established in 1984 by the discovery of the Kumkol deposit. Intensive geological exploration began to be carried out since the late 1970s.

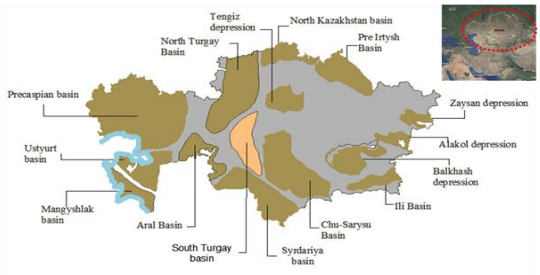

Figure 1 - Map of the sedimentary basins of Kazakhstan [12]

The basin is divided into three structural floors such as characteristic structural and material features of microcontinents. The lower floor is a crystalline foundation consisting of Archean-Lower Paleozoic metamorphic gneisses and various shales that occur at adjacent elevations and are opened by some wells inside and near the edge of the syneclise [13]. The Middle-quasi-platform complex of the Middle and Upper Paleozoic consists of intermittent Devonian, Carboniferous, and Permian deposits up to 1.5-2 km thick. In accordance with the drilling and seismic survey materials in the South Turgay oil and gas basin, there is a wide development of quasi-platform formations of the Upper Paleozoic of considerable power, the distribution of which on its individual geostructural elements is quite complex. The upper platform cover is represented by sedimentary deposits of Triassic-Jurassic, Cretaceous-Miocene, and Pliocene-Quaternary age [14].

The upper structural floor, the most studied by geophysical methods and deep drilling, includes all the sediments of the Mesozoic and Cenozoic and splits into two tiers: the lower-rift, the upper-epirift.

According to the hypsometric position of the foundation, three large structures are distinguished: the Zhylanshik and Aryskum depression with the Mynbulak uplift separating them, complicated, in turn, by structural elements of lower orders.

All the identified deposits are confined to the Aryskum depression, the tectonic characteristics of which are covered in detail in the works of Abdullin A.A., Daukeev S.Zh., Kuandykov B.M., Zholtaev G.Zh., Nazhmetdinova A.Sh., Puzanova I.V., Sapozhnikov R.B., Votsalevsky E.S., Bulekbaev Z.E., etc.

The Aryskum depression is characterized by a complex tectonic structure, has fairly well-defined raised horst–anticlines and lowered foundation blocks - graben-synclines (Figure 2) in length from 100 to 200-250 km and in width up to 25-50 km of north-westerly strike on the western side of the depression, and northerly direction on the eastern side, expanding in width to the northern part of the depression [15].

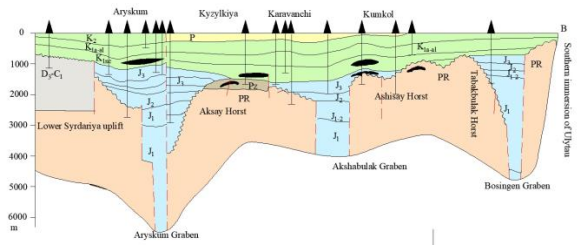

Figure 2 - Geological section of the Aryskum depression [15]

Within the deflection, the Aryskum, Akshabulak (Besoba-Terensai), Sarylan, Bozingen, Daut and Zhinishkekum graben - synclines are distinguished, which are separated by Aksai, Aschisai and Tabakbulak horst - anticlines.

Hydrocarbon systems and deposits. One of the main oils and gas bearing complexes in the section of the Aryskum depression are sandy-clay Mesozoic deposits, within which the Lower Cretaceous (Aryskum horizon), Middle-Upper Jurassic, and Lower Jurassic complexes are distinguished, in addition to which the Upper Paleozoic promising oil and gas complex is also distinguished [16].

The prospects of pre-Mesozoic formations are based on the presence of manifestations of hydrocarbons from weathered basement rocks up to industrial oil inflows (Kyzylkia, Karavanchi, Kenlyk).

Upper Jurassic and Cretaceous sandstones and siltstones deposited in delta and river facies are the main reservoirs in which most of the oil discovered to date is distributed [17].

Within the Jurassic complex, a series of local and zonal clay fluidopores are distinguished [18].

Chalk deposits in the South Turgay oil and gas basin are ubiquitous and are overlain, in turn, by younger Paleogene-Quaternary sediments. They are represented by all age subsections, the deposits are facially sustained over a large area, which allows them to be correlated fairly confidently by logging wells drilled without core sampling.

Oil-producing complexes-sources of hydrocarbons. The forecast hydrocarbon resources are determined based on the reconstruction of the entire complex of natural processes that cause the formation of oil and gas from organic substances of oil and gas mother rocks [19].

Within the South Turgay oil and gas basin, there are effective oil-producing strata of Jurassic sediments, where graben-synclines are associated with lake sedimentation conditions, whose hydrocarbons migrated and accumulated in nearby deposits of the Jurassic and Cretaceous complexes. For the migration of hydrocarbons into Paleozoic traps, sedimentation occurred by overflows from graben along carbonate rocks. Bitumen was found in Devonian carbonate rocks that came to the surface within the Greater Karatau, which indicates the effective migration of hydrocarbons along this complex over a long distance [[20], [21]].

The experimental part

The pyrolytic method on the analyzer of the initial rocks of the samples of stone material of the Kumkol formation of the Upper Jurassic (J_3km) and the Aryskum formation of the Lower Cretaceous (K_1nc1ar) from the wells of the Aryskum depression of the South Turgay oil and gas basin allowed to determine the type of kerogen, hydrocarbon potential and the stage of maturity of organic matter, the geochemical parameters of which are presented in the table below.

Discussion of the results

Generation potential. The results of the study show that the concentration of total organic carbon (TOC) ranges from 0.47 to 1.41%, the parameter S_2 varies from 1.6 to 3.1 mg HC/g of rock in the samples of the Lower Cretaceous and from 1.1 to 9 mg HC/g of rocks of the Kumkol formation of the Upper Jurassic, where values below 2.5 have a low (poor) potential, and above 6 have a good (rich) potential.

Table 1 - Geochemical characteristics of pyrolytic analysis of deposits of the Aryskum depression

Formation	Depth	TOC	S_1	S_2	S_1+S_2	T_{max}	HI	OI	PI
K_1nc_1ar	1682.9	0.52	0.97	1.6	2.57	413.02	298	198.1	0.385
K_1nc_1ar	1686.4	0.53	0.57	2.2	2.77	437.49	417	141.5	0.205
K_1nc_1ar	1687.43	1.12	2.05	3.1	5.15	445.16	277	22.3	0.398
J_3km	1880.45	0.67	0.3	2.6	2.9	434.19	388	16.4	0.103
J_3km	1883.85	0.47	0.24	1.1	1.34	440.33	238	87.2	0.176
J_3km	1887.67	0.57	0.37	2.3	2.67	432.6	407	61.4	0.138
J_3km	1896.54	0.68	0.49	2.8	3.29	330.67	412	47.1	0.149
J_3km	1897.19	0.71	0.22	2	2.22	437.8	283	66.2	0.099
J_3km	1897.36	1.41	1.65	9	10.65	434.11	640	70.2	0.155

Type of kerogen. The dependence of TOC on the hydrocarbon potential indicates type II and type III kerogen of the vast majority of the samples studied, however, the sample from a depth of 1897.36 m is attributed to type I kerogen.

In the studied samples according to the HI hydrogen index, the range of values from 200 to 300 indicates kerogen of type II-III, probably with the generation of oil and gas; from 300 to 600 - kerogen of type II, possible oil and gas generation. However, it should be noted the difference in the sample taken from a depth of 1897.36 m, where the HI value of 640 corresponds to type I kerogen.

The value of the hydrogen index HI, which characterizes the facies-genetic type of organic matter, indicates the humus origin and, less often, the coastal (humus-sapropel) genesis of the studied samples, the organic matter that accumulated under moderately reducing conditions and correspond to kerogen types III and II. In the Van Crevelen diagram (Figure 3), two composite indicators are used to characterize the type of kerogen – the hydrogen index HI and the oxygen index OI, the results of which allow us to draw similar conclusions [22].

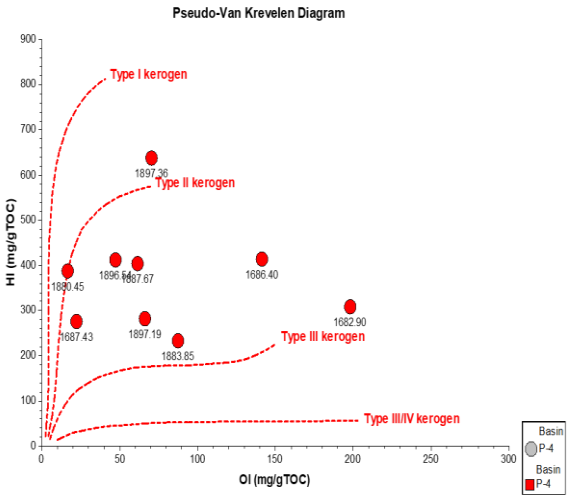

Figure 3 - Correlation between the hydrogen index (HI) and the oxygen index (OI) of the Aryskum depression

Determination of thermal maturity. To determine the thermal maturity, the range of T_{max} values of the studied samples from 435 to 445^{0}C is acceptable for the conditions of the oil window, i.e. oil generation, and allows them to be classified as mature; low T_{max} values are defined as low degree of maturity of organic matter in the studied core samples from a depth of 1682.9 m (Daul formation) and 1896.54 m (Kumkol formation) [23].

The ratio S_1 / S_1+S_2 is the productivity index PI, where the degree of realization of the organic matter of the samples under study varies from 0.103 to 0.398. Thus, samples with a Max in the range of values 435-445^{0}C, as well as PI with more than 0.1 coefficient have an oil-generating potential. However, an indicator of the industrial oil-bearing capacity of the reservoir is a PI value of more than 0.5.

Conclusion

The analysis of the obtained data of the geochemical study of the stone material of the Mesozoic deposits of the South Turgay oil and gas basin allows us to draw the following conclusions:

1. As a result of the study, the studied samples have a rich and very rich generation potential in terms of the content of C_{org} in the range from 0.47 to 1.41, as well as in the parameter S_2 (from 1.1 to 9 mg of HC /g of rock).
2. Most of the studied samples belong to type II and III kerogen, one sample from a depth of 1897.36 m with maximum TOC and S_2 is within the limits of type I kerogen; according to pyrolytic parameters HI, T_{max}, the studied samples belong to type II-III and type I kerogen with probable oil and gas ineftegeneration, respectively;
3. The hydrogen and oxygen indices determining the facies-genetic types of organic matter indicate mainly humus and less often humus-sapropel origin, thereby allowing us to conclude that oil accumulation occurred in moderately reducing conditions and coastal-marine environment.
4. The organic matter in the studied samples is thermally mature according to the T_{max} index. However, there is a low degree of maturity of the organic matter of the Tula formation and the Kumkol formation from a depth of 1682.9 m and 1896.54 m, respectively.

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

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Арысқұм иілуінің Мезозой шөгінділеріндегі органикалық заттардың термиялық пісіп-жетілуі және кероген түрі

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ТҮЙІНДЕМЕ

Бұл жұмыс Оңтүстік Торғай мұнай-газ бассейнінің Арысқұм иілуінің мезозой шөгінділерінің мұнай-газ аналық әлеуетін зерттеуге және геологиялық құрылымның ерекшеліктерін зерттеуге, органикалық заттардың фациалды-генетикалық түрін және жетілу дәрежесін анықтауға арналған. Геохимиялық әдістер мұнай-газ-аналық әлеуетті бағалауда маңызды рөл атқарады, олардың бірі органикалық заттардың түрін және зерттелетін тас материал үлгілерінің термиялық жетілуін анықтау үшін негізгі пиролитикалық талдау болып табылады. Осы мақсатқа жету үшін неоком мен юра шөгінділерінің тас материалын пиролитикалық талдау нәтижелері қолданылды. Геологиялық-геофизикалық материалдарды талдау Арысқұм көкжиегінде жоғары оқшаулағыш қасиеттері бар мұнай-газды құмды қабаттар мен олардың үстіндегі сазды қабаттардың ауданы бойынша таралу заңдылығын байқауға мүмкіндік берді. Алынған мәліметтердің нәтижелері органикалық көміртектің жалпы мөлшері массаның 0,47-ден 1,41%-на дейін екенін көрсетеді. Керогеннің түрін және оның мұнай-газ түзілу аймақтарына қатысты орналасуын анықтау үшін керогеннің элементтік құрамының атомдық қатынастарының координаттарында Ван-Кревелен диаграммасы және оның пиролитикалық деректер үшін модификациясы пайдаланылды, бұл зерттелетін үлгілердің керогені I, II және III типтердің қоспасы екенін көрсетеді. Фациалды-генетикалық түрі органикалық заттар гумусты және гумусты-сапропелге жатады, ал шөгу жағдайлары орташа қалпына келтіру жағдайында жағалау-теңіз ортасы болып табылады.

Түйінді сөздер: Арысқұм ойпаңы, Оңтүстік Торғай мұнай-газ алабы, мұнай-газдылық, органикалық заттар, көмірсутектер, кероген түрі

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Термическая зрелость органического вещества и тип керогена мезозойских отложений, Арыскумский прогиб.

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АННОТАЦИЯ

Данная работа посвящена исследованию нефтегазоматеринского потенциала мезозойских отложений Арыскумкого прогиба Южно-Торгайского нефтегазоносного бассейна и ставит целью изучение особенностей геологического строения, определение фациально-генетического типа и степени зрелости органического вещества. Геохимические методы занимают важную роль в оценке нефтегазоматеринского потенциала, одним из которых является пиролитический анализ керна для определения типа органического вещества и термической зрелости исследуемых образцов каменного материала. Для достижения этой цели были использованы результаты пиролитического анализа каменного материала отложений неокома и юры. Анализ геолого-геофизических материалов позволил проследить закономерность распространения по площади нефтегазоносных песчаных пластов и залегающих над ними глинистых прослоев с высокими изолирующими свойствами в Арыскумском горизонте. Результаты полученных данных показывают, что общее содержание органического углерода составляет от 0,47 до 1,41% масс. Для установления типа керогена и его положения относительно зон нефтегазообразования использовалась диаграмма Ван-Кревелена в координатах атомных отношений элементного состава керогена и ее модификация для пиролитических данных, свидетельствующая о том, что кероген исследуемых образцов представляет собой смесь типов I, II и III, фациально-генетический тип органическое вещество которых относится к гумусовой, гумусово-сапропелевой, а условия осадконакопления - прибрежно-морская среда в умеренно восстановительных условиях.

***Ключевые слова**:* Арыскумская впадина, Южно-Тургайский нефтегазоносный бассейн, нефтегазоносность, органическое вещество, углеводороды, тип керогена

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Earth sciences

Criteria and signs of lead-zinc mineralization within the Maityubinsky anticlinorium

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ABSTRACT
The paper presents research work to establish genetic characteristics of lead-zinc mineralization in the Ulytau-Arganatinsky structural-facial zone. Expanding the mineral resource base of Central Kazakhstan is one of the most urgent tasks because selecting the criteria and characteristics determines the aspects of prospecting and exploration work, as well as their results, which is the goal. In this regard, the following tasks are being solved: identifying the geodynamic position, the genesis of mineralization, the connection of the rock's physical properties with geophysical anomalies, as well as displaying tectonic disturbances and deep faults in them; establishing the connection of mineralization with the carbonaceous-terrigenous package of deposits of the lower subformation of the Zhilandinsky formation of the Upper Proterozoic; structural confinement of mineralization to large faults along which there was a movement of plutogenic hydrothermal solutions forming mineralization, and areas of metamorphically altered rocks, as well as aureole zones of Pb, Zn, Ag, Cd graphite quartz, phyllites and the other shales of the Zhilandysay and Kumolinsky formations, dispersion zones of Cu, Mo, V, Ag, Sc, Ye and REE near the Kyzymchek fault. The established criteria and features can be used when organizing geological exploration work in the search for polymetallic mineralization within the Maityubinsky anticlinorium in zones adjacent to deep mantle faults.

Keywords: Ulutau-Arganatinsky massif, rift structures, tectonic and magmatic cycles, deep faults, hydrotherms.

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Introduction

The Dyusembay deposit is located within the development of the Ulutau-Arganatinsky meganticlinorium, which is subdivided into the Karsakpai synclinorium, the Maityubinsky anticlinorium, and the Baikonur synclinorium. The structure of the studied area is almost completely determined by the effect of the Proterozoic tectonomagmatic megacycle; its western part is covered with Early Caledonian formations [1].

The Central Dyusembay deposit is located on the eastern flank of the Maityubinsky anticlinorium, 15 km east of the large Maityubinsky granitoid massif (S-120 sq. km), and is confined to the periclinal closure of one of the large anticlinal folds (Dyusembay anticline), complicating the Maityubinsky anticlinorium [[2], [3]].

At the end of the Precambrian - the beginning of the Paleozoic, the Ulytau Arganatinsky sialic massif, in the process of the collapse of the Rodinia continent, simultaneously with the formation and development of the Baikonur SFZ, was dissected by

the Karsakpai riftogenic structure (SFZ) into two parts: the western-Maityubinsky, Western-Arganatinsky and Eastern-East-Ulytausky, East Arganatinsky (Figure 1).

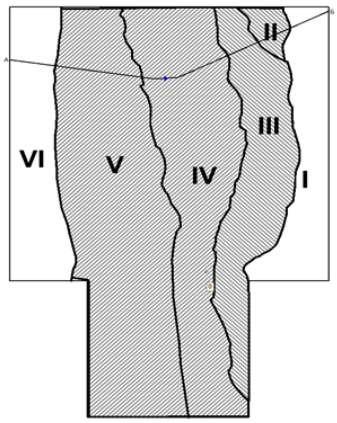

Figure 1 – Scheme of structural and formation complexes of the Baikonur SFZ
I – Zhezkazgan-Sarysu depression; area of rocks of tectonic and magmatic cycles: II-Karelian, III-Gothsky, IV-Baikalsky; V- Isidonsky; VI- Baikonursky synclinorium;

- Area of the Maityubinsky anticlinorium;
- Area of the Karsakpaisky synclinorium

(Perkov I.P. Report on the object "Geological and mineragenic mapping of the Baikonur area, sheets L-42-1,2,13,14; 25-B, G; 26-A,B")

From the west, the Ulutau-Arganatinsky meganticlinorium is limited by the West-Ulutau, and from the east – by the East-Ulutau deep faults. Numerous massifs of hypermafic rocks are confined to the zone of the latter (Figure 2).

Within both the Maityubinsky anticlinorium and the Karsakpai synclinorium, a system of intrusions of ultrabasic rocks exposed to the surface has been identified (Figure 2). Basically, all isolated hypermafic rocks are subalkaline and even alkaline in nature, which can serve as the basis for identifying zones of platform activation in this area [[4], [5]].

Experimental part

There was carried out the analysis of isotope data on the geochronological age of rocks obtained in different years was performed. So, according to the growth zones of accessory zircons that reflect the feldspathization of porphyroids, it is 666 ± 11 million years.

The geochronological age of the Maityubinsky series is 845±17 Ma (Yermolov, Antonyuk, 2012) determined from accessory zircons U-Pb using the SRIMP-II technology, isolated from subvolcanic porphyroids of the Zhaunkar formation with blastoporphyritic quartz crystals and well-preserved fluidity, subjected to feldspathization by the development of porphyroblasts potassium feldspar.

The analysis of materials from early geological and geophysical works [3] shows that rocks are differentiated according to their physical properties. So, according to their density, they can be divided into two groups: these are rocks that fall within the density range of 2.65-2.70 g/cm^3 (sericite, quartz-sericite, quartzite, conglomerates) and rocks with an average density of 2.58-2.65 g/cm^3 (chlorite schists, porphyroids). The densest and most widespread rocks are greenstone strata, which have an excess density of 0.18-2.70 g/cm^3 in relation to the granitized strata and various shales. The effusive strata of acidic composition (porphyroids from tuffs, liparites) characteristic of the Dyusembay and Zhaunkar formations, the deposit region has an average density in the range of 2.60-2.65 g/cm^3 in relation to the underlying greenstone rocks, they have a density deficiency of up to 0.30 g/cm^3 forming local negative gravity anomalies Δg against the background of significant regional anomalies from greenstone strata.

Changing the magnetic field strength ΔTa within the range of +50 to 200 nTl is typical for non-magnetic metamorphic rocks (various salans, quartzites, phylites, porphyroids) of the Lower and Middle Proterozoic. Positive magnetic field anomalies, mostly isometric with an intensity of 200-300 nTl, are caused by diorites and granitoids of Late Devonian age. Positive elongated anomalies (up to 500 nTl) are characteristic of amphibole shales strata occurring among the sediments of the second member of the Zhilandysay formation; anomalies (ΔTa about 500 nTl) are caused by porphyroids.

Rupture faults are identified by a sharp change in the nature of the magnetic field, displacement of linear anomalies and a large horizontal gradient of the gravitational field.

Results and Discussion

The structure of the Baikonur synclinorium, the Maityubinsky anticlinorium and the Karsakpai synclinorium (Figure 2) is characterized by intense dynamometamorphism of all their constituent rocks. The black-shale Vendian-Cambrian strata of the cover are transformed into various

blastosammitic phyllitic and siliceous-carbonaceous shales, micaceous and carbonaceous quartzites. This entire zone is in general characterized by a high degree of schistosity, mainly due to the layering of rocks. Folded forms are quite simple, large in size, most often linear, sometimes brachyform.

In the west, the rocks of the Maityubinsky anticlinorium border on the Baikonur synclinorium (Figure 2). The boundary between them passes along the system of large longitudinal faults that have a long-term and possibly synsedimentary development. It is obvious that this boundary also has paleotectonic significance, delimiting the continental slope and the foot of the Ulytau-Arganatin microcontinent and the Baikonur marginal sea basin of Vendian-Ordovician age [[6], [7]].

The structure of the Maityubinsky anticlinorium is complicated by the presence of large submeridian reverse faults, most likely of Jurassic age, with displacements falling to the north.

The rocks of the Maityubinsky series are feldspatized to varying degrees with the development of potassium spar porphyroblasts, in the zone of maximum development of Riphean and Early Paloezoic intrusive magmatism they were subjected to intense hydrothermal metasomatic transformation and feldspathization with the development of powerful zones of granitization of migmatites and narrow linearly elongated intrusions of porphyroblastic granite-gneisses. The maximum area of their development apparently represents the core of a large lens-shaped swell-shaped granite-gneiss dome.

Figure 2 shows a fragment of the tectonic map of the Ulytau-Arganatinsky meganticlinorium that shows the main faults. The western part of the area (northern part of sheet L-42-VII) covering the Baikonur, Maityubinsky and Karsakpai SFZs, is characterized by discontinuous faults, often grouped into entire systems of close, complexly intertwined, often en echelon-like faults combined with each other, associated with plicative dislocations (Figure 2).

Faults render a significant impact on the overall structure of the region; the largest ones serve as the boundaries of the identified structural-formational zones. Most of the large regional disturbances, especially those associated with the formation and development of rift systems, can be traced to great depths by geophysical methods [[8], [9]].

Almost all the faults are relatively young and formed on newly created continental-type crust. Some of them were updated by the latest tectonic movements, having a significant impact on the development of the hydraulic network.

There are 4 types of discontinuous faults.

The first one is the rift faults of the Proterozoic tectonomagmatic megacycle.

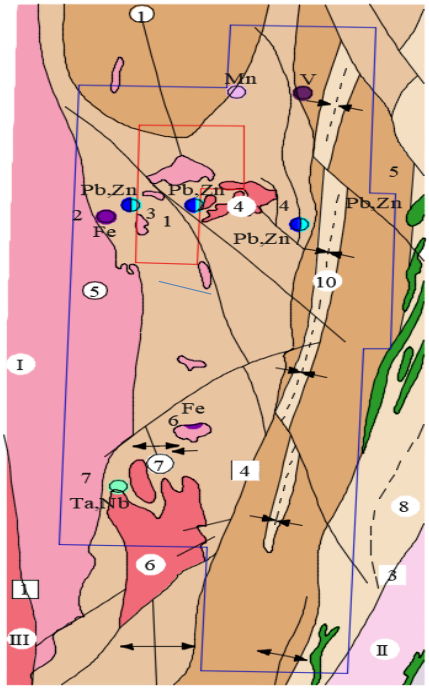

Figure 2 - Geological and tectonic map of the Dyusembay field (Aleksandrov A. E. Detailed exploration project for the Dyusembay Central field (RK)

1-Kulambai fault, 4-Kyzymchek fault, 3-Karsakpai fault;

I-Maityubinsky anticlinorium, II-Karsakpai synclinorium, III-Baikonur synclinorium;

1-Dyusembai anticline, 7-Nasymbai ancticline, 8-Baizhan syncline, 10-Kyzymchek syncline, 4- Dyusembai massif, 5-Maityubinsky massif, 6-Nasymbai massif

The second one is the orogenic reverse faults of the Proterozoic tectonomagmatic megacycle.

The third one is the faults of the Early Caledonian tectonomagmatic cycle.

The fourth one is the Triassic and Jurassic reverse faults.

The chemical composition of the rocks in Table 1 is characterized by silicate analyses of rocks from the Maytyubinsky massif (Zaitsev, 1970) and the “Explanatory Note to GK-500 (1981)”.

Table 1 - Chemical composition of granitoids of the Late Ordovician Krykkuduk complex (ν1, δ1, qδ1, γδ2, γ2, lγ2O3k) [12]

Massif	Rock name	Phase	Index	SiO_2	TiO_2	CaO	Na_2O	K_2O	P_2O_5
Kantyubinsky	qu. diorite	I	$q\delta_1O_3k$	60.81	0.30	5.07	3.71	2.52	-
-"-	qu. diorite	I	$q\delta_1O_3k$	60.91	0.23	5.11	4.72	1.80	-
-"-	Granodiorite	II	$q\delta_2O_3k$	67.35	0.30	2.38	2.56	2.88	-
Maityubinsky	monzo-gabbro	I	$\mu\nu_1O_3k$	48.94	1.48	7.55	2.84	2.13	0.54
-"-	gabbro	I	ν_1O_3k	50.08	1.87	8.55	2.95	1.16	0.50
-"-	monzogabbro diorite	I	$\mu\nu_1\delta_1O_3k$	50.90	1.44	6.64	3.78	3.12	-
-"-	gabbro-diorite	I	$\nu_1\delta_1O_3k$	54.94	0.50	7.45	4.43	0.80	0.36
-"-	monzo	I	$\mu\delta_1O_3k$	55.59	0.88	2.94	4.18	1.96	-
-"-	diorite	I	δ_1O_3k	57.92	1.18	4.10	2.94	1.89	0.46
-"-	diorite	I	δ_1O_3k	57.72	0.87	7.35	3.29	1.60	0.33

In terms of the SiO_2 content (44-74%), the rocks of the complex form a wide range of differentiation from gabbro to granites. The work by Nurzhanov, 2022, describes these rocks and their connection with intrusions.

The first intrusive phase: quartz diorites ($(q\delta_1O_3k)$, gabbro (νO_3k), gabbro-diorites ($\nu\delta_1O_3k$), fine- and medium-grained. The composition varies from gabbro to quartz diorites. In diorite massifs, xenoliths are often observed, and more basic rock varieties are associated with areas enriched in xenoliths. The xenoliths are usually small (up to 10 cm), somewhat flattened in shape, and have a uniform hornblende-plagioclase composition, corresponding to melanocratic diorites of blastic structure [[10], [11]].

The second intrusive phase is fine- and medium-grained granodiorites ($\gamma\delta_2O_3k$), granites (γ_2O_3k) and leucogranites ($l\gamma_2O_3k$). Macroscopically, these are pinkish-gray fine- to medium-grained rocks consisting of plagioclase, potassium feldspar, quartz, amphibole, and biotite.

Thus, the rocks of the first intrusive phase are characterized by gabbro, monzogabbro, gabbro-diorites, monzogabbro-diorites, diorites, monzodiorites, diorites, quartz diorites; the second intrusive phase is represented by granodiorites, granites, and leucogranites.

Thus, the rocks of the first intrusive phase are characterized by gabbro, monzogabbro, gabbro-diorites, monzogabbro-diorites, diorites, monzodiorites, diorites, quartz diorites; the second intrusive phase is represented by granodiorites, granites, and leucogranites.

The main rocks are gabbro, monzogabbro and classified as high-alumina (al'>1); medium rocks: gabbro-diorites, monzogabbro-diorites, diorites, monzodiorites, quartz diorites partially belong to high-alumina (al'>1-2) and very high-alumina (al'>2-10) varieties; acidic rocks: granodiorites, granites and leucogranites are very high-alumina (al'>2-10) [[12], [13]].

The main rocks are mesocratic (f'=10-21), and the middle rocks are divided into mesocratic (f'=10-21) and leucocratic (f'<10).

The rocks of the complex have certain differences in alkalinity: for basic rocks Ka = 0.2-0.3; for medium Ka=0.3-0.4, for acidic Ka=0.04-0.5 [14].

The Middle Proterozoic granite-gneiss complex of the Maytyubinsky anticlinorium is represented by blastoclastic gneiss-granites and granite-gneisses and gneisses genetically related to them.

Granite-gneisses are present in close structural unity with the enclosing folded metamorphic complexes. They form folds, taking the place of stratified strata. Granite-gneisses are connected with the enclosing schists and porphyroids by gradual transitions and the boundaries of the massifs are conditional. The internal structure of the massifs is heterogeneous. In the central parts, gneisse layers are single and thin, and towards the periphery of the massifs they increase in number and thickness [[15], [16]].

The characteristic features of the geological structure of the Dyusembay deposit of the geological structure of the Dyusembay Central deposit site are determined by its location in the zone of influence of the West Ulytau deep fault, the presence of which is established within the site by a series of large faults of submeridional strike, the

most significant of which is the Kyzymchek fault mapped 4 km to the east from the work site (Figure 2). To the west of the Kyzymchek fault is the Maityubinsky anticlinorium, and to the east is the Karsakpaisky synclinorium [[17], [18], [19]].

Dynamometamorphism is most likely associated with pressure from the Turgaisky paleorift; this is reflected in the presence of large reverse faults of a meridian strike with faults dipping to the west. Most likely, these reverse faults are Triassic in age [20].

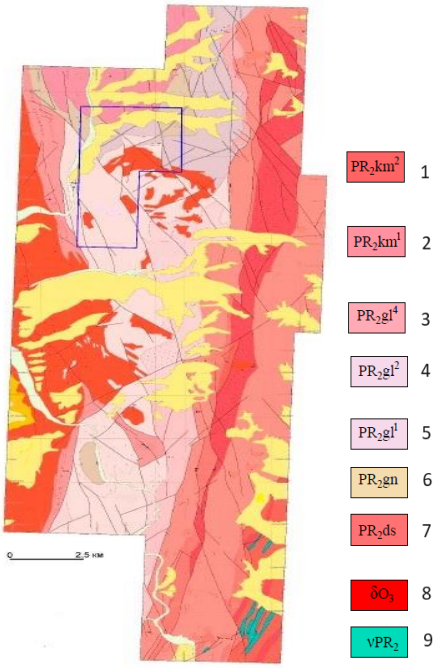

Figure 3 - Geological map (Alexandrov A. E. Detailed exploration project for the Central Dyusembay field (RK)

1-2 Kumolinsky formation: 1-pack of porphyroids, porphyroids on tuffs of rhyolite composition, graphite phyllites, quartzites 2-pack of blastopsammitic quartzite schists and phyllites; 3-5 Zhilandysay formation: 1-pack of porphyroids, partially graphitic and ferruginous, 2-pack of porphyroids and feldspathic shales, 3-pack of conglomerates and porphyroids, graphite quartzites; 6 Zhaunkar formation: porphyroids based on crystalline tuffs; 7 Dyusembai formation: porphyroids based on crystalline tuffs and lavas of liparitic composition; 8 Late Proterozoic intrusions: diorites and granodiorites; 9 Late Proterozoic intrusions: gabbro-diorites.

The internal structure of the Maityubinsky anticlitory is relatively simple: in the axial zone numerous granite-gneiss and granitoid massifs of Paleozoic age are developed, the wings are composed of metamorphic rocks of the Lower-Upper Proterozoic age (packs of sericite-chlorite-albite schists, marbles, ferruginous quartzites, phyllites, rarely graphitic schists, interbedded with packs of porphyritoids), folded into simply constructed brachnoform folds of a submeridional –north-northwest direction.

The core of the Dyusembay anticline is composed of the Dyusembay Formation rocks, which outcrop 30 km northwest of the field. The Zhaunkar and Zhilandysay formations rocks are outcropped in the wings.

Constituting the southern end of the Dyusembay anticline, the rocks of the Zhilandysay formation form a synclinal fold. In the central part of the syncline, porphyroids of the upper pack PR_2gl^4) emerge along the edges of the rocks of the first PR_2gl^1) and second (PR_2gl^2) packs (Figure 3). In general, the deposits of the Zhilandysay formation lying along the eastern flank of the Maityubinsky anticlinorium have a general dip to the east at the angles of 40-60° [21].

Younger Proterozoic rocks are mainly developed far beyond the boundaries of the Central Dyusembay deposit in the western and eastern wings of the Dyusembay anticline (in the contact zone of the Maityubinsky massif and near the Kyzymchek fault.

Conclusions

The considered features of the geological structure and geodynamic processes of the polymetallic mineralization formation in the zone of altered rocks in the vicinity of large tectonic disturbances make it possible to highlight the main criteria and signs of polymetallic type mineralization within the Maityubinsky anticlinorium.

The criteria are as follows:

• Structural: mineralization is confined to large mantle faults with which plutogenic hydrothermal processes are associated.

• Igneous: the presence of intrusions of intermediate composition developed along deep faults that control lead-zinc mineralization, these intrusions are in most cases overlain by more ancient formations.

• Lithological-stratigraphic characteristic of lead-zinc deposits: stratiformity of industrial mineralization corresponding to the hydrothermal-metosomatic stage, the presence of a carbonaceous-terrigenous sediment pack of the lower subformation of the Zhilandinsky formation of the Upper Proterozoic, which is ore-hosting.

The signs are as follows:

• Geophysical: anomalies of gravitational and magnetic fields in the western and northern exocontact of the Dyusembay granitoid massif, coincide with the outcrop of the ore zone of the Dyusembay lead-zinc mineralization to the surface; a set of geophysical methods for identifying ore intervals in wells, assessing the content of main and associated elements is carried out using the methods of GGL-S, GL, RRL and covenometry, inclinometry.

• Geochemical: the presence of aureole zones of Pb, Zn, Ag, Cd associated with mineralization in graphite quartzites, phyllites and other shales of the Zhylandysay and Kumalin formations along the eastern exocontact of the Maityubinsky massif, in the roof of the exocontact zone of the Dyusembay massif in the suture zone of the Kyzymchek fault; dispersion halos of Cu, Mo, V, Ag are confined to graphite schists, quartzites, phyllites of the Kumola formation in the vicinity of the Kyzymchek fault and zones of Sc, Y and REE are confined to graphite schists, quartzites, phyllites of the Zhylandysay and Kumola formations, in the western part of the suture of the Kyzymchek fault and Bestyubinsky strike-slip fault to the north and south of the Dyusembay deposit; specialization of aureole zones in the roof of the Dyusembay massif and along the suture zone of the Kyzymchek fault for polymetallic mineralization, as well as anomalies for copper mineralization (east of the suture zone of the Kyzymchek fault) and anomalies for rare metal mineralization (north of the Dyusembay lead-zinc deposit).

• Geological: mineralization characteristic of the Central Dyusembay deposit is its location in the zone of influence of the West Ulytau deep fault, established along a series of large faults of submeridial strike, with the most significant being the Kyzymchek fault, to the west of which is the Maityubinsky anticlinorium, and to the east the Karsakpai synclinorium.

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

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Майтөбе антиклинорийі шегінде қорғасын-мырыш кенденуінің өлшемшарттары (критерийлері) мен белгілері

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ТҮЙІНДЕМЕ

Жұмыста Ұлытау-Арғанатын құрылымдық-фациалдық аймағы кен орындарының қорғасын-мырыш кенденуінің генетикалық белгілерін анықтау бойынша зерттеу жұмыстары ұсынылған. Орталық Қазақстанның минералдық шикізат базасын кеңейту өзекті болып табылады, өйткені өлшемшарттар мен белгілерді таңдау іздеу-барлау жұмыстарының бағыттарын, сондай-ақ олардың нәтижелерін айқындайды, бұл мақсат болып табылады. Осыған байланысты келесі міндеттер шешіледі: геодинамикалық позицияны, кендеу генезисін, тау жыныстарының физикалық қасиеттерін, аномалиялармен байланыстыру, сондай-ақ олардағы тектоникалық бұзылуларды, терең ақауларды көрсету: кенденудің жоғарғы протерозойдың жыланды формациясының төменгі субсидиясының көміртекті-терригенді шөгінділерімен байланысын орнату; кенденуді қалыптастыратын плутогендік гидротерималдық ерітінділердің қозғалысы жүзеге асырылған ірі ақауларға кенденудің құрылымдық орайластырылуы және метаморфтық өзгерген тау жыныстарының учаскелері, сондай-ақ Pb, Zn, Ag, Cd графитті кварцтардың, филлиттердің және жыландысай және кумолин свиттерінің басқа да тақтатастарының ореолдық аймақтары, Қызымшек ақауының жанында орналасқан Cu, Mo, V, Ag, Sc, Ye және РЗЭ шашырау аймақтары. Белгіленген критерийлер мен белгілер терең мантия ақауларына іргелес аймақтарда Майтөбе антиклинорийі шегінде полиметалл кендерін іздеу кезінде геологиялық барлау жұмыстарын ұйымдастыру үшін пайдаланылуы мүмкін.

Түйін сөздер: Ұлытау-Арғанатын массиві, рифт құрылымдары, тектоно-магматикалық циклдар, терең жарықтар, гидротермдар.

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Критерии и признаки свинцово-цинкового оруденения в пределах Майтюбинского антиклинория

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АННОТАЦИЯ

В работе представлены работы исследований по установлению генетических признаков свинцово-цинкового оруденение месторождений Улытау –Арганатинской структурно-фациальной зоны. Расширение минерально – сырьевой базы Центрального Казахстана является одной из актуальных поскольку выбор критериев и признаков определяет направления поисково-разведочных работ, а также их результаты, что и является целью. В этой связи решается задачи: выявление геодинамической позиции, генезиса оруденения, связь физических свойств горных пород, геофизическими аномалиями, а также отображение в них тектонических нарушений, глубинных разломов: установление связи оруденения с углеродисто-терригенной пачкой отложений нижней подсвиты жиландинской свиты верхнего протерозоя; структурная приуроченность оруденения к крупным разломам по которым осуществлялась движение плутогенных гидротеримальных растворов формирующих оруденение, и участки метаморфически измененных пород, а также ореольные зоны Pb, Zn, Ag, Cd графитовых кварцах, филлитах и других сланцах жиландысайской и кумолинских свит, зоны рассеяния Cu, Mo, V, Ag, Sc, Ye и РЗЭ вблизи Кызымчекского разлома. Установленные критерии и признаки могут быть использованы при организации геолого-разведочных работ при поиске полиметаллического оруденения в пределах Майтюбинского антиклинория в зонах прилегающих к глубинным мантийным разломам.

Ключевые слова: Улутау –Арганатинский массив, рифтогенные структуры, тектоно-магматическае циклы, глубинные разломы, гидротермы.

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Earth sciences

Technological conditions for ensuring the stability of the array of enclosing rocks during the fastening of mine workings

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ABSTRACT

Ensuring the stability of the array of enclosing rocks during the fastening of mine workings is possible only if there is a highly efficient technology for conducting and maintaining workings. For fixing the mining, taking into account the technological stratification of coal-bearing massifs, a method using anchor fastening technology is recommended. The effect of the proposed method of fastening workings is that high reliability of fastening is ensured, and the volume of labor-intensive processes to combat the collapse and stratification of rocks is reduced. The stability of the contours of preparatory workings, taking into account their stress-strain state, depending on mining, geological, and technological factors of factors using the finite element method, is investigated. The boundaries of the area of inelastic deformations are determined by the method of successive loadings. The parameters of deformation of the lateral rocks of the mine workings from the angle of incidence of the formation and the depth of anchoring are considered.

Keywords: mining, fastening parameters, geomechanical processes, anchorage, manifestations of rock pressure, technological schemes.

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Introduction

During the mining and development of coal seams due to the violation of the equilibrium of rocks and redistribution of natural stresses in mines, there is mountain pressure and a variety of geological phenomena, realized in deformation, destruction, movement, and shear of their various array. Geological and mining engineering factors have a decisive influence on the development of mining pressure resulting from the interaction of coal-bearing rocks with mine workings.

The deformed state of the array at the time of monitoring should be considered as an integral picture of a multitude of geological processes occurring and overlapping one another.

The wider application of progressive and used in foreign practice anchoring is limited by the insufficient study of geomechanical processes around mine workings. From the analysis of the

anchoring application, it was established [[1], [2], [3]] that the main reasons for the decrease in the volume of anchoring of workings are: complications of mining and geological and mining engineering conditions with the transition to the depth of development more than 550 - 700 m. Here, the size of the reference pressure zones in the area around the mine workings and the intensity of rock pressure manifestations in the mine workings inside the minefields have significantly increased. The cross-sectional area of mine workings, especially of longwall mine drifts, and the volumes of non-pillar protection of mine workings on the boundary with the excavated space, i.e. in the zone of shear and collapse of rocks of neighboring excavated faces, increased by 35 - 40% (up to 20 - 22m^2); insufficient study of geomechanical processes in rocks around mine workings at the lower horizons and the performance of anchoring in these conditions. This applies most of all to the size of zones of dangerous deformations (mixing, splitting, and destruction) of rocks of the roof and sides of excavations protected by coal pillars and non-pillar methods.

The current trend towards the use of non-pillar mining technology requires finding reliable means of protecting the development workings, primarily those adjacent to the open pit area.

As the depth of the workings increases, the deformations of the enclosing rocks increase intensively, significantly outpacing the growth of the mining depth. The anchoring, working in tension, keeps the anchored rocks from delamination, shearing, and fracture. In rocks with a layered structure, layers of unstable immediate roof are either anchored to the stable main roof or separate rock layers are anchored to form a single monolithic slab, which is able to absorb the load from the overlying rocks. In unstratified rocks, anchors anchored outside the natural collapse vault resist the tensile forces in the vault rocks, and the anchors are set to resist the tensile forces in the rocks of the vault [[4], [5], [6]].

In connection with the above, the objectives of the research were: to establish the regularities of redistribution of rock pressure and rock shear parameters, the nature of shear of anchored rocks with their diverse structural structure and mining-technological factors; to determine the regularities of manifestation of rock pressure on the support, displacements of rocks of the roof, ground, sides of workings; modeling and establishing the parameters of anchoring of mine workings by means of effective strengthening of weakened zones.

The research of the method justifying the application of a limitedly yieldable anchor support, which influences the development of fracture zones in the contour rocks by binding and hardening them within the initial zones of stratification, formed outside the zone of influence of coal-face works, to create a safety bridge, distributing pressure on the vault heels, and playing in the subsequent in the zone of supporting pressure, the role of redistributing the load from the overlying rocks that have come into shear - figure 1 is established [[7], [8]].

Experimental part

To determine the area of stratification of rocks for predicting the stability and collapsibility of the roof rocks and the displacement of the sides of workings and the choice of rational parameters of their carrying out, the control of the stress-strain state of the array was carried out by devices for controlling the deformation of the array CDA-1 (visual control of stratifications in the array) and CDA-2 (quantitative assessment of the displacement of the array and stratification of the roof rocks) - VNIMI design - Figure 2.

Displacements were measured in near-contour rocks in the conveyor drift 78k10-v of the Saranskaya mine of the Karaganda coal basin at a depth of 450 m in three boreholes (central and two at an angle of 45^o to it) in the roof of the workings - Figure 2.

The immediate mine roof of the formation is represented by medium-stable argillites with thickness from 1 to 5 m and strength of 15-20 MPa with a distance between cracks of 0.5 m and the main hard-to-collapse roof with thickness of 24-30 MPa, composed of sandstone with strength of 65-70 MPa.

Outside the zone of influence of coal-face works, the first delamination contour occurred after 0.3 h at a distance of 1.6 m from the workings, after 20 days at a distance of 2.0 m, and after 3 months. - 2,3 м (Figure 3). The most dangerous are tensile stresses located perpendicular to the strata exceeding the strength limits at the contacts and causing detachment of rocks with the separation of layers from each other, and then their collapse is established [[9], [10], [11]]. Rock foliation slippage occurs under the action of tangential stresses directed along the bedding.

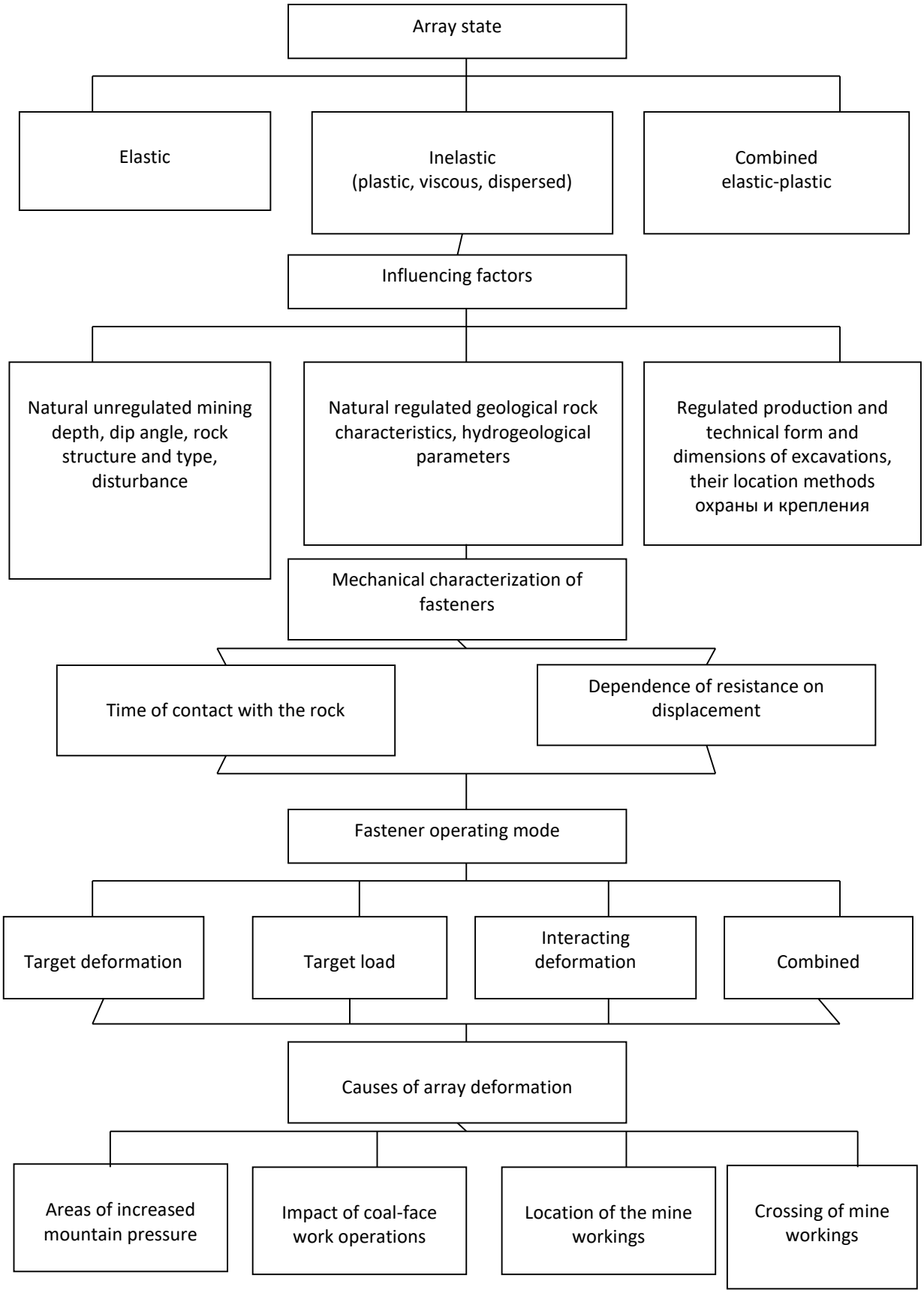
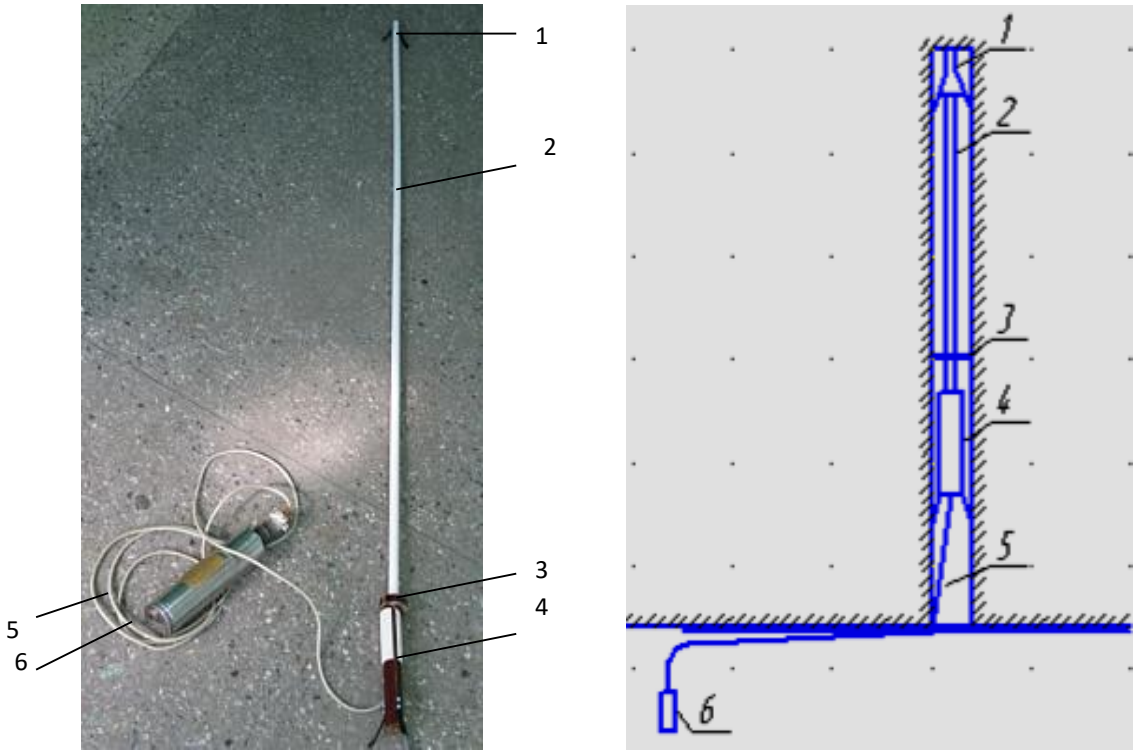


Figure 1 – Complex of basic elements of interaction of underground workings with the rock array



a b

1, 2 - the base checkpoint and its bunch; 3- thrust collar; 4 – strainmeter;
5 – connector cable; 6 – gear CDA - 2.

Figure 2 – Device design (a) and measurement scheme (b)

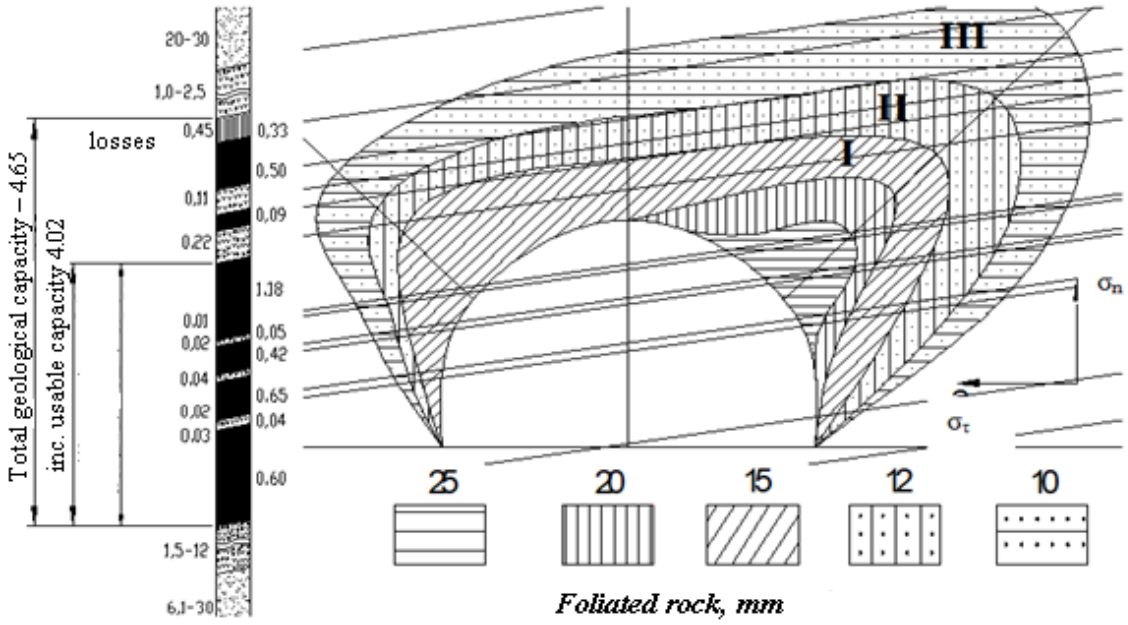


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Figure 3 – Structural column of the formation and the zone of technological stratification of the near-contour rock array of the conveyor drift 78k10-in of the Saranskaya mine

Figure 3, b shows that three foliated contacts of weak rocks (zones I - destructive deformations, II - inelastic, III - elastic) were formed with corresponding zones of technological foliation of the near-contour rock massif.

Discussion of the results

The conducted mine instrumental observations allow us to make the following conclusions established [[12], [13], [14]]:

- activation of rock displacements in the roof and sides of the workings occurs almost immediately, after the face moves 8-10 m away from the measuring sensor;
- destruction of rocks in the sides of the workings leads to the development of roof deformation processes; displacements of rocks on the contour on the side of the workings are at least 1.8 times higher than displacements on the side of the roof;
- the smallest deformations of the roof rocks, within the inelastic deformation zone formed around the workings, outside the anchored thickness, were observed in the sections of the workings with lower values of the loosening coefficients in the sides;
- destruction (extreme deformation) of the roof rocks occurs in the borehole sections located at a distance of at least 1.8 m from the workings contour (no more than 25% of the anchored area of rocks is destroyed).
- the well section located within the anchoring zone is displaced as a single block without significant foliation;
- the zone of the most intensive destruction of rocks in the mine roof is located at a distance of 3.5m or more from the contour and is confined to the place of interlayer contact;
- in the sides of the workings, the rock deformation zone usually has areas of zonal disintegration (at a distance of 0.5 - 1.0 m and 2.0 - 2.5 m from the contour, destruction occurs in the first two days of observation with subsequent development of destruction within the initially undisturbed area of 1.0 - 2.0 m);
- roof rock fractures within the anchoring zone and directly on the workings contour were recorded in the areas of workings with intensive deformations of the side enclosing rocks (lateral displacements exceed vertical displacements by 4-5 times and more), as well as in case of violations of work technology (when the gap between the borehole walls and the anchor rod is exceeded, which leads to incomplete gluing of the anchor in the borehole), in areas with water dripping from the roof and in areas with increased fracturing caused by the presence of small-amplitude geological disturbances.

Determination of the area of initial rock foliation makes it possible to predict the stability and collapsibility of the rocks of the roof and sides of the workings in order to select rational parameters of their conduct. Figure 4 shows the dependences of rock pressure fracture spacing (*l,* cm) on the ratio of geostatic pressure (γH, t/m^2) to the compressive strength of rocks (Rcc , $\frac{\kappa H}{см^2}$), and Figure 5 shows the dependences of fracture modulus (*L*, pcs./m) on the layer thickness (*h*, m) and tensile strength (Rp, $\frac{\kappa H}{см^2}$), fracturing due to the presence of small-amplitude geological disturbances.

Determination of the area of initial rock foliation makes it possible to predict the stability and collapsibility of the rocks of the roof and sides of the workings in order to select rational parameters of their conduct established [[15], [16], [17]]. Figure 4 shows the dependences of rock pressure fracture spacing (*l, cm*) on the ratio of geostatic pressure (γH, t/m^2) to the compressive strength of rocks (Rcc , $\frac{\kappa H}{см^2}$), and Figure 5 shows the dependences of fracture modulus (*L*, pcs./m) on layer thickness (*h*, m) and tensile strength (Rp, $\frac{\kappa H}{см^2}$).

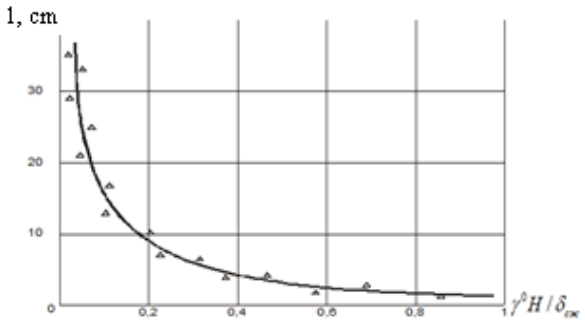


Figure 4 – Dependence of the distance between rock pressure cracks on the ratio of geostatic pressure to the compressive strength of rocks

The obtained results on foliation of rocks allowed to create an effective method for fixing the

mine workings taking into account the technological foliation of coal-rock massifs with the use of anchor fixing technology. In this case, the anchors are installed perpendicular to the force lines of pressure (technological foliation) occurring in the rocks in the contour massif of the workings.

Increasing the load-bearing capacity of the rock anchor is achieved by improving the operational condition of the anchor, ensuring stability, and reducing the displacement and delamination of the enclosing rocks [[18], [19], [20]]. Figure 6 shows the deformation patterns obtained on the basis of analytical modeling using the finite element method with the application of the ANZIS software package for the technology of arch and anchor fixing of the mine workings.

Figure 7 shows the force lines of rock pressure at the anchoring of the mine workings (side view).

When anchoring the workings, anchors are fixed perpendicular to the force lines of rock pressure acting in the rock massif.

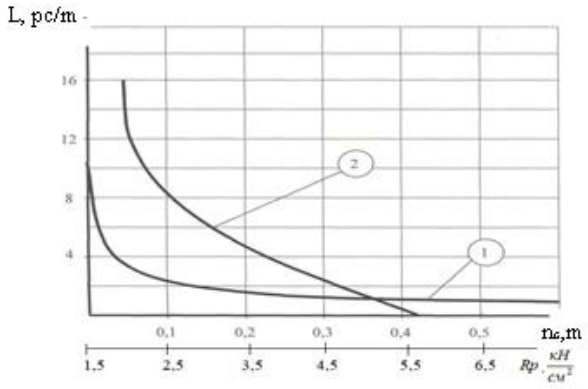
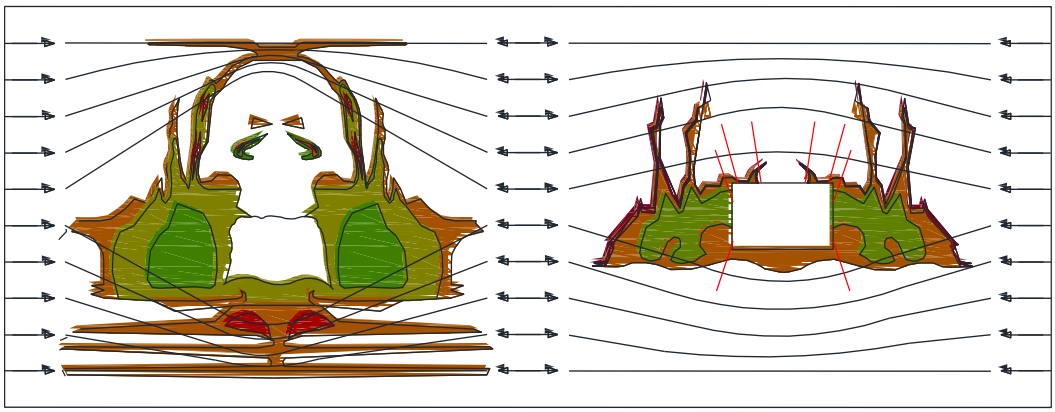
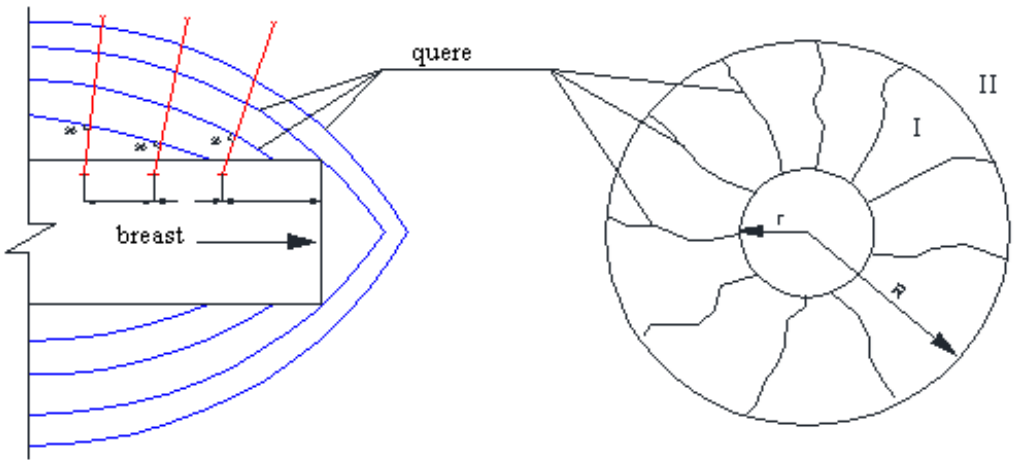


Figure 5 – Dependence of fracture modulus on layer thickness and tensile strength



a b

Figure 6 - Deformation patterns at arch (a) and anchor (b) fastening of the mine workings



I – technological foliation zone; II – sustainable zone of the rock massif

Figure 7 – Anchoring of the mine workings, installed perpendicular to the lines of acting mining pressure

Conclusions

The use of the technology of anchoring the mine workings, installed perpendicular to the force lines of the acting mining pressure, provides for the reduction of displacements and delaminations of the roof rocks and sides of the workings, the possibility of roof collapse and extrusion of the rocks of the sides and ground. The effect of the proposed method of workings fastening is that the high reliability of fastening is provided, and the volume of labor-intensive processes to combat the collapse and separation of rocks is reduced.

The stability of the contours of preparatory workings with regard to their stress-strain state depending on the mining-geological and technological factors was investigated using the finite element method. The boundaries of the inelastic deformation region were determined by the method of successive loading. The parameters of deformation of the lateral rocks of the mine workings from the angle of incidence of the formation and the depth of anchoring are considered.

Limited yielding support is characterized by an elastic-plastic model with unstrengthening. The installation of such anchors in weak rock will result in the activation of the yielding knot at the formation of the nearest fracture zone in time. The formed arch-bridge redistributes the impact of vertical mining pressure from the shear of overlying rocks to the heels of the arch-adjacent side rocks, which stops the process of formation of vertical loading from the fracture zones to the support of the working. The effect of roof rock management is that a load-bearing plate with strong bonds between blocks and increased stability of rock outcrops is formed in the mine roof, preventing the formation of rock foliation cracks (rock pressure cracks) and cross-cutting process cracks.

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

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Кен қазбаларын бекіту кезінде тау жыныстары сілемінің орнықтылығын қамтамасыз етудің технологиялық шарттары

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ТҮЙІНДЕМЕ

Тау-кен қазбаларын бекіту кезінде сыйымды жыныстар массивінің тұрақтылығын қамтамасыз ету қазбаларды өңдеу мен қолдаудың жоғары тиімді технологиясы болған жағдайда ғана мүмкін болады. Көмір жынысты сілемдердің технологиялық стратификациясын ескере отырып, тау-кен қазбаларын бекіту үшін анкерлі бекіту технологиясын қолдану әдісі ұсынылады. Қазбаларды бекітудің ұсынылған әдісінің әсері-бекітудің жоғары сенімділігін қамтамасыз етеді және тау жыныстарының құлауымен және стратификациясымен күресу үшін көп уақытты қажет ететін процестердің көлемі азаяды. Соңғы элементтер әдісін қолданып, тау-кен геологиялық және технологиялық факторларға байланысты олардың кернеулі – деформацияланған күйін ескере отырып, дайындық қазбалары контурларының тұрақтылығы зерттелді. Жүйелі жүктеу әдісімен серпімді емес деформациялар аймағының шекаралары анықталды. Тау-кен қазбасының бүйір жыныстарының қабаттың құлау бұрышынан және анкерлеудің тереңдігінен деформациялану параметрлері қарастырылады.

Түйінді сөздер: тау-кен қазбалары, бекіту параметрлері, геомеханикалық процестер, анкер бекіткіші, тау қысымының көріністері, технологиялық схемалар.

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Технологические условия обеспечения устойчивости массива вмещающих пород при креплении горных выработок

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АННОТАЦИЯ

Обеспечение устойчивости массива вмещающих пород при креплении горных выработок возможно лишь при наличии высокоэффективной технологии проведения и поддержания выработок. Для крепления горной выработки с учетом технологического расслоения угле-породных массивов рекомендуется способ с использованием технологии анкерного крепления. Эффект от предлагаемого способа крепления выработок состоит в том, что обеспечивается высокая надежность крепления, и снижается объем трудоемких процессов по борьбе с обрушением и расслоением горных пород. Исследована устойчивость контуров подготовительных выработок с учетом их напряженно-деформированного состояния в зависимости от горно – геологических и технологических факторов с использованием метода конечных элементов. Определены границы области неупругих деформаций методом последовательных нагружений. Рассмотрены параметры деформирования боковых пород горной выработки от угла падения пласта и глубины анкерования.

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

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Engineering and Technology

Exploring the Impact of Plasmonic Nanoparticles on Photoluminescence of Er^{3+} -Doped Sodium Zinc Tellurite Glass for Solid-State Laser Applications

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ABSTRACT

The present work compares the impact of embedding silver (Ag), gold (Au), titanium (Ti), and titanium nitride (TiN) nanoparticles (NPs) on the absorption, photoluminescence, and Judd Ofelt properties of erbium-doped sodium zinc tellurite glass (TNZE), known as reliable solid-state laser media. Ten absorption bands of Er^{3+} ions in the range of 400–1600 nm are attainable where their bands correspond to their own *4f* transitions. Three prominent photoluminescence (PL) bands of Er^{3+} ions were observed at approximately 525 nm, 545 nm, and 630 nm, corresponding to the transitions $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$ and $^4F_{9/2}\rightarrow{}^4I_{15/2}$, respectively. TZNE with 0.15 mol% of TiN NP inclusion showed the highest PL enhancement factor about 35 times, followed by Ti (17 times), Ag (10 times), and Au NPs (5 times), accordingly. This enhanced PL can be attributed to the strong local field induced by the localized surface plasmon resonance (LSPR) of the plasmonic NPs lies within 490–630 nm, which assists the transitions of Er^{3+} ions. The Judd Ofelt parameter was calculated and the TNZE glass with 0.15 mol% of TiN NPs inclusion disclosed the highest spectroscopic quality with a value of 3.57, compared to the TNZE glass with Ti (1.19), Au (0.59), and Ag NPs (0.90) inclusions. This research revealed several potential glass compositions with plasmonic nanoparticles that are attractive for the development of solid-state laser materials.

Keywords: Nanoparticles, Titanium, Tellurite, Photoluminescence.

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Introduction

Plasmonic nanoparticles (NPs) such as gold [1], silver [2], titanium [3] and titanium nitride [[4], [5], [6]] exhibit unique optical properties by enhancing the local field proximity rare earth ions (REI) doped glass whenever their natural frequency matched with excitation frequency. This phenomenon is known as local surface plasmon resonance (LSPR). It may alter the optical properties of the REIs doped glass for various applications, such as fiber optics, passive solar covers, photonic devices, and optical data storage [[1], [2]]. The tunability of glass properties based on composition makes them versatile as hosts for solid-state lasers. Comparing the effects of different metal NPs on REI luminescence within the same host would offer a systematic approach to navigate the effective plasmonic sensitizer to enhance the photoluminescence (PL) of REIs doped glass.

Sodium zinc tellurite glass doped with erbium (Er^{3+}) ions (TNZE) is an attractive candidate as a host for solid-state lasers. TNZE exhibits photoluminescence (PL) that extends from the visible to the mid-infrared (MIR) region (450–3000nm), making it suitable for a wide range of photonic applications [[7], [8]]. It has a high refractive index (>2.3) and a low phonon energy

(~780 cm−1). TNZE also shows strong up-conversion (UC) emission intensities due to its distinct energy level spacing and sharp spectral features in the *4f* electronic transitions [9]. The spectroscopic quality of sodium zinc tellurite glass doped with erbium (Er^{3+}) is calculated using Judd Ofelt simulations. To determine the most suitable plasmonic nanoparticle (NP) as a sensitizer, various types of NPs such as silver (Ag), gold (Au), titanium (Ti), and titanium nitride (TiN) are incorporated into the system. The main objective is to investigate the influence of these NPs on the laser properties of the glass and identify the most effective plasmonic sensitizer.

Sample Preparation and Characterizations

Composition of the glass with formula 68.85-TeO_2-20ZnO-10Na_2O-1Er_2O_3-0.15 MNPs in mol% is prepared using melt quenching technique. The corresponding glass codes for the MNPs are TNZEAg, TNZEAu, TNZETi, and TNZETiN. High purity analytical grade powders (≈99%) of TeO_2, ZnO, Na_2O, Er_2O_3, Ag, Au, Ti, and TiN NPs from Sigma Aldrich were utilized. Additionally, four MNPs-based glasses without REIs were prepared and coded as Ag_{SPR}, Au_{SPR}, Ti_{SPR}, and TiN_{SPR}, representing glass compositions with Ag, Au, Ti, and TiN NP inclusions, accordingly. These glass is prepared to probe LSPR bands within the host glass. The constituents were placed in an alumina crucible and melted in an electrical furnace at 1000°C for 30 minutes. The liquid-melt was then poured onto a stainless-steel plate and annealed for three hours at 300°C. After cooling to room temperature, the samples were stored in closed containers to prevent moisture attack. Finally, the samples were polished to obtain a smooth surface for luminescence measurement. The room temperature absorption spectra in the range of 400-1600 nm were recorded using a Shimadzu UV-3600PC scanning spectrophotometer (Kyoto, Japan), while the photoluminescence (PL) was measured using a Hitachi F850 Fluorescence spectrometer (Tokyo, Japan). The Judd-Ofelt analysis was performed where their equations are referring to previous published articles [[7], [8]].

Results and Discussion

The UV-Vis-NIR absorption spectra of prepared sample is displayed in in Figure 1. It shown ten absorption bands centred at 407, 444, 452, 489, 522, 653, 800, 976 and 1532 nm which corresponding to transition from the Er^{3+} ions ground state ($^4I_{15/2}$) to excited states of $^2G_{9/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^4H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$, $^4I_{9//2}$, $^4I_{11/2}$ and $^4I_{13/2}$, accordingly [1]. The absorbance bands disclosed almost similar pattern from previous work [1]. These data were used to perform Judd Ofelt (JO) calculations.

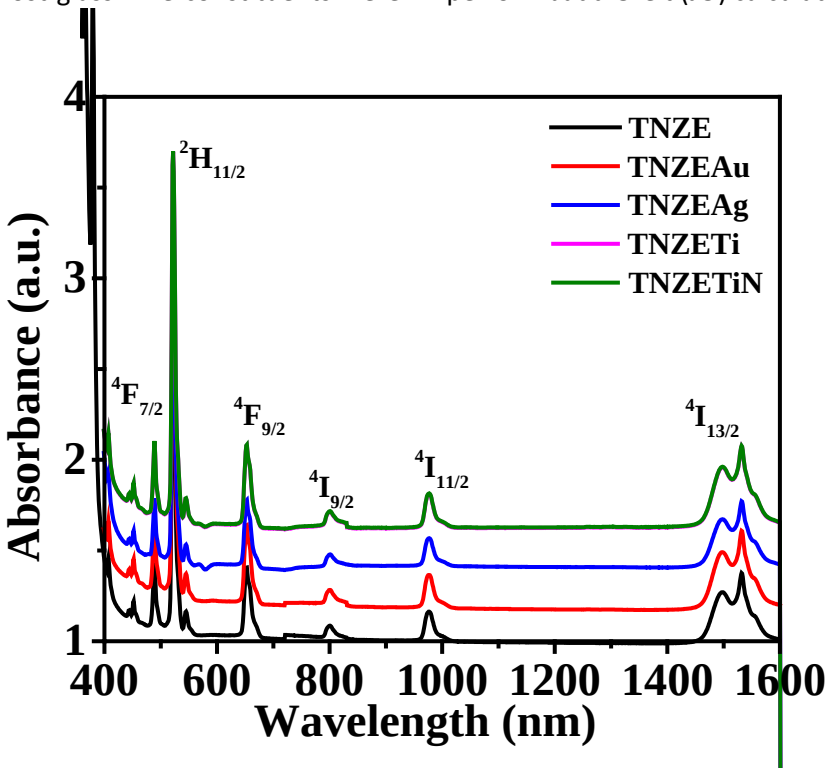

Figure 1 - UV-Vis-NIR absorption spectra of glasses

Table 1 - The JO intensity parameters $(\Omega_2, \Omega_4, \Omega_6)$ and spectroscopic quality factors $\chi = (\Omega_4 / \Omega_6)$ of the glasses

Glass code	Metallic NPs used	Contents (mol%)	Ω_2	Ω_4	Ω_6	Trends of Ω_λ	χ	LSPR band (nm)	Ref.
TNZEAu	Au	0.15	3.38	1.19	2.02	$\Omega_2 > \Omega_6 > \Omega_4$	0.59	630	Present
TNZEAg	Ag	0.15	3.74	2.63	2.93	$\Omega_2 > \Omega_6 > \Omega_4$	0.90	492	Present
TNZETi	Ti	0.15	3.11	2.23	1.88	$\Omega_2 > \Omega_4 > \Omega_6$	1.19	553, 581	Present
TNZETiN	TiN	0.15	4.70	2.71	0.77	$\Omega_2 > \Omega_4 > \Omega_6$	3.57	564	Present
TPBFErAu2	Au	0.2	10.39	2.55	4.98	$\Omega_2 > \Omega_6 > \Omega_4$	0.51	599.652	[12]
TZEAg	Ag	0.5	6.54	2.36	2.82	$\Omega_2 > \Omega_6 > \Omega_4$	0.82	500	[13]
TNZETi	TiO_2	0.1	3.08	2.15	1.88	$\Omega_2 > \Omega_4 > \Omega_6$	1.14	580	[14]

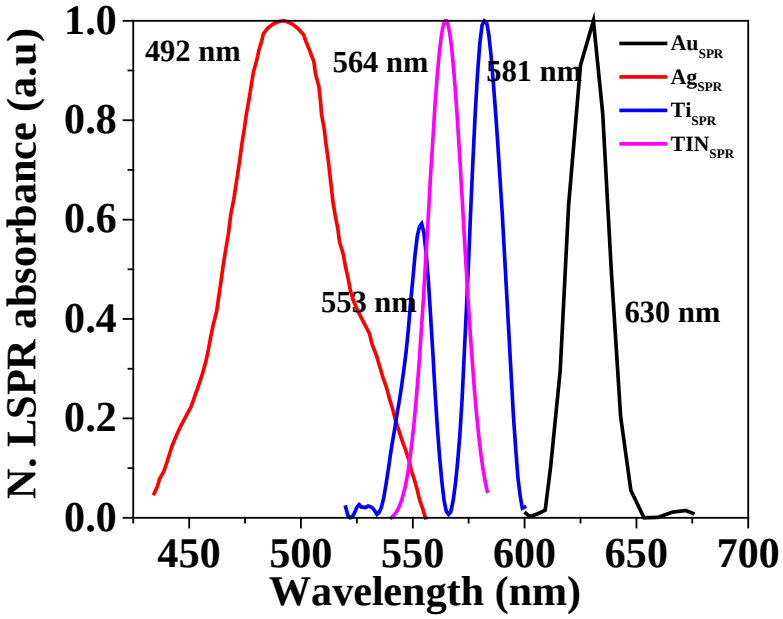

Figure 2 - Normalize LSPR band of plasmonic NPs in host glass

The values of JO intensity parameters $(\Omega_2, \Omega_4, \Omega_6)$ and spectroscopic quality factors $\chi = (\Omega_4 / \Omega_6)$ of prepared samples are summarized in. Glass with 0.15 mol% of Ti NPs shows lowest value of Ω_2 which indicates high symmetrical around Er^{3+} ion. The low Ω_2 value disclosed ionic characteristic of the glass. Meanwhile its lowest Ω_6 values revealed by glass contains TiN NPs indicate its weakest rigidity. The laser strength of the REIs is access through spectroscopic quality parameter, χ. In present case, χ shows highest in TNZETiN follow by TZNETi, TZNEAg and TZNEAu, accordingly.

Figure 2 displayed normalize LSPR bands of Ag, Au and Ti NPs as incorporated into TNZE. The LSPR of Ag, TiN, Ti and Au NPs shows highest peak around 490, 564, 581, and 630 nm, respectively. The Ti NPs exhibit additional LSPR band around 553 due to slight different aspect ratio causes by irregular shape/size [[2], [15]]. This irregular shape tailor different plasma mode and frequency. According to, the localized surface plasmon resonance (LSPR) bands of the plasmonic NPs in present work is comparable with other glass system.

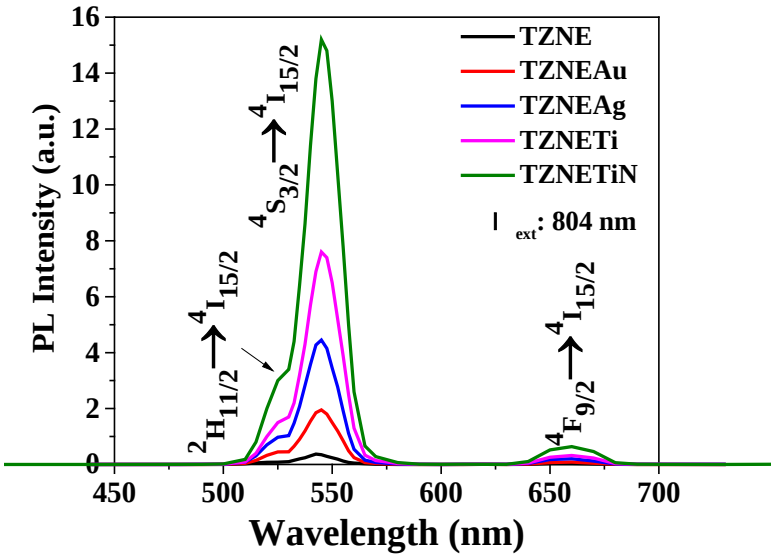

Figure 3 - PL spectra of the glasses with different plasmonic NPs, excited at 804

Figure 3 shows the up-conversion (UC) photoluminescence spectra of Er^{3+} ion as pumped with 804 nm. The photoluminescence (PL) spectra of Er^{3+} ion revealed three prominent bands centred at 525, 545 and 660 nm assigning to $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions, respectively. The PL enhancement factor (η_E) was calculate by dividing the highest PL area of each emission band (525, 545, 660 nm) that incorporated with plasmonic NPs with glass with NPs-free. The highest η_E is revealed by TNZETiN which is about 43, 32, 29 times corresponding to emission band around 525 ($^2H_{11/2} \rightarrow {}^4I_{15/2}$), 545 ($^4S_{3/2} \rightarrow {}^4I_{15/2}$) and 660 nm ($^4F_{9/2} \rightarrow {}^4I_{15/2}$), respectively. Then followed by sample TZNETi (22, 16, 14 times), TNZEAg (13, 10, 9 times), and TNZEAu (6, 5, 3) tally with transitions $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ accordingly. The enhancement is response to local field enlargement that is proximity Er^{3+} ion. The green band at 525 and 545 nm present highest intensification due to overlap TiN and Ti NPs band LSPR band located around 564 and (553 and 581 nm) with the PL bands [[16], [17], [18], [19], [20]] . Ti and TiN NPs reflect potential as new plasmonic sensitizers replacing Au and Ag NPs.

Conclusion

The impact of Ag, Au, Ti, and TiN NPs on the photoluminescence (PL) of TNZE was examined. The localized surface plasmon resonance (LSPR) of the plasmonic NPs was observed in the range of 490-630 nm. The glass with TiN NPs inclusion exhibited the highest spectroscopic quality among other REI-doped hosts in present work, with a value of 3.57. It also demonstrated the most significant enhancement, averagely 35 times for all observed PL bands. The LSPR bands of Ti and TiNPs about 550-580 nm that is overlapped with the Er^{3+} emission (525-545 nm) could be main cause for the utmost PL enhancements where the energy transfer is possible. Present work revealed that different plasmonic NPs able to modify the luminescence intensity of Er^{3+} ions doped sodium zinc tellurite glass. The prepared glass shown potential as a new gain medium for solid-state laser applications.

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Қатты күйдегі лазерлерде пайдалануға арналған Er^{3+}-легирленген натрий мырыш теллюрит әйнегінің фотолюминесценциясына плазмалық нанобөлшектердің әсерін зерттеу

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ТҮЙІНДЕМЕ

Бұл жұмыс күміс (Ag), алтын (Au), титан (Ti) және титан нитриді (TiN) (NPs) нанобөлшектері кірінділерінің эрбиммен легрленген қатты күйдегі лазерлік тасымалдағыш ретінде белгілі шыны (TNZE) натрий мырыш теллуритінің сіңіру, фотолюминесценция және Judd Ofelt қасиеттеріне әсерін салыстырады. Er^{3+} иондарының он жұту жолағы 400-1600 нм диапазонында қол жетімді, мұнда олардың жолақтары өздерінің 4f өтулеріне сәйкес келеді. $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$ and $^4F_{9/2}\rightarrow{}^4I_{15/2}$ өтулеріне сәйкес шамамен 525, 545 және 630 нм-де Er3+ иондарының үш байқалатын фотолюминесценция (PL) жолағы байқалды. Er^{3+} иондарының үш көрнекті фотолюминесценция (PL) жолағы $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$ және $^4F_{9/2}\rightarrow{}^4I_{15/2}$, тиісінше, өтулеріне сәйкес шамамен 525 nm, 545 nm және 630 nm аралығында байқалды. TiN NP қосындысының 0,15 моль% TZNE ең жоғары PL күшейту коэффициентін шамамен 35 есе көрсетті, одан кейін тиісінше Ti (17 есе), Ag (10 есе) және Au NPs (5 есе) болады. Бұл күшейтілген PL 490–630 нм диапазонында жатқан плазмоникалық NP-лердің локализацияланған беттік плазмонды резонансы (LSPR) арқылы индукцияланған күшті жергілікті өріске жатқызылуы мүмкін, бұл Er^{3+} иондарының ауысуларына ықпал етеді. Judd Ofelt параметрі есептелді және Ti (1,19), Au (0,59) және Ag (0,90) қосындылары бар TNZE шынысымен салыстырғанда 0,15 моль% TiN NPs қосылған TNZE шынысы 3,57 мәнімен ең жоғары спектроскопиялық сапаны көрсетті. Бұл зерттеу қатты күйдегі лазерлік материалдарды әзірлеу үшін тартымды болып табылатын плазмоникалық нанобөлшектері бар бірнеше әлеуетті шыны формулаларын анықтады.

Түйін сөздер: нанобөлшектер, титан, теллурит, фотолюминесценция.

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Исследование влияния плазмонных наночастиц на фотолюминесценцию натриево-цинкового теллуритного стекла, легированного Er^{3+}, для применения в твердотельных лазерах

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АННОТАЦИЯ

В настоящей работе сравнивается влияние внедрения наночастиц (NPs) серебра (Ag), золота (Au), титана (Ti) и нитрида титана (TiN) на поглощение, фотолюминесценцию и свойства Judd Ofelt легированного эрбием теллурита натрия-цинка стекло (TNZE), известное как надежный твердотельный лазерный носитель. Достижимы десять полос поглощения ионов Er^{3+} в диапазоне 400-1600 nm, где их полосы соответствуют их собственным 4f-переходам. Наблюдались три заметные полосы фотолюминесценции (PL) ионов Er^{3+} примерно при 525, 545 и 630 nm, соответствующие переходам $^2H_{11/2}\rightarrow{}^4I_{15/2}$, $^4S_{3/2}\rightarrow{}^4I_{15/2}$ and $^4F_{9/2}\rightarrow{}^4I_{15/2}$,

соответственно. TZNE с 0,15 mol% включения TiN NP показал самый высокий коэффициент усиления PL примерно в 35 раз, за ним следуют Ti (17 раз), Ag (10 раз) и Au NPs (5 раз) соответственно. Эту усиленную PL можно объяснить сильным локальным полем, индуцированным локализованным поверхностным плазмонным резонансом (LSPR) плазмонных NPs, лежащим в пределах 490-630 nm, что способствует переходам ионов Er^{3+}. Был рассчитан параметр Judd Ofelt, и стекло TNZE с включением TiN NPs 0,15 mol% показало самое высокое спектроскопическое качество со значением 3,57 по сравнению со стеклом TNZE с Ti (1,19), Au (0,59) и Ag (0,90) включения. Это исследование выявило несколько потенциальных составов стекла с плазмонными наночастицами, которые привлекательны для разработки твердотельных лазерных материалов.

Ключевые слова: наночастицы, титан, теллурит, фотолюминесценция.

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Engineering and technology

Optimal concentration of post-alcohol bard and microsilica in cement-sand mixtures determination

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ABSTRACT

The article presents part of the results of the study of the components of foam concrete made by the two-stage foam injection method, in particular, the influence of microsilica and post-alcohol bard on the setting time and strength of cement. The paper shows the methodology for determining the compressive and flexural strength, selection of the composition of components, analysis, and evaluation of setting times, and strength characteristics of the compared samples. During the study, laboratory experiments were performed to better understand how these additives affect the behavior of cement mixtures. The studies carried out allow us to determine the influence of the modified additive components on the properties of foamed concrete during the production process. The setting time analysis presented in the study revealed that increasing the concentration of the additive significantly reduced the setting time performance of cement. With increasing the content of microsilica and post-alcohol bard at 10% and 30% of the cement weight, the setting initiation and completion times are significantly reduced. To evaluate the change in strength, samples were made and tested in compression and flexure at ages of 3, 7, 14, 21, and 28 days of normal moisture curing. According to the results, it was found that the additive, by accelerating the curing, promotes strength improvement both at an early age and at the design age (28 days). The experimental results showed that the flexural and compressive strength of the material increased as the concentration of the additive increased. The maximum increase in flexural and compressive strength was recorded at additive concentrations of 10% and 30%. This indicates the important role of additives in the strengthening of materials and their potential application in construction. The additive showed an optimum positive effect, therefore, the use of this percentage of additive is the most effective for increasing the compressive and flexural strength of concrete.

Keywords: foam concrete, modified additive, microsilica, post-alcohol bard, setting time, strength characteristics.

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Introduction

The production of construction materials plays a key role in the economy and provides raw materials for the construction industry, which has a high contribution to the total output. In this area, not only the creation of new building materials is actively researched, but also the search for ways to improve the environmental aspects of production, including the utilization of man-made waste and its recycling in building composites.

In modern construction, ensuring the high strength and durability of materials plays a fundamental role. In this context, cement and its compositions, such as foamed concrete, represent some of the most important building materials that

are widely used in various industries. Foamed concrete, due to its lightness, thermal insulation properties and resistance to collapse, is a popular choice for creating a variety of building structures and products. However, its properties and characteristics can be significantly improved with the use of various additives [[1], [2], [3], [4], [5]].

Cellular materials, including foamed concrete, occupy a special place in modern construction due to their outstanding thermal insulation properties and suitability for low-lying buildings. This is particularly important from an environmental and resource efficiency perspective, as improved thermal insulation helps to reduce the consumption of fuel, energy, and natural materials. However, the foam concrete production process includes a worrying problem - the short-lived nature of the foam. This means that there is a need to develop ways to extend the life of foam concrete, and one such method is foam stabilization. There are many methods of foam stabilization, but one of the most promising approaches is the use of special additives. These additives help to increase the stability of the foam and ensure a longer service life [[6], [7], [8]].

It is important to note that the variety of such stabilizing additives and their application methods allow finding the best solutions to strengthen the foam, which ultimately improves the quality and reliability of foam concrete structures. The rapid development of this area of research provides the construction industry with innovative solutions that help to reduce environmental impact and improve energy efficiency [[9], [10], [11], [12], [13]].

An important task is the research and optimization of compositions of construction composites using secondary materials, such as technogenic wastes and products of their processing. This makes it possible to create more environmentally sustainable and efficient building materials, contributing to resource-saving and reducing the impact on nature. This approach promotes the development of innovative solutions in the construction industry and strengthens its position in the field of sustainable development. Research into construction composites and their formulations continues to evolve, introducing new technologies and approaches to improve the quality and environmental performance of building materials. This ensures not only economic growth but also contributes to the environmental sustainability of the industry [[14], [15], [16]].

In recent years, many researchers have obtained and published data showing that the combination of fine aggregate and superplasticizer provides a synergistic effect in concrete, allowing to obtain the best strength results [17]. Today, both builders and researchers are very interested in the use of ferroalloys production waste - microsilica in concrete. The positive effect of microsilica as a fine active mineral additive and the necessity of its use in concrete in combination with superplasticizer was described in publications about 40 years ago [[18], [19], [20]].

The main objective of this work is to methodically analyze the effect of microsilica and post-alcohol bard on the setting time and strength of foam concrete. For this purpose, a study was carried out, which included measuring the compressive and flexural strength of foam concrete samples with different concentrations of these additives. The results of these studies are presented in tables and graphs, which allow us to compare the strength characteristics of different samples and analyze their dependence on the concentration of additives.

Experimental technique

Cement. Cement provided by Kokshe Cement LLP - CEM I 42.5 N was used for this study. This cement, known for its high quality characteristic, represents the main component in the process of foamed concrete production. It was used as a base material for all the compositions subjected to the study.

Components of the modified additive:

Microsilica: To investigate the effect of microsilica on the properties of foamed concrete, amounts of 10%, 20%, and 30% were used. These different percentages of microsilica allowed the evaluation of its effect on the performance of foamed concrete.

Post-alcohol bard: To study the effect of post-alcohol bard on the properties of foamed concrete, quantities of 2.5%, 5.0%, 7.5%, and 10% were used. The variety of bard content allowed the evaluation of different levels of effect on the final material characteristics.

As part of the modified additive study, component tests are performed in two phases, which represent key steps in determining effectiveness and functionality.

In the first stage, the setting time of cement dough using the modified additive is evaluated. Setting time reflects the speed and nature of the cement mixture curing process. It is an important

parameter that determines the possibility of concrete application in specific conditions and production processes. The study of the setting time of cement batter in the first stage is an important step in evaluating the effectiveness and functionality of the modified additive. The obtained results will serve as a basis for further optimization of the additive composition and ensuring the required time characteristics in the production of foam concrete.

The second stage involves the evaluation of the strength characteristics of concrete containing the modified additive. The tests are aimed at determining the mechanical properties of concrete such as compressive and flexural strength. These parameters are key to assessing the quality and reliability of concrete structures. A comprehensive study of the components of the modified additive on cement setting time and strength properties provides a complete picture of the effect of the additive on foam concrete mixtures. These steps provide the necessary information to optimize the additive composition, reference curing processes and achieve the required mechanical properties of concrete.

The research involves the following sequence of activities (Figure 1):

1. Sampling of different types of samples with different percentages.

2. Preparation of samples for testing.

3. Determination of setting time using the methodology provided in GOST 310.3-76.

4. Preparation of sample beams of standard size (40x40x160 mm) in an amount of not less than 6 pieces for each of the compared types.

5. Tests on the strength of sample beams according to the methodology established in GOST 10180, including tests in bending and compression, in order to assess the mechanical properties of the material.

6. Analysis of test results.

A comparison of the results of laboratory tests was carried out for the compositions:

Type 1: Reference sample without additive, standard composition according to GOST 30744-2001;

Type 2: Sample with additive (10% of microsilica);

Type 3: Sample with additive (20% microsilica);

Type 4: Sample with additive (30% microsilica);

Type 5: Sample with additive (2.5% post-alcohol bard);

Type 6: Sample with additive (5% post-alcohol bard);

Type 7: Sample with additive (7.5% post-alcohol bard);

Type 8: Sample with additive (10% post-alcohol bard).

Phase 1: Evaluation of the setting time of cement dough

In the first phase of the study, the components of the modified additive including post-alcohol bard and microsilica in different percentages were tested in order to evaluate and establish the setting time of the cement dough. The tests were carried out by preparing cement tests with different proportions of post-alcohol bard and microsilica as part of the modified additive. Then, the time required for the initiation and completion of the setting process of the cement mixture was measured. For this purpose, standardized methods and equipment were used to ensure the accuracy and reliability of the data obtained.

The aim of this study is to carry out a comparative evaluation of the effect of the modified additive on the setting time of cement dough.

The results of the tests made it possible to determine the effect of different proportions of post-alcohol bard and microsilica on the setting time of cement dough. The optimum ratios of the additive components were identified which provided the desired setting rate of the cement mixture within the required parameters for the production of foamed concrete. Table 1 with the technological composition of samples for the production of foam concrete with different proportions of components (cement, water, microsilica, and post-alcohol bard) is given below.

Phase 2: Evaluation of strength properties

In the second phase of the study, the components of the modified additive including post-alcohol bard and microsilica in different percentages were tested to evaluate their effect on the flexural and compressive strength properties of the cement dough. The data obtained were analyzed and comparatively evaluated to determine the effect of different percentages of additive components on the strength characteristics of cement dough.

Table 1 – Technological composition of samples

Sample	Cement, g	Water, g	Microsilica, g	Post-alcohol bard, g
Type 1	350	98.0	-	-
Type 2	245	98.0	35 (10 %)	-
Type 3	280	98.0	70 (20 %)	-
Type 4	315	98.0	105 (30 %)	-
Type 5	350	88.82	-	8.75 (2.5 %)
Type 6	350	79.63	-	17.50 (5.0 %)
Type 7	350	70.44	-	26.25 (7.5 %)
Type 8	350	61.25	-	35.0 (10.0 %)

Table 2 – Technological composition of samples

Sample	Cement, g	Sand, g	Water, g	Microsilica, g	Post-alcohol bard, g
Type 1	450	1350	180.0	-	-
Type 2	324	1350	180.0	45 (10 %)	-
Type 3	360	1350	180.0	90 (20 %)	-
Type 4	405	1350	180.0	126 (30 %)	-
Type 5	450	1350	88.82	-	168.18 (2.5 %)
Type 6	450	1350	79.63	-	156.37 (5.0 %)
Type 7	450	1350	70.44	-	144.56 (7.5 %)
Type 8	450	1350	61.25	-	132.75 (10.0 %)

a) b) c)

Figure 1 - Testing of samples: a) setting time of cement dough, Vika device;
b) preparation of standard-sized beam samples; c) strength testing of samples, Press Automatic Pilot

Evaluation of the strength characteristics of cement dough in bending and compression allows us to optimize the composition of the additive and achieve the required strength for the production of foam concrete. This contributes to improving the quality and reliability of structures and ensures compliance with the requirements of building codes and standards. Table 2 shows the technological compositions of the compared types of samples for strength characteristics.

Results and Discussion

Setting times. Important data on the setting times of different cement compositions have been obtained in the course of the studies carried out. Setting time, i.e. the time required to initiate and complete the setting process of cement mixture, is an important parameter affecting the nature and applicability of foam concrete structures.

This study presents an analysis of the results of setting time measurements of different compositions including different percentages of microsilica (types 2, 3, and 4) and post-alcohol bard (types 5, 6, 7, and 8). These data are important to understand the effect of this additive on the rate and character of the setting of the cement mixture. Two main peaks can be identified in the setting time diagram (Figure 2). The first peak corresponds to the Start of the setting and the second peak corresponds to the end of the setting. The placement of the types of the compared compositions on the diagram is in ascending order, counting from bottom to top. Here the red color indicates Type 1, which represents the reference sample without additive and serves as a base for comparison. The analysis of the setting time diagram will allow a more detailed study of the effect of the addition of components on the rate and duration of the setting of foam concrete in comparison with the reference sample.

Figure 2 visually demonstrates a comparison of setting times between different types of compositions. It contains information on the Start and end of setting time for each type:

Type 1: Reference sample without additive, with the following values:

- Start of setting time: 2 hours 50 minutes.
- End of setting time: 6 hours 33 minutes.

Type 2 (10% microsilica), which shows shorter setting times compared to Type 1:

- Start of setting time: 1 hour 45 minutes.
- End of setting time: 5 hours 05 minutes.

Type 3 (20% microsilica), which also has shorter setting times:

- Start of setting time: 1 hour 20 minutes.
- End of setting time: 4 hours 30 minutes.

Type 4 (30% microsilica), which exhibits even shorter setting times:

- Start of setting time: 1 hour 15 minutes.
- End of setting time: 4 hours 05 minutes.

Analyzing the data from Figure 2, the following observations can be made:

1. The addition of microsilica significantly accelerates the setting process of the cement mixture. The setting time decreases with increasing microsilica content.

2. The initial setting time decreases more markedly than the setting completion time, indicating an earlier onset of the curing process.

3. These results have important practical implications, as they allow more precise reference and optimization of processes in production using microsilica as an additive.

These data allow a comparison of the setting times of compositions with different additive proportions. They indicate an acceleration of the setting process with the addition of microsilica in proportions ranging from 10% to 30% of the cement weight. As the proportion of additives increases, a decrease in the time required to initiate and complete setting is observed. This information is an important aspect in the design and reference of the foam concrete production process. It allows a more accurate determination of the optimum proportions of components to achieve the required setting time according to specific needs and conditions.

This study presents results that allow analyzing the setting times of different compositions with different proportions of additive, in this case microsilica. The addition of microsilica has a noticeable effect on the setting time of cement mixtures. As the percentage of microsilica increases, the time required to initiate and complete setting decreases. The initial setting time decreases more significantly than the setting completion time, indicating an earlier start of the curing process when microsilica is present in the formulation. This information is of great practical importance in the design and reference of the foam concrete production process. It makes it possible to accurately determine the optimum proportions of components to achieve the required setting time for specific needs and conditions. This helps to improve reference over the production of foamed concrete structures and to ensure that they meet the requirements and quality.

Figure 3 visually demonstrates a comparison of setting times between different types of compositions. It contains information on the Start and end of setting time for each type:

Type 1: Reference sample without additive, with the following values:

- Start of setting time: 2 hours 50 minutes.
- End of setting time: 6 hours 33 minutes.

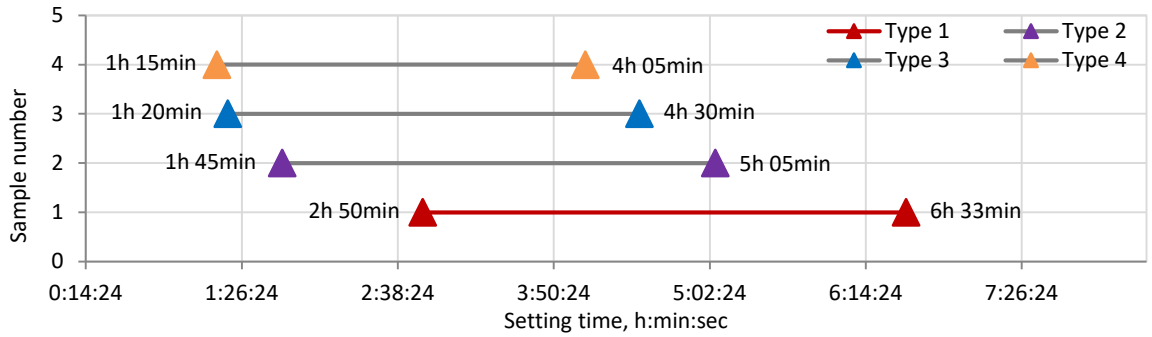

Figure 2 - Effect of additive (microsilica) on setting time

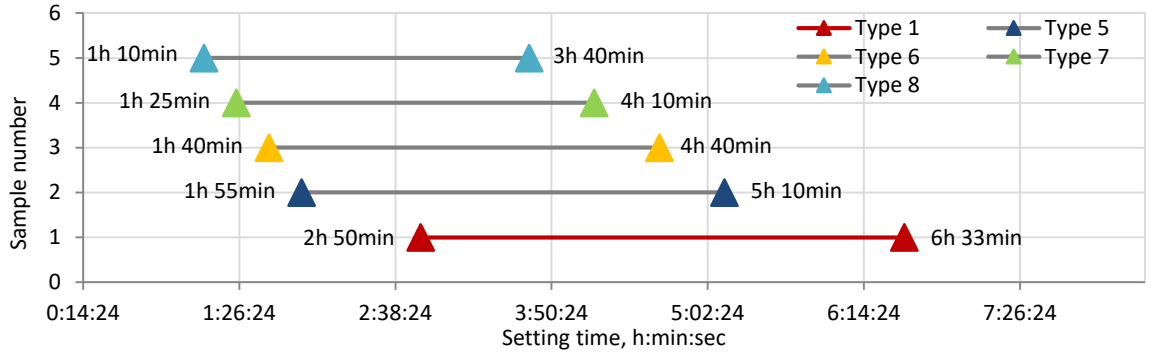

Figure 3 - Effect of additive (post-alcohol bard) on setting time

Type 5 (2.5% post-alcohol bard), which shows shorter setting times compared to Type 1:

- Start of setting time: 1 hour 55 minutes.
- End of setting time: 5 hours 10 minutes.

Type 6 (5.0% post-alcohol bard), which also has shorter setting times:

- Start of setting time: 1 hour 40 minutes.
- End of setting time: 4 hours 40 minutes.

Type 7 (7.5% post-alcohol bard), which exhibits even shorter setting times:

- Start of setting time: 1 hour 25 minutes.
- End of setting time: 4 hours 10 minutes.

Type 8 (10% post-alcohol bard), which also exhibits shorter setting times:

- Start of setting time: 1 hour 10 minutes.
- End of setting time: 3 hours 40 minutes.

Analyzing the data from Figure 3, the following observations can be made:

1. The addition of post-alcohol bard has a significant effect on the setting time of cement mixtures. As the percentage of bard content increases (from 2.5% to 10% of cement weight), the time required to initiate and complete the setting decreases.

2. The initial setting time decreases more significantly than the setting completion time, indicating an earlier onset of the curing process when post-alcohol bard is present in the mix.

3. The obtained data have an important practical significance for designing and reference foam concrete production. They make it possible to determine the optimum proportions of components to achieve the required setting time corresponding to specific needs and conditions.

These data allow the setting times of different compositions with different proportions of additives to be compared. It can be seen that setting times decrease with the addition of increasing amounts of additives. The lower setting time values for sample types 5 through 8, where 2.5% to 10% additive is added, indicate a faster setting process compared to the reference sample type 1. These results help to understand how additives affect the setting time characteristics of foam concrete and can be used to optimize the production process and quality reference. The comparative results of the samples are presented in Table 3.

Table 3 - Comparative results of samples

№	Type	Additive, %	Start of setting time, h-min	End of setting time, h-min
1	Type 1 reference sample	-	2-50	6-33
2	Type 2	microsilica-10	1-45	5-05
3	Type 3	microsilica -20	1-20	4-30
4	Type 4	microsilica -30	1-15	4-05
5	Type 5	post-alcohol bard-2.5	1-55	5-10
6	Type 6	post-alcohol bard-5.0	1-40	4-40
7	Type 7	post-alcohol bard-7.5	1-25	4-10
8	Type 8	post-alcohol bard-10.0	1-10	3-40

Comparative analysis of setting time yields the following key observations:

1. Effect of microsilica addition (Type 2, Type 3, Type 4): It can be seen that as the percentage of microsilica in the composition increases (Type 2 to Type 4), the onset of setting is accelerated and the setting time (second peak) decreases. This indicates that microsilica significantly accelerates the setting process of cement.

2. Effect of post-alcohol bard addition (Type 5, Type 6, Type 7, Type 8): A similar effect is observed with the addition of post-alcohol bard. The higher the percentage of bard (Type 5 to Type 8), the faster the setting starts and the shorter the setting time. This also indicates the ability of post-alcohol bard to accelerate the cement hardening process.

As can be seen from the results, the maximum effect of the additive in the mortar-cement mixture is achieved at a concentration of 10 and 30% relative to the weight of cement at w/c ratio=0.28. The setting time of mortar mixtures significantly depends on the concentration of the additive in them. The additive allows to reduce the setting time by 30% compared to the reference sample. At the same time, the interval between the Start and the end of the setting time is reduced by 40%. Consequently, this additive can be used as a setting time referenceler. Compositions of Types 2-4, containing microsilica in different proportions, are positioned above the reference sample (Type 1), which may indicate faster setting in the presence of this additive. Samples of Types 5-8, which include post-alcohol bard, are even higher and may indicate an even more accelerated setting process.

Strength characteristics. This study examined the strength characteristics of materials, including compressive and flexural strength. These parameters are key indicators that determine how reliably and durably materials can perform their functions. The strength properties were determined on samples made from a cement-sand mixture consisting of cement, sand, additive (for samples of types 2, 3, 4, 5, 6, 7, and 8), and water, curing under normal conditions. The analysis of the results allows us to evaluate how the additive components affect the strength properties of the material. The data obtained represent comparative results between different types of compositions and different additive proportions. The strength values of the sample are shown (at 7, 14, and 28 days) in Figures 4-7.

The results of the bending and compressive strength studies of the sample carried out at the age of 28 days allow us to make a comparative analysis of the different types of compositions and their influence on the strength characteristics of the material.

Type 1, which is a reference sample without additive, has a flexural strength of R = 55.29 kgf/cm² and a compressive strength of R = 420.78 kgf/cm². This sample served as a benchmark for comparison with other types of compositions. The increase in strength was 0%.

Type 2 containing 10% additive shows a significant increase in flexural and compressive strength of 24.63% and 21.39%, respectively, compared to the reference sample. The test results of Type 2 are R = 65.01 kgf/cm² and R = 510.81 kgf/cm².

Type 3 containing 20% additive shows an increase in flexural and compressive strength of 30.49% and 27.01% respectively compared to the reference sample. The test results of type 3 are R= 69.15 kgf/cm² and R = 534.45 kgf/cm^2.

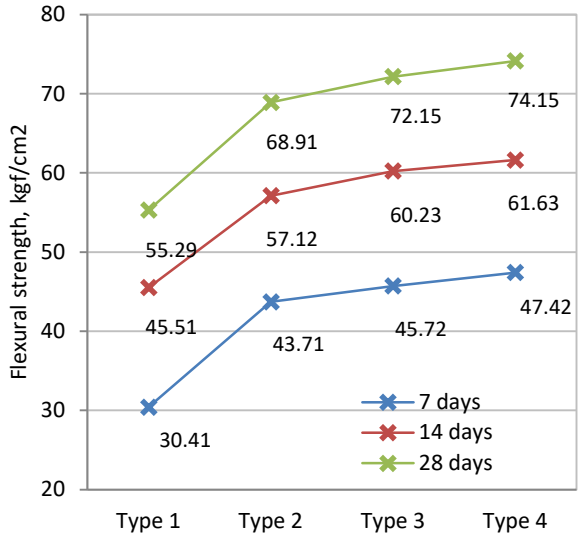

Figure 4 - Flexural strength (microsilica)

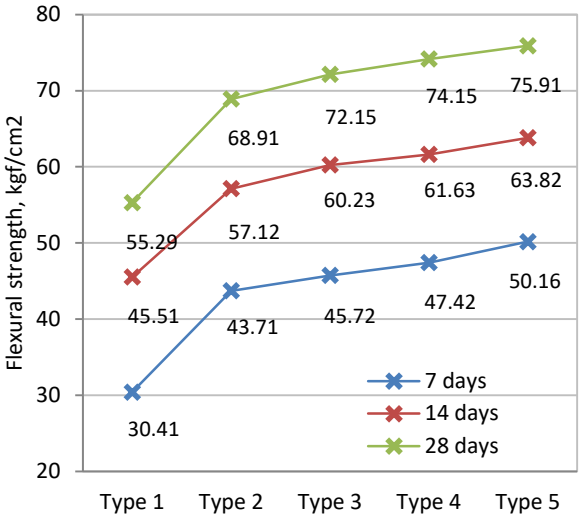

Figure 5 - Flexural strength (post-alcohol bard)

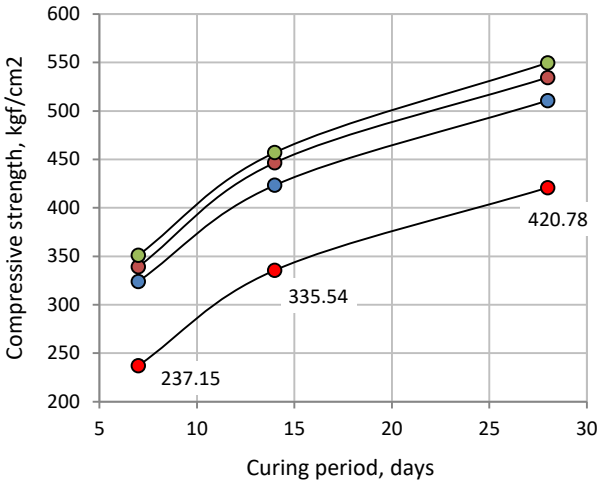

Figure 6 - Compressive strength (microsilica)

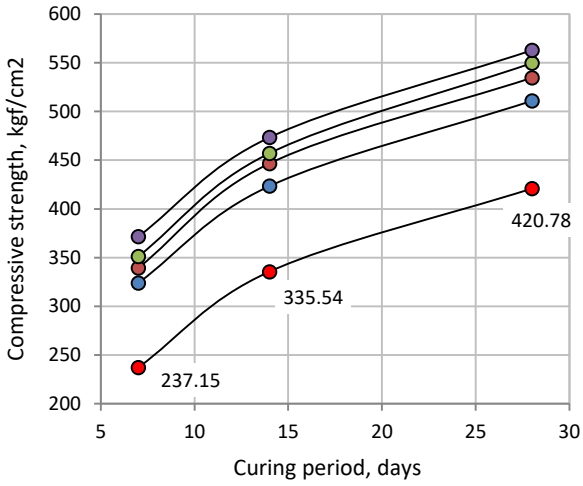

Figure 7 - Compressive strength (post-alcohol bard)

Type 4, maximum increase in flexural and compressive strength by 37.29 and 33.79% was recorded in the sample with 30% additive compared to the reference sample. The test results of type 4 are R= 71.15 kgf/cm² and R = 549.85 kgf/cm².

Type 5, with the addition of 2.5% additive increases the flexural strength by 34.11 and 30.67% compared to the reference sample. Test results for type 5: R= 68.91 kgf/cm² and R=510.81 kgf/cm².

Type 6, when 5.0% additive is added, the flexural strength increases by 34.11 and 30.67% compared to the reference sample. The test results of type 4 are R= 72.15 kgf/cm² and R=534.45 kgf/cm².

Type 7, when 7.5% additive is added, the flexural strength increases by 34.11 and 30.67% compared to the reference sample. The test results of type 4 are R= 74.15 kgf/cm² and R=549.85 kgf/cm².

Type 8. The maximum increase in flexural and compressive strength by 37.29 and 33.79% was recorded for the sample with 10% additive. The test results for type 5 are R= 75.90 kgf/cm² and R=562.98 kgf/cm².

From the analysis of the results, it can be seen that the additive has a significant effect on the strength characteristics of the material. Increasing the concentration of additives leads to a stronger increase in flexural and compressive strength. An important aspect of the curing process is the effect of the additive, which promotes the formation of a strong framework in the material structure. This framework further strengthens the compositions and results in maximizing the strength

Table 4 - Comparative results of samples

Type	Flexural strength, kgf/cm^2			Compressive strength, kgf/cm^2		
	7 days	14 days	28 days	7 days	14 days	28 days
Type 1	30.41	45.51	55.29	237.15	335.54	420.78
Type 2	43.71	55.02	65.01	324.16	423.45	510.81
Type 3	45.72	57.23	69.15	339.35	446.59	534.45
Type 4	47.42	59.63	71.15	351.27	457.19	549.85
Type 5	43.71	57.12	68.91	324.16	423.45	510.81
Type 6	45.72	60.23	72.15	339.35	446.59	534.45
Type 7	47.42	61.63	74.15	351.27	457.19	549.85
Type 8	50.16	63.82	75.90	371.76	473.51	562.98

performance. For a more detailed analysis of the effect of different compositions on strength properties, the results of the studies are shown in Table 4.

The comparative analysis of the test results of the samples allows us to conclude about the influence of the additive concentration on the bending and compressive strength. It was found that increasing the concentration of the additive significantly increases the strength of the material both in bending and in compression. This confirms the important role of additives in strengthening the material. The amount of the introduced additive was set based on the greatest effect of accelerating curing, as well as to obtain the maximum strength gain compared to the analog without additives. The maximum strength gain is achieved at concentrations of 10% and 30% relative to the weight of cement. These formulations have strengths significantly higher than the reference sample (Type 1) and can be considered as optimum for achieving maximum strength. Flexural and compressive strength values show approximately the same increase for most types of compositions, indicating the balanced nature of the effect of the additive. The addition of post-alcohol bard at concentrations of 2.5%, 5%, 7.5%, and 10% also increases strength, although to varying degrees. This provides a choice in developing compositions according to specific needs. Compared to the reference sample (Type 1), all types of compositions show a significant improvement in strength performance.

Conclusion

The results of the conducted research are important to consider in the context of actual problems related to the production of foam concrete and the improvement of its characteristics. The conducted experiments allowed us to reveal a significant influence of additives, such as microsilica and post-alcohol bard, on the setting time and strength characteristics of foam concrete. The results allowed us to draw the following conclusions:

1. The greatest effect was observed when microsilica was used at concentrations of 10% and 30% of cement weight. This resulted in a marked increase in flexural and compressive strengths, as well as a reduction in setting time. Hence, microsilica can be considered as an effective agent for improving the quality of foamed concrete and regulating the setting time.

2. Post-alcohol bard has also shown to be an effective additive for increasing strength and shortening setting time. It should be noted, however, that different additive concentrations can lead to different results, and not always more additive means better performance.

In summary, these results of the study can be used to optimize the production process of foamed concrete, increase its strength and stability, and reduce setting time, which contributes to better performance and more efficient use in construction.

Conflict of interest. The corresponding author declares that there is no conflict of interest.

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Цемент-құм қоспасының құрамындағы барданың (спирттен кейінгі) және микрокремнеземнің оңтайлы концентрациясын анықтау

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ТҮЙІНДЕМЕ

Мақалада екі сатылы көбікті енгізу әдісімен дайындалған көбік бетон компоненттерін зерттеу нәтижелерінің бір бөлігі, атап айтқанда, микрокремнезем мен спирттің кейінгі барданың цементтің қатаю уақытына және беріктігіне әсері көрсетілген. Жұмыста қысу және иілу кезіндегі беріктікті анықтау әдістемесі, компоненттердің құрамын іріктеу, салыстырылатын үлгілердің қатаю уақыттарын және беріктік сипаттамаларын талдау және бағалау көрсетілген. Зерттеу барысында осы қоспалардың цемент қоспаларының әрекетіне қалай әсер ететінін тереңірек түсіну үшін зертханалық тәжірибелер жасалды. Жүргізілген зерттеулер модификацияланған қоспалар компоненттерінің көбікті бетондардың қасиеттеріне әсерін оларды өндіру процесінде анықтауға мүмкіндік береді. Зерттеуде ұсынылған қатаю уақыттарын талдау қоспаның концентрациясының ұлғаюы цементтің қатаюының уақытша көрсеткіштерін айтарлықтай қысқартатынын анықтады. Цемент салмағымен салыстырғанда микрокремнезем және спирттік кейінгі барда мөлшерлерінің 10% және 30% артылғанда, қатаюдың басталу және аяқталу уақыты айтарлықтай қысқарады. Беріктіктің өзгеруін бағалау үшін үлгілер дайындалып, 3, 7, 14, 21 және 28 күн мерзімде қалыпты ылғалдылықта қатайған бетон қысу және иілуге сыналды. Зерттеу нәтижелері бойынша қоспа қатайтуды жеделдете отырып ерте мерзімде де, есептелген (28 тәулік) мерзімде де беріктікті арттыруға көмектесетіні анықталды. Тәжірибе нәтижелері қоспаның концентрациясы жоғарылаған сайын материалдың иілу және қысу беріктігінің жоғарылайтынын көрсетті. Иілу және қысу беріктігінің максималды өсуі 10% және 30% қоспа қосу кезінде болды. Бұл материалдарды нығайтудағы қоспалардың маңызды рөлін және оларды құрылыста қолдану мүмкіндігін көрсетеді. Қоспа оңтайлы оң әсер етті, сондықтан қоспаның осы мөлшерін пайдалану бетонның қысу және иілу беріктігін арттыруда ең тиімді болып табылады.

Түйін сөздер: көбік бетон, модификацияланған қоспа, микрокремнезем, спирттен кейінгі барда, ұстасу мерзімдері, беріктік сипаттамалар.

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Определение оптимальной концентрации послеспиртовой барды и микрокремнезема в составе цементно-песчаной смеси

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АННОТАЦИЯ

В статье представлена часть результатов исследования компонентов пенобетона, изготовленного методом двухстадийного введения пены, в частности влияние микрокремнезема и послеспиртовой барды на сроки схватывания и прочность цемента. В работе показана методика определения прочности при сжатии и изгибе, подбор состава компонентов, анализ и оценка сроков схватывания и прочностных характеристик сравниваемых образцов. В ходе исследования были выполнены лабораторные эксперименты, чтобы более глубоко понять, как эти добавки влияют на поведение цементных смесей. Проведенные исследования позволяют определить влияние компонентов модифицированной добавки на свойства пенобетонов в процессе их производства. Анализ сроков схватывания, представленный в исследовании, выявил, что увеличение концентрации добавки значительно сокращает временные показатели схватывания цемента. С увеличением содержания микрокремнезема и послеспиртовой барды на 10% и 30% от массы цемента, время начала и завершения схватывания существенно сокращается. Для оценки изменения прочности были изготовлены образцы и испытаны на сжатие и изгиб в возрасте 3, 7, 14, 21 и 28 суток нормального влажностного твердения. По результатам исследований установлено, что добавка, ускоряя твердение, способствует повышению прочности, как в раннем возрасте, так и в расчетном возрасте (28 суток). Результаты эксперимента показали, что прочность материала при изгибе и сжатии увеличивается по мере увеличения концентрации добавки. Максимальное увеличение прочности при изгибе и сжатии зафиксировано при добавке в размере 10% и 30%. Это указывает на важную роль добавок в укреплении материалов и их потенциальное применение в строительстве. Добавка показала оптимальный положительный эффект, поэтому использование данного процентного содержания добавки является наиболее эффективным для повышения прочности бетона на сжатие и изгиб.

***Ключевые слова*:** пенобетон, модифицированная добавка, микрокремнезем, послеспиртовая барда, сроки схватывания, прочностные характеристики.

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МАЗМҰНЫ
СОДЕРЖАНИЕ
CONTENTS

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