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## Assessment of the influence of the structural characteristics of granular systems of microsilicon on the properties of thermal insulation materials

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### ABSTRACT

The article discusses experimental studies of the size and shape of structured particles of microsilica small angle x-ray scattering method and a photophonon theoretical description of the heat transfer process in complex heterogeneous structures to assessment of the structural characteristics of granular systems for the properties of thermal insulating materials. The mechanism of heat transfer in granular, porous systems is quite complex, since heat exchange occurs in a material consisting of two phases (solid and gas) and at the phase boundary. Heat transfer in liquid thermal insulation coatings can be carried out from one solid particle to another. In this case, the thermal conductivity will depend on: the chemical and elemental composition of the material; particle granulometry; surface topology - the presence of inhomogeneities, defects on the surface; the number of touches and the contact area between the particles. The heat transfer of gas in the pores is carried out when gas molecules collide. Thermal conductivity will be determined by the ratio of the free path of molecules and linear pore sizes, temperature and dynamic viscosity of the gas phase, the nature of the interaction of gas molecules with the solid phase. Heat transfer by radiation depends on the nature of the particles, the dielectric, magnetic permeability and the degree of blackness of the particle surface. Based on the analysis of possible mechanisms of heat transfer in granular systems, it can be argued that the effective thermal conductivity of the system depends, all other things being equal, on the structure of the pore space of granular materials, topology and the number of particle touches. Considering idealized models of the structure of granular materials in the form of ordered folds of perfectly smooth balls, we can obtain several variants of structures: with tetrahedral; hexagonal; cubic packing of balls.

**Keywords:** x-ray diffractometer, microsilicon, thermal conductivity, diatomite, structure, filler.

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### Introduction

To determine the main structural parameters that affect the thermal conductivity of filled polymer binders, let us consider the mechanisms of heat transfer in solid, liquid, gaseous media.

It is customary to distinguish between three main mechanisms of heat transfer: thermal conductivity (conduction); convection; radiation [[1], [2], [3], [4], [5]].

The conduction mechanism of heat transfer occurs due to the exchange of kinetic energy when

moving molecules collide with each other or with the surfaces of a solid or liquid phase that limits space.

Convection - heat transfer by a moving environment, air or liquid streams.

Radiation - emission of electromagnetic energy emitted by some kind of heat, such as the sun.

In quantum theory, heat transfer in solids by thermal conductivity is considered as a process of nonequilibrium phonon distribution, and thermal conductivity is determined by the deviation of the phonon distribution from the equilibrium state at a given temperature gradient.

Considering the transfer of heat in the gas phase of the composite (in pores, hollow spheres), the molecular kinetic theory assumes the presence of two mechanisms of heat transfer by gas - due to the collision of molecules and radiation.

The efficiency of molecular heat transfer in pores, spheres of liquid heat-insulating coating further (LTC), depends on temperature, pressure, geometry of the pore space, the nature of interaction at the boundary of a solid with gas.

Experimentally established, that the effective thermal conductivity of heterogeneous finely dispersed granular systems, even at atmospheric pressure, may turn out to be lower than the thermal conductivity of the gas filling the pores.

To describe the process of heat transfer in continuous media and determine the coefficient of thermal conductivity, the most often used methods are based on the application of the principle of generalized conductivity, which is based on the analogy (similarity) between the differential equations of stationary heat flux, temperature, mass, current, etc.

It is possible to use topological models, when solving more complex problems to determine the thermal conductivity coefficient. However, they do not take into account the features of the quantum mechanisms of heat transfer through the main matrix of the material [[5], [6], [7]].

### **Analysis of modern research in this area**

To assess the effect of the structural characteristics of granular microsilica systems on the properties of heat-insulating materials, a comprehensive analysis showed that the only mechanism for heat transfer for granular systems would be:

- *heat transfer through a flat, two-layer and multi-layer plate.*

In the works of Krainov A.Yu. To calculate the heat transfer through a flat plate, the value of the heat flux through a plate of thickness  $L$ , having a thermal conductivity coefficient  $\lambda$ , the walls of which have a constant temperature  $T_0$  and  $T_1$ , is determined. The mathematical formulation of the problem consists of a stationary one-dimensional heat equation with boundary conditions of the first kind [8].

- *heat transfer of coatings with a coefficient of thermal conductivity that depends on the temperature of the environment.*

In the works of V.A. Maksimov, S.R. Vitaly. the values of the thermal conductivity coefficient of some ultrathin liquid composite heat-insulating coatings have been experimentally determined. The calculation of the measurement error has been performed. As a result of the work done, the thermal conductivity coefficient of ultra-thin liquid composite heat-insulating coatings was experimentally determined for sample No. 1  $\lambda = 0.086 \text{ W} / (\text{m} \cdot ^\circ \text{C})$ , for sample No. 2  $\lambda = 0.091 \text{ W} / (\text{m} \cdot ^\circ \text{C})$ . But, the real thermal conductivity coefficient of the samples under study in practice turned out to be higher than the declared one.

According to the authors, this discrepancy is possible due to the fact that manufacturers of liquid coatings in laboratory determination of thermal conductivity either used some "ideal" conditions, or the coefficient was obtained by theoretically solving the problem of thermal conductivity in liquid composite heat-insulating environment.

Despite this, the authors consider such liquid thermal insulation coatings to be of great interest for builders, since they allow insulating objects of complex geometric shapes (valve bodies, complex units, etc.), which in some cases makes them practically irreplaceable. Correct consideration of the thermal properties of paints will allow avoiding excessive increases in heat losses of insulated pipelines with a coolant or building enclosing structures, and will also protect them from possible defrosting during periods of negative temperatures [9].

- *heat transfer of a plate with a coefficient of thermal conductivity depending on the coordinate.*

The work of Kolmychkov V.V., Mazhorova O.S. is devoted to the numerical study of convective structures arising near the stability threshold in a non-Bussinesq fluid, the thermal diffusivity of which depends on the vertical coordinate. The main attention is paid to the study of the existence and

stability of a flow in the form of square cells for various values of the Prandtl number [10].

- *phonon-photon model for the theoretical description of the process of heat transfer in complex heterogeneous structures.*

In the works of Gladkov S.O. for an arbitrary type of porous structures, a theoretical approach is proposed for calculating their thermal conductivity coefficient  $\kappa$  as a function of porosity  $\xi$ , temperature  $T$ , density  $\rho$ , and a number of other parameters. The general calculation algorithm is based on the theory of nonequilibrium processes. Its modification in the language of the gas-kinetic approximation allows one to obtain compact formulas for  $\kappa$  and easily estimate the corresponding dependences. On a specific example of such a very important in practical terms refractory substance, like concrete, the theoretical formulas are compared with experimental results and their good agreement is shown [11].

### Methods for determining the structural characteristics of granular systems

1. To study the properties of microdispersed materials, a Hecus S3 - MICRO small-angle X-ray diffractometer was used.

The most important feature of this method is the ability to analyze the internal structure of disordered systems - particles, pore space, interfaces between heterogeneities of heterogeneous substances.

As the scattering coordinate, we used the magnitude of the scattering vector modulus  $s = 4\pi \sin\theta / \lambda$ , where  $2\theta$  is the scattering angle,  $\lambda = 1.5418 \text{ \AA}$  is the wavelength of the radiation used. Scattering intensities were recorded in the range of  $s$  values from 0.0094 to 0.40  $\text{\AA}^{-1}$ , which made it possible to study inhomogeneities with linear dimensions  $L \sim (2\pi) / S$ , in the range of 2 ... 60 nm.

2. One of the most important parameters that determine the thermal insulation properties of materials based on microstructured mineral powders (silica, diatomite) is thermal conductivity. Knowing a number of characteristics of dispersed systems, such as the size, thermal conductivity of the material of primary particles, the method of filling and some other characteristics, it is possible to theoretically calculate the thermal conductivity of granular systems based on the polystructural theory and, as a result, it is possible to assess the structural characteristics of granular systems for

the properties of heat-insulating materials [[12], [13], [14], [15], [16], [17]].

### Assessment of the structural characteristics of granular systems to the properties of heat-insulating materials

For the theoretical description of the process of heat transfer in complex heterogeneous structures, a photophonon model was used, according to which the general expression for the thermal conductivity of a porous system is written in the form of an additive function [[12], [13], [14], [15], [16], [17]].

$$\lambda = \left(1 - \frac{m}{m_p}\right)^2 \lambda_{00} + \frac{m}{m_p} \left(1 - \frac{m}{m_p}\right) \lambda_{01} + \frac{m}{m_p} \left(1 - \frac{m}{m_p}\right) \lambda_{10} + \left(\frac{m}{m_p}\right)^2 \lambda_{11} \quad (1)$$

where  $m$  – porosity of the structure;  
 $\lambda_{00}$  - thermal conductivity of the main matrix;  
 $\lambda_{11}$  - thermal conductivity of pores;  
 $\lambda_{01}$  - phonon-photon thermal conductivity at the interface between pores and the main matrix;  
 $\lambda_{10}$  - photon-phonon thermal conductivity;  
 $m_p$  - percolation threshold for the basic matrix model.

Using the gas-kinetic approximation, we represent the thermal conductivity of the main matrix in the form:

$$\lambda_{00} = \frac{1}{3} c_{fon} v^2 \tau_{fon} \quad (2)$$

where  $c_{fon}$  - phonon heat capacity per unit volume of the main matrix;  
 $v$  - average speed of sound in the material;  
 $\tau_{fon}$  - phonon relaxation time, which is associated with phonon scattering by structural inhomogeneities and at the boundaries of contact of pores with the main matrix.

The phonon heat capacity is determined by the formula (at  $T \gg \theta_D$ )

$$c_{fon} = \frac{3k}{a^3} \quad (3)$$

where  $k$  - Boltzmann constant;  
 $a$  - average interatomic distance of the main matrix material.

The phonon relaxation time satisfies the expression [10]:

$$\tau_{fon} \approx \frac{m_p \rho a^4 v \left(1 - \frac{m}{m_p}\right)}{m k T} \quad (4)$$

where  $\rho$  – base matrix material density;  
 $T$  – absolute temperature (K).

Substituting (3) and (4) into (2), we obtain the expression

$$\lambda_{00} = \left(1 - \frac{m}{m_p}\right) \frac{\rho v^3 a m_p}{T m} \quad (5)$$

Similarly, representing the photon flux as a photon gas, we can write

$$\lambda_{11} = \frac{1}{3} c_{fot} c^2 \tau_{fot} \quad (6)$$

where  $c_{fot}$  - photonic heat capacity per unit pore volume;

$c$  - speed of light in pores;

$\tau_{fot}$  - photon relaxation time within pores.

The work presents an expression for determining the photon heat capacity:

$$c_{fot} \approx k \left(\frac{kT}{\hbar c}\right)^3 \quad (7)$$

( $\hbar$  – Planck's constant), and the photon relaxation time for the case of vacuum or a low concentration of gas molecules in the pores:

$$\tau_{fot} = \frac{L}{c} \quad (8)$$

$L$  – linear pore sizes. Substituting (7) and (8) into (6), we obtain

$$\lambda_{11} = \frac{1}{3} \frac{kL}{c^2} \left(\frac{kT}{\hbar}\right)^3 \left(\frac{kT}{\hbar}\right)^3 \quad (9)$$

It is shown in the work that in formula (1) the terms containing  $\lambda_{01}$  and  $\lambda_{10}$  are small compared to other terms and can be discarded. Then expression (1) will look like this:

$$\lambda = \left(1 - \frac{m}{m_p}\right)^2 \lambda_{00} + \left(\frac{m}{m_p}\right)^2 \lambda_{11}, \text{ and}$$

given  
 (5) and (6):

$$\lambda = \left(1 - \frac{m}{m_p}\right)^3 \frac{\rho v^3 a m_p}{T m} + \frac{1}{3} \left(\frac{m}{m_p}\right)^2 \frac{kL}{c^2} \left(\frac{kT}{\hbar}\right)^3 \quad (10)$$

The resulting formula makes it possible to: estimate the dependence of the thermal conductivity of the LTP on the porosity of the material structure ( $m$ ), linear pore size ( $L$ ), density ( $\rho$ ) on temperature and calculate the effective thermal conductivity of a dispersed porous substance, based only on the knowledge of some macro- and microscopic material parameters; to solve the inverse problem - by measuring the effective thermal conductivity of a dispersed powder by the method of stationary heat flux or by the method of laser flash, knowing the density, speed of sound and average interatomic distances, calculate the characteristic linear dimensions of its pores. At low temperatures, the thermal conductivity of a granular system is determined mainly by its phonon component. With an increase in temperature ( $T \gg \theta_D$ ), this component decreases  $\propto T^{-1}$ , but radiant heat transfer (by photons of electromagnetic radiation)  $\propto T^3$  increases. If the dependence of thermal conductivity on temperature (10) is represented in the form

$$\lambda(T) = \frac{A}{T} + B T^3 \quad (11)$$

then the minimum value of the effective thermal conductivity  $\lambda(T)$  will be observed at a temperature.

$$T_{min} = \sqrt[4]{\frac{A}{3B}} \quad (12)$$

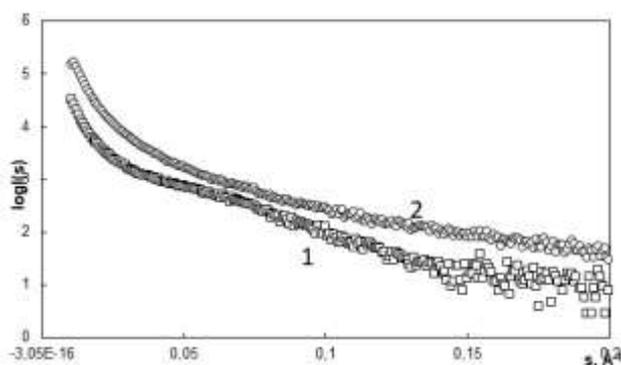
In this case, the photon thermal conductivity (10) will be the smaller, the smaller the dimensions  $L$  of the pores of a given material. Consequently, formulas (10) and (12) make it possible, on the basis of the data obtained as a result of studying the structural characteristics of the pore space of dispersed powders, to reasonably recommend granular systems for use as a filler for LTM. It is proposed to determine and evaluate the structural characteristics of filler powders by the method of small-angle X-ray scattering (SAXS) [1]. The features of structural inhomogeneities of microsilica [[1], [18], [19]] and natural diatomite of the Utesai deposit, as well as a filler powder of the FRONT-VIP vacuum insulating panel from VACU - ISOTEC KG were investigated.

### Experimental part

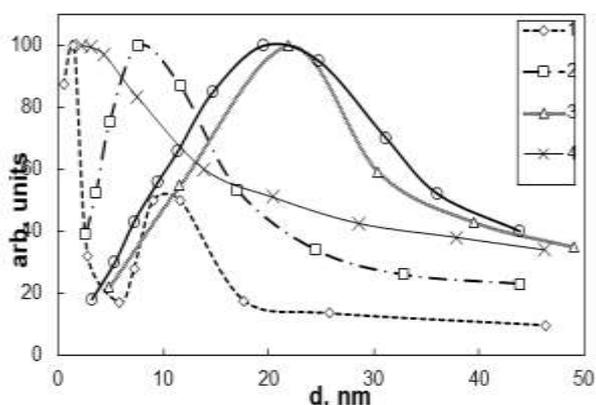
Small-angle X-ray scattering is a diffraction method widely used to study nanoobjects of

various physical nature and state of aggregation, including highly dispersed powders.

The experimental material was obtained in the form of small-angle X-ray scattering indicatrices for all investigated dispersed powders. As the scattering coordinate, we used the magnitude of the scattering vector modulus  $s = 4\pi \sin\theta/\lambda$ , where  $2\theta$  is the scattering angle,  $\lambda = 1.5418 \text{ \AA}$  is the wavelength of the radiation used. Scattering intensities were recorded in the range of  $s$  values from  $0.0094$  to  $0.40 \text{ \AA}^{-1}$ , which made it possible to study inhomogeneities with linear dimensions  $L \sim (2\pi) / S$ , within  $2 \dots 60 \text{ nm}$ . The character of the  $I(s)$  curves indicates that the studied materials contain scattering inhomogeneities (pores) of different linear sizes, and high values of the scattering intensity are due to the sharp contrast caused by the large difference between the density of silica particles and pores. Fig. 1 shows the experimental SAXS curves of the natural diatomite of the Utesayskoye deposit and the filler powder of the FRONT-VIP insulation panel. The scattering indices of the other three microsilia have a similar form to the FRONT-VIP SAXS curve.



**Figure 1** - Curves of small-angle X-ray scattering of dispersed powders: 1 - natural diatomite; 2 - filler powder FRONT-VIP



**Figure 2** - Size distribution of scattering inhomogeneities: 1 - natural diatomite; 2 -

microdispersed silica obtained from diatomite; 3 - condensed silica; 4 - white soot; 5 - FRONT-VIP filler powder.

To find the approximate size distribution functions of scattering inhomogeneities (for spherical particles), the SAXS curves were rearranged into coordinates  $\ln I(s) - s^2$ . Using the Kitaygorodsky method, we obtained the dependencies shown in Fig. 2. Pore size distribution curves of dispersed microsilia have pronounced maxima; a similar function of natural diatomite is bimodal. Table 1 shows the results of the analysis of distribution curves - the maxima of the distribution functions  $d_b$ ; average values of the linear dimensions of the scattering inhomogeneities  $\langle d \rangle$ ; variances of distribution functions  $\Delta d$ .

**Table 1** - Pore size distribution of dispersed microsilia

Powder type	$d_b, \text{ nm}$	$\langle d \rangle, \text{ nm}$	$\Delta d, \text{ nm}$
Natural diatomite	2 10	2 7	7 - 15
Dispersed microsilia obtained from diatomite	8	12	3 - 18
Condensed silica fume	22	26	10 - 34
White soot	2	13	2 - 21
FRONT-VIP	20	20	8 - 37

In general, the average linear dimensions of the scattering inhomogeneities of the investigated dispersed powders are  $\sim 10 - 30 \text{ nm}$ , which, according to the classification of M.M. Dubinin, officially adopted by the International Union of Pure and Applied Chemistry (IUPAC), corresponds to mesopores. Capillary condensation of water molecules occurs in them, which are partially removed during heating (calcination) of dispersed powders [11].

The SAXS indicatrices were rearranged into double logarithmic coordinates  $\lg I(s) - \lg s$ . An analysis of these dependences showed that, in all investigated dispersed materials, a fractal character of scattering by structural inhomogeneities of the nanoscale level is observed. To determine the fractal dimensions of these inhomogeneities, a method was used, which consists in determining the slope of the corresponding linear section of the scattering curve plotted in the indicated coordinates. If the investigated structural elements of the nanoscale, such as pores, pore clusters, and interfaces of inhomogeneities are of a fractal nature, then in certain intervals of values of the modulus of the scattering vector, a power-law

decay of the scattering indicatrix  $I(s) \sim s^{-\alpha}$  with a non-integer value of the exponent should be observed, and  $\alpha < 4$ . At  $1 \leq \alpha < 3$ , the power-law decay of  $I(s)$  is characteristic of scattering from fractal clusters or aggregates of nanoparticles (mass fractals) with the dimension  $D = \alpha$ . In the case when  $3 < \alpha < 4$ , scattering from nanoparticles with a nonsmooth fractal surface is observed, the fractal dimension of which is determined as  $D_s = 6 - \alpha$ . The exponent  $I(s)$  in this case is defined as  $\alpha = \Delta \lg I(s) / \Delta \lg s$ .

On the SAXS curve of diatomite from the Utesai deposit, three rectilinear sections are distinguished, corresponding to the values of the scattering vector  $0.013 - 0.026 \text{ \AA}^{-1}$ ,  $0.031 - 0.061 \text{ \AA}^{-1}$ , and  $0.067 - 0.095 \text{ \AA}^{-1}$ . The parameter  $\alpha$  for these sections is 2.59, 1.56 and 3.73. Sizes of inhomogeneities are 24 - 48 nm, 10 - 20 nm, and 7 - 9 nm, respectively. The most large-scale scattering objects behave like mass fractals with a fractal dimension  $D = \alpha = 2.59$ , which is typical for branched self-organized porous structures. The second rectilinear segment of the indicatrix  $\lg I(s) - \lg s$  corresponds to inhomogeneities with fractal dimension  $D = 1.56$ , which can be clusters in the form of curved chains of spherical pores of nano- and micrometer scale, possibly pore channels. In addition to mass fractals, the natural diatomite of the Utesayskoye field exhibits inhomogeneities with a fractal interface. The dimensions of such inhomogeneities are 7 - 9 nm, and the fractal dimension is  $D_s = 6 - \alpha = 2.27$ . This value of the fractal dimension corresponds to a

slightly indented surface, if we take into account that a perfectly smooth surface has  $D_s = 2.0$ , and a highly indented porous surface - 3.0. Fractal characteristics of all studied materials are shown in Table 2.

Dispersed microsilica obtained from natural diatomite also contains three types of scattering inhomogeneities, two of which are mass fractals with dimensions 2.32 and 2.13. The scale of such objects is 8 - 40 nm. Small-scale pores 4 - 8 nm have rather heavily indented interfaces ( $D_s = 2.64$ ). Condensed silica fume, in contrast to other investigated dispersed powders, does not have X-ray scattering inhomogeneities that could be attributed to mass fractals. The interfaces of the  $\text{SiO}_2$  particles - the pores have a fractal dimension  $D_s = 2.40$ . White microsilica contains fractal clusters of pore space with linear dimensions of 4 - 25 nm. The interfaces of larger scattering formations (25 - 40 nm) are strongly indented - their fractal dimension is  $D_s = 2.83$ . The scattering curve  $\lg I(s) - \lg s$  of the FRONT - VIP filler powder has two crossover points: branched porous aggregates 20 - 40 nm in size have a fractal dimension  $D = 2.59$ , and inhomogeneities on a scale of 12 - 20 nm have highly irregular surface with  $D_s = 2.70$ . In addition, the data of small-angle X-ray scattering allow us to suggest that on the surface of the smallest elements of the structure of the filler powder (4 - 12 nm), there may be layers of scattering inhomogeneities with a lower electron density than that of silicon dioxide (parameter  $\alpha = 4,10$ ).

**Table 2** - Fractal characteristics of the investigated materials

№	Material	$\Delta s, \text{ \AA}^{-1}$	$\alpha$	D	$D_s$	d, nm
1	Natural diatomite	0.013 - 0.026	2.59	2.59	2.27	24 - 48
		0.031 - 0.061	1.56	1.56		10 - 20
		0.067 - 0.095	3.73			7 - 9
2	Dispersed microsilica obtained from diatomite	0.016 - 0.025	2.32	2.32	2.64	25 - 40
		0.025 - 0.080	2.13	2.13		8 - 25
		0.080 - 0.160	3.36			4 - 8
3	Condensed microsilica	0.016 - 0.160	3.60		2.40	4 - 40
4	White soot	0.016 - 0.025	3.17		2.83	25 - 40
		0.025 - 0.160	2.66	2.66		4 - 25
5	FRONT - VIP	0.016 - 0.032	2.59	2.59	2.70	20 - 40
		0.032 - 0.056	3.30			12 - 20
		0.056 - 0.160	4.10			4 - 12

Analysis of the data obtained gives grounds to believe that the studied granular systems are suitable: for the creation of new generation heat-

insulating materials; as fillers for LTC, VIP. At the same time, condensed microsilica and white soot do not require preliminary heat treatment, since

their low moisture content is determined by the production conditions (subject to the rules of storage and transportation of bulk material). Dispersed microsilica obtained from diatomite and natural diatomite must be calcined at temperatures not lower than 400 - 500 °C for 3 - 5 hours. This modification of dispersed powders leads to their deep dehydration and helps to remove residues of organic material of sedimentary origin present in natural diatomites.

### Conclusions

1. It was found that dispersed microsilica obtained from natural diatomite also contains three types of scattering inhomogeneities, two of which are mass fractals with dimensions 2.32 and 2.13. The scale of such objects is 8 - 40 nm. Small-scale pores 4 - 8 nm have rather heavily indented interfaces ( $D_s = 2.64$ ). Condensed silica fume, in contrast to other investigated dispersed powders, does not have X-ray scattering inhomogeneities that could be attributed to mass fractals. The interfaces of the  $\text{SiO}_2$  particles - the pores have a fractal dimension  $D_s = 2.40$ . White microsilica scoot contains fractal clusters of pore space with linear dimensions of 4 - 25 nm. The surface of the larger scattering formations (25 - 40 nm) are strongly indented - their fractal dimension is  $D_s = 2.83$ . The scattering curve  $\lg I(s) - \lg s$  of the FRONT - VIP filler powder has two crossover points: branched porous aggregates 20 - 40 nm in size have a fractal dimension  $D = 2.59$ , and inhomogeneities on a scale of 12 - 20 nm have highly irregular surface with  $D_s = 2.70$ . In addition, the data of small-angle X-ray

scattering allow us to suggest that on the surface of the smallest elements of the structure of the filler powder (4 - 12 nm), there may be layers of scattering inhomogeneities with a lower electron density than that of silicon dioxide (parameter  $\alpha = 4.10$ ).

The results obtained confirm the presence of a developed pore space of particles and agglomerates of dispersed silicon dioxide of nanometer sizes, can be used to calculate the effective thermal conductivity of heterogeneous systems, for example, mineral silica powders of various origins. The investigated dispersed materials have similar parameters of the pore system at the nanometer level.

2. As a result of the analysis of the influence of the structural parameters of a granular system formed from synthesized silicon dioxide particles, it was found that during the production of LTC, their heat-shielding properties can be adjusted by changing: pressure, viscosity of the molecular weight of the gas; porosity of the macrostructure and clusters; thermal conductivity of the solid and gas phase of the system; accommodation coefficient; coordination number; size of primary particles; fractal dimension that characterizes the topological features of the structure of particles, aggregates, globules, clusters and their tendency to dissipate the energy of gas molecules.

### Conflict of interests

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

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## Түйіршіктелген микрокремний жүйелерінің құрылымдық сипаттамаларының жылу оқшаулағыш материалдардың қасиеттеріне әсерін бағалау

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**ТҮЙІНДЕМЕ**

Мақалада азбұрышты рентгендік шашырау әдісімен құрылымдалған микрокремнезем бөлшектерінің мөлшері мен формасын эксперименттік зерттеу және жылу оқшаулағыш материалдардың қасиеттері үшін түйіршіктелген жүйелердің құрылымдық сипаттамаларын бағалау мақсатында күрделі гетерогенді құрылымдардағы фотофонды жылу беру процесінің теориялық сипаттамасы қарастырылған. Түйіршікті, кеукті жүйелердегі жылу беру механизмі өте күрделі, өйткені жылу алмасу екі фазадан (қатты және газ) тұратын материалда және фазалық шекарада жүреді. Сұйық жылу оқшаулағыш жабындарда жылу беру бір қатты бөлшектен екіншісіне берілуі мүмкін. Бұл жағдайда жылу өткізгіштік: материалдың химиялық және элементтік құрамына; бөлшектердің гранулометриясына; бет топологиясына – беттің әртектілігіне, бетте ақаулардың болуына; бөлшектердің жанасу саны мен жанасу аймағына байланысты болады. Кеуктерде газдың жылу беруі газ молекулаларының соқтығысуы арқылы жүзеге асырылады. Жылу өткізгіштік - молекулалардың бос жүрісі мен кеуктердің сызықтық өлшемдерінің қатынасы, газ фазасының температурасы мен динамикалық тұтқырлығы, газ молекулаларының қатты фазамен өзара әрекеттесу сипаты арқылы анықталады. Сәулемен жылу беру бөлшектердің табиғатына, диэлектрлік, магниттік өткізгіштікке және бөлшектердің бетінің қаралық деңгейіне байланысты. Түйіршікті жүйелердегі жылу берудің мүмкін болатын механизмдерін талдауға сүйене отырып, жүйенің тиімді жылу өткізгіштігі түйіршікті материалдардың кеук кеңістігінің құрылымына, топологияға және бөлшектердің жанасу санына байланысты болады деп айтуға болады. Мінсіз теріс шарлардың реттелген қатпарлары түріндегі түйіршікті материалдар құрылымының идеалдандырылған модельдерін қарастыра отырып, біз құрылымның бірнеше нұсқасын аламыз, олар: төрт қырлы, алтыбұрышты, кубтық қаптамасы бар шар тәріздес.

**Түйін сөздер:** рентгендік дифрактометр, микрокремний, жылу өткізгіштік, диатомит, құрылым, толтырғыш.

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## Оценка влияния структурных характеристик зернистых систем микрокремнезема на свойства теплоизоляционных материалов

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**АННОТАЦИЯ**

В статье рассматриваются экспериментальные исследования размера и формы структурированных частиц микрокремнезема методом малоуглового рентгеновского рассеяния и теоретическое описание фотофонного процесса теплопередачи в сложных гетерогенных структурах с целью оценки структурных характеристик гранулированных систем для свойств теплоизоляционных материалов. Механизм теплопередачи в гранулированных, пористых системах довольно сложен, поскольку теплообмен происходит в материале, состоящем из двух фаз (твердой и газовой) и на

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границе раздела фаз. Передача тепла в жидких теплоизоляционных покрытиях может осуществляться от одной твердой частицы к другой. В этом случае теплопроводность будет зависеть от: химического и элементного состава материала; гранулометрии частиц; топологии поверхности - наличия неоднородностей, дефектов на поверхности; количества касаний и площади контакта между частицами. Теплопередача газа в порах осуществляется при столкновении молекул газа. Теплопроводность будет определяться соотношением свободного пробега молекул и линейных размеров пор, температурой и динамической вязкостью газовой фазы, характером взаимодействия молекул газа с твердой фазой. Передача тепла излучением зависит от природы частиц, диэлектрической, магнитной проницаемости и степени черноты поверхности частиц. Основываясь на анализе возможных механизмов теплопередачи в гранулированных системах, можно утверждать, что эффективная теплопроводность системы зависит, при прочих равных условиях, от структуры порового пространства гранулированных материалов, топологии и количества соприкосновений частиц. Рассматривая идеализированные модели структуры зернистых материалов в виде упорядоченных складок идеально гладких шариков, мы можем получить несколько вариантов структур: с четырехгранной; шестиугольной; кубической упаковкой шариков.

**Ключевые слова:** рентгеновский дифрактометр, микрокремний, теплопроводность, диатомит, структура, наполнитель.

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## Determination of optimal oil pumping plans

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### ABSTRACT

This paper presents the results of determining the optimal plans for pumping oil through the main oil pipelines of Kazakhstan. The calculation methodology is based on determining the minimum unit cost of pumping depending on oil flow rate. Oil pumping energy-saving modes are determined under optimal operating conditions of pumping units and heating furnaces at stations. Determination of the optimal pumping plan is implemented as a separate module of the SmartTranPro software. Pumped oil volumes on the oil pipeline sections were determined on the basis of the automated system of control and metering of electrical energy data of KazTransOil JSC. Optimal pumping plans for monthly oil volumes in the Kalamkas – Karazhanbas and Dzhumagaliev – Atasu pipeline sections for cold and warm periods were calculated on the basis of the found dependence of the pumping unit cost. For each range of oil mass flow rate, specific costs for oil pumping and a list of operating pumps at oil pumping stations located along the pipeline section are indicated.

**Keywords:** oil pipeline, flow rate, optimal pumping plan, energy-saving mode, unit cost.

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## Introduction

Increasing energy consumption efficiency when transporting oil by main pipelines mostly depends on the system of organization and management of technological modes of oil pipeline operation and is achieved by modeling optimal conditions of its operation [[1], [2], [3], [4]].

Optimizing the process of pipeline transportation of oil is of great practical importance, and a number of works are devoted to the problem of optimizing distribution of cargo flows through the system of main pipelines [[5], [6], [7], [8], [9], [10], [11], [12], [13], [14], [15], [16], [17]].

When considering this problem, the question of choosing rational volumes of pumped oil naturally

arises. Pumping units must be able to pump the amount of oil that is required according to optimal operation of the oil pipeline. Therefore, associated with the problem of choosing rational oil volumes along oil pipeline routes is the problem of choosing the most effective modes of operation of pumping and power equipment for reliable operation of the main oil pipeline.

Management of energy-saving modes is determined under optimal operating conditions of equipment of oil pumping stations and technological modes of oil pumping through main oil pipelines. Determination of energy-saving modes of pumping is important for estimating the efficiency of operation of main oil pipelines.

### Methodology for finding the optimal oil pumping plan

The optimal pumping mode is considered to be such the mode in which the least amount of financial costs is consumed for given performance. Oil pumping costs are the sum of electricity expenses consumed by pumps and fuel for operation of heating furnaces.

The problem of finding the optimal pumping mode of a given volume of oil is as follows:  $G$  is the total volume of oil (in tons), which must be pumped optimally over a period of time  $T$ ;  $Q_i$  is the capacity (in t/h) of the pipeline at the mode No.  $i$  without using a pressure regulator (PR) or a variable frequency drive (VFD);  $t_i$  is the total operating time of the pipeline in the mode No.  $i$  during the period  $T$ ;  $E_i$  is the unit costs per unit of time (in tenge/h) when pumping oil in the mode No.  $i$ ;  $Q_i^{\min}$  is the minimum specified capacity (in t/h) of the pipeline at the mode No.  $i$ , which can be achieved using a PR or a VFD.

Each optimal plan is represented by one of the following three cases:

1) The mode No.  $i$  with shutdowns, i.e. the plan consists of alternating states: pumping in the mode with the capacity  $Q_i$  (total  $t_i$  hours) and stopping pumping (total  $(T - t_i)$  hours):

$$Q_i t_i = G, \quad t_i \leq T$$

2) The combination of modes No.  $i$  and No.  $j$ , i.e. the plan consists of alternating states: pumping in the mode with the capacity  $Q_i$  (total  $t_i$  hours) and in the mode with the capacity  $Q_j$  (total  $t_j$  hours):

$$Q_i t_i + Q_j t_j = G, \quad t_i + t_j = T, \\ E_i t_i + E_j t_j \rightarrow \min$$

3) The mode No.  $i$  with the selection of rotor speed:

$$Q_{VFD} = \frac{G}{T}, \quad Q_i^{\min} \leq Q_{VFD} \leq Q_i$$

In this case, the pumping plan consists of one mode with the constant capacity  $Q_{VFD}$ . Required pump rotor speed is determined based on the value of  $Q_{VFD}$ .

The energy efficiency of oil transportation can be estimated by specific electric energy consumption according to the work performed [18]:

$$E_p = \frac{W}{G \cdot H_{loss}} \quad (1)$$

where  $W$  is the amount of consumed electricity, kWh;  $G$  is the volume of pumped oil, t;  $H_{loss}$  is the required head for pumping the volume of oil  $G$  through the pipeline, m.

In practice, in addition to specific electric energy consumption  $E_p$ , specific electric energy consumption by pipeline capacity is used:

$$E_{cap} = \frac{W}{G \cdot L} \quad (2)$$

where  $L$  is the oil pipeline length, km;  $E_{cap}$  has the dimension of kWh/(thousand tons · km).

The energy-saving mode of main oil pipeline operation is estimated by specific electric energy consumption for pumping one ton of oil. Specific electric energy consumption in kWh/t is found by the formula [[18], [19]]:

$$E_{spj} = \frac{1}{\rho Q_j} \left( N_{consjn} + \sum_{i=1}^{n_{Hj}} N_{consij} \right) \quad (3)$$

where  $N_{consjn}$  is the power consumed by electric motors of booster pumps of the head pumping station (PS) when operating in the  $j$ -th mode;  $N_{consij}$  is the same for electric motors of mainline pumps of the  $i$ -th PS;  $n_{Hj}$  is the total number of mainline pumps at stations in the  $j$ -th mode.

Power consumed by the pumping unit when operating in the  $j$ -th mode is found from the expression [[18], [19], [20]]:

$$N_{consj} = \frac{\rho g H_j Q_j}{\eta_{1j} \eta_{2j} \eta_{3j}} \quad (4)$$

where  $H_j$ ,  $Q_j$ ,  $\eta_{3j}$  are the head, the flow rate and the efficiency of the pump, respectively, when operating in the  $j$ -th mode,  $\eta_{1j}$  is the efficiency of the electric motor in the  $j$ -th mode,  $\eta_{2j}$  is the efficiency of the mechanical transmission, for the mechanical clutch can be taken  $\eta_{2j} = 0.99$ .

Pump efficiency is calculated by the formula [[18], [19]]:

$$\eta_{3j} = c_0 + c_1 Q_j + c_2 Q_j^2 + c_3 Q_j^3$$

where  $c_0$ ,  $c_1$ ,  $c_2$ ,  $c_3$  are the empirical coefficients, which are determined for each type of rotor.

The efficiency of an electric motor is expressed by the formula [19]:

$$\eta_{1j} = \left[ 1 + \frac{1 - \eta_{nom}}{2\eta_{nom}k_{load}} (1 + k_{load}^2) \right]^{-1}$$

where  $\eta_{nom}$  is the efficiency of an electric motor at nominal loading,  $k_{load}$  is the operation factor of an electric motor.

Thus, to assess the efficiency of energy-saving modes of pumping oil blends along oil pipeline routes, it is possible to use specific electric energy consumption (3), specific electric energy consumption for the work performed (1) or specific electric energy consumption for cargo turnover (2).

### Calculation results

Determination of the optimal pumping plan is implemented as a separate module for the SmartTranPro software package [21]. The software module selects the most optimal combination of pumps for each flow rate  $Q$  in the interval  $(10, Q_{max})$  with a step of 0.5 t/h and calculates specific energy consumption  $E(Q)$ .

Using this module for the Kalamkas – Karazhanbas and the Dzhumagaliev – Atasu oil pipeline sections, optimal modes of pumping oil and oil blends were calculated. According to production data, the lowest ground temperature value is observed in March, and the highest – in September, therefore calculations were carried out for these two months.

To calculate financial costs, tariffs for electricity and fuel in respective regions for 2020 were used. Pumped oil volumes on considered sections of oil pipelines were determined on the basis of the ASCAPC (Automatic System for Commercial Accounting of Power Consumption) system data of KazTransOil JSC.

The following data were used as initial parameters:

- average monthly values of soil temperature along the pipeline;
- an actual value of the pumped oil volume during the month.

When carrying out optimization calculations, the following restrictions are taken into account, which are necessary for safe operation of oil pipelines:

- maximum allowable pressure at the station outlet;
- maximum allowable pressure at the oil pumping station outlet (up to the PR);

- minimum allowable pressure at the pump inlet;
- a safe range of pump flow rate;
- minimum allowable rotor speed.

For listed sections of oil pipelines, dependences of the minimum unit cost of pumping on capacity were plotted. Based on the found dependence, optimal pumping plans were calculated for various values of monthly planned volumes.

Optimal pumping plans are presented in a tabular form, which displays a list of ranges of monthly planned volumes with corresponding optimal pumping modes.

Tables show lists of pump operating modes in ascending order of obtained performance. A performance range corresponds to each individual table mode. If, opposite to the performance range in the list of operating pumps, any pump is indicated "with a VFD" (for example, "mainline pumping unit (MPU) No. 1 with a VFD"), it is assumed that any performance value from the corresponding range can be obtained by adjusting rotor speed of the specified pump. If, opposite to the performance range in the list of operating pumps, no pump is indicated "with a VFD", it is assumed that any performance value from the corresponding range can be obtained using a VFD at the starting station, or by creating backpressure at the inlet to the terminal station. In addition, if names of pumps are indicated in a cell on one line, then this means that given pumps operate in parallel, if on different lines of one cell, then sequentially.

### The Kalamkas - Karazhanbas oil pipeline

At the Kalamkas – Karazhanbas section (Fig. 1) of the Kalamkas – Karazhanbas – Aktau main oil pipeline, Buzachi oil with constant physical and chemical composition is pumped [22]. Optimization calculations were carried out using the actual data of the SCADA system [23].

Initial parameters for performing optimization calculations are given in Table 1. At 0.6 km and 23 km of the Kalamkas - Karazhanbas pipeline, there are associated oil pumping points of Buzachi neft LLP and Arman JV. Based on the archival data of the SmartTranPro database for 2019, monthly pumping volumes from Buzachi neft LLP and Arman JV are 15-16 thousand  $m^3$  and 10-12 thousand  $m^3$ , respectively. Therefore, in order to take this fact into account, monthly average values of pumping flow rate were used as the initial calculation parameter.

Figure 2 shows the dependency curve of unit costs for pumping oil for the Kalamkas –

Karazhanbas oil pipeline section from performance obtained for the cold period. Tables 2 and 3 show optimal pump operation modes for different performances and optimal pumping plans for different monthly volumes for the Kalamkas – Karazhanbas oil pipeline.

As a result of the calculation, two optimal pump operation modes were selected for this section: in the range of mass flow rate values 100 – 231 t/h, the pipeline can operate in the mode No. 1 with shutdowns, in the range of flow rates 232 – 740 t/h – in the mode No. 2 with the selection of required rotor speed.



Figure 1 – Diagram and profile of the Kalamkas - Karazhanbas pipeline section

Table 1 – Initial parameters for calculating unit costs in the section of the Kalamkas – the Karazhanbas

Parameter names	Parameter value	
	March	September
Initial oil temperature, °C	+52.5	+54
Initial pressure, bar	0.5	0.5
Flow rate of pumping from "Buzachi neft" LLP, t/h	20	20
Flow rate of pumping from "Arman" JV, t/h	14	14
Residual pressure at the inlet of the terminal station, bar	1.2	1.2
Soil temperatures, °C	+9.2 (0 km) +10.6 (62 km)	+24.8 (0 km) +25.5 (62 km)
Electricity tariff, kWh/tenge	19.49	19.49

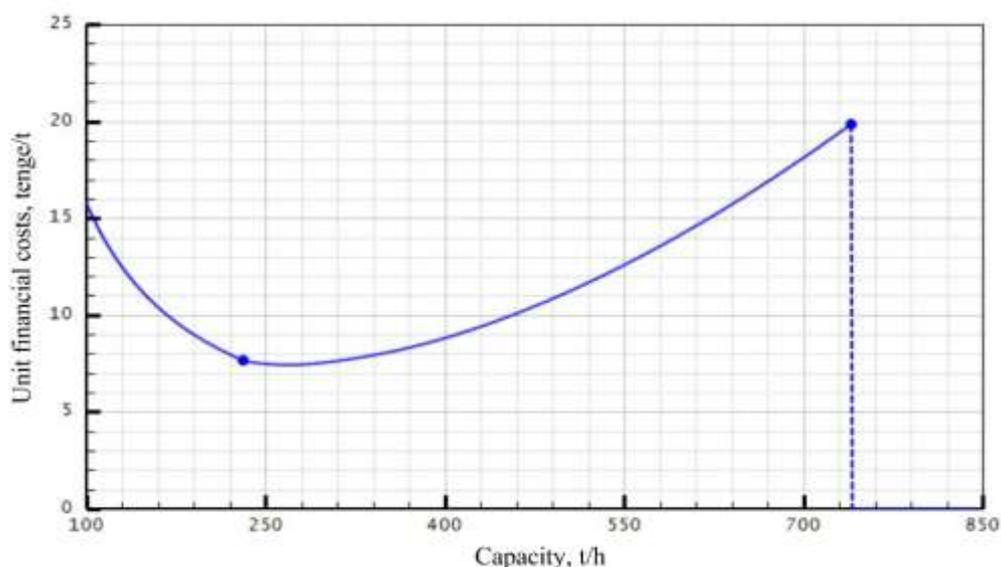


Figure 2 – Dependence of unit costs on capacity in the Kalamkas – Karazhanbas section for March

**Table 2** – Optimal operating modes of pumps for various performance values of the Kalamkas – Karazhanbas section

Mode No.	Flow rate, t/h	Costs, thousand tenge/h	Unit costs, tenge/t	Operating pumps
1	100 - 231 (March) 100 - 242 (September)	1.6 - 1.8 (March) 1.6 - 1.8 (September)	15.8 - 7.7 (March) 15.8 - 7.4 (September)	booster pump unit (BPU) No. 1
2	232 - 740 (March) 243 - 750 (September)	1.8 - 14.7 (March) 1.8 - 14.9 (September)	7.6 - 19.8 (March) 7.4 - 19.8 (September)	BPU No. 1 MPU No. 3 with a VFD

**Table 3** – Optimal pumping plans at different monthly volumes for the Kalamkas – Karazhanbas section

Pumping volume, t	Required modes
0 – 171000 (March) 0 – 174000 (September)	Mode No. 1 with shutdowns
171000 – 550000 (March) 174000 – 540000 (September)	Mode No. 2 with the selection of required rotor speed

**Table 4** – Initial parameters for calculating unit costs in the Dzhumagaliev – Atasu oil pipeline section

Parameter names	Parameter value	
	March	September
Initial oil temperature, °C	+10	+24
Initial pressure, bar	0.6	0.6
Residual pressure at the inlet of the terminal station, bar	1	1
Soil temperature, °C	+ 4.3 (0 km) +1.4 (175.7 km) +3.3 (267.6 km) +2.7 (427.3 km)	+ 22.1 (0 km) +18 (175.7 km) +19.2 (267.6 km) +16.4 (427.3 km)
Electricity rate, kWh/tenge	15.49	15.49

**The Dzhumagaliev – Atasu oil pipeline**

For optimization calculations of the Dzhumagaliev – Atasu section (Fig. 3) of the Pavlodar – Atasu main oil pipeline, parameters of Aktope oil at the outlet of the Pavlodar - head oil pumping station (HOPS) were used.

Initial data for optimization calculations are given in Table 4: initial oil temperature, pressure at the inlet of the booster pump at the Dzhumagaliev HOPS, residual pressure at the inlet of the Atasu – oil pumping station (OPS), soil temperature values at main points and electricity tariffs.



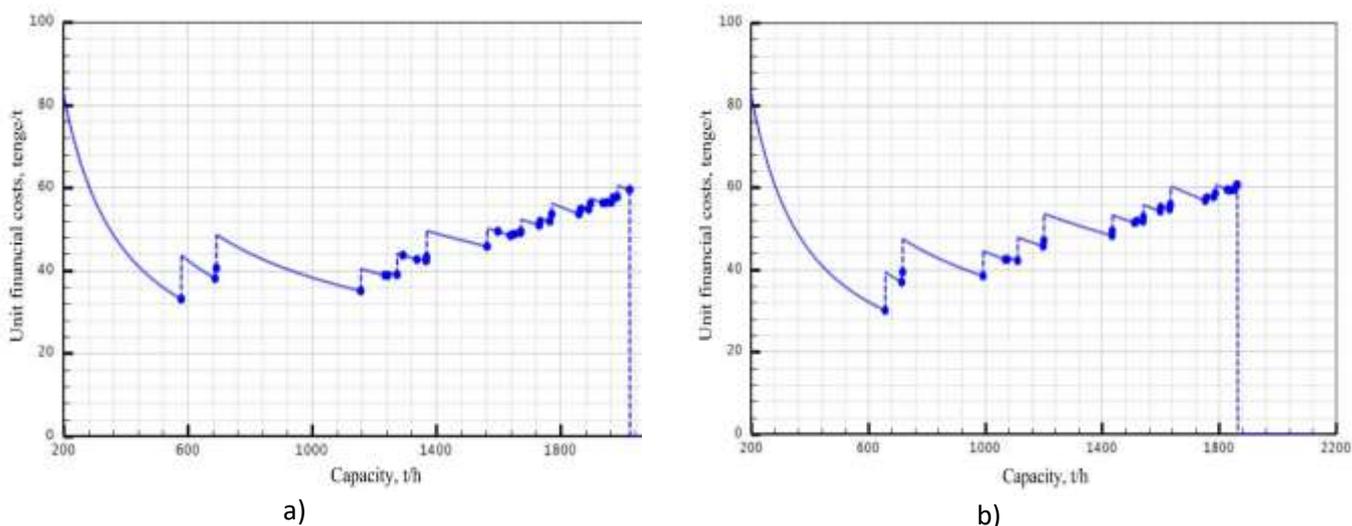
**Figure 3** – Diagram and profile of the Dzhumagaliev – Atasu pipeline section

Figure 4 shows the dependency curve of unit costs on performance obtained for cold and warm periods of Dzhumagaliev – Atasu pipeline section operation. The zigzag change in specific energy consumption on the graph is explained by switching to another pump or a group of pumps.

Table 5 shows found optimal operating modes of pumps for various performance values of the Dzhumagaliev – Atasu section for the cold period. For each range of oil mass flow rate, specific pumping costs and lists of pumps that operated at oil pumping stations of the considered section

(Dzhumagaliev HOPS and Barsengir OPS) are indicated. If the cell is empty, then this pumping station is not turned on. In accordance with obtained modes for the Dzhumagaliev – Atasu pipeline section, optimal plans for pumping oil were found at various monthly volumes.

Table 6 shows data on optimal pumping plans for the cold period. For example, in the range of monthly oil flow rates from 738,000 to 1,066,000 tons, the most optimal for energy saving is the use of a combination of modes No. 4 and No. 13 when pumping oil in this section.



**Figure 4** – Dependence of unit costs on performance at the Dzhumagaliev – Atasu pipeline section: a) cold period (March); b) warm period (September)

**Table 5** – Optimal operating modes of pumps for various performance values of the Dzhumagaliev – Atasu oil pipeline section in the cold season

Mode No.	Flow rate, t/h	Unit costs, tenge/t	Operating pumps	
			Dzhumagalieva HOPS	Barsengir OPS
1	2	3	4	5
1	200 - 658	82.6 - 30.1	BPU No. 1 MPU No. 1 (Q=0.5)	
2	659 - 715	39.4 - 36.9	BPU No. 1 MPU No. 3	
3	716 - 718	39.5 - 39.4	BPU No. 1 MPU No. 4 (D=465mm)	
4	719 - 993	47.4 - 38.5	BPU No. 1 MPU No. 1 (Q=0.5)	MPU No. 3 (Q=0.5)
5	994 - 1069	44.5 - 42.5	BPU No. 1 MPU No. 1 (Q=0.5) MPU No. 3	
6	1070 - 1076	42.6 - 42.5	BPU No. 1 MPU No. 3	MPU No. 3 (Q=0.5)
7	1077 - 1078	44.0 - 44.0	BPU No. 1 MPU No. 4 (D=465mm)	MPU No. 3 (Q=0.5)
8	1079 - 1086	44.1 - 43.9	BPU No. 1 MPU No. 1 (Q=0.5)	MPU No. 1
9	1087 - 1128	49.4 - 48.2	BPU No. 1 MPU No. 3 MPU No. 4 (D=465mm)	
10	1129 - 1172	48.3 - 46.9	BPU No. 1 MPU No. 3	MPU No. 1
11	1173 - 1174	48.4 - 48.3	BPU No. 1 MPU No. 4 (D=465mm)	MPU No. 1
12	1175 - 1187	49.0 - 48.8	BPU No. 1	MPU No. 3 (Q=0.5)

			MPU No. 1 (Q=0.5)	MPU No. 4
13	1188 - 1434	54.0 - 48.3	BPU No. 1 MPU No. 1 (Q=0.5) MPU No. 3	MPU No. 3 (Q=0.5)
14	1435 - 1435	49.4 - 49.4	BPU No. 1 MPU No. 1 (Q=0.5) MPU No. 4 (D=465mm)	MPU No. 3 (Q=0.5)
15	1436 - 1511	53.2 - 51.4	BPU No. 1 MPU No. 1 (Q=0.5) MPU No. 3	MPU No. 1
16	1512 - 1518	51.9 - 51.8	BPU No. 1 MPU No. 2 MPU No. 3	MPU No. 3 (Q=0.5)
17	1519 - 1519	52.5 - 52.5	BPU No. 1 MPU No. 3 MPU No. 4 (D=465mm)	MPU No. 3 (Q=0.5)
18	1520 - 1599	56.3 - 54.2	BPU No. 1 MPU No. 2 MPU No. 3	MPU No. 1
19	1600 - 1600	55.0 - 55.0	BPU No. 1 MPU No. 2 MPU No. 3	MPU No. 2
20	1601 - 1601	55.2 - 55.2	BPU No. 1 MPU No. 3 MPU No. 4 (D=465mm)	MPU No. 1
21	1602 - 1602	56.0 - 56.0	BPU No. 1 MPU No. 3 MPU No. 4 (D=465mm)	MPU No. 2
22	1603 - 1685	57.0 - 54.8	BPU No. 1 MPU No. 1 (Q=0.5) BPU No. 2	MPU No. 3 (Q=0.5) MPU No. 4
23	1686 - 1688	55.2 - 55.1	BPU No. 1 MPU No. 1 (Q=0.5) MPU No. 3	MPU No. 3 (Q=0.5) MPU No. 4
24	1689 - 1753	58.6 - 56.8	BPU No. 1 MPU No. 1 (Q=0.5) MPU No. 2	MPU No. 1 MPU No. 3 (Q=0.5)
25	1754 - 1757	57.5 - 57.4	BPU No. 1 MPU No. 1 (Q=0.5) MPU No. 3	MPU No. 1 MPU No. 3 (Q=0.5)
26	1758 - 1766	57.7 - 57.5	BPU No. 1 MPU No. 2 MPU No. 3	MPU No. 3 (Q=0.5) MPU No. 4
27	1767 - 1770	59.2 - 59.2	BPU No. 1 MPU No. 3 MPU No. 4 (D=465mm)	MPU No. 3 (Q=0.5) MPU No. 4
28	1771 - 1828	61.1 - 59.4	BPU No. 1 MPU No. 1 (Q=0.5) MPU No. 2	MPU No. 1 MPU No. 2
29	1829 - 1839	59.6 - 59.3	BPU No. 1 MPU No. 2 MPU No. 3	MPU No. 1 MPU No. 3 (Q=0.5)
30	1840 - 1843	60.4 - 60.4	BPU No. 1 MPU No. 2 MPU No. 3	MPU No. 2 MPU No. 3 (Q=0.5)
31	1844 - 1844	61.4 - 61.4	BPU No. 1 MPU No. 3 MPU No. 4 (D=465mm)	MPU No. 1 MPU No. 3 (Q=0.5)
32	1845 - 1848	62.5 - 62.5	BPU No. 1 MPU No. 3 MPU No. 4 (D=465mm)	MPU No. 2 MPU No. 3 (Q=0.5)
33	1849 - 1863	63.9 - 63.5	BPU No. 1 MPU No. 2 MPU No. 3	MPU No. 1 MPU No. 2

**Table 6** – Optimal pumping plans at different values of monthly volumes for the Dzhumagaliev – Atasu section for March

Pumping volume, thousand tons	Required modes
0 – 489000	Mode No. 1 with shutdowns
489000 - 738000	a combination of mode No. 1 and mode No. 4
738000 – 1066000	a combination of mode No. 4 and mode No. 13
1066000 - 1304000	a combination of mode No. 13 and mode No. 24
1304000 – 1368000	a combination of mode No. 24 and mode No. 29
1368000 - 1386000	a combination of mode No. 29 and mode No. 33

Thus, for each range of monthly flow rates, the most optimal pump operating modes were determined for the coldest and warmest periods of time for the Dzhumagaliev – Atasu oil pipeline section.

### Conclusions

With the use of the control module of optimal oil pumping modes of SmartTranPro SP for the Kalamkas – Karazhanbas and the Dzhumagaliev – Atasu oil pipeline sections:

- dependences of the minimum unit cost of pumping on performance for warm and cold periods were plotted;

- on the basis of the found dependence of the unit cost, optimal pumping plans were calculated for various values of monthly planned volumes for warm and cold periods of time.

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

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## Мұнай айдаудың оңтайлы жоспарларын анықтау

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### ТҮЙІНДЕМЕ

Бұл мақалада Қазақстанның магистральдық мұнай құбырлары арқылы мұнай айдаудың оңтайлы жоспарларын анықтау нәтижелері келтірілген. Есептеу әдістемесі мұнай шығынына байланысты айдау бірлігінің минималды меншікті құнын анықтауға негізделген. Мұнай айдаудың энергия үнемдеу режимдері станциялардағы сорғы қондырғылары мен жылыту пештерінің оңтайлы жұмыс жағдайларында анықталды. Айдаудың оңтайлы жоспарын анықтау SmartTranPro бағдарламалық пакеті үшін жеке модуль ретінде жүзеге асырылды. Мұнай құбырларының учаскелері арқылы айдалатын мұнай көлемі «ҚазТрансОйл» АҚ ASKUE жүйесінің деректері бойынша анықталды. Анықталған бірлік құнының ағын жылдамдығына тәуелділігі негізінде «Қаламқас – Қаражанбас» және «Жұмағалиев – Атасу» учаскелеріндегі суық (наурыз) және жылы (қыркүйек) уақыт аралығындағы мұнайдың айлық көлеміне айдаудың оңтайлы жоспарлары есептелді. Әрбір шығын диапазоны үшін мұнай айдауға арналған нақты шығындар және құбыр учаскесінің бойында орналасқан мұнай айдау станцияларындағы жұмыс істейтін сорғылардың тізімі көрсетілді.

**Түйін сөздер:** мұнай құбыры, массалық шығын, оңтайлы айдау жоспары, энергияны үнемдеу режимі, меншікті шығындар.

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## Определение планов оптимальной перекачки нефти

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	<b>АННОТАЦИЯ</b> В данной статье приведены результаты определения оптимальных планов перекачки нефти по магистральным нефтепроводам Казахстана. Методика расчета основана на определении минимальной удельной стоимости перекачки в зависимости от расхода нефти. Энергосберегающие режимы перекачки нефти определяются при оптимальных условиях работы насосных агрегатов и печей подогрева на станциях. Определение оптимального плана перекачки реализовано в виде отдельного модуля для программного комплекса SmartTranPro. Объемы перекачиваемой нефти по участкам нефтепроводов были определены по данным системы АСКУЭ АО «КазТрансОйл». На основании найденной зависимости удельной стоимости от расхода были рассчитаны оптимальные планы перекачки для месячных объемов нефти на участках «Каламкас – Каражанбас» и «Джумагалиева – Атасу» для холодного (март) и теплого (сентябрь) периодов времени. Для каждого диапазона расхода указаны удельные затраты на перекачку нефти и перечень работающих насосов на нефтеперекачивающих станциях, расположенных вдоль участка нефтепровода. <b>Ключевые слова:</b> нефтепровод, массовый расход, оптимальный план перекачки, энергосберегающий режим, удельные затраты.
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## Synthesis and characterization of new biodegradable gels based on 2,2'-(ethylenedioxy) diethanethiol and pentaerythritol triacrylate

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### ABSTRACT

The work is devoted to the synthesis and characterization of gels based on the monomers pentaerythritol triacrylate (PETriA) and 2,2'-(ethylenedioxy)diethanethiol (EDODET) by thiol-ene "click" polymerization. The properties of the obtained gels were investigated by IR, Raman spectroscopy, mechanical analysis. Sol-gel analysis of obtained networks was carried out and the degradability was investigated. The results of IR spectroscopy confirmed the presence of -C = O and -C-O-C- groups in the composition of the obtained gels. The presence of unreacted C = C bonds conjugated with C = O, as well as thiol groups, varies depending on the composition of the initial monomer mixture (IMM). Raman spectroscopy results correlate well with IR data. Raman spectra also show C-S, S-S and SH characteristic bands that are difficult to identify by IR spectroscopy. It was found that the composition of MM affects the physicochemical properties of the synthesized gels. The highest yield of the gel fraction of obtained polymers was found in samples with an equimolar composition of IMM. The analysis of mechanical properties showed that gels with an excess of PETriA exhibit more elastic properties, and an excess of EDODET leads to the formation of networks with a higher crosslinking density. The study of the ability of obtained PETriA-EDODET gels to degrade in a 3% solution of hydrogen peroxide showed that the polymer network degrades by 12% within 60 days. This property of the obtained gels can find application in the creation of targeted drug delivery systems with their prolonged release.

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## Introduction

The popularity of thiol-ene "click" polymerization for the synthesis of various polymer materials is growing every year. These reactions are very versatile and can be carried out using radical conditions including photochemical initiation, or can simply be promoted with polar solvents such as N, N-dimethylformamide (DMF) [1].

Thiols and unsaturated compounds are often used in stoichiometric ratios (1:1) to achieve complete conversion and increase the mechanical properties of the target product by thiol-ene polymerization [2]. However, the resulting materials usually have inactive surfaces with such a ratio of the starting components. The work [3] reports the first use of nonstoichiometric thiol-unsaturated compound ratios leading to the production of

materials with residual unreacted functional groups both in the bulk and on the surface. The presence of unreacted thiol groups on the surface of nanoparticles as a result of nonstoichiometric thiol-ene interactions can impart mucoadhesive properties to materials - the ability to adhere and retain on the surface of the mucous membrane due to the formation of disulfide bonds with cysteine residues of mucins [4].

Recently, the use of thiol-ene polymers is mainly concentrated in the biomedical field, mostly in the form of gels [5]. A wide variety of polymer systems have been successfully synthesized using various types of multifunctional unsaturated compounds and thiols [[6], [7]]. Biodegradable thiol-ene systems are of particular interest [8]. Biodegradation in the case of biomaterials for medical use focuses on biological processes within the body that cause

gradual destruction of the material [9]. The following mechanisms of destruction are distinguished: hydrolytic and enzymatic [10]. In this work, we studied polymeric materials that contain hydrolysable bonds in the polymer chain, such as an ester group, and, accordingly, degrade by a hydrolytic mechanism.

### Experimental part

**Materials.** Pentaerythritol triacrylate (PETriA) manufactured by Aldrich Chemical Co (USA), containing 350 ppm of hydroquinone monomethyl ester as an inhibitor, was used without further purification.

2,2'-(ethylenedioxy)diethanethiol (EDODET) manufactured by Aldrich Chemical Co (USA) was used without additional purification.

N,N-Dimethylformamide (DMF) manufactured by Aldrich Chemical Co (USA) was used without additional purification.

**Gel synthesis.** Synthesis of gels of various compositions (the ratio of monomers [PETriA:EDODET] = [2:1], [1:1] and [1:2] mol/mol) was carried out in closed glass penicillin vials in a DMF solvent (50 mass.% solvent and 50 mass.% monomer mixture) with constant stirring on a laboratory shaker GFL 3005 (Germany) for 24 hours at 30°C. The formation of a crosslinked gel structure was carried out within 24 hours, depending on the composition of the initial monomer mixture (IMM). Then the resulting gels were washed from unreacted monomers for 1 hour in DMF, 6 hours in acetone (3 changes of acetone) and 24 hours in water (3 changes of water). The washed polymers were dried in a lyophilic freeze-dryer to constant weight.

**Physicochemical research methods.** The study of the kinetics and equilibrium degree of swelling in distilled water was carried out by the gravimetric method. The equilibrium degree of swelling was calculated by the formula

$$\alpha = \frac{m_{\text{swollen}} - m_{\text{dry}}}{m_{\text{dry}}} \quad (1)$$

where  $m_{\text{swollen}}$  and  $m_{\text{dry}}$  – mass of swollen and dry samples, respectively.

For sol-gel analysis the synthesized gel samples were washed from unreacted monomers for 1 hour in a DMF solution, then in an acetone solution (3 changes of solvent), and then in water. After that washed gels were dried in a freeze-dryer to constant weight.

The content of sol and gel fractions was calculated using the formulas

$$G\% = \frac{m_{\text{dry w.}}}{m_{\text{synt}}} \times 100\% \quad (2)$$

$$S\% = 100\% - G\% \quad (3)$$

where  $m_{\text{synt}}$  – mass of the synthesized gel;  $m_{\text{dry w.}}$  = mass of the washed and dried gel.

An analytical balance Sartorius BP 121S (Germany) with an accuracy of 0.0001 g was used to determine the mass of synthesized and washed dried gels. Labconco FreeZone freeze-dryer (USA) was used for drying the samples.

In order to confirm the chemical composition of the synthesized samples, the methods of IR and Raman spectroscopy were used. IR spectroscopy was performed on a Carry 660 Agilent IR Fourier spectrometer (USA).

Raman spectroscopy was performed using a Solver Spectrum setup (Russia). Dried gel samples with a diameter of 0.5 mm were used for the analysis.

The physicochemical characteristics of the synthesized samples were determined on a TA.XTplus Stable Micro Systems instrument (UK) in the compression mode.

**Biodegradation degree.** The degradability of the resulting gels was studied in a 3% hydrogen peroxide solution. The experiments were carried out in closed glass penicillin vials at a constant temperature of 37 °C in an incubator with occasional stirring. Determination of degradable properties was carried out in several parallel experiments. The degree of degradation (DD) was investigated by the gravimetric method to a constant value of the mass of the samples and was calculated by the formula:

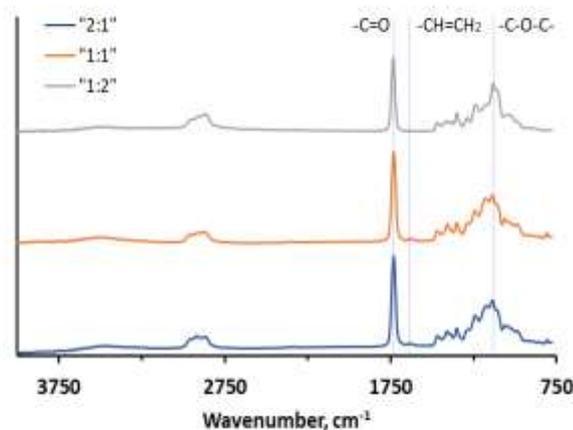
$$DD = \frac{m_0 - m_x}{m_0} \times 100\% \quad (4)$$

where  $m_x$  – mass of degraded gel;  $m_0$  – initial mass of gel.

### Discussion of results

In this work, the thiol-ene "click" polymerization method was used to synthesize gels based on pentaerythritol triacrylate (PETriA) and 2,2'-(ethylenedioxy)diethanethiol (EDODET) with different ratios of components in the IMM [PETriA:EDODET] = [2:1], [1:1] and [1:2] mol/mol in the presence of DMF.

The chemical composition of the synthesized PETriA-EDODET gels was studied by IR and Raman spectroscopy. IR spectra of dry samples of PETriA-EDODET gels of various compositions are shown in Figure 1. All three presented spectra have a high peak in the range of 1745-1725  $\text{cm}^{-1}$ , which corresponds to vibrations of the  $-\text{C}=\text{O}$  group. A broader peak of lower intensity in the region of 1180-1140  $\text{cm}^{-1}$  indicates the presence of ( $-\text{C}-\text{O}-\text{C}-$ ) groups in the composition of the resulting gels [11]. It is also worth paying attention to the peaks in the region of 1640-1630  $\text{cm}^{-1}$  for compositions 2:1 mol/mol and 1:1 mol/mol which confirm the presence of unreacted  $-\text{C}=\text{C}-$  bonds conjugated with  $-\text{C}=\text{O}$ . At the same time, for the 1:2 mol/mol composition with a predominance of the thiol component, no characteristic bands are observed in this region, which proves that all double bonds have reacted with  $-\text{SH}$  groups.



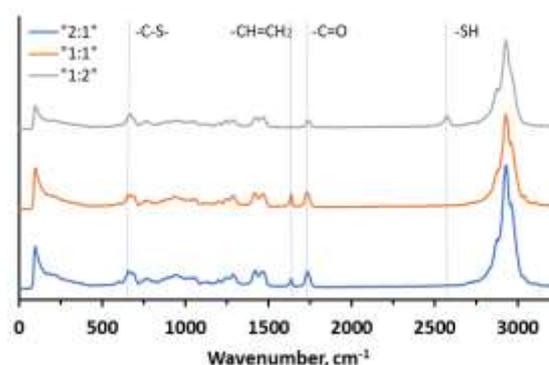
**Figure 1** - IR spectra of PETriA-EDODET gels with various compositions of the IMM. [PETriA-EDODET] = [2:1], [1:1] and [1:2] mol/mol

It is known from the literature that the determination of  $-\text{SH}$  groups content requires the use of Raman spectroscopy, since thiol groups show a weak signal in the IR spectra. Figure 2 shows the results of Raman spectroscopy of PETriA-EDODET based gels. It was found that peaks at 700-650  $\text{cm}^{-1}$  are responsible for vibrations of the  $\text{C}-\text{S}$  bond. The peak at 525  $\text{cm}^{-1}$  indicates vibrations of the  $\text{S}-\text{S}$  bonds. The absorption band at 2590-2550  $\text{cm}^{-1}$  confirms the presence of  $\text{SH}$ -groups, which indicates an excess of EDODET in the PETriA-EDODET gel with a monomer ratio of 1:2 mol/mol.

The absorption bands in the region of 1680  $\text{cm}^{-1}$  are responsible for the vibrations of the  $-\text{CH}=\text{CH}_2$  bond which confirms the presence of a large number of multiple bonds characteristic of PETriA-EDODET gels structure obtained with an excess of PETriA in

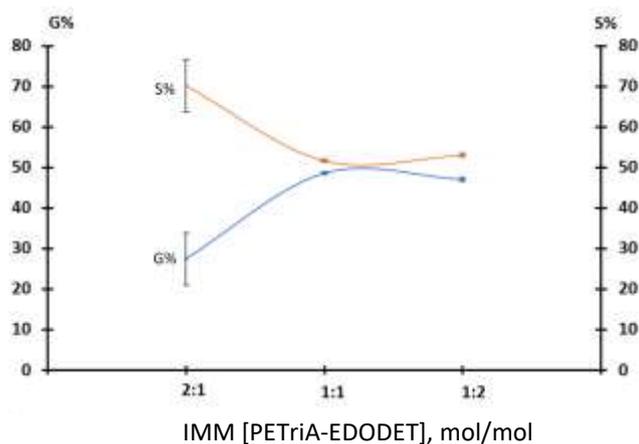
the composition of the IMM (2:1 mol/mol) and correlates with IR spectroscopy data.

Based on the results obtained by IR and Raman spectroscopy a mechanism for the formation of crosslinked gel structure was proposed. During the polymerization reaction, the interaction of monomers with the formation of covalent bonds occurs through the reaction of functional groups such as double bonds of PETriA and thiol groups of EDODET. With an excess of PETriA in the IMM, gels with unreacted multiple bonds in their composition are formed, while an excess of EDODET leads to the formation of gels with unbound thiol groups. Thus, in this work, the formation of such gel structures was confirmed by the data of IR and Raman spectroscopy.



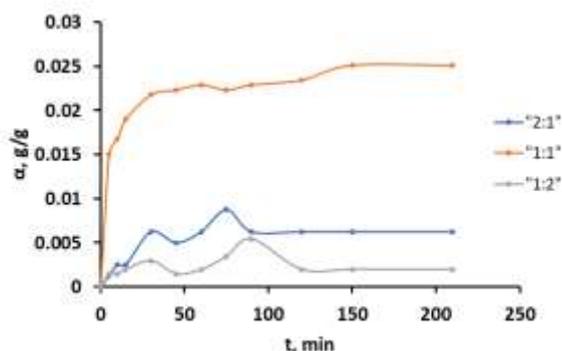
**Figure 2** - Raman-spectra of PETriA-EDODET gels with various compositions of the IMM. [PETriA-EDODET] = [2:1], [1:1] and [1:2] mol/mol

Sol-gel analysis is one of the main characteristics of gels. This method allows determination of the polymer network yield. According to the results of sol-gel analysis of PETriA-EDODET gels (Figure 3), the highest yield of gel fraction is observed for the gel sample with the IMM composition of 1:1 mol/mol. This may be due to the fact that for the given IMM composition, the starting monomers PETriA and EDODET are taken in an equimolar ratio. When the ratio of monomers PETriA and EDODET in IMM is 2:1 or 1:2 mol/mol, the yield of the gel fraction decreases. It is likely that with a lack of one of the monomers in IMM, the amount of reacted monomer molecules decreases. Then, unreacted monomers are washed out of the polymer network during washing. In this case, the yield of the gel fraction at 1:2 mol/mol monomer ratio in the IMM is higher than at 2:1 mol/mol ratio. This may be due to the high activity of thiols to form disulfide bonds, which leads to the formation of PETriA-EDODET gel of a higher crosslinking density with an excess of 2,2'-(ethylenedioxy) diethanethiol in the IMM.



**Figure 3** - Dependence of sol and gel fractions yield of PETriA-EDODET gels on IMM composition

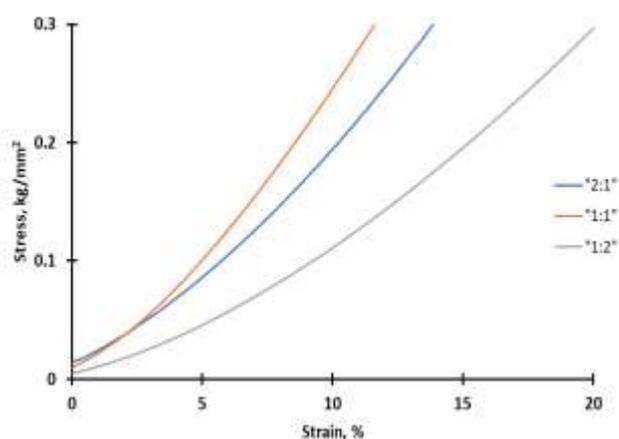
In this work, the swelling ability of obtained PETriA-EDODET gels in distilled water was investigated. Figure 4 shows data on the change in the swelling degree of PETriA-EDODET gels over time. It can be seen from the results obtained that the ratio of the starting monomers affects swelling rate of the gels. With an increase in the content of 2,2'-(ethylenedioxy) diethanethiol, the swelling capacity of PETriA-EDODET gels decreases. This behavior may be due to the high content of -SH groups in the gel structure, which form additional disulfide bridges and increase the density of the polymer network.



**Figure 4** - Dependence of the swelling rate of PETriA-EDODET gels on IMM composition in distilled water

The study of the mechanical characteristics of the gels makes it possible to draw conclusions about the mechanical strength of the gels and indirectly judge their composition. In this work, the mechanical strength of the synthesized gels based on PETriA-EDODET in the compression mode was investigated. Figure 5 shows the deformation curves of PETriA-EDODET gels of various compositions. It was found that all gel samples are sufficiently strong and elastic and do not undergo significant

mechanical destruction. The figure also shows a noticeable effect of the ratio of monomers in the IMM on strength of the resulting gels. The presence of an excess amount of EDODET in the composition of the IMM contributes to a slight decrease in elasticity of the polymer network and an increase in its strength (hardness). This is probably due to the formation of a larger number of crosslinks in the gel, which reduce the mobility of macromolecules. Gels with an excess of PETriA in the IMM composition are more elastic, which may be due to the presence of a larger number of multiple bonds in the gel composition.



**Figure 5** - Deformation curves of PETriA-EDODET gels of various IMM compositions

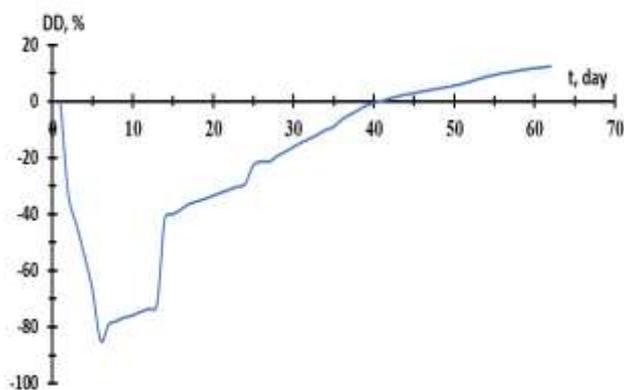
According to the mechanical analysis data, the elastic modulus was also calculated for each gel sample presented in Table 1. The elastic modulus was calculated as the slope of the initial straight section of the gel deformation curve obeying Hooke's law. It was found that an increase of EDODET concentration in IMM composition of PETriA-EDODET gel promotes an increase in the elastic modulus.

**Table 1** - Values of the elastic modulus of PETriA-EDODET gels of various compositions of IMM

IMM composition [PETriA:EDODET], mol/mol	Elastic modulus, Pa
2:1	17500
1:1	21428
1:2	25745

It is known from the literature that in the human body in places of inflammation, including in places of formation of oncological tumors of various thiology,

hydrogen peroxide is released in small quantities. The release of hydrogen peroxide prevents the spread of infection and serves as a signal to attract leukocytes [12]. Various concentrations of hydrogen peroxide can be found in the literature to study oxidative degradation in vitro, mimicking in vivo conditions. While the ISO 10993-13 standard implies the use of 3 wt.% (approximately 1 M)  $H_2O_2$ , Cosgriff-Hernandez and colleagues used 20%  $H_2O_2$  with 0,1 M  $CoCl_2$ , Sun and colleagues used 5 mM  $H_2O_2$  with 50 mM  $CuSO_4$  [13]. In this work, the degradation degree of gels based on PETriA-EDODET was studied in 3% hydrogen peroxide solution. Based on the data obtained, a graph of the dependence of the degradation degree of gels on the residence time in solutions was plotted, which is shown on Figure 6. This figure shows that the degradation of the sample with a composition of 2:1 mol/mol occurs after 40 days and the stage of swelling precedes the degradation of the gel. In the first week, the gel swells rapidly, that can be noticed by a significant increase in its mass, then it decreases and the degree of degradation increases, respectively, this behavior correlates with the research data [13], where the degradability of gels based on pentaerythritol tetrakis (3-mercaptopropionate) and tri-/tetraacrylates synthesized by thiol-ene "click" reaction was studied. The degree of degradation of gels based on PETriA-EDODET by day 60 amounted  $\sim 12\%$ . Polymers with hydrolyzable bonds generally undergo slow degradation from several weeks to a year [14].



[PETriA:EDODET] = [2:1] mol/mol

**Figure 6** - Dependence of the degree of degradation of PETriA-EDODET gels on time in a 3% solution of hydrogen peroxide

## Conclusions

In this work, gels based on the monomers pentaerythritol triacrylate (PETriA) and 2,2'-(ethylenedioxy) diethanethiol (EDODET) in various ratios and in the presence of a solvent dimethylformamide (DMF) were synthesized by the thiol-ene "click" polymerization method. The properties of the obtained gels were investigated by various physicochemical methods. The results of IR spectroscopy confirmed the presence of  $-C=O$  ( $1745-1725\text{ cm}^{-1}$ ),  $-C-O-C-$  ( $1180-1140\text{ cm}^{-1}$ ) groups in the composition of the obtained gels. Bands in the region  $1640-1630\text{ cm}^{-1}$  for compositions 2:1 mol/mol and 1:1 mol/mol established the presence of unreacted  $C=C$  bonds, conjugated with  $C=O$ , whereas for 1:2 mol/mol composition with a predominance of the thiol component, there are no characteristic peaks in this region. Obtained results of Raman spectroscopy correlate well with IR spectroscopy results and confirm them. Raman spectra also show  $C-S$ ,  $S-S$  and  $-SH$  characteristic bands that are difficult to identify by IR spectroscopy. It was found that IMM composition affects physicochemical properties of the synthesized gels. Analysis of mechanical properties showed that gels with an excess of PETriA exhibit more elastic properties, while an excess of EDODET leads to the formation of networks with a higher crosslinking density.

The ability of the obtained PETriA-EDODET gels to biodegradation in 3% hydrogen peroxide solution was investigated. It was found that the polymer network degrades by 12% within 60 days. This property of the obtained gels can find application in medicine as a targeted drug delivery system with their prolonged release.

## Conflict of interests

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

## Acknowledgment

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## 2,2'- (этилендиокси) диэтантриол мен пентаэритритол триакрилат негізінде биологиялық деградацияға ұшырайтын жаңа гельдердің синтезі мен сипаттамасы

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### ТҮЙІНДЕМЕ

Жұмыс тиол-ен «клик» полимеризациясы арқылы пентаэритритол триакрилат (ПЭТриа) және 2,2'- (этилендиокси) диэтантриол (ЕДОДЭТ) мономерлері негізінде гельдерді синтездеуге және оларды сипаттауға арналған. Алынған гельдердің қасиеттері ИҚ-, Раман спектроскопиясы, механикалық талдау арқылы зерттелді. Алынған торларға золь-гельдік талдау жүргізілді және деградацияға қабілеттілігі зерттелді. ИҚ-спектроскопиясының нәтижелері алынған гельдердің құрамында С=О және -С-О-С- топтарының болатындығын растады. С=О-мен түйскен реакцияға түспеген С=С байланыстары, сондай-ақ тиол топтары бастапқы мономер қоспасының (БМҚ) құрамына байланысты өзгереді. Раман спектроскопиясының нәтижелері ИҚ деректерімен жақсы корреляцияланады. Раман спектрлері сонымен қатар ИҚ спектроскопиясымен анықтау қиын С-С, S-S және SH-тән жолақтарды көрсетеді. БМҚ құрамы синтезделген гельдердің физикалық-химиялық қасиеттеріне әсер ететіні анықталды. Алынған полимерлердің гельдік фракциясының ең жоғары шығымы БМҚ эквимольерлік құрамы бар үлгілерде табылды. Механикалық қасиеттерді талдау көрсеткендей, ПЭТриа мөлшері артық гельдер серпімді қасиеттерге ие, ал ЕДОДЭТ-тің артық болуы өзара тығыздығы жоғары торлардың пайда болуына әкеледі. Алынған ПЭТриа-ЕДОДЭТ гельдерінің сүтегі асқын тотығының 3% ерітіндісінде ыдырау қабілетін зерттеу полимерлік желінің 60 күн ішінде 12% ыдырайтынын көрсетті. Алынған гельдердің бұл қасиеті дәрі-дәрмектердің таргетті (мақсатты) жеткізу жүйелерін құруда қолдануға болады.

**Түйін сөздер:** (2,2'- (этилендиокси) диэтантриол, пентаэритритол триакрилат, гель, биодеградация, тиол-ен «клик» полимерленуі).

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## Синтез и характеристика новых биодеградируемых гелей на основе 2,2'- (этилендиокси) диэтантриола и пентаэритритол триакрилата

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### АННОТАЦИЯ

Работа посвящена синтезу и характеристике гелей на основе мономеров пентаэритритол триакрилат (ПЭТриа) и 2,2'- (этилендиокси) диэтантриол (ЭДОДЭТ) методом тиол-ен «клик» полимеризации. Свойства полученных гелей были исследованы методами ИК-, Раман спектроскопии, механическим анализом. Были проведены золь-гель анализ полученных сеток и исследована способность к деградации. Результаты ИК-спектроскопии подтвердили наличие С=О и -С-О-С- групп в составе полученных гелей. Наличие непрореагировавших С=С связей, сопряженных с С=О, а также тиольных групп варьируется в зависимости от состава исходной мономерной смеси. Результаты Раман-спектроскопии хорошо коррелируют с данными ИК-анализа. Раман-спектры также показывают С-С-, S-S и SH- характеристические полосы, которые тяжело идентифицируются методом ИК-спектроскопии. Установлено, что состав исходной мономерной смеси (ИМС) влияет на физико-химические свойства синтезированных гелей. Наибольший выход гель фракции полученных полимеров обнаружен у образцов с эквимольным составом ИМС. Анализ механических свойств показал, что гели с избытком ПЭТриа проявляют более эластичные свойства, а избыток ЭДОДЭТ приводит к образованию сеток с большей плотностью сшивания. Исследование способности полученных гелей ПЭТриа-ЭДОДЭТ к деградации в 3% растворе перекиси водорода показало, что полимерная сетка деградирует на 12% в течении 60 суток. Данное свойство полученных гелей может

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найти применение при создании систем таргетной доставки лекарственных средств, с их пролонгированным высвобождением.

**Ключевые слова:** (2,2'-(этилендиокси) диэтантол, пентаэритритол триаакрилат, гель, биодegradация, тиол-ен «клик» полимеризация).

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## Hybrid Sorbents for Removal of Arsenic

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### ABSTRACT

The paper analyzes data on the removal of arsenic by sorption methods using materials that have prospects for large-scale application in water treatment. These materials include transition metal oxides in the micro- and nano-dimensional form, including those in the composition of composite materials with inorganic matrices, or hybrid sorbents in the composition with polymer resins or natural biopolymers. Examples of the use of composite (hybrid) sorbents for the removal of arsenic from solutions with low concentrations (at the level of MPC) are given. The objective of this article was to sum the up-to-date information about the most important features of chitosan-containing and chitosan-carbon materials we developed in view their use in arsenic removal processes at low concentrations to concentrations that meet WHO requirements. The paper presents data on the sorption properties of Mo-containing activated carbon fibers and chitosan-carbon composite materials towards arsenic (V) when it is extracted from bidistilled and tap water under static and dynamic conditions. The factors of the different behavior of the sorbents depending on the form of a biopolymer deposited on the fiber and the stability of the sorbents during the sorption of arsenic are discussed.

**Keywords:** arsenic, sorption, composites, hybrid sorbents, carbon fiber, chitosan.

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## Introduction

Various technologies are used to solve numerous environmental problems. In particular, the following methods are used for the removal of toxic pollutants from water: oxidation/precipitation, coagulation, co-precipitation, sorption, ion exchange, and membrane technologies [[1], [2], [3], [4]]. Among them, sorption/adsorption is considered as a relatively simple, effective, and cost-efficient techniques for removing pollutants, it is also suitable for the use in rural areas. In addition, no sludge is formed when applying this technology.

Arsenic is known to be one of the most toxic chemical elements at very low concentrations [[1], [5], [6], [7], [8]]: it is one of the most well-known environmental pollutants. Arsenic affects the human body at very low concentrations, so that the World Health Organization (WHO) recommended reducing

the maximum permissible concentration (MPC) of As in drinking water down to 10 µg/L [1].

Arsenic enters the environment from geothermal and ground waters, as a result of weathering, soil erosion, and volcanic activity. In addition, arsenic contamination has anthropogenic origins, such as the use of pesticides, mining processing, and burning of fossil fuels [[1], [2], [3]].

Although most of the indicated methods, provided that they are carried out under optimal conditions, allow reducing the arsenic concentration below 10 µg/L, the majority of them are rather costly, especially the membrane technologies [[1], [2]].

At present, a wide range of materials was tested for the purpose of removing As at low concentrations: natural ores, minerals, activated carbons (AC), ion exchange resins, agricultural and industrial waste, natural biopolymer chitosan [[1], [2], [7], [8], [9], [10]].

Among the materials recommended for use as adsorbents in water treatment, the following transition metal oxides were studied:  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{MnO}_2$ , and iron oxides/hydroxides [[6], [11], [12], [13]]. The latter ones are of the greatest interest, since their application allows isolating powders (nanopowders) from the media to be decontaminated by magnetic separation on the condition that the oxide has magnetic properties. Of iron oxides, goethite ( $\alpha\text{-FeOOH}$ ) and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) are non-magnetic, whereas magnetite ( $\text{Fe}_3\text{O}_4$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), and hydrated iron oxides are characterized magnetic properties [[13], [14]].

The separation of iron hydroxides, which are considered as among the most effective sorbents for arsenic, requires sedimentation or filtration and is hard to perform due to their low mechanical strength [[13], [15]].

The solution to this problem consists in the immobilization of iron oxides into a carbon or polymer matrix to obtain composite materials [[13], [14], [15], [16], [17], [18]].

Another group of materials that are widely studied as sorbents for arsenic includes carbon materials (CM) in various forms like conventional commercial carbons or carbon nanotubes. However, activated CM, despite their high specific surface area, the presence of surface functional groups, and a well-developed porous structure, are not very suitable for removing anionic pollutants, which include arsenic compounds. At the same time, CMs comprise one of the most suitable matrices for the production of composites, even despite their high cost and the method of their production, which is not particularly environmentally friendly [[19], [20]].

In recent years, numerous works were devoted to nanoscale metal (hydro)oxides, such as  $\text{Fe}_3\text{O}_4$ , hydrated iron oxide (HGO),  $\text{TiO}_2$ ,  $\text{MnO}_2$ , etc., which demonstrate high sorption efficiency towards heavy metals. However, these hydroxides cannot be directly used in the flow-through systems due to high pressure in the columns caused by the ultra-fine particle sizes. These technological disadvantages can be avoided by placing the oxide on to conventional porous adsorbents, including activated carbons, cellulose granules, alginate beads, or polymer adsorbents to produce hybrid sorbents for further application [15].

Another approach to obtaining composite materials consists in the immobilization of iron oxides directly into polymer matrices. Cation-exchange and anion-exchange synthetic resins are

used for immobilization [[13], [15], [16], [21], [22], [23], [24], [25], [26], [27]].

Commercial arsenic sorbents were synthesized on the basis of industrial ion-exchange resins by immobilization of iron oxides in them. Among these, the ArsenX<sup>®</sup> hybrid sorbents show high efficiency in removing arsenic from model solutions [[21], [23], [24]].

Currently, the development of highly effective sorbents is tending to low-price sorbents based on natural biopolymers, the most preferred of which is the natural polymer chitosan (CS) [[7], [10], [28], [29], [30], [31], [32], [33]].

The use of biopolymers as sorbents is determined by their unique combination of properties: non-toxicity, biodegradability, biocompatibility, bioactivity, and production from renewable sources [[30], [31]].

Chitosan is a natural aminopolysaccharide synthesized by alkaline hydrolysis of chitin (a cheap natural raw material, among other sources, it is a by-product of the fishery industry). Chitosan can be considered as the most suitable material for the removal of anions (including some charged forms of arsenic), since it contains a large number of amino groups protonated in an acidic medium. This ensures the removal of anionic forms of arsenic by an ion exchange mechanism [29].

However, there are several factors that prevent the full-scale use of chitosan. The modification of CS is necessary to overcome its solubility in an acidic medium, low porosity, and residual crystallinity.

The best sorption properties are demonstrated by the materials based on modified chitosan, which include grafting functional groups or compounds of other compounds (that have a strong affinity for arsenic) incorporated into a biopolymer matrix [10].

Impregnation with metal oxides or metals was suggested to increase the sorption capacity or improve the selectivity towards arsenic [[10], [30], [31], [32], [33], [34]]. A large group of modifier compounds consists of metal oxides (Al, Ti, Mn, Fe, Ce, Cu, and Mo) [[5], [7], [10], [31], [34]]. Molybdenum oxide is especially remarkable of these due to the different mechanism of interaction with As as a result of the formation of an arsenomolybdate complex [[6], [10]].

It is necessary to single out a group of sorbents in which the biopolymer (polysaccharide) chitosan is modified with molybdenum, which has a strong affinity for both chitosan and As: this allows the use of Mo-containing chitosan as a sorbent for arsenic [[6], [7], [10], [31], [35], [36]]. Mo-containing

**Table 1** - Examples of hybrid sorbents based on metal oxides

Sorbent	Initial concentration	Solution	Mode	Passed volume*	Final concentration, $\mu\text{g/L}$	Reference
Polystyrene (polyHIPE) coated with iron hydroxide	50-200 $\mu\text{g/L}$ As(III), As(V)	deionized and tap water	dynamic		<10	[38]
Layers of sand coated with manganese oxide and iron oxide	1 mg/L As(III), As(V)	0.01 M $\text{NaNO}_3$ solution	pilot unit, dynamic		<50	[39]
Iron coated chitosan flakes, Iron doped chitosan granules	500 $\mu\text{g/L}$ As(III), As(V)	real ground water	dynamic	147 b.v. As(III) 180 b.v. As(V)	<10	[40]
$\text{TiO}_2$ /montmorillonite	120-410 $\mu\text{g/L}$	real ground water	column	4300-10500 b.v.	<10	[41]
FeO/activated carbon	0,5 mg/L	potable water	column	1,250 ml of solution	<10	[42]
$\text{Al}_2\text{O}_3$ /chitosan	91 mg/L As(III), 101 mg/L As(V)	deionized water	dynamic	40 b.v. As(III) 120 b.v. As(V)	<10	[43]
Activated carbons impregnated with iron hydroxide	40-60 $\mu\text{g/L}$ 70-75% As(V) 25-30% As(III)	real ground water	dynamic	20000 b.v.	<10	[44]
Activated carbon fiber impregnated with nanosized magnetite	<1000 $\mu\text{g/L}$	water solution	static	m/v = 0.7 g/L	<10	[45]
Macroporous anion exchanger D-201 loaded with hydrated ferric oxide	1 mg/L As(V)	solution in the presence of $\text{SO}_4^{2-}$ , $\text{Cl}^-$ , $\text{PO}_4^{3-}$ , $\text{SiO}_2$ , $\text{HCO}_3^-$	dynamic	max 2000 b.v.	<10	[15]
npRio gel-type strong base anion exchange resin Impregnated iron oxide ArsenX <sup>np</sup>	20 $\mu\text{g/L}$	solution in the presence of 30 $\mu\text{g}$ of $\text{SiO}_2$	dynamic	~7500 b.v. 17500 b.v.		[23]
Strong base anion exchange resin based on styrene-divinylbenzene loaded hydrated ferric hydroxide	600 $\mu\text{g/L}$ As(V)	solution in the presence of $\text{PO}_4^{3-}$ , $\text{SiO}_2$	dynamic	~12000 b.v.	<10	[22]
ArsenX <sup>np</sup>	80-100 $\mu\text{g/L}$ 140-180 $\mu\text{g/L}$			25000 b.v. 20000 b.v.	<50	[21]
Natural zeolite coated with nanocomposites of Mn-Fe oxides	50 $\mu\text{g/L}$ As(III), As(V)	potable water	pilot unit, dynamic	10000 b.v.	<3	[46]
Purolite A-500P resin filled with hydrated iron oxide	100 $\mu\text{g/L}$ As(III)	solution in the presence of $\text{SO}_4^{2-}$ , $\text{Cl}^-$ , $\text{HCO}_3^-$		12000 b.v.	10	[47]

Note: \*) b.v - empty bed volumes,  
m/v – mass to volume ratio

chitosan resins can be synthesized in the form of magnetic sorbents [37]. Some examples of the use of hybrid sorbents for the removal of arsenic at low

concentrations close to the MPC are shown in Table 1.

The objective of the present work was to study the sorption properties and stability of Mo-

containing sorbents based on both pristine carbon fiber and fiber modified with chitosan during the processes of arsenic removal from model solutions with low concentrations in bidistilled and tap water.

### Experimental part

Carbon fiber and chitosan-carbon materials modified with molybdenum oxide were chosen as the objects of the research. To produce chitosan carbon materials, chitosan (in various forms) was deposited by different methods on the initial carbon fiber Aktilen (grade brand B) produced by St. Petersburg Research Institute Chemical Fiber "Khimvolokno".

The chitosan-carbon material CCM(-900) was produced by depositing chitosan from a solution on a carbon fiber (CF), which was used as a working electrode, in a standard electrochemical cell, while it was polarized into the cathode region with holding at the reached potential of -900mV for a given time. The deposition potential was measured relatively to the Ag/AgCl reference electrode.

The sample of CCM(SO<sub>4</sub>) was prepared by deposition of nanoscale chitosan on the surface of CF by ionotropic gelation method. To do this, the carbon fiber was pre-soaked in a chitosan solution and then the wet fiber was treated with a concentrated solution of the strong electrolyte Na<sub>2</sub>SO<sub>4</sub>. The fiber was washed with water to remove the excess of the electrolyte and dried in the air.

The preparation of chitosan-carbon materials is described in detail in [48].

The modification of carbon fiber and chitosan-carbon materials with molybdenum oxide was performed by adsorption of molybdenum from solutions of sodium molybdate with different concentrations at pH 3, at which the maximum sorption of molybdenum from the solution was observed. The sorption of molybdenum was carried out under static conditions at a ratio of  $m : V = 1 : 1000$ . The concentration of molybdenum in the sorbent was determined by the difference between the initial and equilibrium concentrations from a given volume of the solution to the carbon sample.

The sorption properties of composite sorbents were studied under static conditions with a phase ratio of  $S : L = 1 : 1,000$ . The sorption kinetics was studied on the model solutions prepared with tap water by the limited volume method (0.05 mg sorbent: 50 ml solution, pH 3.0). In accordance with this method, probes were taken from the solution, the initial concentration of which is known, at certain intervals of time, in which the concentration

of the element was determined during its extraction by the sorbent. Arsenic(V) sorption isotherms were obtained by the method of variable concentrations in the solutions prepared with bidistilled water from 50 to 1000 µg/L (pH 3.0) and tap water from 50 to 1500 µg/L (pH 6.4–6.5). To prepare model solutions, a standard solution of Na<sub>2</sub>HAsO<sub>4</sub>·7H<sub>2</sub>O in 1 M HCl with 25 mg/L As was used. Standards for the determination of arsenic were prepared with tap and bidistilled water.

To study the sorption dynamics, a model solution was prepared with bidistilled water with a concentration of arsenic(V) of ~100 µg/L, pH 2.9. Arsenic breakthrough curves were taken in a polyethylene column of a diameter of 0.9 cm and a height of 5.8 cm at a solution passing rate of 1 ml/min. The volume of the loaded sorbent layer was 1 cm<sup>3</sup> with a packing density of 0.15-0.16 g/cm<sup>3</sup>. The samples were analyzed for the content of As(V) as 50 ml of the solution was passed. The following sorbents were tested in the dynamic mode: initial CF–Mo, CCM(-900)–Mo, CCM(SO<sub>4</sub>)–Mo.

### Results and discussion

Despite the advantages of using chitosan as a sorbent for the removal of certain pollutants, there are a number of objective reasons that prevent its widespread use as a sorbent for the removal of arsenic, in particular. These include: 1) weak stability of chitosan at pH optimal for As extraction, 2) low sorption capacity, especially towards As(III), 3) difficulty in standardization of initial chitosans due to heterogeneity depending on the degree of deacetylation, 4) low porosity of chitosan and, accordingly, low availability of sorption sites, 5) physicochemical characteristics of granules that prevent their use in industrial units in a dynamic mode [[30], [31]].

Although chitosan can sorb arsenate ions [[29], [49], [50]], the sorption capacity towards arsenic is very low, it rarely reaches 10 mg of As (V)·g<sup>-1</sup>, and only a few mg of As(III)·g<sup>-1</sup>[35]. Therefore, chitosan undergoes modification by physical or chemical methods [7]. The choice of a metal modifier (specifically, a metal oxide) is determined by both the nature of the interaction of this metal directly with the matrix and its interaction with the extracted toxic agent. The immobilization of metal oxides into chitosan implies an increase in arsenic sorption capacity and the emergence of selectivity over other metals and related ions [7]. As was mentioned above, metals such as molybdenum and iron are

effectively used to obtain sorbents due to their strong affinity for chitosan.

The removal of arsenic using granules of a chitosan sorbent containing molybdenum depends on the characteristics of the granules, as does the sorption of molybdenum by granules of the original chitosan. This is related to the fact that the sorption of molybdenum is influenced by both the degree of deacetylation and the molecular weight of chitosan. The correlation between the parameters is not direct. However, it was shown that the sorption of molybdenum depended on the degree of crystallinity of the polymer. High degree of crystallinity reduces the availability of water and metal ions to binding (reactive) amino groups [51].

On the other hand, the sorption of molybdenum is completely controlled by the pH of the solution and the concentration of molybdenum in the solution, which determine the appearance of charged poly-nuclear hydrolyzed forms of molybdenum at pH 3-3.5, which are most preferable for its sorption by chitosan [[52], [53]].

Thus, some part of molybdenum is well sorbed due to electrostatic interactions with polymer molecules, while the other part is in the form of clusters adjacent to the polymer structure [54].

Chitosan sorbents containing molybdenum can be prepared in various ways: 1) impregnation of chitosan granules with molybdate, 2) coagulation of CS granules in a solution of molybdate. The first process is essentially an adsorption process and is largely determined by the properties of chitosan, which cause different sorption of molybdate. The second method of production is based on ion gelation of chitosan using molybdate as gelling agent, which leads to the formation of micro and nanoparticles of chitosan [[35], [36], [55]]. Ionic gelation with molybdate is an analog of the processes of ionotropic gelation of chitosan in

solutions of tripolyphosphate or sodium sulfate. The difference between the materials obtained in different media was confirmed by electron microscopy. The granules obtained in sodium hydroxide are characterized by large open porous structure (with a thin outer layer). When the gel is coagulated with molybdate, then treated with sodium hydroxide solutions, the structure is heterogeneous. The external layer is relatively compact (100  $\mu\text{m}$ ) without obvious pores, and the inner part is characterized by a small pores structure [[54], [56]].

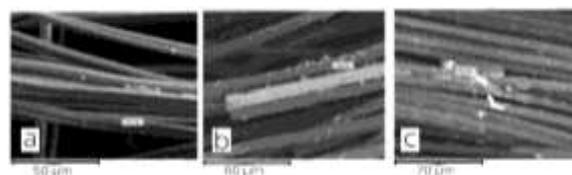
The sorbents used in the work were based on activated carbon fiber (ACF) and were obtained using these fiber modification techniques. Chitosan

deposition on the fiber surface in the base form was performed by electrodeposition on the cathode from CF, that is, by gelation of chitosan with sodium hydroxide generated at the cathode at a potential of -900 mV [57]. Another sample was prepared by coagulation of chitosan with sodium sulfate in the presence of CF as a carrier [48]. The modification of the prepared samples with molybdenum was carried out by adsorption of Mo from a solution of sodium molybdate. The use of CF as a carrier creates favorable conditions for the sorption of arsenic. The deposition of CS on a highly developed CF surface contributes to the increase of the chitosan surface and, accordingly, the availability of amino groups of CS molecules [[58], [59]].

The features of Mo sorption by carbon fiber and chitosan-carbon materials, and the characterization of materials by atomic adsorption and electron microscopy were described in [[58], [59], [60]]. In order not to repeat the published data, we included only the part related to the sorption of arsenic.

The surface morphology of the initial CF and composite chitosan-carbon materials with chitosan deposited in various forms were characterized by scanning electron microscopy (Figure 1). When carbon fibers are modified with chitosan, two different films are deposited: an insoluble chitosan film in the base form under cathodic polarization and a film in the sulfate form, both of them are solid, homogeneous, completely covering the pores of the original carbon fiber.

The non-modified materials (in the absence of Mo) do not virtually sorb arsenic. On the contrary, as the test results show, the materials modified with Mo effectively decontaminate solutions from arsenic under static conditions: at initial arsenic concentrations of 50–1500  $\mu\text{g/L}$ , the equilibrium concentration reaches 10  $\mu\text{g/L}$ . The effectiveness of Mo-containing sorbents can be explained by the formation of an open porous structure formed in a film deposited on the carbon fiber surface, similar to the structure in chitosan gels, which were prepared by the interaction of chitosan with molybdate polyoxyanions as crosslinking agents [[54], [61]].



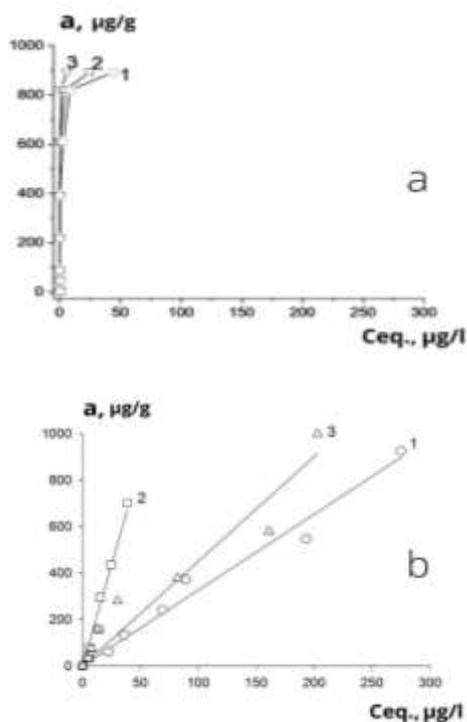
**Figure 1** - SEM image of the surface of composite sorbents based on CF modified with molybdenum: a) CF-Mo; b) CCM(-900)-Mo; c) CCM(SO<sub>4</sub>)-Mo

The difference between the sorbents is displayed in the processes of arsenic(V) extraction. From the analysis of the sorption isotherms, it can be seen that in bidistilled water in the studied concentration range, the sorbents differ slightly from each other (Figure 2a). While in tap water, the best sorbent is a Mo-containing chitosan-carbon material in which the polymer is deposited on the carbon fiber surface in the sulfate form (Figure 2b).

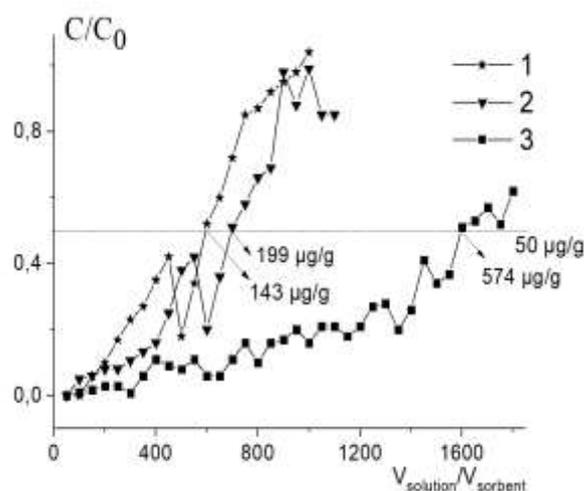
The difference in the behavior of chitosan-carbon materials is clearly displayed in the dynamic mode of arsenic removal from aqueous solutions.

As follows from the data presented in Figure 3, the sorbents CCM(-900)-Mo and CF-Mo have approximately the same full dynamic capacity, which is achieved when passing 900-950 bed volumes of the solution.

At the same time, the total exchange capacity of sorbent CCM(SO<sub>4</sub>)-Mo is not achieved even when passing 1800 ml (b.v.) of the solution. The numbers at the intersection of the output curves with the line of 50 µg/L correspond to the dynamic capacity before the slip. Here, at the selected sorbent loading density and a given solution passing rate, sorbents containing Mo, in which CF is coated with a chitosan film in various forms, show satisfactory characteristics: CCM(-900)-Mo retains a concentration of up to 10 µg/L when passing 300 bed volumes, and CCM(SO<sub>4</sub>)-Mo when passing 750 bed volumes.



**Figure 2** - Isotherms of sorption of As(V) on Mo-containing sorbents from a) bidistilled and b) tap water, 1) CCM(-900)-Mo, 2) CCM(SO<sub>4</sub>)-Mo, 3) CF-Mo. a – sorption capacity, Ceq. – equilibrium concentration



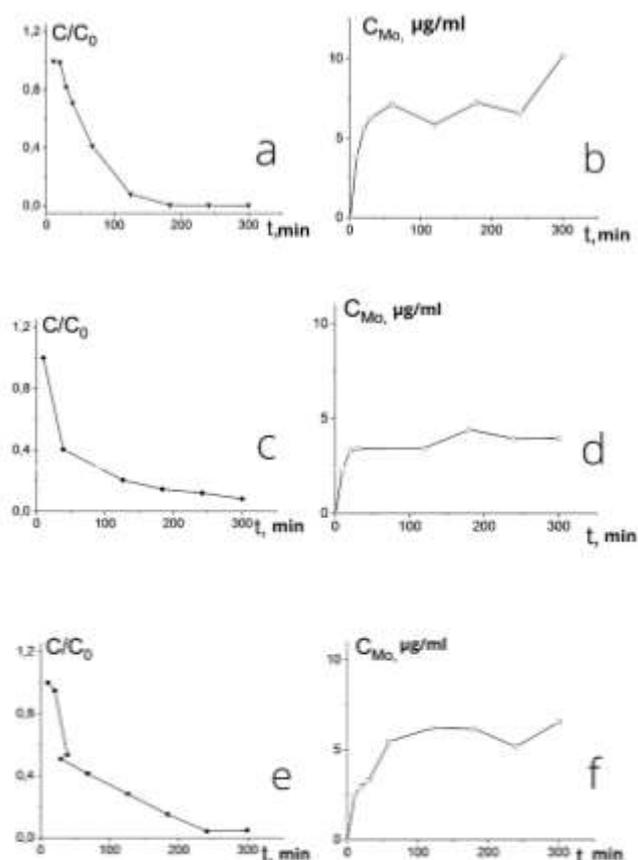
**Figure 3** - Output curves of sorption of As (V) by the sorbents: 1) CF-Mo, 2) CCM(-900)-Mo, 3) CCM(SO<sub>4</sub>)-Mo, pH 2.9, Co ~105 µg/L; C/C<sub>0</sub> -- the ratio of the concentration of As (V) in the eluate to the initial concentration

The isolation of arsenic is known to be based on a complexation reaction in a solution between Mo(VI) and As(V). The structure of these complexes, the so-called heteropolyanions, is very complex and depends on both the initial Mo/As ratio and the pH of a solution [6].

However, the monolybdate ion, which is located in the chitosan film in various bound forms (strongly bound and labile), can be released into the solution, leading to secondary contamination. Also, a weakly bound form of molybdate, partially released into the solution, can form complexes with arsenic, thereby reducing the efficiency of the sorption process.

The curves of Mo leaching from the sorbents in comparison with the kinetic data of arsenic extraction are shown in Figure 4.

As follows from the above data, during the sorption of arsenic, labile molybdate is washed out of the sorbent into the solution, which leads to contamination of the solution with molybdenum in concentrations significantly exceeding the MPC of molybdenum (250 µg/L). Mo leaching is not accompanied by an increase of the concentration of As in the solution, which is probably due to the bond strength of the arseno-molybdate complex with the carbon matrix. The problem of reducing the leaching of molybdate and increasing the bond strength of molybdate with the sorbent can be solved by treating the sorbent with phosphate ions before using the Mo-chitosan sorbent to prevent the leaching of mobile molybdate [[6], [36], [55]].



**Figure 4** - Kinetics of the sorption of As(V) (a, c, e) and the kinetics of leaching of molybdenum (b, d, f) from the composite sorbents: a, b) CF–Mo; c, d) CCM(-900)–Mo; d, e) CCM(SO<sub>4</sub>)–Mo; C/C<sub>0</sub>– the ratio of the concentration of As(V) at the time t to the initial concentration, C<sub>Mo</sub> is the concentration of molybdenum at time t.

## Conclusions

1. Oxides of transition polyvalent metals in an ultradispersed state in the composition of composite sorbents, being deposited on an inorganic carrier or included in a polymer matrix, can be successfully used to remove arsenic from solutions with low concentrations to a level that meets WHO standards.

2. Sorption of As(V) by Mo-containing sorbents based on carbon fiber and chitosan-modified fiber in various forms under static and dynamic conditions has been studied.

3. The determining role of the form of chitosan deposited on the surface of carbon fiber on the sorption properties of composite Mo-containing sorbents has been shown.

4. During the removal of As(V) from acidic solutions, the composite sorbents are destroyed, which is accompanied by the release of Mo into the solution to be cleaned. Therefore, the synthesized sorbents can be used in combined schemes of purification of industrial water and technological solutions.

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

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## Мышьякты кетіруге арналған гибриді сорбенттер

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### ТҮЙІНДЕМЕ

Мақалада суды тазартуда кең көлемде қолданылатын материалдарды пайдалана отырып сорбциялық әдістермен мышьякты кетіру бойынша мәліметтер талданады. Оларға микро және нано мөлшерлік күйдегі ауыспалы металдардың оксидтері кіреді, олардың ішінде органикалық емес матрицалы композициялық материалдар құрамында немесе полимерлі шайырлар немесе табиғи биополимерлері бар гибриді сорбенттер болады. Концентрациясы төмен ШРК (шекті рұқсат етілген концентрация) деңгейде ерітінділерден мышьякты кетіру үшін композиттік (гибриді) сорбенттерді қолдану мысалдары келтірілген. Бұл мақаланың мақсаты – ДДСҰ талаптарына сәйкес келетін төмен концентрацияда мышьякты кетіру процестерінде қолдану үшін Мо-бар хитозан мен біз жасаған хитозан-көміртекті материалдардың маңызды ерекшеліктері туралы соңғы ақпаратты жинақтау. Мақалада статикалық және динамикалық жағдайда алынған бидистилденген және ағынды судан бөліп алған кезде мышьякқа (V) қатысты құрамында Мо бар белсендіріген көмір талшықтары мен хитозан-көміртекті композициялық материалдардың сорбциялық қасиеттері туралы деректер келтірілген.

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Талшық түрінде тұнбаға түсетін биополимер формасына және мышьяк сорбциясы кезінде сорбенттердің тұрақтылығына байланысты сорбенттердің әр түрлі әрекеттерінің себептері талқыланады.

**Түйін сөздер:** мышьяк, сорбция композиттер, гибриді сорбенттер, көміртекті талшық, хитозан.

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## Гибридные сорбенты для удаления мышьяка

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### АННОТАЦИЯ

В работе анализируются данные по извлечению мышьяка сорбционными методами с использованием материалов, имеющих перспективы широкомасштабного применения в водоподготовке. К ним отнесены оксиды переходных металлов в микро- и нано- размерном состоянии, в том числе в составе композитных материалов с неорганическими матрицами, или гибридных сорбентов в составе с полимерными смолами или природными биополимерами. Приведены примеры использования композитных (гибридных) сорбентов для извлечения мышьяка из растворов с низкими концентрациями (на уровне ПДК). Цель настоящей статьи – обобщить актуальную информацию о наиболее важных особенностях Мо-содержащих хитозановых и разработанных нами хитозан-углеродных материалах для использования их в процессах удаления мышьяка на уровне низких концентраций до концентраций, удовлетворяющих требованиям ВОЗ. В работе представлены данные по сорбционным свойствам Мо-содержащих активированных углеродных волокон и хитозан-углеродных композиционных материалов по отношению к мышьяку (V) при извлечении его из бидистиллированной и водопроводной воды, полученные в статических и динамических условиях. Обсуждаются причины различного поведения сорбентов в зависимости от формы осажденного на волокно биополимера и устойчивость сорбентов в процессе сорбции мышьяка.

**Ключевые слова:** мышьяк, сорбция, композиты, гибридные сорбенты, углеродное волокно, хитозан.

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## Study of the horizontal sidetracking efficiency using hydrodynamic modeling (on the example of a Kazakhstani field)

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### ABSTRACT

One of the modern approaches for the effective development of small deposits is the construction and operation of wells with a complex architecture: horizontal wells (HW), sidetracks (BS, BGS), multilateral wells (MLW). Sidetracking makes it possible to reanimate an old well that is in an emergency state or inactivity for technological reasons, by opening layers that have not been previously developed, bypassing contamination zones, or watering the formation. This study examines the possibility of using horizontal sidetracks in the operating wells of the field of the Zhetybai group. To select the optimal length of the horizontal sidetrack of the wells, graphs of the dependences of the change in flow rate versus length of the horizontal well were built, taking into account the pressure losses due to friction. It can be seen from the dependence of NPV versus length of the horizontal wellbore that the maximum NPV is achieved with a horizontal wellbore length of 100 m. A further increase in the length of the horizontal wellbore leads to a decrease in NPV. This is due, firstly, to a decrease in oil prices, and secondly, interference of wells, a small number of residual reserves, and a small oil-bearing area. As a result of a comparison of technical and economic criteria, the optimal length of a horizontal wellbore is from 100-300 meters. Comparison of the flow rates of vertical wells and wells with horizontal sidetracks showed a clear advantage over the latter in all respects.

**Keywords:** horizontal sidetrack, hydrodynamic modeling, flow rate, friction pressure loss, Net present value – NPV.

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## Introduction

One of the current approaches for the efficient development of small reservoirs is the drilling and operation of complex design wells - horizontal wells (HW), sidetracks (S, HS) and multilateral wells (MLW).

Sidetracking makes it possible to reanimate an old well that is in a breakdown state or inactivity for technological reasons, by penetrating layers that have not been previously developed and bypassing zones of contamination or water encroachment.

In the United States, multilateral drilling began in 1930. The first wells with two sidetracks each about 7 m long drilled in Texas at a depth of 900 m.

The oil flow rate of one of these wells increased from 0.25 to 9.6 tons/day (during the first ten days). Steady flow rates of sidetrack wells was 5-7 tons/day.

The first experimental work of drilling multilateral wells in the Soviet Union was carried out in 1952 at the Kartashovskoye field in wells 65-45. Almost 80% of the well length was drilled directly through the producing formation. The distance between the individual sidetracks bottomhole were increased to 300 m [1].

The works of the authors [[2], [3], [4], [5], [6], [7], [8], [9]] are devoted to the analysis of the horizontal sidetracks exploitation, determination of

well flow rates, drilling problems, planning and location of the horizontal sidetracks.

Differences in the horizontal wells production rate determination were defined as a result of statistical analysis in [[10], [11], [12]]. The main factor affecting the productivity of high-flow wells is reservoir pressure, for low-flow wells - the length of the horizontal section of the wellbore.

To enhance oil recovery and improve well productivity formation stimulation methods are considered in [[13], [14]].

This study is devoted to horizontal sidetracks application in the operating wells of the X oil field of the Zhetybai group.

### Experimental part

Field X, related to the satellite of the Zhetybai field, is located in the steppe flat part of the Mangyshlak peninsula and is territorially included in the Mangistau region. This is one of the small fields in terms of oil reserves, which is part of the Production Office "Zhetybaimunaigaz". The oil-bearing capacity of the field was established in 1975, when a gush of oil was obtained from the J-IX horizon in exploration well 3.

One production zone the J-IX horizon was identified based on the analysis of geological field data and the results of the X oil field development analysis.

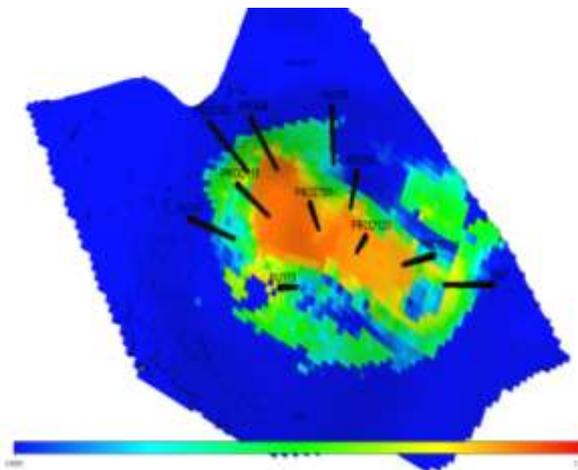
The initial geological and physical characteristics of the production zone are shown in Table 1.

**Table 1** - Initial geological physical characteristic J-IX horizon of the X oil field of the Zhetybai group

Parameter	Horizon J-IX
Average depth, m	1861
Reservoir type	поровый
Oil Productive area, thous m <sup>2</sup>	3853
Gas Productive area, thous m <sup>2</sup>	-
Porosity, unit fraction	0.19
Average oil saturation, unit fraction	0.67
Absolute permeability, 10 <sup>-3</sup> mkm <sup>2</sup> ( from core/from hydrodynamic study)	0.0215 (core) / 0.0615 (hydrodynamic)
Reservoir temperature, °C	85
Reservoir pressure, MPa	18.2
Reservoir oil viscosity, mPa*s	2.31
Reservoir oil density, ton/m <sup>3</sup>	0.783
Formation volume factor, unit fraction	1.166
Bubble point pressure, MPa	5.96
Gas-oil ratio, m <sup>3</sup> /ton	48

The production well stock includes six wells: 2 exploration and 4 production wells (108, 110, 114 and 120).

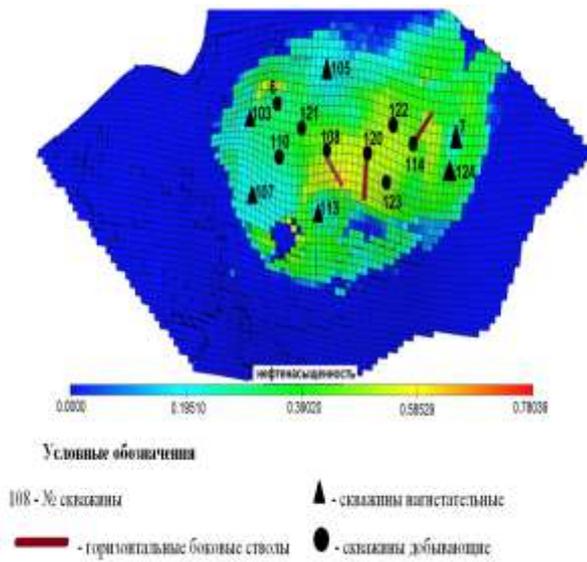
The hydrodynamic model uploaded a total of 11 wells placed according to depth, geological and physical characteristics and productive zone capabilities in accordance with development project production data (see Figure 1).



**Figure 1** - Location of production and injection wells on the hydrodynamic model

At 2015, the remaining reserves of the X oil field of the Zhetybai group amounted to 3123.5 thousand tons of oil and it was the initial criteria for the selection of the candidate wells from the old stock. At the same time, when choosing wells for sidetracking operation, it is necessary to take into account the degree of formation waterflooding. In this regard, for each well it was necessary to carry out a detailed analysis of adjacent wells sections and the nature of the reservoir distribution in the formations that are the objects for sidetracking.

It was significant to determine the location of candidate wells, when designing the sidetrack wells. To determine the trajectory and justify the length of the horizontal sidetrack of the well, horizontal well (HW) production rates were calculated using various formulas. First, the areas of maximum residual oil reserves were determined using the hydrodynamic model of the field. As can be seen from Figure 2, the areas with the maximum residual oil saturation are located along the paleo channel in the central part of the field. Based on this, candidate production wells were identified in which horizontal sidetracks (HS) were designed (Figure 2). In total, three production wells were selected: 108, 114 and 120, which are located in the central part of the paleo-channel deposits with the highest effective oil saturation.



**Figure 2** - Trajectory of horizontal sidetracks in producing wells (108, 114, 120)

After determining the maximum residual oil reserves areas, various options for the horizontal sidetracks trajectory were calculated, which differed in many directions.

One of the characteristic features of the field is the occurrence of the aquifer below the oil reservoir, and due to intensive waterflooding, the water cut of the selected wells in 2015 was up to 95%. Therefore, it was decided to design the horizontal sidetracks trajectory along the paleochannel, closer to the top of the reservoir to reduce the water cut in the wells.

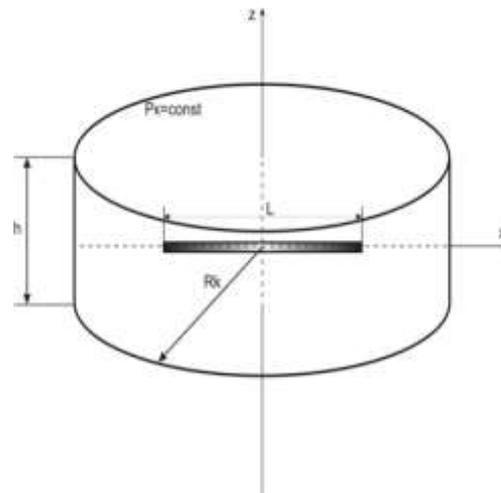
Fluid inflow to vertical and horizontal wells differs significantly. Thus, the inflow to a vertical well is radial, and streamlines are distributed parallel to the top and bottom of the formation, because a vertical well penetrates the entire thickness of the formation. With an increase in the penetrated formation thickness, the flow rate increases, the pressure distribution in the vertical plane does not change. For horizontal wells, fluid flow occurs both vertically and horizontally. Well flow rate is affected by horizontal and vertical permeability, reservoir boundaries, horizontal borehole length, presence of local depressions in the borehole (water and gas accumulate in them) and the behavior of the bottomhole formation zone [15].

In cases when horizontal sidetracks are drilled at a late stage of development, it is necessary to take into account the effect of continuously changing field conditions (the presence of residual reserves not covered by waterflooding, current

water cut, formation depletion, etc.) [15]. Application of hydrodynamic modeling allows these changes to be taken into account to the maximum extent.

The results of theoretical research carried out by P.Ya. Polubarinova-Kochina [16] can be used when the reservoir thickness is many times greater than the wellbore length. If the reservoir thickness is comparable to the length of the deviated well, then the formulas cannot be used.

In work [1] Yu.P. Borisov, an approximate solution to the problem of inflow to horizontal and deviated wells in a homogeneous reservoir was presented. Based on the method of equivalent filtration resistance, simple expressions were obtained to determine the productivity of horizontal and deviated wells in a reservoir with a circular external reservoir boundary (Figure 3).



**Figure 3** - Model of a circular formation with a central location of horizontal well

The total filtration resistance can be represented as the sum of two resistances: external - the inflow from external reservoir boundary to a rectilinear vertical gallery, and internal - the fluid flow in the vertical plane to the linear drain:

$$Q = \frac{2\pi kh\Delta P}{\mu \left[ \ln \frac{4R_c}{L} + \frac{h}{L} \ln \frac{h}{2\pi r_c} \right]} \quad (1)$$

In the work of S.D. Joshi [17] was considered a steady fluid flow to a single horizontal well located in an elliptical formation.

The summation of the filtration resistances of the two flat solutions allows obtaining an expression for determining the productivity of a horizontal well:

$$Q = \frac{2\pi kh}{\mu B \left[ \ln \left( \frac{a + \sqrt{a^2 - (L/2)^2}}{L/2} \right) + \frac{h}{L} \ln \frac{h}{2r_c} \right]} \quad (2)$$

где

$$a = \frac{L}{2} \left\{ 0,5 + \left[ 0,25 + \left( \frac{R_k}{L/2} \right)^4 \right]^{0,5} \right\} \quad (3)$$

Joshi's formula for calculating the production rate of a horizontal well taking into account the formation anisotropy is as follows:

$$Q = \frac{2\pi kh \Delta P}{\mu B \left[ \ln \left( \frac{a + \sqrt{a^2 - (L/2)^2}}{L/2} \right) + \frac{h\beta^2}{L} \ln \left( \frac{h}{2\pi r_c} \right) \right]} \quad (4)$$

denoting the anisotropy coefficient

$$\beta = \sqrt{\frac{k_h}{k_v}} \quad (5)$$

The most accurate formula for calculating the horizontal well flow rate is Joshi's formula, taking into account heterogeneity (anisotropy). Thus, for calculation the flow rate of the selected wells (108, 114, 120) with horizontal sidetracks, Joshi's formula was used, presented below:

$$Q = \frac{2\pi kh(P_e - P_{wf})}{B_o \mu \left[ \ln \left( \frac{a + \sqrt{a^2 - (L/2)^2}}{L/2} \right) + \frac{h\beta^2}{L} \ln \left( \frac{h}{2\pi r_c} \right) + S \right]} \quad (6)$$

where  $L$  is the length of the horizontal wells, m;  $R_k$  is the radius of the circular external reservoir boundary, m;  $r_w$  is the well radius, m;  $h$  is the effective formation thickness, m;  $a$  is the main semiaxis of the drainage ellipse in the horizontal plane;  $k_h$  is the formation horizontal permeability,  $m^2$ ;  $k_v$  is the formation vertical permeability,  $m^2$ ;  $P_e$  is the reservoir pressure, Pa;  $P_{wf}$  is the well pressure, Pa;  $\mu$  is the reservoir oil viscosity, Pa·s;  $B_o$  is the oil formation volume factor;  $S$  is the skin factor.

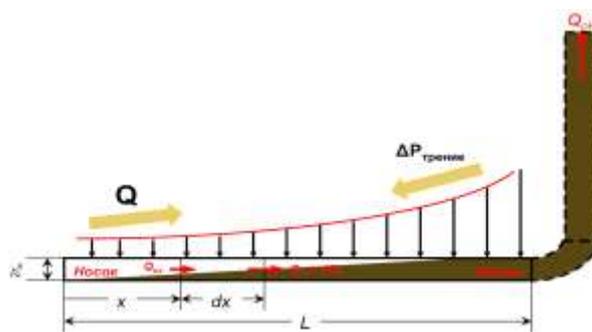
Consider a calculation of the flow rates of the wells (108, 114, 120) with the horizontal sidetracks, taking into account the reservoir parameters and different length of horizontal sidetracks. For all

selected wells, we take the general values of the parameters presented in Table 2.

**Table 2** - General parameters for calculating the horizontal wells flow rate

Parameter	Sign	Value	Unit
Well radius	$r_c$	0.057	m
External boundary radius	$R_k$	150	m
Reservoir oil viscosity	$\mu_{o\ res}$	2.31	mPa·s
Reservoir oil density	$P_{o\ res}$	783	$m^3/d$
Oil formation volume factor	$B$	1.166	unit fraction
Average reservoir permeability	$k_{av}$	0.0215	$mkm^2$
Formation anisotropy	$\beta$	3.162	unit fraction

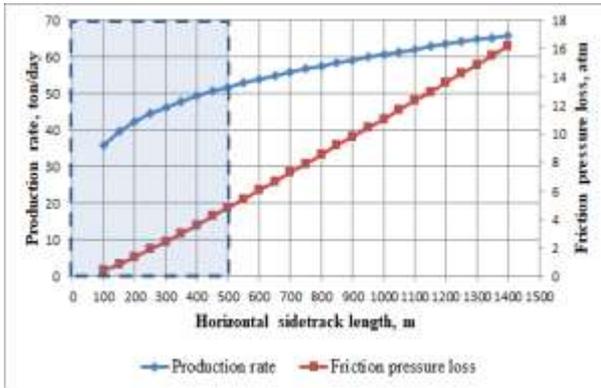
An increase of the wellbore horizontal length leads to an increase in hydraulic losses and a continuous decrease in the drawdown in the lateral direction of the well. Studies by various authors [[15], [16], [17], [18]] have shown that when opening high-permeability sections of horizontal wells, frictional pressure losses along the length of the horizontal section can lead to a significant decrease in well productivity. Friction pressure losses in a horizontal wellbore depend on the horizontal wellbore length, the diameter of the well (liner), fluid velocity, roughness of the inner pipe surface, fluid density and flow pattern (Figure 4). Therefore, it is important to choose the optimal length of the horizontal wellbore, which will provide high rates of flow rate and NPV with minimum well drilling costs.



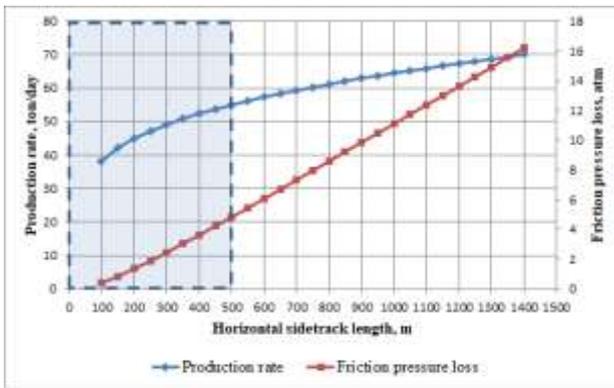
**Figure 4** - Friction pressure loss in horizontal wellbore

To select the optimal length of the horizontal sidetrack of the wells, curves of production rate versus length of the horizontal sidetracks were built

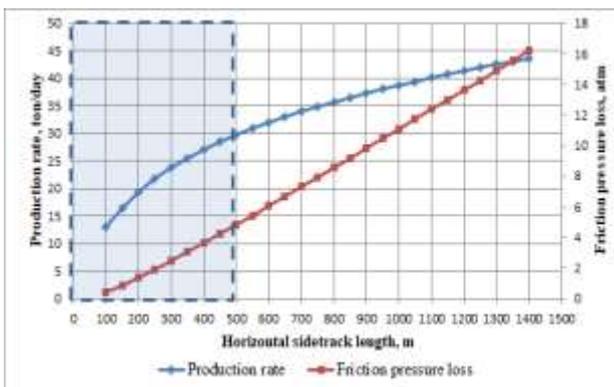
taking into account the friction pressure losses (Figures 5-8). As can be seen from Figures 5-8, the optimal length of a horizontal wellbore is a length not exceeding 500 m.



**Figure 5** - Production rate versus horizontal sidetrack 108 length with the friction pressure loss



**Figure 6** - Production rate versus horizontal sidetrack 120 length with the friction pressure loss



**Figure 7** - Production rate versus horizontal sidetrack 114 length with the friction pressure loss

The anisotropy over the reservoir was taken equal to 3.16. It can be seen from the graphs 5-7 that the drop in drawdown (as a result of friction) along the length of the wellbore horizontal section limits the flow rate only after 600-700 meters. It is

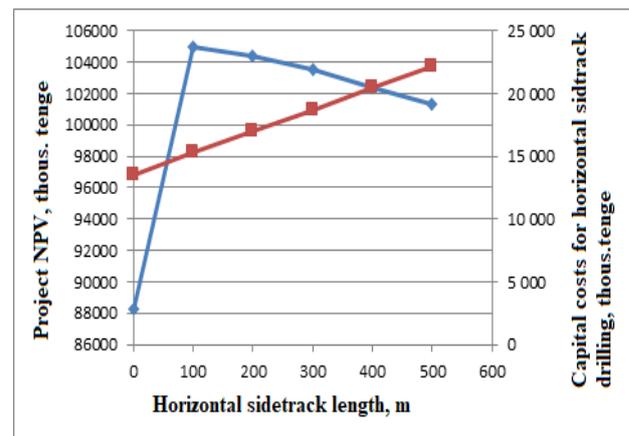
also necessary to take into account the technological criteria - pump productivity and economic criteria - capital costs for the horizontal wellbore drilling. The economic criteria is the accumulated discounted cash flow - NPV. The optimal well length is at which the NPV will be maximum.

$$NPV = -K + \sum_{i=1}^T D^i \lambda_i \quad (7)$$

where  $D^i$  is the cash flow in the  $i$ -th year;  $\lambda_i$  - discounted rate;  $K$  - capital expenditures.

For the calculation of the economic criteria field hydrodynamic simulation conducted with changing the horizontal length of the well. The length increases from 100 to 500 meters. Further increase in the horizontal length of the well is impractical due to the small reservoir drainage area. As a result, the diagram of NPV versus horizontal length of the well was obtained (Figure 8).

From the digram of the NPV versus horizontal length, it can be seen that the maximum NPV is achieved with a horizontal wellbore length of 100 m (Figure 8). A further increase in the length of the horizontal wellbore leads to a decrease in NPV. This is due, firstly, to a decrease in oil prices, and secondly, interference of wells, a small amount of residual reserves, and a small oil-productive area. By comparing the technical and economic criteria of the optimal horizontal wellbore length was obtained of 100-300 meters.



**Figure 8** - NPV project versus horizontal sidetrack length

### Results discussion

The parameters of the horizontal sidetrack wells, as well as the results of the calculated flow rates of horizontal sidetracks wells according to the Joshi formula are shown in Table 3.

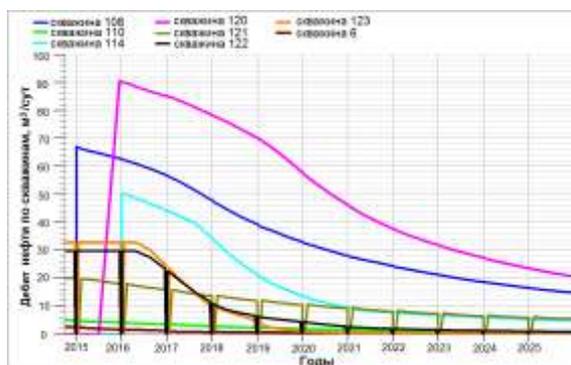
**Table 3** - Well parameters with horizontal sidetracks

Parameter	Well #		
	108	114	120
Horizontal length (L), m	236	230.9	263
Reservoir thickness (h), m	19	20	18.8
Draw-down pressure ( $\Delta P$ ) – the difference in external boundary and bottomhole pressure, MPa	3.3	2.5	3.1
Calculated well flow rate, m <sup>3</sup> /d	98.5	70.7	109.8

The calculated flow rates were used in the hydrodynamic model to define the input parameters oil and water flow rates. As a result, the field development parameters were obtained depending on the geological and physical conditions of the reservoir, the properties of reservoir fluids and the production capabilities of the wells in the hydrodynamic model.

**Table 4** - Wells production rate on X oil field of the Zhetybai group (in 01.2016)

Well #	Oil production rate, m <sup>3</sup> /d	Water production rate, m <sup>3</sup> /d	Watercut, %
6	1.5	28.4	94.9
108 с ГБС	67.07	47.4	41.4
110	4.1	52.3	92.7
114 с ГБС	50.3	39.6	44.04
120 с ГБС	90.4	59.7	39.7
121	17.2	25.6	59.8
122	29.6	22.9	43.6
123	24.5	33.06	57.4



**Figure 9** - Oil production dynamics by wells (2015-2025)

Comparison of the results of the vertical wells flow rates and horizontal sidetrack wells showed a clear advantage of wells with horizontal sidetrack in all criteria (Table 4, Figure 9). Figure 9 shows that

the horizontal sidetrack wells flow rates are higher than drilled new wells flow rates for the analyzed period from 2015 to 2025, except for well 114, the flow rate of which decreases from 2021 to 10 m<sup>3</sup>/day. Oil flow rates vary from 4.7 to 90.4 m<sup>3</sup>/day, with an average of 35.7 m<sup>3</sup>/day. The inlet water cut of horizontal sidetrack wells at the beginning of production reached 40%, which is explained by the close location of the bottom water and water flooding by the injected water.

In general, the oil production rates of wells operating with horizontal sidetracks are on average 5-6 times higher (35.7 m<sup>3</sup>/day versus 6.2 m<sup>3</sup>/day), water cut is 1.2 times lower for conventional wells (70.65% versus 88.2%) (Figure 9). Taking into account that the water cut is 1.2 times lower for wells operating with horizontal sidetracks, it can be assumed that previously not drained layers will be involved.

### Conclusions

Based on the study results, the following brief conclusions can be drawn:

1. To select the optimal length of the horizontal sidetrack of the wells, curves of the production flow rate versus horizontal sidetrack length were built, taking into account the friction pressure losses. It can be seen from the graphs that the drawdown drop (as a result of friction) along the horizontal section length of the wellbore limits the flow rate only after 600-700 meters.

2. From the NPV versus the horizontal length, it can be seen that the maximum NPV is achieved with a horizontal wellbore length of 100 m. A further increase in the horizontal length leads to a decrease in NPV. This is due, firstly, to a decrease in oil prices, and secondly, interference of wells, a small amount of residual reserves, and a small oil-productive area. By comparing the technical and economic criteria of the optimal horizontal wellbore length was obtained of 100-300 meters.

3. Comparison of the results of the vertical wells flow rates and horizontal sidetrack wells showed a clear advantage over the latter in all respects. The flow rates of horizontal sidetrack wells are higher than the new drilled wells flow rates for the analyzed period from 2015 to 2025.

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

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## Гидродинамикалық модельдеу әдісімен көлденең бүйірлік ұңғыманың тиімділігін зерттеу (Қазақстандық кен орны мысалында)

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### ТҮЙІНДЕМЕ

Шағын кен орындарын тиімді игерудің заманауи тәсілдерінің бірі күрделі архитектурасы бар ұңғымаларды (көлденең ұңғымалар, көлденең бүйір ұңғымалар, көп оқпанды ұңғымалар) салу және пайдалану болып табылады. Көлденең бүйір ұңғыманы бұрғылау арқылы апаттық жағдайдағы немесе технологиялық себептермен жұмыс істемей тұрған ескі ұңғыманы қалпына келтіруге мүмкіндік береді. Бұл бұрын игерілмеген қабаттарды ашып, ластанған немесе суланған аймақтарды айналып өту арқылы іске асады. Бұл зерттеуде Жетібай тобына кіретін кен орнындағы жұмыс істеп тұрған ұңғымаларда көлденең бүйір оқпанды пайдалану мүмкіндігі қарастырылған. Ұңғымалардың көлденең бүйірлік оқпанының оңтайлы ұзындығын таңдау үшін үйкеліске байланысты қысымның жоғалуын ескере отырып, дебиттің көлденең ұңғыманың ұзындығына тәуелділік графиктері салынды. NPV көлденең ұңғыма оқпанының ұзындығына тәуелділігінен максималды NPV көлденең ұңғыма оқпанының ұзындығы 100 м болғанда қол жеткізілетінін көруге болады. Көлденең ұңғыма оқпаны ұзындығының одан әрі ұлғаюы NPV төмендеуіне әкеледі. Бұл, біріншіден, мұнай бағасының төмендеуімен, екіншіден, ұңғымалардың интерференциясымен, қалдық қорының аздығымен және мұнайлы аймақтың аз болуымен байланысты. Техникалық-экономикалық критерийлерді салыстыру нәтижесінде көлденең ұңғыма оқпанының оңтайлы ұзындығы 100-300 метр аралығында болады. Тік ұңғымалар және көлденең ұңғыма оқпаны бар ұңғымалардың дебитін салыстыру барлық жағынан екіншісінің айқын артықшылығын көрсетті.

**Түйін сөздер:** көлденең бүйір оқпан, гидродинамикалық модельдеу, дебит, үйкеліске байланысты қысымының шығыны, таза дисконтталған мән – NPV.

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## Исследование эффективности горизонтальных боковых стволов скважин с помощью гидродинамического моделирования (на примере Казахстанского месторождения)

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### АННОТАЦИЯ

Одним из современных подходов для эффективной разработки небольших залежей является строительство и эксплуатация скважин со сложной архитектурой: горизонтальных скважин (ГС),

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боковых стволов (БС, БГС), многозабойных скважин (МЗС). Бурение боковых стволов дает возможность реанимировать старую скважину, находящуюся в аварийном состоянии или бездействии по технологическим причинам, за счет вскрытия пластов, ранее не разрабатываемых, обхода зон загрязнения или обводнения пласта. В настоящем исследовании рассмотрена возможность применения горизонтальных боковых стволов на действующих скважинах месторождения Жетыбайской группы. Для выбора оптимальной длины горизонтального бокового ствола скважин были построены графики зависимостей изменения дебита от длины горизонтальной скважины с учетом потерь давления на трение. Из зависимости NPV от длины горизонтального ствола видно, что максимальный NPV достигается при длине горизонтального ствола 100 м. Дальнейшее увеличение длины горизонтального ствола приводит к снижению NPV. Это обусловлено, во-первых, снижением цен на нефть, во-вторых интерференцией скважин, небольшим объемом остаточных запасов, малой площадью нефтеносности. В результате сравнения технических и экономических критериев оптимальная длина горизонтального ствола составляет от 100 до 300 метров. Сопоставление результатов дебитов вертикальных скважин и скважин с горизонтальными боковыми стволами показало явное преимущество за вторыми по всем показателям.

**Ключевые слова:** горизонтальный боковой ствол, гидродинамическое моделирование, дебит, потери давления на трение, чистый дисконтированный доход – NPV.

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## Smelting options for carbon ferrochrome based on ore raw materials, middlings and their technological evaluation

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### ABSTRACT

The article presents the results of large-scale laboratory tests carried out in the conditions of the Chemical and Metallurgical Institute named after V.I. Zh. Abishev on the use of briquetted mono-charge in the smelting of carbon ferrochrome on a 250 kVA furnace. The purpose of these studies was to determine the technological parameters of the use of briquetted mono-charge containing in its composition chrome ore, wastes from the production of high-carbon ferrochrome, middlings and various carbonaceous reducing agents. The main idea of using these briquettes was to multiply the contact surface of the reductant and ore, which should speed up the technological process. The principal possibility of smelting a standard alloy using briquetted mono-charge is shown. The alloy for individual charge options meets the requirements of the standards. In comparison with the technology without the use of briquettes, the mono-charge technology has shown advantages in all main parameters. The technology with the use of briquettes from the dust of the AktZF gas cleaning system is distinguished by a low yield of non-standard metal and slag, the bulk of the material goes into the gas collection system. Technologies from briquettes from fines pellet production area of Donskoy ore mining and processing plant and flash have very low specific technical and economic indicators and cannot be recommended for industrial use. Improvement of briquetting modes and technology of their smelting is required. The technical and economic indicators were higher than the current one, showed briquettes from ore and coke of the People's Republic of China, briquettes of ore from borlin and shubarkol coals of Kazakhstan.

**Keywords:** ferroalloy, carbon ferrochrome, mono-charge, reducing agent, slag, briquette.

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### Introduction

In the conditions of the Chemical and Metallurgical Institute named after Zh. Abishev, large-scale laboratory tests were conducted on the use of briquetted mono-charge for the smelting of carbonaceous ferrochrome in a 250 kVA furnace. The duration of the experimental company was 9

days. Six variants of briquettes containing various reducing agents were tested. As a comparative variant, the charge materials used at the AktPF were used. A total of 98 swimming heats were held.

The furnace is lined with magnesite brick. The furnace hearth is made of a packed hearth mass that has been coked for 11 hours under current with periodic shutdown of the furnace [[1], [2], [3],

[4]]. The furnace transformer has four voltage stages: 18.2 V; 24.4 V; 36.6 V and 48.8 V. During the experiments, they worked at a voltage of 36.6 V and 48.8 V. The furnace has a graphite electrode with a diameter of 150 mm. The heating of the furnace began on a traditional charge.

After heating the furnace for 0.92 days on a traditional charge, they switched to a charge using briquettes.

The following is a consistent description of the technologies:

- 1 – traditional charge (China coke+special coke+Borly coal);
- 2 – briquettes with Shubarkol coal;
- 3 – briquettes with Borly coal;
- 4 – briquettes with coke ChNR;
- 5 – briquettes made of gas cleaning dust;
- 6 – briquettes from a small product from Pallet Production Site;
- 7 – briquettes from obloy;

Technical and economic indicators of the smelting of carbonaceous ferrochrome using briquetted mono-charge in enlarged laboratory conditions are shown in table 8.

### Calculated part

**Stage No. 1 (traditional charge).** The tests began with a comparative version, as which the technology was chosen as close as possible to the technology at the Aktobe ferroalloy plant. According to this option, they worked for 0.92 days, carried out 11 melt. The average chemical analysis of melting products during this period was: metal – 67.05% Cr; 1.23% Si; 9.30% C; 0.024% S; 0.012% P; slag – 5.48% Cr<sub>2</sub>O<sub>3</sub>; 31.05% SiO<sub>2</sub>; 0.74% CaO; 44.20% MgO; 17.01% Al<sub>2</sub>O<sub>3</sub>; 1.12% FeO; 0.215% S; 0.010% P.

The grate worked without fistulas, with uniform gas release over the entire surface of the grate. The charge sits down by self-propelled. The furnace capacity was 155.0 kg Cr/day, chromium extraction was 79.3%.

**Stage No. 2 (briquettes with Shubarkol coal).** At this stage, smelting was carried out using

briquettes with Shubarkol coal in the charge in the amount of 42.4 kg per ear. According to this option, we worked for 0.75 days, conducted 9 melt. The average chemical analysis of melting products during this period was: metal – 69.12% Cr; 0.85% Si; 9.71% C; 0.020% S; 0.011% P; slag – 5.33% Cr<sub>2</sub>O<sub>3</sub>; 32.16% SiO<sub>2</sub>; 1.09% CaO; 42.36% MgO; 17.29% Al<sub>2</sub>O<sub>3</sub>; 1.28% FeO; 0.206% S; 0.011% P.

The transition to briquettes with Shubarkol coal in general led to an intensification of the process with a more stable current load. The grate worked without fistulas, with uniform gas release over the entire surface of the grate. The furnace capacity was 165.9 kg Cr/day, chromium extraction was 88.17%.

**Stage No. 3 (briquettes with Borly coal).** At this stage of large-scale laboratory tests, smelting was carried out using briquettes with Borly coal in the charge in the amount of 42.0 kg per ear. According to this option, we worked for 0.5 days, conducted 6 melt. The average chemical analysis of melting products during this period was: metal – 70.28% Cr; 1.21% Si; 9.22% C; 0.027% S; 0.015% P; slag – 4.63% Cr<sub>2</sub>O<sub>3</sub>; 34.03% SiO<sub>2</sub>; 1.10% CaO; 36.08% MgO; 20.57% Al<sub>2</sub>O<sub>3</sub>; 0.35% FeO; 0.210% S; 0.011% P.

The grate worked without fistulas, with uniform gas release over the entire surface of the grate. The charge sits down by self-propelled. The furnace capacity was 152.6 kg Cr/day, chromium extraction was 84.91 %.

**Stage No. 4 (briquettes with coke ChNR).** In this test period, briquettes from ore fractions of 0-10 mm and coke of the ChNR in the amount of 30 kg per ear were used in the charge. According to this option, they worked for 1.25 days, spent 15 melt. The average chemical analysis of melting products during this period was: metal – 69.4 %Cr; 0.85%Si; 5.83%C; 0.018%S; 0.042%P; slag – 8.29%Cr<sub>2</sub>O<sub>3</sub>; 27.77% SiO<sub>2</sub>; 3.03% CaO; 36.25% MgO; 8.41% Al<sub>2</sub>O<sub>3</sub>; 1.64% FeO; 0.011% P.

The compressive strength of the briquettes ranged from 154-238 kg per briquette. Such high strength ensured their safety during transportation from Aktobe to Karaganda.

**Table 1** – Chemical composition of dust from the gas capture system during the testing of briquettes from the dust of the gas purification of the AktPF

Material	Chemical composition, %								
	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	C	S
Dust from the furnace No. 1	69.74	0.68	3.07	11.98	-	0.033	-	3.21	1.3
Dust from the furnace No. 2	46.74	1.36	5.31	14.1	-	0.044	-	6.05	1.2

**Stage No.5 (briquettes made of gas cleaning dust).** The use of gas cleaning dust briquettes had very serious distinctive features. The braces themselves were made without the addition of additional binders. The gas cleaning dust itself, when water is added, sets like cement and acquires sufficient strength during subsequent pressing and drying.

During the melting, there was an intense release of dust, unlike other options. Dust was taken from the gas capture system, the chemical composition of this dust is shown in table 1.

As can be seen from these data, the dust is characterized by a relatively high MgO content and high dispersion. It is quite possible to use it as an additive to a mixture for the manufacture of periclase bricks or for a mixture in shotcrete masses for the shotcrete lining of converters. The output of slag and metal was insignificant. As can be seen from this table, the metal is characterized by large fluctuations in chromium and other impurities. It does not correspond to standard compositions and it is almost difficult to implement such a ferrochrome [[5], [6], [7]].

The chemical composition of the slag is also unstable. The output of metal and slag from melting to melting is also unstable, often either slag or metal came out in small quantities. This mode of operation is unacceptable and cannot be recommended for industrial development. At the same time, this technology is of particular interest for further research and possible improvement with the use of electric arc units for remelting steel scrap. Such briquettes can be put into the chipboard furnace together with scrap for direct alloying of steel or cast iron with chromium. The technology is characterized by a high energy consumption per 1 ton of chromium and low other indicators (table 2).

**Stage No. 6 (briquettes from a small product from Pallet Production Site).** The small product of Pallet Production Site DGOK is a dropout from the site for the production of pellets with a size of less than 5 mm. Currently, this material does not find proper use, although it contains an average of 50 % Cr<sub>2</sub>O<sub>3</sub> in its composition. Using this material, we have obtained briquettes. The chemical composition of the briquettes is given in table 3.

**Table 2** – Technological parameters of the smelting of high-carbon ferrochrome using briquettes from the dust of the gas purification of AktPF

Name of the articles	Unit of measurement	Parameters
Briquettes consumed	kg	1260
Metal received	kg	277.05
Slag is obtained	kg	226.2
Multiplicity of slag		0.816459123
Melt were carried out	pieces	25
Specific power consumption	kWh/t Cr	22166.3
Specific consumption of briquettes	kg/t Cr	7651.2
Working hours	day	2.17
Efficiency	Cr kg/day	75.95
Average Cr content in the metal	%	59.4

**Table 3** – Chemical composition of briquettes from a small product of Pallet Production Site DGOK

Name of materials	Chemical composition, %								
	Cr <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MgO	CaO	FeO	Al <sub>2</sub> O <sub>3</sub>	P	S	C
Briquette from the Pallet Production Site	31.8	13.0	14.9	3.5	13.9	6.2	0.01	0.16	11.4

At this stage of large-scale laboratory tests, smelting was carried out using briquettes from the

finest of the Pallet Production Site DGOC product in the amount of 30.0 kg per ear in the charge.

According to this option, they worked for 1.83 days, carried out 22 melt. The average chemical analysis of melting products during this period was: metal – 67.5% Cr; 2.09% Si; 5.35% C; 0.003% S; 0.024% P; slag – 9.38% Cr<sub>2</sub>O<sub>3</sub>; 28.0% SiO<sub>2</sub>; 4.94% CaO; 39.24% MgO; 12.67% Al<sub>2</sub>O<sub>3</sub>; 2.65% FeO; 0.040% P.

The grate worked without fistulas, with uniform gas release over the entire surface of the grate. The charge sits down by self-propelled. The furnace capacity was 114.45 kg Cr/day, chromium extraction was 84.1 %. The main technological parameters are presented in table 4.

The strength of briquettes made of small items of the Pallet Production Site DOK ranged from 43-81 kg per briquette, which is significantly lower than the strength of briquettes made of gas cleaning dust of the AktPF. In addition, this material is heavily subjected to briquetting by the vacuum-extrusion method, the yield of briquettes is not more than 30 % of the total mass of materials

passed through the press. In addition, the technology is distinguished by a very high specific energy consumption per 1 ton of chromium (10266.6 kWh/t Cr). The resulting metal complies with the standard. This technology with the use of briquettes from small things of Pallet Production Site DGOK can not yet be recommended for industrial use due to the above negative aspects. It is required to work out the briquetting modes and the technology of conducting the melting process.

**Stage No. 7 (briquettes from obloy).** Obloy is a fine-dispersed waste from the production of briquettes in the conditions of DGOK. This material does not find proper use, although it also contains an average of 49.96 % Cr<sub>2</sub>O<sub>3</sub> in its composition. Using this material, we have obtained briquettes by the vacuum-extrusion method. The chemical composition of the briquettes is given in table 5.

The ratio of reducing agent, ore and binders is presented earlier in table 6.

**Table 4** – Technological parameters of the smelting of high-carbon ferrochrome using briquettes from small of Pallet Production Site DGOK

Name of the articles	Unit of measurement	Parameters
Briquettes consumed	kg	1380
Metal received	kg	308
Slag is obtained	kg	458.5
Multiplicity of slag		1.49
Melt were carried out	pieces	22
Specific power consumption	kWh/t Cr	10266.6
Specific consumption of briquettes	kg/t Cr	6637.78
Working hours	day	1.83
Efficiency	Cr kg/day	113.6
Average Cr content in the metal	%	67.5

**Table 5** – Chemical composition of briquettes from a small product of Pallet Production Site DGOK

Name of the articles	Chemical composition, %								
	Cr <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MgO	CaO	FeO	Al <sub>2</sub> O <sub>3</sub>	P	S	C
Briquettes from obloy	24.8	11.2	19.4	1.1	13.3	5.6	0.04	0.39	9.7

At this stage of large-scale laboratory tests, smelting was carried out using briquettes from the chip in the charge in the amount of 30.0 kg per ear. According to this option, we worked for 0.83 days, conducted 10 melt. The average chemical analysis of melting products during this period was: metal – 61.54% Cr; 1.59% Si; 5.17% C; 0.026% S; 0.033% P; slag – 13.63% Cr<sub>2</sub>O<sub>3</sub>; 24.27% SiO<sub>2</sub>; 3.01% CaO;

41.24% MgO; 10.83% Al<sub>2</sub>O<sub>3</sub>; 2.78% FeO; 0.057% P<sub>2</sub>O<sub>5</sub>.

The grate worked unsatisfactorily with frequent emissions. The charge sits down with difficulty. The furnace capacity was 95.57 kg Cr/day; chromium extraction was 72.3 %. The main technological parameters are presented in table 7.

**Table 6** – Compositions of experimental versions of briquettes made of chromium ore and carbon reducing agents

Option no.	Type of technology	Materials	Ratio, %
1	Traditional without briquetting	Chrome ore	77.24
		Coke ChNR	9.03
		Shubarkol coal	5.15
		Borly coal	8.58
2	Briquettes with Shubarkol coal	Chrome ore	71.94
		Shubarkol coal	28.06
3	Briquettes with Borly coal	Chrome ore	72.63
		Borly coal	27.37
4	Briquettes with coke ChNR	Chrome ore	74.0
		Coke ChNR	18.5
		Binder	7.5
5	Briquettes made of gas cleaning dust	Gas cleaning dust without additives	-
6	Briquettes from a small product from Pallet Production Site	A small product of Pallet Production Site	71.43
		Coke ChNR	21.43
		Binder	7.14
7	Briquettes from obloy	Obloy	71.43
		Coke ChNR	21.43
		Binder	7.14

**Table 7** – Technological parameters of the smelting of high-carbon ferrochrome using briquettes from the chip

Name of the articles	Unit of measurement	Parameters
Briquettes consumed	kg	750
Metal received	kg	129.5
Slag is obtained	kg	502.9
Multiplicity of slag		3.9
Melt were carried out	pieces	10
Specific power consumption	kWh/t Cr	21777.5
Specific consumption of briquettes	kg/t Cr	9417.1
Working hours	day	0.83
Efficiency	Cr kg/day	95.57
Average Cr content in the metal	%	61.5

### The discussion of the results

The strength of briquettes made of scrap ranged from 41-67 kg per briquette, which is lower than the strength of briquettes made of gas purification dust of the AktPF. In addition, this material is heavily subjected to briquetting by the vacuum-extrusion method, the yield of briquettes is not more than 20 % of the total mass passed through the press of materials. In addition, the technology is distinguished by a very high specific energy consumption per 1 ton of chromium

(21777.5 kWh / t Cr). The resulting metal differs from the standard one. This technology using briquettes made of scrap can also not be recommended for industrial use due to the above negative aspects. It is necessary to work out the briquetting modes and the technology of conducting the melting process [[8], [9], [10]].

Below are the main technical and economic indicators of single-charge technologies, which, in our opinion, can be recommended for industrial testing, since they have significant advantages compared to traditional technologies (table 8).

**Table 8** – Technical and economic indicators of carbon ferrochrome smelting with the use of briquetted mono-charge

Indicators	Unit of measurement	Periods			
		Traditional without briquetting	Briquettes with coke ChNR	Briquettes with Shubarkol coal	Briquettes with Borly coal
1. Working hours	day	0.92	1.25	0.75	0.50
2. The number of melt	pieces	11	15	9	6
3. The charge is set					
Dry briquettes	kg		930	555.1	350.1
including chrome ore content Cr <sub>2</sub> O <sub>3</sub>	kg		688.2	392.5	250.1
it has chromium in it	%		50.0	52.5	52.5
	kg		234.0	141.1	89.9
Coke ChNR	kg		172.05		
Shubarkol coal	kg			162.6	
Borly coal	kg				100.1
Chrome. ores of fr. 0-10 mm content Cr <sub>2</sub> O <sub>3</sub>	kg	162.9	688.2		
it has chromium in it	%	52.5	50.0		
	kg	58.6	234.0		
Chrome. ores of fr. 10-80 mm content Cr <sub>2</sub> O <sub>3</sub>	kg	337.9			
it has chromium in it	%	52.2			
	kg	120.6			
Total ore 50% Cr <sub>2</sub> O <sub>3</sub>		523.7	688.2	412.5	262.8
it has chromium in it		179.2	234.0	141.1	89.9
Quartzite	kg			14.0	
Carbon reducing agents:					
Coke ChNR	kg	56.4	172.05		
special coke	kg	34.0			
Shubarkol coal	kg			162.6	
Borly coal	kg	56.1			100.1
The restorer of everything	kg	146.5	172.05	162.6	100.1
4. Electric power	kWh	1680.0	2448	1408.0	888.0
5. Metal received					
Total	kg	211.9	307.29	180	108.6
	kg Cr	142.1	212.95	124.4	76.3
Chemical composition of the metal					
Cr	%	67.05	69.4	69.12	70.28
Si	%	1.23	0.85	0.85	1.21
C	%	9.30	5.83	9.71	9.22
S	%	0.024	0.018	0.020	0.027
P	%	0.012	0.042	0.011	0.015
6. Slag is obtained	kg	243.5	372.36	176.7	118.0

It has chromium in it	kg Cr	9.13	20.99	6.44	3.74
Multiplicity of slag		1.15	1.21	0.98	1.09
Chemical composition of slag					
Cr <sub>2</sub> O <sub>3</sub>	%	5.48	8.29	5.33	4.63
SiO <sub>2</sub>	%	31.05	27.77	32.16	34.03
CaO	%	0.74	3.03	1.09	1.10
MgO	%	44.20	36.25	42.36	36.08
Al <sub>2</sub> O <sub>3</sub>	%	17.01	8.41	17.29	20.57
FeO	%	1.12	1.64	1.28	0.35
S	%	0.215	0.204	0.206	0.210
P	%	0.010	0.011	0.011	0.011
7. Technical and economic indicators					
Efficiency	kg Cr/day	155.0	170.36	165.9	152.6
Average melting weight	kg Cr	12.92	14.19	13.82	12.72
Extracting chromium	%	79.30	90.0	88.17	84.91
Specific consumption of materials					
chrome. ore 50% Cr <sub>2</sub> O <sub>3</sub>	kg/ t Cr	3685.9	3224.73	3315.2	3442.7
reducing agent	kg/ t Cr	1031.2	806.18	1306.9	1311.1
Coke ChNR	kg/ t Cr	397.0	806.18		
special coke	kg/ t Cr	239.3			
Shubarkol coal	kg/ t Cr			1306.9	
Borly coal	kg/ t Cr	394.9			1311.1
Quartzite	kg/ t Cr			112.5	
Specific consumption of electric energy	kWh/ t Cr	11824	11470.69	11317	11635

## Conclusions

The technology using briquettes from the dust of the gas purification of the AktPF is characterized by a low yield of metal and slag, the bulk of the material goes into the gas capture system. During these melts, the resulting ferrochrome does not correspond to the standard composition. The dust caught in the gas cleaning system contains a high concentration of MgO, which is a prerequisite for its use in the refractory industry. The technology has low specific technical and economic indicators, especially high power consumption. It is not recommended to use briquettes from the gas purification dust of the AktZF with a complete replacement of the traditional charge, they can be used as an additive to the usual charge in a certain proportion. Technologies made of briquettes from

small pieces of of Pallet Production Site DGOK and debris have very low specific technical and economic indicators and cannot be recommended for industrial use. It is necessary to finalize the briquetting modes and the smelting technology.

Technical and economic indicators are higher, compared to the current one, showed briquettes from ore and coke of the People's Republic of China, briquettes from Borlin and Shubarkol coals of Kazakhstan.

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

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## Кен шикізаты мен өнеркәсіп өнімдері негізінде көміртекті феррохромды балқыту нұсқалары және оларды технологиялық бағалау

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### ТҮЙІНДЕМЕ

Мақалада Ж.Әбішев атындағы химия-металлургия институты жағдайында қуаты 250 кВА пеште көміртекті феррохромды балқыту кезінде брикеттелген моношекқұрам қолдану бойынша жүргізілген кеңейтілген зертханалық зерттеулердің нәтижелері келтірілген. Бұл зерттеулердің мақсаты құрамында хром кені, жоғары көміртекті феррохром өндірісінің қалдықтары, аралық өнімдер және әртүрлі көміртекті тотықсыздандырғыштар бар брикеттелген моношекқұрамды пайдаланудың технологиялық көрсеткіштерін анықтау болды. Басты идея осы брикеттерді қолдану барасында тотықсыздандырғыш пен кеннің әрекет ету үрдісін ұлғайту болып табылады. Брикеттелген моношекқұрамды қолдана отырып, стандартты қорытпаны балқытудың негізгі мүмкіндігі көрсетілген. Шекқұрамның жекелеген нұсқалары бойынша қорытпа стандарттардың талаптарына сәйкес келеді. Брикеттерсіз технологиямен салыстырғанда моношекқұрам технологиясы барлық негізгі параметрлер бойынша артықшылықтарды көрсетті. АктЗФ газдан тазарту шаңынан брикеттерді пайдалану технологиясы стандартты емес металл мен шлақтың төмен шығысымен сипатталады, материалдың негізгі бөлігі газды ұстау жүйесіне түседі. Дон тау-кен байыту комбинатының шекемтастар өндіру учаскесі мен облойдің ұсақ-түйек брикеттерінен жасалған технологиялар өте төмен техникалық-экономикалық көрсеткіштерге ие және оларды өнеркәсіптік пайдалану үшін ұсынуға болмайды. Брикеттеу режимдерін және оларды балқыту технологиясын жетілдіру қажет. Техникалық-экономикалық көрсеткіштер Қытай Халық Республикасы кені мен коксынан алынған брикеттер, Қазақстанның борлы және шұбаркөл көмірінен алынған кен брикеттері ағымдағы көрсеткіштермен салыстырғанда жоғары.

**Түйін сөздер:** ферроқорытпа, көміртекті феррохром, моношихта, тотықсыздандырғыш, қож, брикет.

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## Варианты выплавки углеродистого феррохрома на основе рудного сырья, промпродуктов и их технологическая оценка

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### АННОТАЦИЯ

В статье изложены результаты укрупненно-лабораторных испытаний, проведенные в условиях Химико-металлургического института им. Ж. Абишева по применению брикетированной моношихты при выплавке углеродистого феррохрома на печи мощностью 250 кВА. Целью этих исследований было определение технологических показателей применения брикетированной моношихты, содержащей в своем составе хромовую руду, отходы производства высоко

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углеродистый феррохром, промпродукты и различные углеродистые восстановители. Главная идея применение этих брикетов заключалась в многократном увеличении поверхности контакта восстановителя и руды, что должно форсировать технологический процесс. Показана принципиальная возможность выплавки стандартного сплава с использованием брикетированной моношихты. Сплав по отдельным вариантам шихты соответствует требованиям стандартов. В сравнении с технологией без применения брикетов моношихтовая технология показала преимущества по всем основным параметрам. Технология с использованием брикетов из пыли газоочистки АктЗФ отличается низким выходом нестандартного металла и шлака, основная масса материала уходит в систему улавливания газов. Технологии из брикетов из мелочи участка производства окатышей Донского горно-обогатительного комбината и облоя имеют очень низкие удельные технико-экономические показатели и не могут быть рекомендованы для промышленного использования. Требуется доработка режимов брикетирования и технологии их выплавки. Более высокие технико-экономические показатели, по сравнению с текущей, показали брикеты из руды и кокса Китайской Народной Республики, брикеты из борлинских и шубаркольских углей Казахстана.

**Ключевые слова:** ферросплав, углеродистый феррохром, моношихта, восстановитель, шлак, брикет.

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## Research on development of nanotechnology in the Republic of Kazakhstan

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### ABSTRACT

In the history of civilization, materials and technology that defined the face of the era have appeared more than once. It is enough to recall the “age” of bronze and iron, steam and electricity, the atomic “age” and the computer age. Nanomaterials (NM) are undoubtedly among such materials, and the 21st century opens the era of nanotechnology. Most experts in the field of science and technology policy, strategic planning and investment are confident that in the next decade nanorevolution is expected in all areas of science, production, defense, medicine, mode of life, recreation and entertainment. Its consequences will be more extensive than the consequences of the computer revolution in the last third of the 20th century, i.e., a large-scale and systematic invasion of nanostructured materials, products and methods of their production will literally come to all spheres of life. The paper analyzes the ways of nanotechnology development and the use of various nanomaterials and nanoproducts in various sectors of the world economy and environmental protection. Nanotechnology is a field of fundamental and applied science that provides theoretical justification for practical methods of research, production, and products application with an atomic structure by manipulating atoms and molecules. The aim of the work is to study the development of nanotechnology and its role in the modern economy. The article considers the ways of development of nanotechnology in Kazakhstan, as well as promising directions of their development and application in the field of mechanical engineering and industry in general.

**Keywords:** nanotechnology, nanomaterials, nanoscience, nanosystem technology, nanoproducts, nanomarket, nanotechnology development program, nanoproducts application, nanoindustry.

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### Introduction

Manipulation at the atomic level enables to control features of new materials and nanomaterials. A material with measurement of one to 100 nm controls nanotechnology. Moreover, nanotechnology consists of showing, measuring, modeling and developing substances in mentioned measurement range and they can be used in new ways [[1], [2]].

The main feature of nanomaterials to the nanosphere is that their size allows us to attribute objects in the nanoscale range from 1 to 100

nanometers by two or three dimensions. Except the main nanomaterials (nanofibers, nanotubes, and nanoparticles), there is a category of derived nanomaterials, which are complex structures formed from the main nanomaterials. Representatives of nanomaterial derivatives include nano-ceramics obtained by pressing and synthesizing initial nanoparticles, for instance, complex metal oxides. In this case, the composition of nanoceramics includes an amorphous (glassy) binder component as well as the crystalline nanoscale phase. Another example of nanomaterial derivatives are nanocomposites consisting of initial

nanoparticles, nanopipettes, nanophiles and (or) nanotubes interconnected by a polymer bond [[2], [3]].

This derivative provides nanomaterials by new useful properties such as increased strength, more elasticity, heat resistance, thermal and electrical conductivity, etc.

### Experimental part

Worth to say, some previously known materials with nanoparticles were not considered as nanomaterials. Academician Tretyakov Yu.D. stated that faience, decorated with colored glaze to give ceramics a special shine, was the first nanoparticle. The technology of creating a nanoproduct like faience was used by Umbrian potters in Italy in the 15th century. At that time, the reflectivity of nanoparticles (gold, silver and other metals) was used to give the faience an appropriate glitter of gold, silver, etc. Porcelain, created in China during Qin dynasty, is also a nanostructure, however, only in 1980-s when a scanning tunneling microscope was invented it became possible to distinguish nanostructures, that is, the necessary tool base appeared [[4], [5]].

With the development of nanotechnology, a number of new concepts have emerged in science: nanomaterials, nanosystem technique, nanotechnology, nanoappliances and nanoindustry. In the nanoindustry, markets of various directions are being formed and developed as nanocomplexes: nanoproducts (sale of licenses, certificates and industrial models); nanotechnology; nanoproducts; nanostructures and devices for monitoring nanoparticles.

Any of these markets is a “nanotechnological and economic paradigm” as a system representing a set of government bodies (at the macro level, supporting the development of nanotechnology and nanosciences), intersectoral regional scientific and production centers (at the level conducting research and development of nanoproducts), organizations and individuals interacting in order to realize their interests, nano projects and plans, scientific and technical and industrial programs (at the micro level, producing nanoproducts and having a targeted effect at micro-level). At the microlevel, nanoparticle producers (sellers) and buyers (legal entities – organizations and individuals) represent nanoparticle markets, each of them are trying to earn a commercial profit from sale-purchase transaction (Figure 1) [[5], [6]].

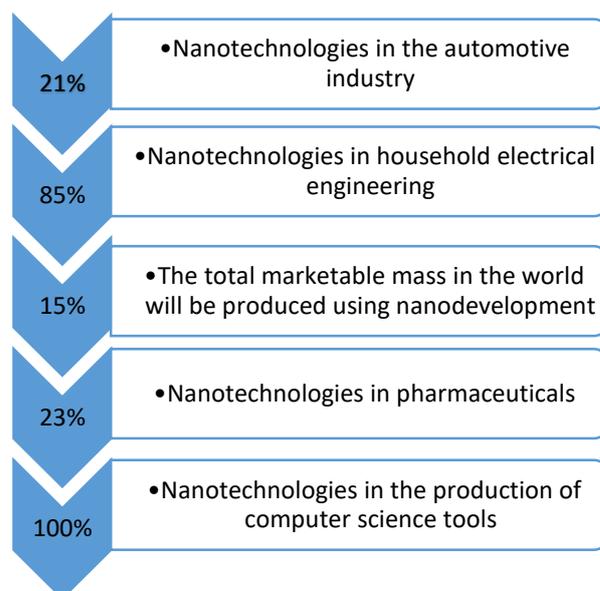


Figure 1 - The share of nanoredevelopment in the commercial mass of industrial goods [5]

15% of the total marketable mass in the world will be produced using nanodevelopments. Today, there are more than 800 consumer products manufactured using nanotechnology on the world market – electronics, clothing, cosmetics, food, pharmaceuticals and household appliances [5].

The United States was the first to understand that nanotechnology is the near future of all mankind. Annual public and private investments in the US over the recent seven years amounted to about 2.5 billion US dollars. The state programs of americans for developing nanotechnology led to the leading positions in volumes of research in nanoindustry and output. The share of the United States (more than three thousand units in the sum of companies and individuals) accounts for about forty percent of patents in the field of nanotechnology obtained in all countries of the world [[6], [7], [8]].

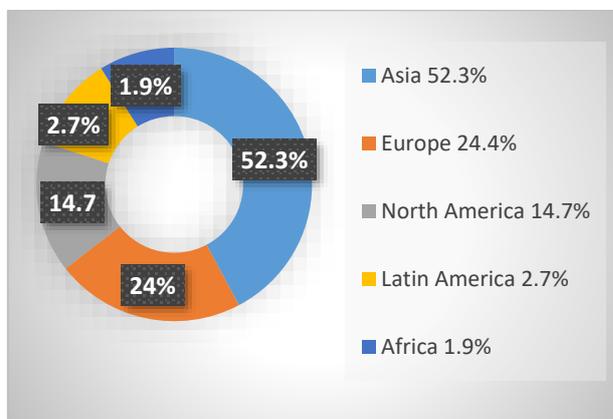


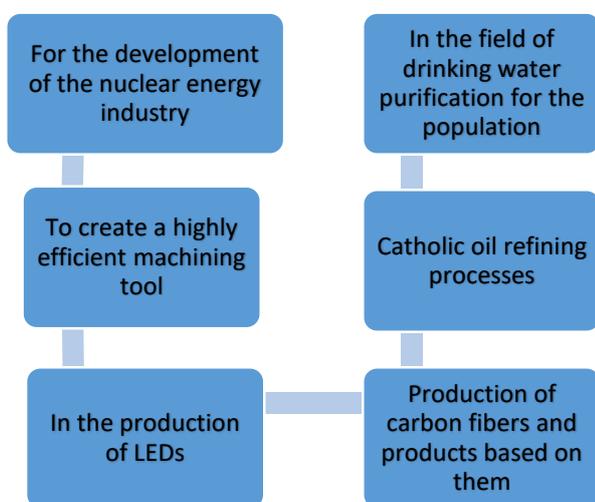
Figure 2 - Geographical distribution of publications on nanotechnology [9]

At the same time, according to the study, the largest number of scientific papers on nanotechnology falls on the countries of Asia and Oceania, more than half – on European countries and America, the smallest is on Africa (1.9%).

In the global nanoindustry, nanotechnology is used in the production of 600 types of primary nanomaterials and components and 80 groups of consumer goods.

Herein, 46% of the global nanoproducts and nanomaterials production is accounted for companies of the US nanoindustry, 28% of the nanoproducts production is accounted for European companies and 20% is accounted for East Asian countries (China, Japan, South Korea, and Taiwan). The rest of the world accounts for about 6% of the global production of nanomaterials and nanoproducts. The most popular material used in the production of nanoproducts are silver nanoparticles, using which about 320 types of nanomaterials and nanoproducts are produced. About 100 types of nanoproducts are produced using carbon nanoparticles (carbon nanotubes and nanopowders), 60 types using titanium dioxide and more than 40 types using silicon (Figure 2) [[9], [10], [11]].

The leaders of the rating are China, the United States, India, South Korea and Iran. At the same time, Russia took 12<sup>th</sup>, Belarus - 58<sup>th</sup>, Armenia - 81<sup>st</sup>, Uzbekistan - 86<sup>th</sup>, Georgia-89<sup>th</sup>, Tajikistan - 93<sup>rd</sup>, Kyrgyzstan-98<sup>th</sup>, Turkmenistan - 101<sup>st</sup> places. At the same time, according to the study, the largest number of scientific papers on nanotechnology falls on the countries of Asia and Oceania, more than half – on European countries and America, the less on Africa (1,9%) [11]



**Figure 3** - Analysis of promising areas of nanotechnology use [14]

The importance of nanotechnologies [12] presents a specific research work in the field of nanoscale building materials carried out by the Federal Institute for Materials Research and Testing in Berlin.

Nanotechnologies create incredibly useful structures from individual atoms or molecules, the study [13] discusses the latest innovations in the field of oral health, nanocorporated products, patient safety and occupational safety.

The issues of using the historical penetration of nanotechnologies as a contribution to a reliable assessment of technological capabilities and a critical assessment of technological manifestations are considered (Figure 3) [14].

### Research results and discussion

The analysis shows that there are research teams in Kazakhstan that carry out research and development in the field of nanotechnology and related disciplines. Nevertheless, the implementation of the program titled "Development of nanoscience and nanotechnology in the Republic of Kazakhstan for 2007-2009" showed that the country lacks a developed infrastructure that ensures the production of the necessary clean primary materials, the disposal of harmful waste, etc. All this hinders the development of fundamental and applied research, as well as the creation of nanomaterials and nanotechnologies, small innovative companies designed to become the driving force of the country's innovative development strategy.

Research centers that contribute to scientific and technical research in the field of nanotechnology are: Nazarbayev University, National Laboratory, National Nanotechnology Laboratory on the basis of KazNU named after al-Farabi, laboratory of the Institute of Physics and Technology, laboratory of engineering profile at TarSU, SKSU n.a. M. Dulati, SKSU n.a. M. Auezov, KazNU named after al-Farabi, Satpayev university, JSC "NSMC", EKSTU n.a. D. Serikbayev, as well as the National Scientific Laboratory at East Kazakhstan State University n.a. S. Amanzholov. A significant contribution to the solution of scientific and technical problems in the field of nanotechnology was made by Nazarbayev University, national laboratories, in particular, the National Nanotechnology Laboratory on the basis of al-Farabi Kazakh National University, the laboratory of the Institute of Physics and Technology, the laboratory

of engineering profile at TarSU, SKSU n.a. M. Dulati, SKSU n.a. M. Auezov, KazNU named after al-Farabi, Satpayev university, JSC "NSMC", EKSTU n.a. D. Serikbayev, as well as the National Scientific Laboratory at East Kazakhstan State University n.a. S. Amanzholov.

National Scientific Laboratory for Collective Use at the EKSU named after Sarsen Amanzholov was set up on October 8, 2009. The laboratory is equipped with a modern avance-III 500 nuclear magnetic resonance spectrometer manufactured by Bruker (Germany), X-ray diffractometers, electronic and optical microscopes, a vacuum station and other technological equipment that allows conducting studies of the structural and phase state and properties of materials. An experimental-industrial site has been created at the Laboratory.

A hydraulic press, 3D-draft and molding equipment for angular pressing of an equal channel were developed and manufactured with the support of the Foundation of the First President of the Republic of Kazakhstan. The mechanical properties of aluminum have significantly increased using them, namely, the hardness is 3 times, the yield strength is 18 times, the tensile strength is 5 times, the hardness of Titanium is 1.5 times.

The Laboratory of New Materials and Energy Saving Systems is known for its innovations, best practices and novelties, with a reputation as a world-class research institution that attracts the best students and employees not only in Kazakhstan, but also around the world. The laboratory closely cooperates with international researchers from leading world universities and research centers, such as the Tokyo Institute of Technology (Japan), the University of Warwick (Great Britain), Chungnam National University (Korea), Tokyo Metropolitan University (Japan), Sejong University (Korea), Tokyo University (Japan), Hanyang University (Korea), Hebei University of Technology (China), the French National Research Center (France), etc.

The National Laboratory for Nanotechnology "Nanofab" was established in 2008 at the South Kazakhstan State University (Shymkent city) to implement promising projects of nanotechnology and nanoindustry in order to implement state policy in the field of nanotechnology, create and develop innovative infrastructure in the field of nanotechnology, form the sector of Kazakhstani researchers in the nanoindustry as a whole. To conduct research and development work in the laboratory, it is planned to create conditions for the world's leading scientists and the possibility of training highly qualified domestic specialists. The

laboratory plans to develop breakthrough projects in the field of nanotechnology based on the raw materials of Kazakhstan.

The laboratory is equipped with a scanning electron microscope of the Japanese company JEOL, as well as a system of energy-dispersion microanalysis and structural analysis of polycrystalline objects manufactured in the UK. Such a complex allows us to study the fine structure of organic and inorganic substances at the nanoscale.

The activity of the laboratory of engineering profile in the mining metallurgical and oil and gas sectors at KazNTU n.a. K. I. Satpayev is aimed at strengthening the material and technical base of the university, as well as at training highly qualified engineering personnel and developing innovative technologies in the field of earth sciences, metallurgy, mechanical engineering, oil and gas, ecology, bio- and nanomaterials, information systems [15].

"IRGETAS" Regional University Laboratory of engineering profile at the East Kazakhstan University is in the direction of "high technology for obtaining new materials based on the integrated use of resources of the mining and metallurgical industry." It conducts research on natural nanomaterials, technologies for obtaining natural carbon nanoparticles, nanotechnology for opening ores of non-ferrous and precious metals, nanotechnology for obtaining nanofilms and nanowires, technical ceramics based on rare metal compounds, etc.

The laboratory of engineering profile "nanoengineering research methods" was established at Taraz State University to create a new generation of food products with high nutritional value based on the use of nanostructured food materials; to develop a technology for producing nanofiber from carbon-containing gas raw materials of the Amangeldy deposit; to conduct a complex of studies on improving the technology for obtaining composite materials on the basis of industrial waste; on the development of nano- and biotechnologies for obtaining new materials for the production of textile and light industry products based on vegetable and cellulose fibers; on the development of nanostructured coatings for natural and artificial leather with high performance property.

However, the development of nanotechnology in Kazakhstan also has weaknesses, in particular:

- there is no tradition of creating and developing nanotechnology;
- there is no coordination center for the implementation of state policy in the field of nanotechnology, the development of innovative

infrastructure in the field of nanotechnology, the implementation of projects to create promising nanotechnology and nanoindustry;

- insufficient funding of research and development projects in the field of nanotechnology;

- lack of long-term scientific and technical programs; Laboratories are practically not provided with modern technological equipment for the production of nanomaterials;

- lack of qualified personnel to support the industry; there are no permanent large-scale nanotechnology forums and world-class conferences;

- low level of information support on nanotechnology issues, lack of information in the state language;

- there is no unified terminology on nanotechnologies and nanomaterials that regulates the regulatory and methodological framework for conducting measurements, tests and control, establishing criteria for compliance, quality and safety of nanoobjects, nanomaterials and other nanotechnological products;

- low share of production of high-tech and knowledge-intensive types of products.

The main reason for the problems of technology development is the neglect of humanity to the core of its civilization – science – over the past few decades.

Fundamental science is a civilizational resource accumulated by past generations, wasted for profit. Kazakhstan now needs an innovative breakthrough in the nanotechnology of new plants, workshops and factories for the production of high-tech products based on domestic developments [[16], [17], [18]].

For the development of nanotechnology in Kazakhstan, the scientific side is being developed and the necessary specialists are being trained.

In mechanical engineering, there is an opportunity to increase the resource of metal cutting and processing tools using special coatings and emulsions due to the widespread introduction of nanotechnological developments and nanomaterials both in the modernization of the existing fleet of high-precision and precise machines, and in the production of new nanotechnological equipment.

## Conclusions

Nowadays, there is a rapid growth of the market for consumption products based on nanotechnology. For example, the size of the global electronics and IT market using nanotechnology is more than \$ 0.5 billion in 2010. Up to \$ 1.8 billion by 2015, that is, more than three times. At that time, enterprises should be ready to develop high-tech products, otherwise new technologies may be sold abroad and not bring the necessary income to the country. As practice shows, many Russian enterprises cannot create competitive products based on high technologies.

As for nanomaterials, their fields of application and sales markets are growing very rapidly. The forecast for 10-12 years is that their volume will amount to more than 350 billion US dollars. The total volume of sales of nanoproducts per year is \$ 1000 billion. Currently, nanomaterials are used in various spheres of human life, in the near future the scope of their application will significantly expand.

Kazakhstan's science is only taking the first steps in the field of production and use of nanomaterials and nanotechnologies, so in the future we can expect positive results from it.

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

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## Қазақстан Республикасындағы нанотехнологияның дамуын зерттеу

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<p>Мақала келді: 16 Сәуір2021 Сараптамадан өтті: 11 шілде 2021 Қабылданды: 02 желтоқсан 2021</p>	<p><b>ТҮЙІНДЕМЕ</b></p> <p>Өркениеттің қазіргі тарихында дәуірдің келбетін анықтаған материалдар мен технологиялар бірнеше рет пайда болды. Қола мен темірдің, бу мен электрдің "ғасырын", атом "ғасырын" және компьютер ғасырын еске түсіру жеткілікті. Наноматериалдар (НМ) сөзсіз осындай материалдардың қатарына жатады және 21 ғасыр нанотехнология дәуірін ашады. Ғылыми-техникалық саясат, стратегиялық жоспарлау және инвестициялар саласындағы сарапшылардың көпшілігі алдағы онжылдықта нанореволюцияның ғылым, өндіріс, қорғаныс, медицина, өмір, демалыс және ойын-сауықтың барлық салаларында күтілетініне сенімді. Оның салдары ХХ ғасырдың соңғы үшінші бөлігіндегі компьютерлік революцияның салдарларынан да үлкен болады, яғни наноқұрылымды материалдар, бұйымдар мен оларды өндіру әдістері өмірдің барлық салаларына кең ауқымды және жүйелі түрде басып кіреді. Мақалада нанотехнологияны дамыту және әлемдік экономика мен қоршаған ортаны қорғаудың әртүрлі салаларында әртүрлі наноматериалдар мен наноөнімдерді пайдалану жолдары талданады. Нанотехнология – бұл атомдар мен молекулаларды басқару арқылы атом құрылымы бар өнімдерді зерттеудің, өндірудің және қолданудың практикалық әдістерін теориялық негіздеуді қамтамасыз ететін іргелі және қолданбалы ғылымның саласы. Жұмыстың мақсаты – нанотехнологияның дамуын және олардың қазіргі экономикадағы маңыздылығын зерттеу. Мақалада Қазақстандағы нанотехнологияларды дамыту жолдары, сондай-ақ оларды дамыту мен машина жасау және жалпы өнеркәсіп саласында қолданудың болашақтағы бағыттары қарастырылады.</p> <p><b>Түйін сөздер:</b> нанотехнологиялар, наноматериалдар, наноғылым, наножүйелік техника, наноөнімдер, нанонарығы, нанотехнологияны дамыту бағдарламасы, наноөнімдерді қолдану, наноиндустрия.</p>
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## Исследование развития нанотехнологий в Республике Казахстан

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### АННОТАЦИЯ

В современной истории цивилизации материалы и технологии, определившие облик эпохи, появлялись не раз. Достаточно вспомнить "век" бронзы и железа, пара и электричества, атомный «век» и компьютерный век. Наноматериалы (НМ), несомненно, относятся к числу таких материалов, и 21 век открывает эру нанотехнологий. Большинство экспертов в области научно-технической политики, стратегического планирования и инвестиций уверены, что в ближайшее десятилетие нанореволюция ожидается во всех сферах науки, производства, обороны, медицины, быта, отдыха и развлечений. Ее последствия будут более масштабными, чем последствия компьютерной революции последней трети ХХ века, то есть масштабное и систематическое вторжение наноструктурированных материалов, изделий и методов их производства придет буквально во все сферы жизни. В статье анализируются пути развития нанотехнологий и использования различных наноматериалов и нанопродуктов в различных отраслях мировой экономики и охраны окружающей среды. Нанотехнология – это область фундаментальной и прикладной науки, обеспечивающая теоретическое обоснование практических методов исследования, производства и применения продуктов с атомной структурой путем манипулирования атомами и молекулами. Целью работы является изучение развития нанотехнологий и их значения в современной экономике. В статье рассматриваются пути развития нанотехнологий в Казахстане, а также перспективные направления их развития и применения в области машиностроения и промышленности в целом.

	<b>Ключевые слова:</b> нанотехнологии, наноматериалы, нанонаука, наносистемная техника, нанопродукты, нанорынок, программа развития нанотехнологий, применение нанопродуктов, наноиндустрия.
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## Fluoroammonium method for processing of cake from leaching of titanium-magnesium production sludge

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### ABSTRACT

We present the results of the physical and chemical properties of cake from nitric-acid leaching of titanium production sludge. It was found that all silicon in the cake is in the form of quartz, albite, sillimanite, sodium aluminosilicate. In total, these minerals make up the majority of the cake 60.24%. Titanium is presented in the form of rutile, titanium aluminum oxide, which in total is 35.56%. Iron is part of sillimanite and hematite, the total content of which is about 4.2%. The optimal parameters of fluoroammonium processing of cake were determined: silicon distillation into sublimates at 300°C for 6 hours, sublimation of titanium in the form of titanium tetrafluoride at 800°C for 2 hours. The process of alkaline hydrolysis of sublimates of fluoride compounds and cinder was carried out. Purification of impurities and calcination of hydrated titanium dioxide were carried out. The resulting titanium and silicon dioxide products contain: 96.2% TiO<sub>2</sub>, 88 % SiO<sub>2</sub>, respectively; a niobium-containing intermediate product with a content of 11.6 % Nb<sub>2</sub>O<sub>5</sub> was also obtained.

**Keywords:** cake, sublimates, cinder, fluoroammonium processing, alkaline hydrolysis, titanium dioxide.

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## Introduction

The Kroll process is the main method for producing titanium sponges in all countries manufacturing titanium sponges [1], which consists of magnesium-thermal reduction of titanium tetrachloride at 850°C. The production chain of this process includes the production of magnesium metal from its molten salts by electrolysis. Dehydrated carnallite is the raw material for the production of electrolytic magnesium, and the spent electrolyte is used in the chlorination of titanium slags. Natural carnallite is preliminarily enriched and dehydrated. At the stages of titanium slag chlorination and magnesium electrolysis, a significant amount of chloride waste is formed.

Industrial waste is a hazard to the environment, as it contaminates soil and groundwater during neutralization and storage of solid waste in sludge dumps and the resulting industrial wastewater [2].

Part of the titanium production chloride waste is leached with water and neutralized with calcium

hydroxide to pH 7-8.5. The resulting slurry is pumped into sludge collectors and accumulates therein. The reserves of sediments or sludge of titanium production are about 320 thousand tons. The multicomponent composition thereof is present in the form of oxides, oxychlorides, and carbonates [3].

In Russia, the Bereznikovsky Titanium-Magnesium Plant (AVISMA JSC) obtains iron oxide pigments from waste [4]. However, the available research on hydrometallurgical processing of titanium-magnesium production waste was economically ineffective and lengthy due to the low filtration rate of slurries after leaching of chloride waste from titanium-magnesium production. Therefore, according to the existing technology, the Bereznikovsky Titanium-Magnesium Plant, washes out this waste with water and neutralizes acidic effluents with alkaline effluents of soda production, and sends to a sludge dump.

Thus, titanium-magnesium plants usually do not process solid chloride waste and often discharge

wastewater that contains chlorides and harmful substances into water bodies, polluting the soil and water of the surrounding area [5]. The plant has to pay huge fines for waste maintenance. The creation of integrated technology for the processing of this technogenic raw material will make it possible to obtain additional products in the form of titanium dioxide and calcium nitrate. Titanium dioxide can be returned to production for chlorination of titanium slags and calcium nitrate will be used as a fertilizer and a component in the cement industry, so these products will be in demand both in Kazakhstan and on the world market.

In recent years, fluoroammonium processing of multicomponent raw materials has been of great interest [6]. Ammonium bifluoride is a white crystalline substance with good solubility in water of 434 g/L, a melting point of 126.2°C, and a boiling point of 238°C, accompanied by decomposition into  $\text{NH}_3$  and HF.

The interaction of oxygen-containing compounds of titanium and other metals with ammonium bifluoride is of great importance in terms of the technological attractiveness of the method for extracting components from raw materials through the formation of ammonium fluorometallates [7] that, due to their physical and chemical properties, ensure the solubility of products and the possibility of separating mixtures by sublimation. Fluorination by-products (water vapor, ammonia, hydrogen fluoride) in gas-collecting systems are regenerated into ammonium fluoride and, upon drying, are formed into ammonium bifluoride, which ensures environmental safety of production and allows such by-products to be used in the circulation of a fluorinating agent.

[[8] and [9]] show the possibility of separating aluminosilicates with ammonium bifluoride into alumina and silicon oxide by sintering. In the complex processing of kaolin concentrates, ammonium bifluoride ( $\text{NH}_4\text{HF}_2$ ) was used as a fluorinating reagent. Under normal conditions, ammonium bifluoride does not pose a significant environmental hazard and is a strong fluorinating reagent when heated. Its melting and decomposition points are 126.2°C and 238°C, respectively. This is because each reaction needs to be activated, and the activation of hydrogen fluoride and halogen fluorides requires less energy than gaseous fluorine, so such reactions can be carried out at a lower temperature. The kaolin concentrate with  $\text{NH}_4\text{HF}_2$  is sintered at 190-200°C with the formation of a powdery product. This product is

desilicized under oxidizing conditions at a temperature above 320°C. Gaseous ammonia and water vapor are trapped and enter the absorption apparatus; ammonium fluoride enters the same place. Evaporation of the resulting solution obtains regenerated  $\text{NH}_4\text{HF}_2$  which goes to the head of the process. The method for processing [10] titanium-containing raw material of ilmenite concentrate includes the fluorination of the raw material by sintering with a fluoride reagent, heat treatment of the fluorinated mass to separate fluorination products by sublimation, pyrohydrolysis of post-sublimation residues to obtain iron oxide. Fluorination uses ammonium fluoride, ammonium bifluoride, or their mixture in a stream of inert gas as a fluoride reagent. The sublimation products are trapped in water when obtaining an ammonium fluorotitanate solution, and hydrated titanium dioxide is precipitated with an aqueous solution of ammonia, then the precipitate is heat-treated to obtain titanium dioxide.

In the available patent and scientific literature, almost all presented information about the fluoroammonium treatment is related to the processing of ores or concentrates, but not to the processing of titanium production waste by this method. Taking into account the differences in the physical and chemical properties of ammonium fluorometallates, we can select the conditions for the complete separation of the mineral product fluorinated with ammonium bifluoride into individual components. All this is a prerequisite for the development and creation of a more progressive and promising fluoride technology for processing titanium-containing raw materials.

The main purpose of this work was to study the physical and chemical properties of the previously obtained cake [11] from nitric-acid leaching of sludge from Ust-Kamenogorsk Titanium Magnesium Plant JSC and the processing of cake from leaching of sludge by the fluoroammonium method to obtain marketable products.

### Experimental part and discussion of results

This research proposes to use a cake from nitric-acid leaching of sludge from Ust-Kamenogorsk Titanium Magnesium Plant JSC as a raw material source; its phase composition is shown in Table 1. Based on the results of X-ray fluorescence and chemical analyzes, the elemental composition of the cake was determined as follows, wt. %: 19.7 Ti, 3.1

Fe, 1.2 Ca, 3.3 Al, 0.4 S, 20.5 Si, 0.1 V, 3.6 Nb, 51.03 O, 0.4 F, 0.7 Zr, 0.2 Cr, 0.06 Mn, 0.4 W.

The polished surface of a polished section prepared from the cake from nitric-acid leaching of sludge was examined using an EDAX ORBIS MICRO-XRF X-ray fluorescence spectrometer. The research results are shown in Figure 1.

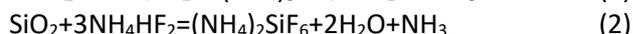
**Table 1** – Phase composition of the cake

Phase	Formula	S-Q, %
Quartz	SiO <sub>2</sub>	37.8
Rutile	TiO <sub>2</sub>	25.5
Albite	(Na,Ca)Al(Si,Al) <sub>3</sub> O <sub>8</sub>	13.2
Niobium-aluminum-titanium oxide	Ti <sub>0.8</sub> Al <sub>0.1</sub> Nb <sub>0.1</sub> O <sub>2</sub>	10.0
Sillimanite	(Al <sub>1.98</sub> Fe <sub>0.02</sub> )SiO <sub>5</sub>	5.7
Iron oxide	Fe <sub>2</sub> O <sub>3</sub>	4.2
Sodium aluminum silicate	Na(AlSi <sub>2</sub> O <sub>6</sub> )	3.6

The results of physical and chemical studies draw the following conclusions: all silicon is in the form of quartz, feldspar as albite, sillimanite, sodium aluminosilicate. In total, these minerals make up the majority of the cake (60.24%). Titanium is presented in the form of rutile, titanium aluminum oxide, which in total is 35.56%. Iron is part of sillimanite and hematite with a total content of about 4.2%.

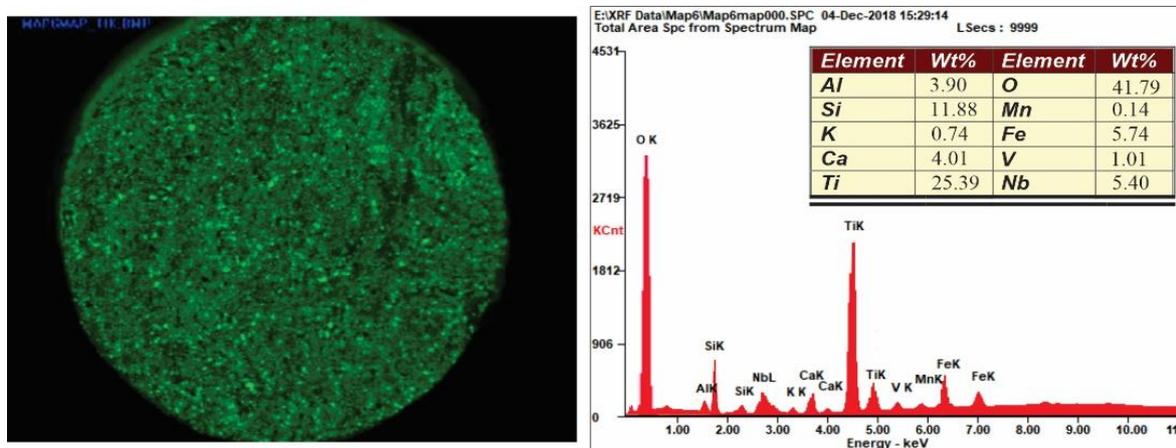
Experiments on fluoroammonium processing of cake from sludge leaching were carried out. For the interaction of ammonium bifluoride with cake, preliminary sintering was carried out. Preliminary sintering of the cake with ammonium bifluoride and a small amount of water (25% of the initial mixture) was carried out in a vertical furnace at 200°C for 60 min in a fluoroplastic crucible. The cake sintering at 200°C with ammonium bifluoride is necessary for the interaction of the silicate components of the

cake with ammonium bifluoride [12]. The following reactions occur during fluoridation:



At the same time, the sinter yield for each experiment was stably in the range of 85-87%; the rest was losses with the gas phase in the form of ammonia, water vapor, and hydrogen fluoride. Silicon and titanium were sublimated in a stainless steel tube with an argon supply at a rate of 1 to 1.5 dm<sup>3</sup>/min. Silicon was sublimated at 200°C and 300°C with a change in the duration of the process from 60 to 360 min. The results of studies on the sublimation of silicon are shown in Table 2. Based on the results of silicon sublimation, a histogram of silicon extraction into sublimates and a cinder was built (Figure 2).

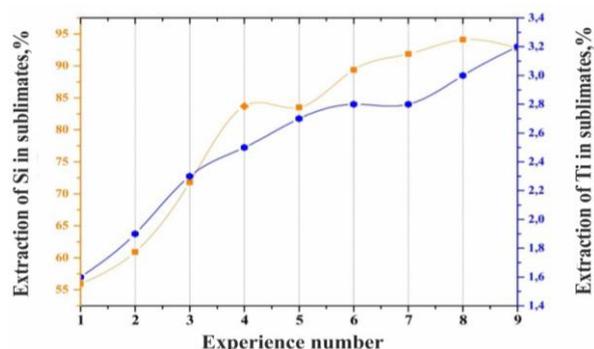
According to Table 2 and the diagram in Figure 2, the increase in the time of the sublimation process from 60 to 360 min at both temperatures increased the extraction of silicon into sublimates from ~55 to ~91-94%, respectively. At the same time, the extraction of titanium into sublimates increased in a small amount, in the range from ~1.6 to ~3.2%, respectively. The best results were shown by experiment 8, which was carried out at a sublimation temperature of 300°C for 360 min, at an argon flow rate of 1.2 dm<sup>3</sup>/min, where the extraction of silicon into sublimates was 94.2%. The content of silicon and titanium in sublimates was 25.9% and 1.9%, respectively. The sublimate yield was 29.5%, the cinder yield in the boat was 29.0%, the rest was the gaseous phase trapped in the flask with 10% ammonia water for the regeneration of ammonium bifluoride.



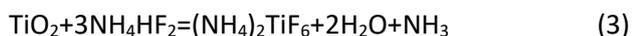
**Figure 1** – Energy Dispersive X-ray (EDX) Analysis

**Table 2** – Study of the process of silicon sublimation after sintering cake with ammonium bifluoride

Exp. No.	Sinter yield, %	T, °C	τ, min	Argon, dm <sup>3</sup> /min	Sublimate yield, %	Cinder yield, %
1	85.64	200	60	1	8.95	57.98
2	86.55	200	120	1	10.33	48.05
3	86.35	300	120	1	12.81	43.26
4	85.39	300	180	1	17.9	38.02
5	85.90	300	240	1	17.22	38.43
6	87.00	300	300	1	25.18	35.5
7	86.71	300	360	1	26.43	30.23
8	85.85	300	360	1.2	29.53	29.04
9	86.10	300	360	1.5	30.15	29.43

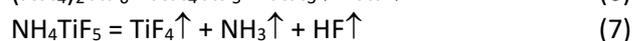
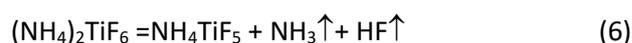
**Figure 2** – Diagram of silicon and titanium extraction in silicon sublimates

Titanium sublimation was the next stage. For sublimation of titanium, cinders from experiments 5-9 were combined. The resulting material was crushed, averaged, and divided into 5 experiments. For each sample, an additional amount of ammonium bifluoride was added to maintain the ratio with the amount of cinder equal to 1:1. The samples were preliminarily sintered at 200°C for 60 min. The sinter yield for each experiment was in the range of 90-94%. The second sintering of the cinder at 200°C with ammonium bifluoride was carried out for the complete fluorination of titanium oxides and impurity components according to the following reactions:



Impurity compounds such as Mg, Mn, Nb, Al, Fe, emerging during fluorination, form simple and complex fluorides, which remain in the cinder.

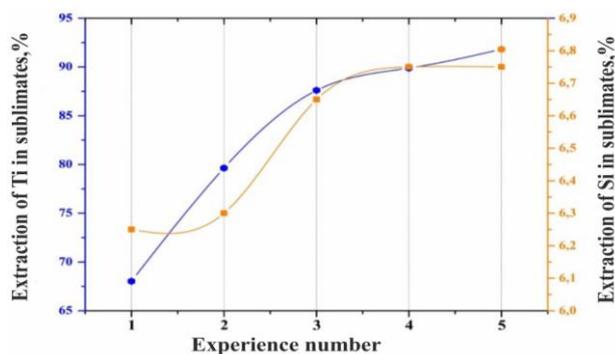
The ammonium hexafluorotitanate formed during fluorination with an excess of ammonium bifluoride decomposes to titanium tetrafluoride stepwise with the elimination of the ammonium fluoride molecule from the complexes according to the following reactions:



If there is not enough ammonium bifluoride, part of the titanium dioxide is not completely fluorinated to the formation of ammonium oxyfluorotitanates, which form titanium oxyfluoride (TiOF<sub>2</sub>) upon thermal decomposition [13].

Titanium tetrafluoride was sublimated at 700-800°C during 60-120 min. The argon supply rate in all experiments was maintained at 1.2 dm<sup>3</sup>/min. The results of studies on titanium sublimation are presented in Table 3. Figure 3 shows the extraction of titanium into sublimates and cinder.

The research results presented in Table 3 and on the diagram (Figure 3) show that the increase in the process temperature from 700 to 800°C and duration from 60 to 120 min increases titanium extraction into sublimates from ~68 to ~92%. The extraction of silicon into sublimates was in the range of ~6.25 to ~6.75%. The best performance was achieved at the temperature of 800°C, duration of 120 min, argon flow rate of 1.2 dm<sup>3</sup>/min, while titanium extraction into sublimates was 91.82%. The content of titanium and silicon in the sublimates was 35.75% and 2.56%, respectively. The sublimate yield was 33.41%; the cinder yield in the boat was 17.5%.

**Figure 3** – Diagram of titanium and silicon extraction in titanium sublimates

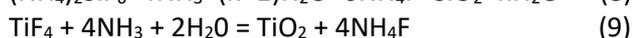
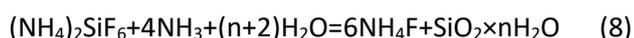
**Table 3** – Study of the titanium sublimation process

Exp. No.	Sinter yield, %	T, °C	τ, min	Argon, dm <sup>3</sup> /min	Sublimate yield, %	Cinder yield, %
1	93.5	700	60	1.2	21.67	24.24
2	90.95	750	60	1.2	27.61	20.36
3	92.9	750	90	1.2	27.54	17.45
4	92.98	800	90	1.2	32.5	18.85
5	93.98	800	120	1.2	33.41	17.50

Table 4 shows the chemical composition of the products of fluoroammonium processing.

According to Table 4, the titanium content in the initial cinder was 24.45%; after fluoroammonium processing with its transfer to sublimes, the residual titanium content in the final cinder was 3.1%. At the same time, the content of such impurities as iron, calcium, aluminum, niobium, and sodium in the final cinder increased in comparison with their value in the initial cinder supplied to the ammonium fluoride processing. Only an insignificant part of iron, a little calcium with aluminum, and a residual amount of silicon passed into titanium sublimes.

To transfer the obtained fluoride products into oxides, experiments on alkaline hydrolysis were carried out. To carry out studies of the alkaline hydrolysis process, batches of fluoride sublimes of silicon and titanium, as well as cinder, were preliminarily produced under the established optimal conditions of previous experiments. Alkaline hydrolysis of ammonium hexafluorosilicate and titanium tetrafluoride was carried out according to the following reactions [[13], [14]]:



Experiments on alkaline hydrolysis of titanium fluorides were carried out to remove fluorine and

obtain titanium dioxide. For this, 20 g of titanium fluoride sublimes were taken, placed in a glass with 400 ml of 10% ammonia water at a S:L ratio of 1:20, and heated to 50°C with stirring at 50 rpm. Upon reaching the desired temperature, the mixture was kept for 60 min, then cooled and defended for 30 min. The clarified part was decanted, water was added to the precipitate at a S:L ratio of 1:20, stirred for 10 min, and filtered. Then, the precipitate was dried at 105-110°C to constant weight. Hydrated titanium dioxide with the following composition was obtained, wt. %: 45.54 Ti, 1.6 Fe, 0.8 Si, 0.59 Al, 0.1 Nb, 0.03 Ca (75.9 TiO<sub>2</sub>, 1.7 SiO<sub>2</sub>).

The resulting hydrated titanium dioxide contains impurities of iron, aluminum, etc., which may affect the quality of the final product. For purification from impurities, the obtained hydrated titanium dioxide was subjected to nitric-acid processing.

Nitric acid purification was carried out under the following conditions: 10% HNO<sub>3</sub>, at 60°C, at a S:L ratio of 1:10, for 60 min. After washing, the titanium dioxide precipitate was dried at 105-110°C to constant weight, then calcined in a chamber furnace at 500°C for 120 min. As a result, we obtained a product corresponding to a rutile concentrate in terms of chemical composition, %: 57.7 Ti, 1.1 Fe, 0.64Si, 0.28Al, 0.03Ca, 39.5O, etc. (96.2 TiO<sub>2</sub>, 1.57 Fe<sub>2</sub>O<sub>3</sub>, 0.52 Al<sub>2</sub>O<sub>3</sub>, 1.37 SiO<sub>2</sub>, 0.014 CaO, etc.).

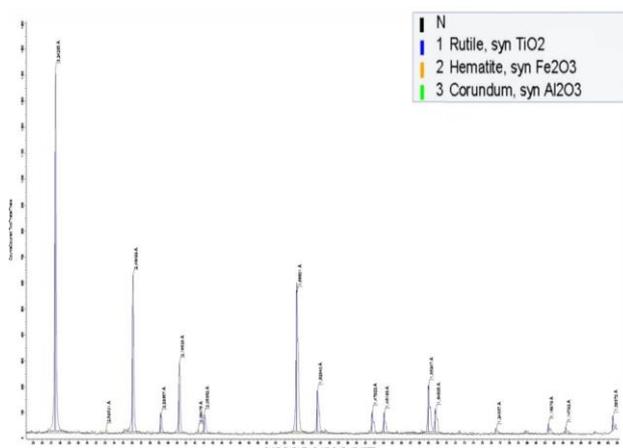
**Table 4** – Chemical composition of fluoroammonium processing products

Name	Sinter	Silicon sublimes	Cinder	Titanium sublimes	Final cinder
Element	Content, %				
Ti	7.65	1.85	24.45	35.75	3.1
Fe	0.98	0.24	3.13	1.0	11.6
Ca	0.15	0.14	0.37	0.06	1.56
Al	1.15	0.4	3.50	0.40	15.06
Si	8.10	25.85	1.61	1.56	0.10
Nb	0.79	0.01	2.62	-	5.5
Cr	0.07	-	-	-	-
P	0.23	0.03	-	-	-
Na	0.70	-	0.85	-	3.9
F	61.96	65.38	35.86	53.02	39.54
O	12.74	2.90	23.39	4.50	17.84
Other	5.48	3.2	4.22	3.71	1.8

According to the results of the XRD analysis of the titanium dioxide obtained, which is presented in Table 5 and Figure 4, the product mainly consists of rutile ( $\text{TiO}_2$ ) and has small amounts of iron impurities in the form of hematite, as well as aluminum oxides.

**Table 5** – Phase composition of the titanium dioxide product

Phase	Formula	Content, %
Rutile	$\text{TiO}_2$	95.2
Iron oxide	$\text{Fe}_2\text{O}_3$	4.0
Aluminum oxide	$\text{Al}_2\text{O}_3$	0.8



**Figure 4** – Diffractogram of the titanium dioxide product

Alkaline hydrolysis of silicon sublimates and final cinder was carried out according to a similar scheme. Amorphous silica, wt. %: 41.8 Si, 4.2 Ti, 0.075 Ca, 0.054 Al, 0.027 P, 0.08 Fe, 0.16 F (88.07  $\text{SiO}_2$ , 7  $\text{TiO}_2$ ) and a niobium-containing product of the following composition, wt. %: 6.7 Ti, 0.35 Si, 20.5 Fe, 19.3 Al, 8.1 Nb, 4.2 Na, 0.7 Ca, 0.1 F. (11.17  $\text{TiO}_2$ , 0.75  $\text{SiO}_2$ , 29.32  $\text{Fe}_2\text{O}_3$ , 36.45  $\text{Al}_2\text{O}_3$ , 11.6  $\text{Nb}_2\text{O}_5$ , 5.7  $\text{Na}_2\text{O}$ ) were additionally obtained.

Thus, according to the results of the studies, titanium dioxide of rutile modification, containing

96.2  $\text{TiO}_2$ , was obtained. In terms of titanium dioxide as the main component and the content of impurities, the obtained one corresponds to the rutile concentrate according to GOST 22938-78.

## Conclusions

The results of the investigated physical and chemical properties of cake from nitric-acid leaching of titanium production sludge show that all silicon in the cake is in quartz, feldspar in the form of albite, sillimanite, sodium aluminosilicate; in total, these minerals make up most of the cake (60.24%). Titanium is presented in the form of rutile, titanium aluminum oxide, which in total is 35.56%.

For the selective extraction of silicon and titanium, the fluoroammonium method of cake processing was chosen. The optimal parameters of fluoroammonium processing of cake were determined: silicon distillation into sublimates at 300°C for 6 hours, sublimation of titanium in the form of titanium tetrafluoride at 800°C for 2 hours.

The alkaline hydrolysis process for titanium tetrafluoride sublimates was carried out. Hydrated titanium dioxide was obtained and subjected to nitric-acid treatment, drying, and calcination at 500°C for 120 min. As a result, rutile titanium dioxide containing 96.2%  $\text{TiO}_2$  was obtained. Alkaline hydrolysis of fluoride silicon compounds and the final cinder additionally gave amorphous silica with a content of 88%  $\text{SiO}_2$  and a niobium-containing intermediate product with a content of 11.6%  $\text{Nb}_2\text{O}_5$ .

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

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## Титан-магний өндірісіндегі шламды шаймалау барысында алынған сүзіндіні (кекті) фторлы аммоний әдісімен өңдеу

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<p>Мақала келді: 15 тамыз 2021 Сараптамадан өтті: 08 қараша 2021 Қабылданды: 15 желтоқсан 2021</p>	<p><b>ТҮЙІНДЕМЕ</b> Титан өндірісіндегі шламды азот қышқылымен шаймалау барысында алынған сүзіндінің (кектің) физико-химиялық қасиеттерінің нәтижелері келтірілген. Кремнийдің сүзінді құрамында кварц, альбит, силлиманит, натрий алюмосиликаты түрінде кездесетіні анықталды. Тұтас алғанда бұл минералдар сүзіндінің ауқымды 60,24 % бөлігін құрайды. Титан рутил, титаналюмониобий оксиді күйінде кездеседі және олардың жиынтығы 35,56%-ды құрайды. Темір силлиманит пен гематит құрамына кіреді, жалпы мөлшері 4,2%. Сүзіндіні фтор-аммонийлік өңдеудің оңтайлы параметрлері анықталды: кремний 300 °С температурада, 6 сағат ішінде бұға айналып айдалады, титан титан тетрафториді түрінде 2 сағат ішінде 800 °С бұға айналады. Фторлы қосылыс возгондары мен күйіндіге қатысты сілтілі гидролиз процесі жүргізілді. Қоспалардан тазарту және гидратталған титан диоксидін қыздыру жұмыстары жүргізілді. Алынған титан мен кремний диоксиді өнімдерінде, сәйкесінше: 96,2% TiO<sub>2</sub>, 88% SiO<sub>2</sub> бар және құрамында 11,6% Nb<sub>2</sub>O<sub>5</sub> бар ниобийқұрамды аралық өнім алынды. <b>Түйін сөздер:</b> сүзінді, возгондар, күйінді, фтораммонийлік өңдеу, сілтілі гидролиз, титан диоксиді.</p>
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## Фтороаммонийный метод переработки кека от выщелачивания шлама титаномагниевого производства

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<p>Поступила: 15 августа 2021 Рецензирование: 08 ноября 2021 Принята в печать: 15 декабря 2021</p>	<p><b>АННОТАЦИЯ</b> Приведены результаты физико-химических свойств кека от выщелачивания азотной кислотой шлама титанового производства. Установлено, что весь кремний в кеке находится в форме кварца, альбита, силлиманита, алюмосиликата натрия. В сумме эти минералы составляют большую часть кека 60,24%. Титан представлен в виде рутила, титаноалюмониобиевого оксида, которые в сумме составляют 35,56 %. Железо входит в состав силлиманита и гематита, общее содержание которых составляет около 4,2 %. Установлены оптимальные параметры фтороаммонийной переработки кека: отгонка кремния в возгоны при 300 °С в течение 6 часов, возгонка титана в виде тетрафторида титана при 800 °С в течение 2-х часов. Проведен процесс щелочного гидролиза возгонов фторидных соединений и огарка. Осуществлена очистка от примесей и прокаливание гидратированного диоксида титана. Полученные продукты диоксидов титана и кремния содержат: 96,2% TiO<sub>2</sub>, 88 % SiO<sub>2</sub>, соответственно, также получен ниобийсодержащий промежуточный продукт с содержанием 11,6 % Nb<sub>2</sub>O<sub>5</sub>. <b>Ключевые слова:</b> кек, возгоны, огарок, фтороаммонийная переработка, щелочной гидролиз, диоксид титана.</p>
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## The effectiveness of the kit portable PLC on electrical motors course among vocational school students in Aceh, Indonesia

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### ABSTRACT

This research aims to test the effect of the kit Programmable Logic Controller (PLC) on the achievement of vocational school students' competencies in electrical motor control courses for form 3 students in Aceh, Indonesia. Constructivist theory and Bloom's Taxonomy are referenced in this study in relation to learning. While the ADDIE model is used in relation to product development. This study used a quasi-experimental design with pre- and post-tests. The population (N = 333) in this study was level 3 vocational students in Aceh, Indonesia. The number of samples was 98 people, consisting of the experimental group (n = 50) and the control group (n = 48) selected by cluster random technique. The instruments used in this study included pre- and post-test interview protocols. The values of the KR20 reliability coefficient of the question items on the knowledge aspect were 0.97 and 0.81 on the skills aspect. The results of the descriptive analysis found that the experimental group (mean = 64.08; SD = 4.548) showed better competency achievement than the control group (mean = 63.06; SD = 5.487). The result of hypothesis test using Mann Whitney test is [Asymp. Sig. (2-tailed) = .000, p < 0.05] which means that the teaching aids developed have successfully had a positive effect in improving the achievement of student competencies. The implications of this study have produced a teaching aid that can be used as a template by teachers to build teaching aids that are more affordable, easy and safe to use so that they can be motivated to innovate in learning and become a new career opportunity. Given that the Covid-19 epidemic has affected face-to-face learning, the proposal for further research is the need to integrate logic control programming (PLC) learning aids into a technology-based learning trend. Researchers, on the other hand, suggest a broader scope of study whether teachers and students in a wider area and other fields of knowledge related to the utilization of PLC programming.

**Keywords:** effectiveness, teaching aid, programmable logic controller, motor electric installation, vocational schools.

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### Introduction

Vocational education is an education that trains graduates with employment skills. Entering the era the needs of the industry. The Indonesian industrial world needs high-quality human resources. Graduates of vocational schools with skills can meet the needs of Indonesian industry. Thus, graduates of vocational schools that suit the

of Industrial Revolution 4.0, the skills needs of all walks of life and workers have undergone remarkable changes [1]. The skills possessed by graduates of vocational schools must correspond to industrial world can reduce the unemployment rate in Indonesia [2]. With the government's policy through the Ministry of National Education, it is expected that the number of vocational schools will exceed public schools in the next 10 years at 70%

compared to 30%. Given that Indonesia needs a large number of mid-level skilled workers to meet the needs of the world of employment and industry, this consideration seems logical.

However, it is certainly not easy to realize this hope, needed the support of all sectors of society, the business community, and industry [3]. Currently, there is an impression that the skills of vocational school graduates are not good enough, and they are worried about losing competition with existing foreign workers. With good quality of graduates of vocational schools, it is hoped that they will not only work in their home countries, but are also expected to compete with the foreign workforce globally [4]. It is often heard that on the one hand, there are a large number of graduates from vocational schools, but on the other, there are still very few (limited) graduates who are able to work independently and according to their capabilities [5].

Certain factors that can influence the achievement of students in this programming topic have also been identified. Among them are the factors of knowledge, skills and interests of the students themselves. Thus, the use of teaching aids is expected to have an influence in the learning process. There is a lot of talk about the use of teaching aids for teachers in teaching and learning activities. Some of the obstacles or constraints faced by teachers in the implementation and provision of teaching kit in the teaching and learning process include insufficient teaching materials, heavy teaching burden, lack of time, impracticality, inability to write teaching materials on their own, and insufficient funds [6].

According to Mohd Yasin et al [7], the use of teaching aids in teaching and learning activities in vocational schools has not reached satisfactory and inadequate levels, especially involving the use of the latest technical skills. Facilities in the process of inadequate teaching and learning are one of the factors that hinder the implementation of the vocational school curriculum. The next factor is due to the knowledge, skills and attitude of the teacher himself, if laboratory facilities are insufficient for practical training, no steps will be taken [8]. According to Pheng [9], teachers do not have enough time to provide teaching and learning equipment and perform system maintenance on practical equipment. Moreover, the old method of using blackboards by teachers is boring and less effective in giving students understanding. This can lead to a lack of teaching growth in institutions and an inability to consistently coordinate to support

learning in a more complex and challenging teaching environment.

Based on the initial studies conducted in learning the topic of logical control programming (PLC) in the electrical machine installation course, it was found that there are weaknesses in the practical teaching process due to various factors, among which is that the absence of teaching aids is enough to cause students to lack understanding of the teaching and learning process. Existing teaching aids are very simple and will not encourage students to think creatively about programming system solutions. In addition, simply applying theoretical concepts to practical activities will not directly affect the performance of students. In addition, insufficient funding, teachers with no experience, inexperienced management staff and lack of materials in the library [8]. Therefore, portable PLC kit, It is hoped that it will help the teaching and learning process as a training media in vocational schools.

*The objective of this study is to test the effect of portable teaching aids programming logic control (PLC) for electric motor control courses among students of form 3 vocational school in Aceh, Indonesia.*

*The research question of study: What is the effect of teaching portable PLC kit on student competency achievement for electric motor control courses among students of form 3 vocational schools in Aceh, Indonesia?*

*A hypothesis should be built to answer the questions studied to find out the impact of portable PLC teaching aids in learning electric motor control in students. Here are the hypotheses in this study: Ho = There is no difference in the effect of portable PLC kit for electric motor control courses among students of form 3 vocational school in Aceh, Indonesia; Ha = There is a difference in the effect of portable PLC kit on electric motor control courses among students of form 3 vocational school in Aceh, Indonesia.*

## Theoretical Framework

In this study, researchers used the theory of Constructivism founded by Vygotsky, Piaget and Bruner. This Constructivism Theory was also co-adapted with the ADDIE development model by Branch [10] and Dick & Carey [11].

Constructivist learning theory is one of the learning methods based on the student's experience related to existing knowledge. This theory emphasizes student activity. The learning process is

not only dominated by the teacher but the student is also active in it. One of the learning strategies that actively involves students is constructivism. The method of constructivism places students in the main role in the student centered process [12].

In the context of constructivism learning related to assists in the learning process, students are required to be actively involved and interact to make learning more meaningful. One of the challenges teachers face in applying constructivism methods is adapting and changing instructional design strategies to enable students to actively participate in effective project activities and assignments, thus encouraging students to explore, test, build, collaborate, and reflect on what is being studied [13].

It is believed that constructivist learning related to the use of teaching aids can help students solve problems more quickly, since this process emphasizes aspects of group thinking and discussion, and can establish bilateral communication between students and teachers, students and students [14].

Referring to Bloom's Taxonomy theory, general instruments, competencies are divided into three parts: attitude, knowledge, and skills. Taxonomy Bloom is one of the development of cognitive theory, usually associated with problems setting learning goals and standard problems assessing or measuring learning outcomes, as curriculum development [15].

The attitude aspect covers all things related to emotions, such as feelings, values, appreciations, passions, interests, motivations and attitudes. According to Gunawan & Palupi [16], the aspect of attitudes related to a student's attitude and interest towards subjects among them is receiving attitude,

which is related to the sensitivity of students in receiving external stimuli in either in the form of problems or specific conditions. Feedback, is a reaction to the stimulus given from the external one. Assessing (valuing), this has to do with value or belief in a stimulus. Organization, that is, the attitude of aligning values into an organization. The characteristics of values that are the integration of the values that a person possesses are reflected in attitude and personality.

Cognitive aspects are a field that deals with the purpose of learning that deals with mental processes that begin at the level of knowledge up to the evaluation stage [17]. Knowledge level is a person's skill in recalling terms, formulas, names and so on

The psychomotor aspect is a student's skill in acting related to physics skills including a physical movement and coordination to achieve learning outcomes [18]. Psychomotor aspects include physical mobility and coordination, practical skills and physical skills. These skills can be measured in terms of speed, accuracy, distance, method/implementation technology. In PLC programming competencies, the psychomotor aspect can be interpreted as a student's skill in applying PLC programming that covers practical knowledge and skills.

The level of teaching aids is to refer to the ADDIE model. This stage includes the design and development of PLC teaching aids [19]. While the evaluation section is to test the usability and impact of PLC teaching aids on students' competency achievement through expert assessment and post-testing. The resulting PLC teaching aids are expected to have a positive impact on teachers and students during the teaching and learning process. Figure 1 shows the theoretical framework of the study.

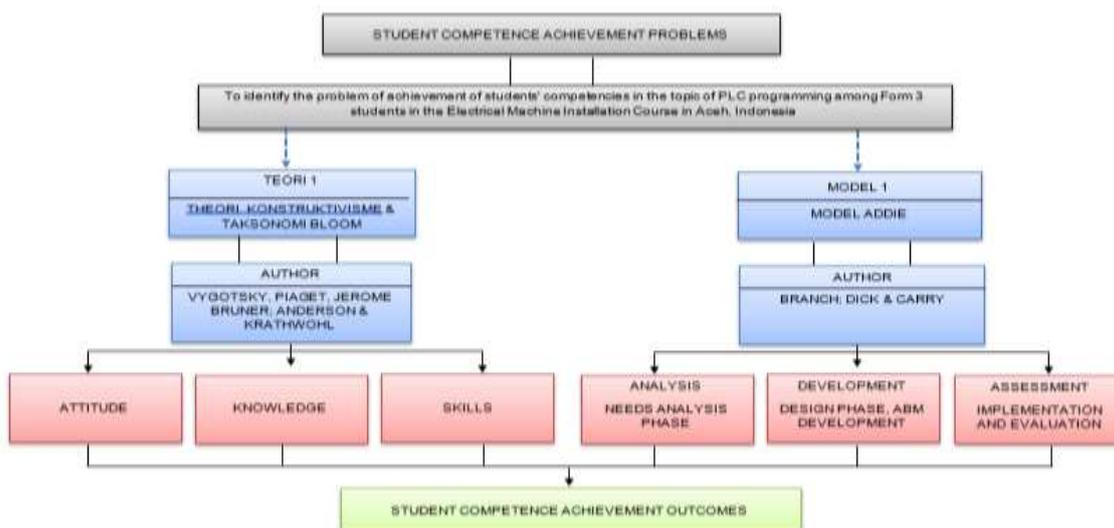
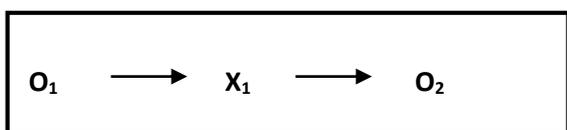


Figure 1 - Study theory framework

### Research Methodology

*Study Design.* The study used quasi-experimental design through quantitative approach. Quantitative approaches are used because this study requires data in the form of figures. Sang [20] believes that the use of quantitative approaches can demonstrate the discovery of comprehensive information, differences and consequences. This study aims to study the impact of the development of portable PLC kit on the achievement of student competencies on electrical machine installation courses for form three students of vocational schools in Aceh area, Indonesia. Figure 2 is a flow chart from this study.



Note:  
 O1 = Pre-Test  
 X1 = Learning through experience  
 O2 = Post Test

**Figure 2** - Study framework. Adapted from Hastjarjo in Chook & Campbell [21]

*Population.* Based on the data obtained from the database of institutions that manage the vocational school data, the number of form 3 students in electrical engineering of vocational schools in Aceh area, Indonesia is 539 people. The number of schools identified is 16 schools which in turn are categorised as urban and rural schools to focus on the selection of sample studies. The determination of the urban or rural school category is based on the geographical position of the school. Referring to Table 1 below, there are 6 schools that fall into the rural school category in the field of electrical engineering. The total number of students in rural schools is 126. Table 1 shows data on the number of schools and students categorised as rural schools in the field of electrical engineering in Aceh, Indonesia.

**Table 1** - Data of students and vocational schools in the field of electrical engineering in Aceh rural area

No	School Name	Area	Number of Student
1	Lhok Nga Aceh Besar Vocational School	Rural	5 Student
2	Darul Kamal Aceh Besar Vocational School	Rural	22 Student

3	Tanah Luas Vocational School No. 1	Rural	9 Student
4	Bener Meriah Vocational School No. 1	Rural	28 Student
5	Bener Meriah Vocational School No. 2	Rural	9 Student
6	Abdya Vocational School No. 1	Rural	32 Student
7	Sinabang Vocational School No. 2	Rural	21 Student
Total			126 Student

Source: Ditpsmk, 2020.  
<http://peta.ditpsmk.net/peta2/index.php/chome/pencariansekolah/>

Based on Table 2 below, there are 9 schools that fall into the urban area school category. The total number of students in schools in the urban area is 413. But the actual number was 333 people who went on to become the population in this study.

**Table 2** - Data of students and vocational schools in the field of electrical engineering in the Aceh urban area

Bill	School Name	Area	Number of Student
1	Banda Aceh Vocational School No. 2	Urban	48 Student
2	Sigli Vocational School No.2	Urban	50 Student
3	Bireuen Vocational School No.1	Urban	51 Student
4	Lhokseumawe Vocational School No.5	Urban	15 Student
5	Langsa Vocational School No.2	Urban	100 Student
6	Karang Baru Aceh Tamiang Vocational School No.2	Urban	54 Student
7	Takengon Middle Aceh Vocational School No. 2	Urban	28 Student
8	Peureulak East Aceh Vocational School No.2	Urban	23 Student
9	Meulaboh West Aceh Barat Vocational School No.2	Urban	44 Student
Total			413 Student

Source: Ditpsmk, 2020.  
<http://peta.ditpsmk.net/peta2/index.php/chome/pencariansekolah/>

Based on the two tables above, researchers chose urban area schools as the place where the study was conducted as it was easily accessible thus minimizing the production of study costs. In addition, the number of urban school students has more students than the number of students in rural schools. Therefore, researchers only need to choose the two schools that are the place of study until the implementation of the study becomes simpler, simpler and time-saving.

*Sample.* The samples in this study consist of form 3 students from electrical engineering vocational school who took courses in electrical motor courses. Refers to school and student data of designated urban areas. Next, out of the 9 schools in the city area, researchers selected the schools that were used as study places by randomly selecting using cluster sampling techniques. From the 9 schools in the town area, one school was chosen randomly by voting method, until it was found Peureulak East Aceh Vocational School No.2. The purpose of this school selection is to be used as a school for pilot studies to carry out the analysis of the needs of kit development and testing of research instruments [22]. According to Panahbehagh [23], this technique is used when the population is not made up of individuals, but consists of groups or groups of individuals or clusters. District sampling techniques are used to determine samples when objects to be studied or data sources are very extensive [24]. Figure 3 shows a map of population dissemination and samples of studies.

When it was obtained from the school used as a place of study, researchers selected two schools that were used as places of study. Out of the remaining 8 urban schools, researchers selected two schools using the voting method until 2 schools, namely Banda Aceh Vocational School No. 2 and Karang Baru Aceh Tamiang Vocational School No.2. But, as early as 2020, almost the entire country was faced with a Covid-19 pandemic. Indonesia is one of the countries affected by the Covid-19 pandemic. The spread of covid-19 has rapidly spread throughout the 34 existing areas, not to mention the westernmost area of Aceh.

Banda Aceh as an area city and being one of the places to conduct this study itself has a fairly high number of covid-19 positive cases compared to other districts in Aceh area. The area has been designated as a red zone for the spread of covid-19 with the number of victims continuing to increase, until the local government designates the area as an area that applies social blocking, this includes the blocking of teaching and learning activities in schools [25]. Therefore, researchers made changes by aborting Banda Aceh Vocational School No.2 as one of the places to conduct studies and replace them with other urban area schools whose rate of spread of Covid-19 was lower. Thus, the remaining 6 schools were re-elected by voting for a replacement school that had been dropped previously, hence found Langsa Vocational School No. 2 as a replacement school. It is one of the urban schools that is still implementing the teaching and learning process during the Covid-19 pandemic. Figure 4 is the sampling technique in this study.

Based on Figure 4, Langsa Vocational School No.2 was selected as an experiment group, while Karang Baru Aceh Tamiang Vocational School No.2 was selected as the control group. As for the purpose of selection of the two schools, it is to avoid internal threats to the validity of the study. The 3 table below shows that the samples were 98 people comprising 48 students of control school and 50 students from experiment school. The number of non-permanent students per semester makes it difficult to accurately state the number of students. In addition, the Covid-19 pandemic has an impact on the number of students who are following the teaching and learning process.

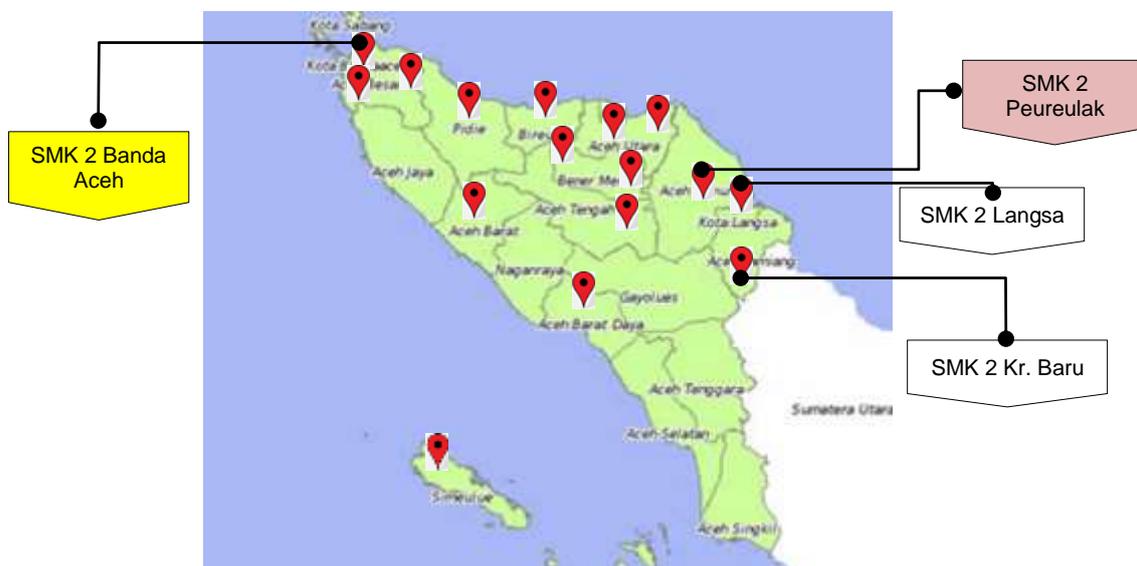


Figure 3 - Population dissemination study

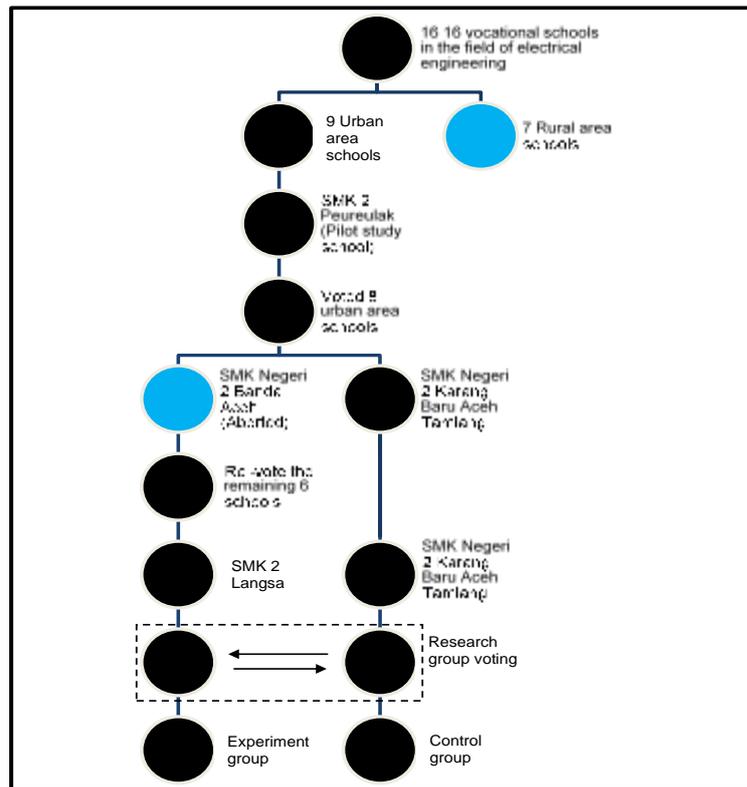


Figure 4 - Sampling technique

The characteristics of the subject in the population are inaccurate, the population can be considered as an abstract element as well as difficult or unquantifiable or accurately calculated [26]. According to Table 3, the sample number is 154 students. But the number of samples during the study was 98 students only. The number is based on the attendance list of students owned by the teacher who teaches at the course

Table 3 - Number of study samples

School	Class A	Class B	Total
Karang Baru Aceh Tamiang Vocational School No.2 (control)	24 Student	24 Student	48 Student
Langsa Vocational School No.2 (Experiment)	26 Student	24 Student	50 Student
			98 Student

**Instruments.** The study used pre-tests and post-tests. Testing is a measurement tool with objective standards, so it has multiple uses and can be used to measure and compare the behavior of an individual or group. Pre- and post-test tests are used to measure students' competency achievement before and after using developed teaching aids. Pre- and post-test tests are conducted in the form of

written tests, since written tests are a common way to test students' cognitive abilities [27].

The preparation of pre-test and post-test questions is aimed at seeing the extent of the impact of portable plc teaching aids on the achievement of students' competencies through the use of such teaching aids. These questions are first tested through a pilot study test before doing an actual study. Students are given 30 minutes to answer the pre-test. Then at other sessions the student conducts a 4-hour laboratory session. As for the post-test session, students are given 30 minutes to answer all questions. In the actual test, the answer paper was reviewed by 3 experts in the field based on the schemes provided to ensure the reliability of the results obtained.

The instruments that have been constructed have been reviewed by three experts comprising vocational teachers in electrical engineering in Aceh and senior lecturers of the Sultan Idris Education University of Malaysia with experience teaching over 10 years. The instrument of the test question item also tested its validity and reliability.

The validity and reliability of the instrument is important to ensure that the results obtained are reliable and indisputable [28]. The value of the test item is calculated using the Kuder-Richardson 20 formula (K-R20). According to Yap et al. [29], the Kuder-Richardson formula is used to avoid giving

tests twice and avoiding problems dividing tests into two parts. This formula can be used for homogeneous tests where each test item measures the same factors of general or personality abilities. According to him, the Kuder-Richardson formula depends on the consistency of individual performance of an item by item based on the standard deviation of the test. The value of  $KR_{20}$  is between zero (0) and 1.00, although a negative value is possible. A high  $KR_{20}$  value indicates that the test has internal consistency. For Carey [30], a value above 0.90 showed very high reliability. The coefficient value of reliability is .974 on the knowledge aspect and .811 on the skills aspect. According to Ghafar [31], in case the coefficient value is high (0.8 and above), it can be concluded that the test set has high reliability.

Besides, researchers also use protocol instruments. The interview protocol in this study is also an in-depth source of data on the most important teaching practices. Through the interview method, researchers were able to meet several key conditions, which involve students' knowledge of motor installation based on PLC programming. The interview method can also make it easier for researchers to conduct deeper exploration, since new information obtained can only be known through students' experiences, opinions, feelings and ideas about motor control systems and PLC programming knowledge. In addition, the interviews carried out can provide new information to researchers, especially information related to the practice of using teaching aids in programming learning. Researchers were also able to explore important information of a subjective nature to understand situations and things that are not directly visible.

Researchers also used the technique of dissenting in conducting interviews so that the respondent can give a complete opinion, explain and elaborate each question asked. Researchers will minimize questions so that the respondent can explain further the answers stated. Additionally, researchers will avoid asking questions by giving respondents a shadow of answers to avoid the researchers' biases.

### Data Analysis

The findings were analyzed using *statistical package for social science (SPSS) ver. 23.0*. Researchers used descriptive statistics to illustrate the study data that covered the amount of data,

maximum value, minimum value, mean value and so on. The researchers will then test the normality of the data to find out whether the data obtained is scattered normally or not. If the study data is found to be normal, researchers will use the Parametric t-test while if the data is abnormal, researchers will use the Non-Parametric Wilcoxon and Mann Whitney tests.

To analyze the results of the interview protocol, researcher begin writing the transcription of the interview immediately after the interview session. Researchers also examined and referenced field notes to help parse data, such as feelings, thoughts and intentions that cannot be measured.

*Document Analysis.* According to Bungin [32], document analysis is one of the methods of data collection used to search historical data in social study methodologies. Guba and Lincoln in Moleong [33], explain the difference between document and record terms. A record definition is any written statement provided by an individual/organization to test an event. Documents are data sources for additional research, including written material, films, drawings, and monumental works, all of which provide information for the research process. Documents can be used to analyze values and track what can be obtained in one document [34]. Through document analysis, researchers were able to identify the extent to which the learning on the Electrical Machine Installation course on the topic of logical control programming (PLC) had an impact on the achievement of students' competencies.

*Pre and Post Test Tests.* Assessments were conducted to test the impact of PLC teaching aids on students' academic achievements that can be measured through pre-tests and post-tests. This test method is used to assess students' level of understanding, mastery and skills. Pre-tests are used to obtain data showing students' weaknesses so that these vulnerabilities can be detected and early assistance can be planned. The post-test is aimed at looking at progress and weakness after carrying out interventions. The set of questions for pre-tests and tests are the same set of questions.

*Video and Picture Documentation.* Researchers used photo and video recordings for the purpose of observing the implementation of teaching. The use of photo and video recordings can make it easier for researchers to record each teaching execution activity more accurately. The use of these two audio visual materials is to reduce any possibility of important data dropped throughout the observation. The use of photo and video recordings

is a very suitable way to gather information in the form of voice and movement and can overcome the weaknesses of researchers who are only able to record a portion of the observations from the entire findings [35].

### Research Results

*Research Question:* What is the effect of kit portable PLC on the achievement of student competency for electric motor courses among students of form 3 vocational school in Aceh, Indonesia?

Prior to the introduction of the programming topic, a Pre Test was administered to 98 students to see the students' existing knowledge on the subtopic installation of electrical machines based on PLC programming as well as to see the equivalence of both groups. Table 4 shows the results of the Pre Test score for the electrical machine assembly course obtained by the experimental group respondents and the control group respondents.

Based on the results of the pre-test results, it was found that the students who obtained the pre-test score at a weak level (50-59) for the experimental group of 5 people (10%), whereas the control group was 8 (16.67%). The students who scored moderately (60-69) in the experimental group were 35 students (70%) and for the control group 32 students (66.67%). Next, the number of students who obtained the pre-test scores with satisfactory levels (70-80) in the experimental group was 10 students (20%), while the number of students in the control group was 8 (16.67). At the level of excellence (81-100), there were no students who scored at excellent levels in both groups, thus it was concluded that both groups of students had the equivalent of pre-test scores.

**Table 4** - Pre-test score

Level	Experiment Group (n = 50)		Control Group (n = 48)	
	f	(%)	f	(%)
Excellent (81-100)	0	0	0	0
Satisfactory (70-80)	10	20	8	16.67
Medium (60-69)	35	70	32	66.67
Weak (50-59)	5	10	8	16.67
Very Weak (0-49)	0	0	0	0
Total	50	100	48	100

To determine the equality of both groups, a descriptive analysis to compare the mean values is

performed. Table 5 below shows a comparison of the mean values of Pre Test. The mean value of the control group was 63.06 while the mean value of the segment group was 64.08. Both mean values are in the weak level category by reference to Table 5. Therefore, it can be concluded that both groups in terms of pre-test scores are equivalent.

**Table 5** - Comparison of Pre Test Mean Values

	n	Min	S. D	S. D Error
Control Group Pre-Test	48	63.06	5.487	.792
Experimental Group Pre-Tests	50	64.08	4.548	.643

Researchers have statistically descriptive data such as Table 6 below to reflect the study data that includes the amount of data, maximum value, minimum value, mean value and so on. The researchers then performed normality tests on all data obtained through the research instruments (Pre Test, Post Test) used to ensure that the data were normally buried.

**Table 6** - Descriptive Data Analysis

	n	Min	Max	Mean	S.D
Control Group Pre-Test	48	50	70	63.06	5.487
Experimental Group Pre-Tests	50	50	70	64.08	4.548
Control Group Post-Test	48	60	78	71.02	3.987
Experimental Post-Test Group	50	65	85	80.56	3.477
Number of valid Samples	48				

Table 7 below shows the findings from the Data Normality Test. From data normality analysis, significant value (Sig) for Kolmogorov-Smirnov test and Shapiro-Wilk test, it was found that three of them were less than 0.05 (<0.05). This can be concluded that the data obtained is not normally sown. To that end, the data needs to be analyzed with non-parametric statistics using the Mann-Whitney Test.

**Table 7** - Data Normality Test

Class	Kolmogorov-Smirnov	Shapiro-Wilk
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	Statistics	df	Sig.	Statistics	df	Sig.
Pre-Experimental Test	.140	50	.015	.919	50	.002
Post-Experimental Test	.171	50	.001	.844	50	.000
Pre-Control Test	.201	48	.000	.898	48	.001
Post-Control Test	.170	48	.001	.958	48	.086

**Note:** df = degree of freedom, Significant at level  $p < 0.05$ .

**Study Hypothesis.** Researchers conducted the Mann-Whitney Test because the number of samples for both groups was not the same as the control group of 48 people and the experimental group of 50 people. The hypothesis that was constructed in this study is:  $H_0$  = There is no difference in the effect of portable PLC kit for electrical motor control courses among students of form 3 vocational school in Aceh, Indonesia; and  $H_a$  = There are differences in the effect of the portable PLC kit on electrical motor control courses among vocational student's form 3 in Aceh, Indonesia compared to students who follow conventional learning methods. This hypothesis will be accepted if the Asymp.Sig value is less than 0.05 ( $< 0.05$ ), while if the Asymp.Sig value is more than 0.05 ( $> 0.05$ ), then the study hypothesis is rejected.

Table 8 and Table 9 show findings from the Mann-Whitney Test. The statistics showed that the value of Asymp.Sig (2-tailed) was .000, and that it was less than 0.05 ( $< 0.05$ ). Then it can be proved that the hypothesis is accepted. Thus, it can be concluded that there is a difference in the outcome of students' competency achievements in the Electrical Machine Installation Course between form 3 vocational students who follow the learning method using portable PLC kit and students who follow conventional learning methods.

**Table 8** - Mann-Whitney Test (Rank)

Group		n	Min Rank	Total Rank
Student Competency Achievement	Control Group	48	25.91	1243.50
	Experiment Group	50	72.15	3607.50
	Total	98		

**Table 9** - Mann-Whitney Test (Statistical Test<sup>a</sup>)

	Student Competency Achievement
Mann-Witney Test	67.500
Wilcoxon W Test	1243.500

Z Test	-8.076
Asymp. Sig. (2-tailed)	.000
Exact Sig. [2*(1-tailed Sig.)]	.000b

**Note:** a = the variables grouped: group, b = not corrected for bonding.

### Discussion

A total of 50 students of the experimental class were exposed to learning that took advantage of portable PLC kit to test the usability of the device and to see the impact of learning on the electrical motor control course among of vocational schools form 3 in Aceh, Indonesia. Meanwhile, the other 48 students who are the control class group are implemented using conventional learning methods. Both groups were given tests both before and after the learning activities were carried out to see the comparative results of students' achievements.

The results of the analysis of the mean value of the tests before the study was carried out as in Table 5.2 are equivalent. Both groups are categorised as having weak mean values. Meanwhile, the results of the descriptive data analysis on Table 5.3 showed significant results at the mean value of the experimental group test after the study was performed compared to the experimental group. The gap between the mean values before and after treatment was carried out in the experimental group was 16.48. Meanwhile, the gap in the value of the mean before and after the study activities carried out on the control group was 7.96. The mean value gap between the two groups was 9.54. So it can be concluded that significant differences occurred in the experimental group treated with portable PLC kit. On the other hand, on the control group, the value of the difference did not show a significant increase.

The hypothetical test results based on a nominee (Rank) referring to Table 5.5 showed significant differences in mean values between the two groups after the study was conducted. The experimental group had a higher mean value of 72.15, compared to the control group (25.91), the difference in the mean values between the two groups was 36.24. This illustrates that there has been a significant improvement in the outcome of the competency of experimental group students after being given treatment with learning that benefited portable PLC kit compared to before being given treatment. The control group, with conventional learning, did not show the results of competency achievements that were significant both before and after the study.

Next, the statistical test results of the hypothesis of the study as shown in Table 5.6, the value of Asymp.Sig (2-tailed) is .000, and it is less than 0.05 ( $<0.05$ ). It can then be explained that Ha's hypothesis that there is a difference in the effect of using portable PLC kit on the electrical motor control course among students of form 3 vocational school in Aceh, Indonesia is accepted. This means that the use of portable PLC kit has been effective in improving the outcome of the competency of experimental group students as opposed to the achievements of control groups that implement conventional learning.

In addition, portable PLC kit has been developed to provide understanding and thus improve students' academic achievement in related topics. Through portable PLC's kit utilization of practical learning activities, students can gain a fun new experience as they learn programming topics. Overall, it has successfully produced interventions that positively impact learning and teaching for the topics learned.

The developed tool teaches portable PLC kit equipped with electrical circuits using plug and unplug wiring systems. According to Intan study [36], the effect of using teaching aids with plug and unplug systems is higher compared to using conventional wiring systems. In line with a study conducted by Zahri and Osman [37], they argue that teaching aids that use plug-in components make it easier for students to process circuits for understanding purposes. The use of teaching aids can also increase the level of understanding of students and thus improve the number of scores obtained. In addition, the amount of time in practical activities can also be reduced and thus provides an opportunity for students to try practically repeatedly. This teaching aid can also make it easier for teachers to stage demonstrations and in turn spark students' interest in practical practice in the laboratory.

The portable PLC kit were developed with the aim of wanting students to know and understand the application of PLC programming-based electrical machine control systems in the industry. This can stimulate students' learning motivation in following the teaching and learning process and is very supportive of students' competencies before entering the world of work [38]. PLC programming competencies are indispensable in the industry. PLC has been successfully applied to every industry segment, including steel mills, paper mills, food processing plants, chemical plants and power plants. PLC performs a variety of regulatory tasks, from

recurring on/off settings from simple machines to sophisticated manufacturing and process settings. Automation systems in the industry include operations such as processing, installation, inspection and handling of materials, in many cases solving more than one of these operations in the same system. Figure 5 shows the activities of students doing programming the motor control system with the portable PLC kit.



**Figure 5** - Students do programming of motor control systems on computer software and PLC teaching aids

Meanwhile Rowe et al. [39] has successfully created a kit to guide PLC hands-on learning in undergraduate engineering education at the University of Colorado Boulder. As a result, students provided positive feedback on the use of teaching aids in merging theoretical learning in classes and practicality into PLC programming activities. Based on the results of Suparta's [40] study, it was found that PLC teaching aids can be used as learning media to improve students' learning outcomes. In addition, the use of PLC teaching aids as a learning media in creating electrical machine control wiring systems has had a positive impact in improving students' learning outcomes.

Such portable PLC kit can be highlighted to be a trend of hands-on knowledge delivery besides practicing active learning pedagogy, and also, engineering subjects [[41], [42]]. Teachers from other technical and vocational schools can take this idea to be applied to their learning and teaching delivery process so that the level of mastery of basic programming concepts for technical and vocational school students especially in the field of electrical engineering increases and thus helps the students when pursuing work in the industry and or furthering their studies at Polytechnics or Universitas.

## Conclusions

Overall, this study was successfully conducted to see the impact of PLC portable kits on electric motor courses especially on

programming topics among vocational school students in Aceh, Indonesia. The PLC portable kit has also tested its usability on students, where the use of portable PLC kit has achieved the objectives of the study that the researchers have built and has a positive impact whether in terms of academic achievement, interest and motivation of students in studying programming topics. Through this study, researchers are directly or indirectly able to support the government's idea of a teaching factory by motivating teachers to be more creative and innovative in producing business-based learning that refers to the standards and

procedures that occur in the industrial world in real terms by producing marketable kit products. This creates a new job opportunity that has the potential to reduce the unemployment rate which is more dominated by graduates of vocational schools.

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

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## Ачех кәсіптік-техникалық училищесінің (Индонезия) оқушыларына арналған «Электр қозғалтқыштағы портативті БЛК-ның тиімділігі» курсы

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### ТҮЙІНДЕМЕ

Бұл зерттеу Индонезияның Ачех қаласындағы 3 курс студенттеріне арналған электр қозғалтқышын басқару пәні бойынша кәсіптік-техникалық училище оқушыларын оқыту үшін бағдарламаланатын логикалық контроллер (БЛК) жинағының әсерін тексеруге бағытталған. Бұл зерттеуде конструктивизм теориясы мен Блум таксономиясы туралы айтылады. ADDIE моделі өнімді әзірлеуге қатысты қолданылады. Бұл зерттеуде алдын ала және тесттен кейінгі сынақтармен квазиэксперименттік дизайн қолданылды. Осы зерттеуге Индонезияның Ачех қаласындағы кәсіптік білім беретін 3-деңгейдегі студенттер (N = 333) қатысты. Таңдалынған адамдар кездейсоқ кластерлік іріктеу әдісімен таңдалған эксперименттік топтан (n = 50) және бақылау тобынан (n = 48) тұратын 98 адамды құрады. Бұл зерттеуде пайдаланылған құралдарға тестілеуге дейінгі және кейінгі сұхбат хаттамалары кірді. Сұрақтардың KR20 сенімділік коэффициентінің мәндері – білім аспектісі бойынша 0,97 және дағдылар аспектісі үшін 0,81 болды. Сипаттамалық талдау нәтижелері эксперименттік топтың (орта = 64,08; SD = 4,548) бақылау тобына қарағанда (орта = 63,06; SD = 5,487) жақсы құзыреттілікке қол жеткізгенін көрсетті. Манн-Уитни сынағы арқылы гипотезаны тексеру нәтижесі: [Асимп. Sig. (Екі жақты) = 0,000, p < 0,05], яғни әзірленген оқу құралдары оқушылардың оқу үлгерімін арттыруға сәтті әсер етті. Бұл зерттеудің нәтижелері мұғалімдерге оқудағы инновацияларға ынталандыру және жаңа мансаптық мүмкіндіктерді ашу үшін қол жетімді, қарапайым және қауіпсіз оқыту құралдарын жасау үшін үлгі ретінде пайдалануға болатын оқыту құралын жасауға мүмкіндік берді. Ковид-19 эпидемиясының бетпе-бет оқытуға әсер еткенін ескере отырып, бағдарламалатын логикалық бақылау (БЛК) оқулықтарын біріктіру қажеттілігіне қатысты қосымша зерттеулер ұсынылады. Зерттеушілер, сонымен қатар зерттеулердің қосымша кең ауқымын ұсынады.

**Түйін сөздер:** эффектілер, ПЛК оқулықтары, қосымша ақпарат, электр машиналарын орнату курсының құзыреттіліктері.

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## Курс "Эффективность портативного ПЛК на электродвигателях" среди учащихся профессионально-технических училищ в Ачехе, Индонезии

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### АННОТАЦИЯ

Это исследование направлено на проверку влияния комплекта программируемого логического контроллера (ПЛК) для обучения учащихся профессиональных технических училищ по дисциплине управление электродвигателями для студентов 3-го курса в Ачехе, Индонезия. Теория конструктивизма и Таксономия Блума упоминаются в этом исследовании. Модель ADDIE используется в отношении разработки продукта. В этом исследовании использовался квазиэкспериментальный план с предварительными и последующими тестами. Население (N=333), участвовавшее в этом исследовании, были студентами профессионального образования 3 уровня в Ачехе, Индонезия. Количество выборок составило 98 человек, состоящих из экспериментальной группы (n=50) и контрольной группы (n=48), выбранных методом случайного кластерного отбора. Инструменты, использованные в этом исследовании, включали протоколы интервью до и после тестирования. Значения коэффициента достоверности KR20 вопросов по аспекту знаний составили 0,97 и 0,81 по аспекту навыков. Результаты описательного анализа показали, что экспериментальная группа (среднее=64,08; SD=4,548) показала лучшее достижение компетентности, чем контрольная группа (среднее=63,06; SD=5,487). Результат проверки гипотезы с использованием критерия Манна-Уитни: [Асимп. Sig. (Двусторонний) = 0,000, p < 0,05] означает, что разработанные учебные пособия успешно оказали положительное влияние на повышение уровня успеваемости учащихся. Результаты этого исследования привели к созданию учебного пособия, которое учителя могут использовать в качестве шаблона для создания более доступных, простых и безопасных учебных пособий, чтобы они могли быть мотивированы на инновации в обучении и открывать новые возможности для карьерного роста. Учитывая, что эпидемия Covid-19 повлияла на очное обучение, предлагается провести дальнейшие исследования в связи с необходимостью интеграции учебных пособий по программированию логического управления (ПЛК). Исследователи, с другой стороны, предлагают более широкий круг изучения вопроса.

**Ключевые слова:** эффекты, учебные пособия по ПЛК, дополнительная информация, компетенции курса по установке электрических машин.

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## Studies of the rate of gold sorption by the AM-2B anionite from cyanide-alkaline solutions

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### ABSTRACT

The paper presents the results of studies on the sorption leaching of gold-containing ore of the Vasilkovskoye deposit. Kinetic dependences of the sorption of gold and associated metals from cyanide-alkali solutions under different physical and chemical factors were obtained. It was found that gold on the AM-2B resin sorbed at a higher rate than, for example, copper and zinc. The solutions were analyzed using modern devices of a new generation: FT-IR spectrometer "Avatar 370". Laboratory studies were performed to determine the gold sorption rate by the AM-2B anionite from cyanide-alkaline solutions. It was found in the process of sorption of gold from multicomponent cyanide-alkali solutions on AM-2B anionite of mixed basicity, with the macroporous structure containing benzyl dimethylamine and dibenzyl dimethyl ammonium functional groups, that an important factor of qualitative and quantitative separation of gold and impurity metals is the concentration of cyanide and hydroxyl ions in solution. The temperature effect on the sorption rate of gold from cyanide-alkali solutions was studied with the temperature dependences  $F$  of  $t$ ,  $Bt$ , of  $t$ ,  $\ln(1-F)$  of  $t$ , and  $D$  of  $t$  that show that the sorption process of dicyanoaurate ions is controlled by mixed diffusion.

**Keywords:** ore, gold, sorption leaching, anionite AM-2B, cyanidation.

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## Introduction

The Republic of Kazakhstan is one of the most important gold-producing provinces in the Central Asian region in terms of gold reserves and production. The most important problem of gold hydrometallurgy is the search for rational methods of its extraction from low-grade refractory ores. It is becoming increasingly important as new deposits are discovered and exploited, allowing the gold

reserve of the Republic of Kazakhstan to be increased. Theoretical and technological results of the research performed, tests of the main processes intended to process gold-bearing raw materials - leaching of the material, sorption of gold on ion-exchange resins can be used to design and construct production facilities at various gold-bearing deposits in Kazakhstan.

Kazakhstan has significant potential reserves of gold-containing minerals [1]. Geotechnological

methods, in particular heap leaching, are currently considered the most suitable for gold-containing raw materials.

The kinetic characteristics of the process were studied with the purpose to develop a technology intended for the sorption extraction of the target metal (gold). Anion exchanger AM-2B, an effective, easily regenerated sorbent with high mechanical strength and macroporous structure widely used in metallurgy has been applied as sorbents [[2], [3]].

The search for rational ways to increase the gold extraction completeness is an urgent task due to the annual growth in the processing amount of poor, refractory gold-bearing ores and secondary raw materials.

Modern technology for extracting gold and silver from leach solutions widely uses processes of sorption of cyanide complexes of these metals. Two principal directions were developed: a) sorption with activated carbons [[2], [3], [4]], b) sorption with synthetic ion-exchangers [5].

The study is relevant, since the concentration of the recovered metal in the external solution and the temperature of the solution are the main factors affecting the ion-exchange sorption rate.

The study of the sorption kinetics is of practical interest, since the rate that determines the ion exchange stage revealed during the experiment, plays a major role with the purpose to solve such practical problems as the choice of conditions for the ion exchanger synthesis or the finished sorbent type.

The objective of this work was to study the gold sorption rate with the AM-2B anionite from cyanide-alkaline solutions

### Experimental part

The ion exchange process has been actively developed in the CIS countries and is the most promising for the mining industry in Kazakhstan. Gold was one of the first metals that people tried to extract from dilute solutions using ion exchange.

The object of research was the cyanide-alkaline solutions for leaching ore from the Vasilkovskoye deposit.

Experiments intended to obtain productive solutions and sorption extraction were performed under the standard methods. The chemical composition of the test solution is represented by the following main components, mg/dm<sup>3</sup>: 0.6-2.0 Au; 8.3-40 Cu; 1.1-6.2 Zn; 0.4-8.5 Fe; 0.1-0.5 Co; 0.1-0.5 Ni; 0.07-0.94 Stot. g / dm<sup>3</sup>; 0.1-0.2 CN- mg/dm<sup>3</sup>; 0.9-1.2 OH- mg/dm<sup>3</sup>. The initial cyanide-alkaline

solutions were obtained by leaching gold-bearing ores of the Vasilkovskoye deposit, containing 1.4 - 3.4 g/t of gold. Sorption products. i.e. solution and cake were subjected to atomic adsorption and assay types of analysis, respectively. The research used AM-2B grade resin. produced by "Resins" State Enterprise, Ukraine.

Before sorption, the resin was pre-saturated with OH-ions, by treatment with a 5% NaOH-solution to convert the sorbent into the OH-form. The process was controlled by the solution pH

### Discussion of the results

Productive gold-containing solutions obtained from agitation leaching are sent for sorption extraction. Ion-exchange resins or activated carbons are used as sorbents in industrial practice [[6], [7], [8], [9], [10], [11], [12]].

The ion exchange process in the anionite - solution system was studied in a static mode in thermostated Plexiglas cells equipped with a mechanical stirrer. Sampling was performed periodically. The total number of samples taken for analysis did not exceed 5% of the initial amount of the solution.

Tests on sorption extraction of gold from multicomponent solutions obtained by leaching-filtration scheme were performed in laboratory conditions. Gold was leached with the cyanide-alkali solution. AM-2B anionite was used as sorbents. Anionite AM-2B is a macroporous ion-exchange resin based on a copolymer of styrene with divinylbenzene, containing strong and weakly basic functional groups in its structure. The presence of bifunctional tertiary groups containing nitrogen atoms capable of forming active groups with metals (i.e., forming complexes) in combination with a high exchange capacity and a good (due to the macroporous matrix) exchange rate makes it possible to selectively extract anionic metal complexes.

Obtaining the kinetic characteristics is necessary to justify the regime of the proposed sorption technology for the extraction of gold from solutions.

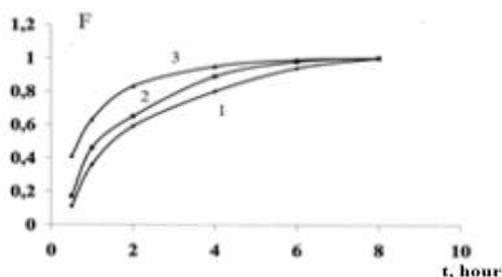
One of the main factors affecting the rate of ion-exchange sorption is the concentration of extractable metal in the external solution and solution temperature.

*Effect of the concentration of gold in the solution on the sorption rate.* Rate changes during sorption under static conditions were studied depending on gold concentration, temperature, and the presence of impurities in the solution. In the experiments

presented, the concentration of gold in the initial solutions varied within the range of 0.005-0.11 mg-eq / dm<sup>3</sup>; the concentration of CN<sup>-</sup> and OH<sup>-</sup> was constant and amounted to 0.04 and 0.56, respectively; the same amount of sorbent (V, ml) was added to the sorbent weight (m, g) V: m = 2000.

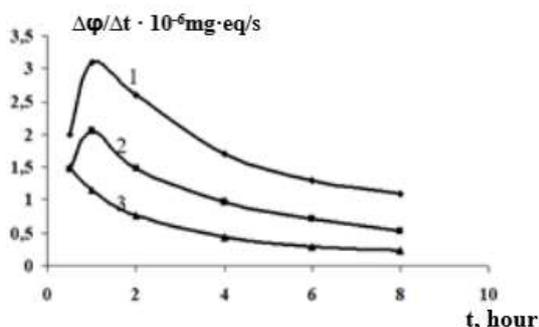
Sampling was performed in 30 minutes, then in an hour during the day. The gold concentration in the solution after sorption was determined by atomic absorption spectrometry.

Experimental data on the effect of the concentration of dicyanoaurate ions on the degree of gold exchange are presented in the form of curves in Figure 1, and the rate of gold sorption on Figure 2. It is noted that the degree of exchange (F) of dicyanoaurate ions increases depending on the time of contact of the phases and the concentration of gold in the initial solution; the sorption rate increases proportionally with an increase in the concentration of the external solution concerning the extracted ion. The experimental data obtained indicate that the sorption process is limited by both external and internal diffusion, that is, the process proceeds in a mixed region with the predominance of either external diffusion or intra-diffusion limitations at each stage of sorption.



Gold concentration, g-eq / dm<sup>3</sup>: 1 - 0.005; 2 - 0.025; 3 - 0.11.

**Figure 1** - Effect of the concentration of dicyanoaurate ions on the degree of gold exchange

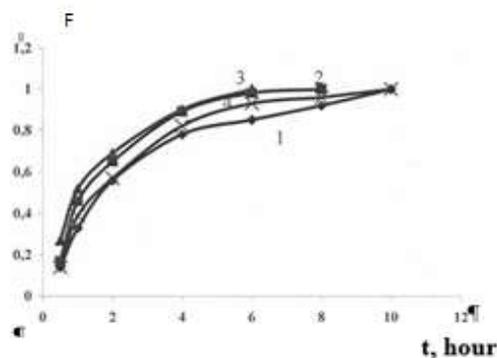


Concentration of gold, g-eq/dm<sup>3</sup>: 1 - 0,005; 2 - 0,025; 3 - 0,11.

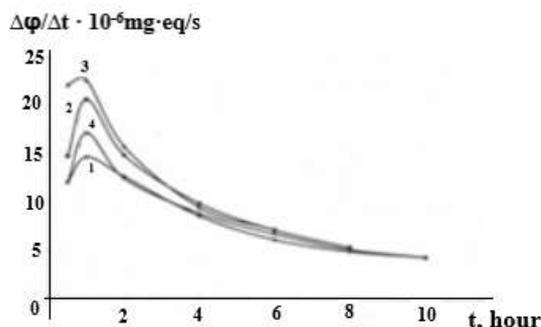
**Figure 2** - Effect of the concentration of dicyanoaurate ions on the sorption rate of gold

The temperature dependences F of t, Bt, of t, ln(I-F) of t, and D of t were determined when studying the effect of temperature on the sorption rate of gold from cyanide-alkali solutions that show that the sorption process of dicyanoaurate ions is controlled by mixed diffusion (Figures 3 and 4). Curvilinear relations F on t, ln(I-F) on t and W on t confirm the mixed nature of the gold sorption kinetics (Table 1).

Studies on the temperature effect on the gold sorption from cyanide-alkaline solutions with a low content of cyanide and hydroxyl ions have found that the most favorable temperature for the dicyanoaurate ions sorption is 298 K. An increase in temperature to 308 - 318 K, as well as a decrease to 288 K is negative affects the gold sorption rate and depth [[13], [14], [15], [16]].



**Figure 3** - Effect of temperature on the degree of gold exchange



Temperature, K: 1 - 288; 2 - 294; 3 - 303; 4-313. Axis abscissa - time, h; ordinate axis - sorption rate, DF / At x 10<sup>-6</sup> mg-eq / s.

**Figure 4** - Effect of temperature on the gold sorption rate

As can be seen from the data obtained, with an increase in temperature to 303 K, the exchange degree insignificantly but evenly increased during 6 sorption hours at a temperature of 288; 294; 303 K and was 0.85; 0.98 and 1.0, respectively. The exchange degree begins to decrease and in 6 hours of sorption reaches only 0.93 with an increase in temperature over 303 K.

**Table 1** - Effect of temperature on the exchange degree, diffusion coefficient and sorption rate of gold ( $C_{Au} = 0.025 \text{ mg-eq/dm}^3$ )

Temperature, K	Time t, hour	Exchange degree, F	ln(I-F)	Diffusion coefficient t D, cm <sup>2</sup> /s	B, s <sup>-1</sup>	$\Delta\Phi/\Delta t$ , mg-eq / s
288	0.5	0.14	-0.15	$6.9 \cdot 10^{-7}$	$985 \cdot 10^{-3}$	$120 \cdot 10^{-6}$
	1.0	0.33	-0.40	$3.5 \cdot 10^{-6}$	$9.9 \cdot 10^{-2}$	$146 \cdot 10^{-6}$
	2.0	0.56	-0.82	$5.5 \cdot 10^{-6}$	$9.94 \cdot 10^{-1}$	$12.6 \cdot 10^{-6}$
	4.0	0.78	-1.51	$9.0 \cdot 10^{-6}$	1.03	$85 \cdot 10^{-6}$
	6.0	0.85	-1.9	$2.0 \cdot 10^{-5}$	3.43	$6.1 \cdot 10^{-6}$
	8.0	0.92	-2.53	$1.0 \cdot 10^{-5}$	2.28	$4.9 \cdot 10^{-6}$
	10.0	1.0		$9.0 \cdot 10^{-6}$	2.57	$4.3 \cdot 10^{-6}$
294	0.5	0.17	-0.19	$2.1 \cdot 10^{-6}$	$3.1 \cdot 10^{-2}$	$14.7 \cdot 10^{-6}$
	1.0	0.46	-0.62	$10.9 \cdot 10^{-6}$	$3.1 \cdot 10^{-2}$	$20.6 \cdot 10^{-6}$
	2.0	0.65	-1.05	$20.0 \cdot 10^{-6}$	1.14	$14.8 \cdot 10^{-6}$
	4.0	0.89	-2.21	$30.0 \cdot 10^{-6}$	3.42	$9.8 \cdot 10^{-6}$
	6.0	0.98	-3.91	$18.0 \cdot 10^{-6}$	3.08	$7.1 \cdot 10^{-6}$
	8.0	1.0		$9.0 \cdot 10^{-6}$	3.08	$5.3 \cdot 10^{-6}$
	303	0.5	0.27	-0.31	$6.91 \cdot 10^{-6}$	$9.86 \cdot 10^{-2}$
1.0		0.52	-0.73	$10.9 \cdot 10^{-6}$	$3.11 \cdot 10^{-1}$	$22.6 \cdot 10^{-5}$
2.0		0.63	-0.99	$17.2 \cdot 10^{-6}$	$9.71 \cdot 10^{-1}$	$15.7 \cdot 10^{-5}$
4.0		0.90	-2.3	$30.0 \cdot 10^{-6}$	3.43	$9.4 \cdot 10^{-5}$
6.0		1.0		$18.0 \cdot 10^{-6}$	3.08	$7.1 \cdot 10^{-5}$
313	0.5	0.14	-0.15	$6.9 \cdot 10^{-7}$	$985 \cdot 10^{-3}$	$120 \cdot 10^{-6}$
	1.0	0.39	-0.49	$3.5 \cdot 10^{-6}$	$9.9 \cdot 10^{-2}$	$17.1 \cdot 10^{-6}$
	2.0	0.57	-0.84	$5.5 \cdot 10^{-6}$	$3.14 \cdot 10^{-1}$	$12.4 \cdot 10^{-6}$
	4.0	0.82	-1.71	$9.0 \cdot 10^{-6}$	1.03	$8.8 \cdot 10^{-6}$
	6.0	0.93	-2.66	$2.0 \cdot 10^{-5}$	3.43	$6.7 \cdot 10^{-6}$
	8.0	0.96	-3.22	$1.0 \cdot 10^{-5}$	2.28	$5.4 \cdot 10^{-6}$
	10.0	1.0		$9.0 \cdot 10^{-6}$	2.57	$4.3 \cdot 10^{-6}$

It can be stated that an increase in temperature to 303 K slightly increases the process of gold sorption on the AM-2B anionite from cyanide-alkaline solutions, and with a further increase in temperature (more than 303 K), the rate of gold sorption decreases.

Changes in the rate during sorption were studied depending on the concentration of cyanide and hydroxyl ions in the solution, as well as gold and temperature.

The results are presented in tables 2 and 3. The sorption rate is directly proportional to its concentration in the solution: the higher the concentration of the external solution, the more ions penetrate deep into the sorbent. The rate of penetration of counterions of the boundary layer into the inner layers of the sorbent also increases as the concentration of the external solution increases [[15], [16]]. Similar dependencies were obtained when studying the effect of temperature on the sorption rate of gold (Table 3).

As the temperature increases, the sorption rate decreases that can be explained by the following

reasons. A dynamic equilibrium between the ions entering and leaving the resin at each period is established in the sorption process. Probably, as the time increases above a certain temperature, the rate of reverse desorption of gold ions increases reducing the rate of direct sorption.

**Table 2** - Change in the gold sorption rate overtime at different concentrations in solution, mg-eq / dm<sup>3</sup>

Time, h	$C_{Au} - 0.005$	$C_{Au} - 0.025$	$C_{Au} - 0.110$
0.5	5	15	150
1	13	28	122
2	6	18	74
4	3	10	41
6	3	8	30
8	3	7	23

**Table 3** - Change in the gold sorption rate overtime at different process temperatures mg-eq / s

Time, h	288 K	294 K	303 K	313 K
0.5	12	12	14.5	21.9
1	15	17	20.8	22.6
2	12.5	13.6	14.8	15.7
4	8.3	8.8	9.5	9.2
6	6.2	6.7	7.2	7.3
8	4.7	5.4	5.3	5.3

The IR-spectroscopic method of studying the materials was performed using an "Avatar 370" IR-Fourier spectrometer. According to the results, the infrared spectroscopy analysis showed that absorption bands of valence  $\nu(\text{OH}) - 3439 \text{ cm}^{-1}$ , strain  $\delta\text{HOH} - 1647 \text{ cm}^{-1}$ , and librational  $\nu \text{ L H}_2\text{O} - 632 \text{ cm}^{-1}$  vibrations of molecular water were recorded in the spectrum (Figure 5) [17]. Group  $[\text{NCS}]^- - 1118, 995 \text{ cm}^{-1}$  [17]. The optical density at the maximum of the absorption bands characterizing oscillations  $\nu \text{ OH}, \delta \text{ HOH}, \nu \text{ L H}_2\text{O}$  were measured. Optical density at the maxima of absorption bands corresponding to stretching vibrations of water  $\nu \text{ OH}$  was 1.452; deformational vibrations of water  $\delta \text{ HOH} - 0.548$ ; librational water fluctuations  $\nu \text{ L H}_2\text{O} - 0.495$ . The optical density at wave number  $1118 \text{ cm}^{-1}$  was 0.034 at the maximum absorption band that characterizes the  $\nu_4(\text{E})$  fluctuation of the cyanide ion. The optical density at the absorption band maximum at wave number  $995 \text{ cm}^{-1}$  that characterizes the  $\nu_1(\text{A1})$  cyanide ion vibration, was 0.035.

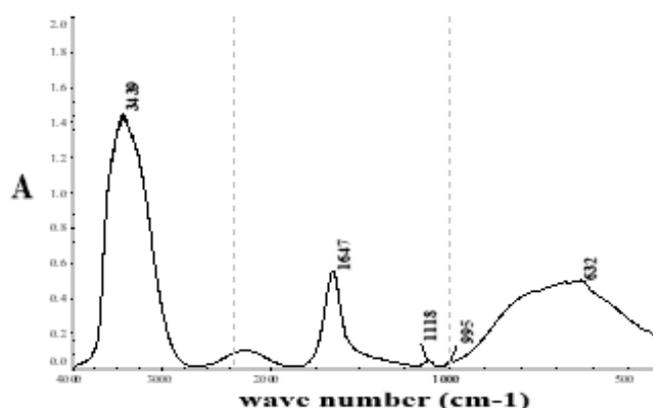


Figure 5 - Results of infrared spectroscopy analysis of the solution

Thus, it can be concluded based on the studies performed to determine the rate of gold sorption by the AM-2B anion exchanger from alkaline cyanide solutions that the amount of gold in the ion exchanger after treatment does not change and decreases with the use of alkaline cyanide solutions. Anionite of mixed basicity AM-2B shows high selectivity for gold [[18], [19], [20], [21]].

### Conclusions

Laboratory studies to determine the gold sorption rate by the AM-2B anion exchanger from cyanide-alkali solutions were performed. It was found in the process of gold sorption from multicomponent cyanide-alkali solutions on AM-2B anionite of mixed basicity with the macroporous structure containing benzyl dimethylamine and

dibenzyl dimethyl ammonium functional groups, that an important factor of qualitative and quantitative separation of gold and impurity metals is the concentration of cyanide and hydroxyl ions in solution. The temperature effect on the gold sorption rate from cyanide-alkali solutions was studied with the temperature dependences  $F$  of  $t$ ,  $Bt$ , of  $t$ ,  $\ln(I - F)$  of  $t$ , and  $D$  of  $t$  that shows that the sorption process of dicyanoaurate ions is controlled by mixed diffusion.

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

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## Цианид-сілтілі ерітінділерден АМ-2В анионитімен алтынның сіңу жылдамдығын зерттеу

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### ТҮЙІНДЕМЕ

Бұл жұмыста Васильков кен орнының алтынды кендерін сорбциялық сілтісіздендіру бойынша зерттеулердің нәтижелері ұсынылған. Әртүрлі физика-химиялық факторлар кезінде цианид-сілтілі ерітінділерден алтын мен ілеспе металдар сорбциясының кинетикалық тәуелділігі алынды. АМ-2В шайырындағы алтын мыс пен мырышқа қарағанда жоғары жылдамдықпен сорбцияланатыны анықталды. Ерітінділер заманауи жаңа буын құрылғысы: "Avatar 370" ИК-Фурье спектрометрін қолдана отырып талданды. Цианид-сілті ерітінділерінен АМ-2В анионитімен алтынның сорбция

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жылдамдығын анықтау бойынша зертханалық зерттеулер жүргізілді. Бензилдиметиламин және дибензилдиметил-аммоний функционалдық топтары бар макрокеукеті құрылым, аралас негіздегі АМ-2Б анионитінде көп компонентті цианид-сілтілі ерітінділерден алтынды сіңіру процесінде алтын мен қоспалы металдардың сапалық және сандық бөлінуінің маңызды факторы ерітіндідегі цианид-, және гидроксил - иондардың концентрациясы болып табылады. Цианид-сілтілі ерітінділерден алынған алтынның сорбциялау жылдамдығына температураның әсерін зерттеу кезінде t-ден F, t-ден Bt, t-ден ln(I - F) және t-ден және D температуралық тәуелділіктер анықталды, бұл дицианоаурат иондарының сорбциялау процесі аралас диффузиямен басқарылатындығын көрсетеді.

**Түйін сөздер:** кен, алтын, сорбциялық сілтісіздендіру анионит АМ-2Б, циандау.

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## Исследования скорости сорбции золота анионитом АМ-2Б из цианидно-щелочных растворов

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### АННОТАЦИЯ

В работе представлены результаты исследований по сорбционному выщелачиванию золотосодержащей руды Васильковского месторождения. Получены кинетические зависимости сорбции золота и сопутствующих металлов из цианидно-щелочных растворов при различных физико-химических факторах. Установлено, что золото на смоле АМ-2Б сорбируется с большей скоростью, чем, например меди и цинк. Растворы анализировали с использованием современных приборов нового поколения: ИК-Фурье спектрометра «Avatar 370». Проведены лабораторные исследования по определению скорости сорбции золота анионитом АМ-2Б из цианидно-щелочных растворов. В процессе сорбции золота из многокомпонентных цианидно-щелочных растворов на анионите АМ-2Б смешанной основности, макропористой структуры с бензилдиметиламинными и дибензилдиметил-аммониевыми функциональными группами, установлено, что важным фактором качественного и количественного разделения золота и примесных металлов являются концентрации цианид-, и гидроксил- ионов в растворе. При изучении влияния температуры на скорость сорбции золота из цианидно-щелочных растворов установлены температурные зависимости F от t, Bt, от t, ln(I - F) от t и D от t, которые показывают, что процесс сорбции дицианоаурат-ионов контролируется смешанной диффузией.

**Ключевые слова:** руда, золото, сорбционное выщелачивание, анионит АМ-2Б, цианирование.

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## Features of the crystallization of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in the system $\text{AlCl}_3 - \text{MeCl}_x - \text{HCl} - \text{H}_2\text{O}$

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### ABSTRACT

A laboratory setup has been developed to study the regularities of crystallization of aluminium chloride hexahydrate from hydrochloric acid solutions. The influence of the  $\text{AlCl}_3$  content in the initial solution, the consumption of gaseous HCl, and the behavior of impurities on the crystallization of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  from aluminium chloride solutions of leaching cinder obtained as a result of chlorinating ash burning from thermal power plants in Kazakhstan have been studied. The behavior of impurity metals in the process of crystallization of aluminium chloride solution has been studied, and their distribution between the products of the crystallization process has been established. It is shown that aluminium chloride content in the solution decreases with an increase in the consumption of hydrochloric acid. It was found that under the conditions of crystallization of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , all impurities, except for barium, pass by 98% into the mother liquor. To reduce barium and other impurities in the obtained crystals of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , it is proposed to carry out multiple washing of the crystals with hydrochloric acid (32% HCl). It has been shown that a decrease in the acidity of the washing solution from pH = 10 to pH = 5.5 ensures the isolation of ACH crystals with a minimum content of impurity metals, ppm: 3-5 Ca; 3-6 Fe; 1-3 Mg; 0.1-0.5 Ti; 1-3 Na; 20-30  $\text{P}_2\text{O}_5$ . The moisture content of the obtained crystals is 4-5%; the particle size is 400-900 microns. As a result of mathematical processing, regression equations were constructed that adequately predict aluminium chloride content in the solution and its extraction into crystalline hydrate, depending on the consumption of hydrochloric acid. The optimal parameters of the crystallization process have been established: T = 60 °C, HCl concentration in the solution - 26-30%, HCl gas consumption = 0.5 l/min, duration 1 hour.

**Keywords:** crystallization, aluminium chloride hexahydrate, solution, hydrochloric acid, impurities, washing, acidity, extraction.

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### Introduction

The selective precipitation (salting out) of aluminium chloride hexahydrate (ACH) from aluminium-containing solutions with hydrochloric acid are based on the different degrees of solubility of compounds in the acid. Many works are devoted to studying the crystallization of aluminium chloride from hydrochloric acid solution [[1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11], [12]].

It was shown in [[1], [2]] that with an increase in HCl concentration, the solubility of aluminium and chromium chlorides in the systems  $\text{AlCl}_3\text{-HCl-H}_2\text{O}$  and  $\text{AlCl}_3\text{-NaCl-H}_2\text{O(-HCl)}$  decreases. Detailed studies on the solubility of iron chloride in aqueous solutions were carried out in [3]. The authors found that the solubility of iron chloride in the system  $\text{AlCl}_3 + \text{FeCl}_3 + \text{H}_2\text{O}$  at 298.15 K increases with an increase in the content of iron chloride in the solution. This trend was observed in studies of a complex multicomponent system  $\text{AlCl}_3\text{-}$

$\text{FeCl}_3\text{-MgCl}_2\text{-CaCl}_2\text{-KCl-NaCl-HCl-H}_2\text{O}$  carried out by the authors of [5].

In the crystallization of ACH ( $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ ) was carried out with gaseous hydrogen chloride (HCl) obtained as a result of the interaction of NaCl with concentrated (94%) sulfuric acid according to the reaction:  $\text{H}_2\text{SO}_4 + 2\text{NaCl} = 2\text{HCl}\uparrow + \text{Na}_2\text{SO}_4$  [7]. The authors found that within 15 minutes of the crystallization process, the solution is saturated with HCl vapours, then the first crystals of ACH appear. After 30 minutes of the beginning of the experiment, the authors observed a sharp increase in the number of crystals in the solution. After an hour, the formation of crystals slowed down and practically stopped. The authors' data obtained from studying the effect of temperature on the crystallization of ACH has a great interest. It was found that with an increase in the temperature of the process, the content of the main impurities decreases sharply: chromium by 3.5 times, iron by 2.1 times. The content of Mg and Na is almost halved; the proportion of other impurities does not exceed  $10^{-2}\%$ .

An important aspect of the ACH crystallization process is washing the crystals obtained from the residues of the hydrochloric acid solution. The results of works [[6], [7]] on the study of washing aluminium chloride hexahydrate with hydrochloric acid of various concentrations (20, 25, 30, 35.5%) showed good agreement with each other. In experiments with an acid concentration of up to 30%, partial dissolution of the obtained crystals was observed. When using a more concentrated acid (> 30%), the moisture content of the crystals was 25%. As an alternative, an organic reagent, acetone, was chosen, using which the reverse dissolution of ACH was not observed. Humidity was in the range of 3.5-4.5%.

To optimize the crystallization process, it is necessary to have information about the influence of various factors [[8], [9], [10], [11], [12]], which include four parameters that are important for controlling the crystallization of ACH: (1) - the concentration of aluminium chloride in the initial solution for crystallization, (2) - the consumption of gaseous hydrogen chloride, (3) - temperature and (4) - concentration of impurities in the initial solution. Parameters (1), (2) and (3) have a strong influence on the formation of crystals. The crystallization temperature below 60 °C reduces the purity of the crystals, and its increase does not significantly affect the growth of ACH crystals. Nevertheless, the result of parameter (4), the combined effects are also significant since some impurities, in particular phosphorus and magnesium, are concentrated in crystals at the early stages of crystal growth.

The analysis of the results of published works shows the fundamental possibility of crystallising ACH from hydrochloric acid solution with further alumina production by its thermal decomposition. Comparative analysis of the effects of well-known studies, both in terms of the mechanism of the crystallisation processes of ACH and in terms of optimal parameters, shows good agreement with each other. Minor deviations in the quality of the obtained products can be explained by the presence of impurities in the initial solutions and various equipment and techniques for their implementation.

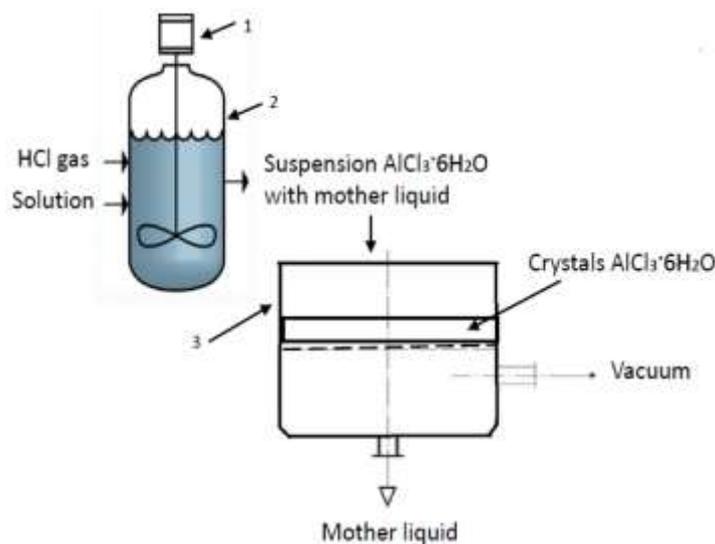
The purpose of this work is to study the effect of the  $\text{AlCl}_3$  content in the initial solution, the consumption of gaseous HCl, and the behavior of impurities on the crystallization of  $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$  from aluminium-containing salt solutions obtained after leaching the cinder of chlorinating ash roasting from thermal power plants in Kazakhstan [[13], [14]].

## Research methods

To study the crystallization process, synthetic solutions were used with the following composition:  $\text{AlCl}_3$  - 11-15%,  $\text{CaCl}_2$  - 12-16%,  $\text{TiCl}_4$  - 0.2-0.3%, HCl - 3-5% and others typical for solutions obtained after leaching the cinder with hydrochloric acid and their filtration. The density of solutions is 1.25-1.29  $\text{g/cm}^3$ .

The experimental technique was as follows. A crystallizer vessel was charged with 1 l of an aluminium chloride solution obtained after leaching and filtration. The concentration of aluminium chloride in the solution varied from 10 to 15%. After pouring the solution into the crystallizer, the solution was stirred at a stirrer speed of 250 rpm. The process temperature was maintained at 60 °C. Next, hydrogen chloride gas was fed into the crystallizer at a 0.5 l/min until its concentration reached 26%. The total duration of the process was 1 hour. The obtained crystals of aluminium chloride was separated from the mother liquor by filtration and washed with 26% HCl solution. Then the crystals were dried at a temperature of 80-100 °C.

The mother liquors were sent for the extraction of non-ferrous metals containing rare-earth metals from them. The products obtained in the process of crystallization - crystals of aluminium chloride, mother liquors and solutions after washing the crystals with ACH, were subjected to elemental analysis for the content of aluminium, non-ferrous, rare-earth metals, as well as impurities - phosphorus, iron, sodium, potassium, calcium, magnesium, titanium, barium, etc.



1 - automatic stirrer; 2 - reactor; 3 - suction filter.

Figure 1 - Schematic diagram of a laboratory setup for crystallization of ACH

### Results and discussion

A schematic diagram of a laboratory setup for crystallizing aluminium chloride from a solution is shown in Fig. 1.

In crystallization, two products were obtained - mother liquor and crystals of ACH ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ).

The mother liquor composition obtained during the crystallization of ACH from an aluminium chloride solution is shown in Table 1.

Table 1 – Composition of mother liquor obtained during crystallization

Components	Composition	
	g/l	%
CaCl <sub>2</sub>	527.21	40.55
AlCl <sub>3</sub>	11.32	0.87
FeCl <sub>3</sub>	37.22	2.86
MgCl <sub>2</sub>	31.48	2.42
TiCl <sub>4</sub>	2.37	0.18
KCl	0.42	0.03
NaCl	5.65	0.43
H	85.25	6.82
O	611.88	48.95
Cu	0.013	10.25 ppm
Ni	0.167	128.8 ppm

The consumption of hydrochloric acid determines the yield of ACH crystals. The dependence of the aluminium chloride content in the solution on the increase in the concentration of HCl, constructed from the results of the experiments (Fig. 2), shows a close relationship between these values. The content of aluminium

chloride in the solution decreases with an increase in the concentration of hydrochloric acid in the solution.

The obtained results of experimental studies were subjected to mathematical processing with the data of work [5], obtained in similar conditions of the crystallization process. As a result of mathematical processing, a regression equation was obtained that predicts the content of aluminium chloride in solution (y) depending on the concentration of HCl in solution (x), which has the following form:

$$y = 23.162 - 0.675x, \quad r = 0.83 \quad (1)$$

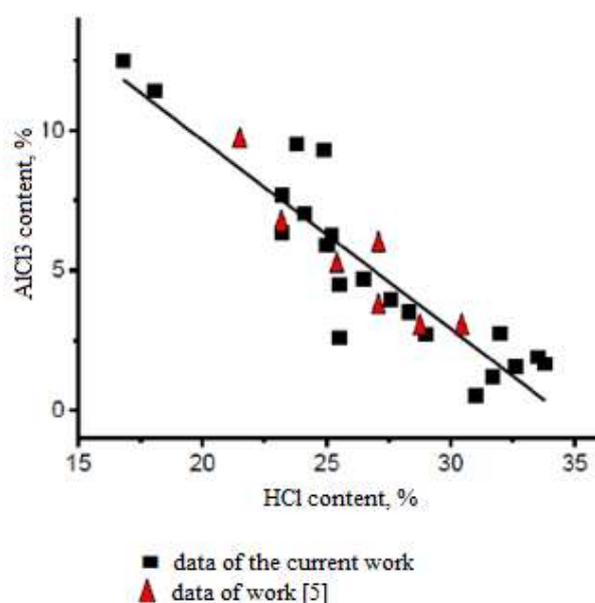
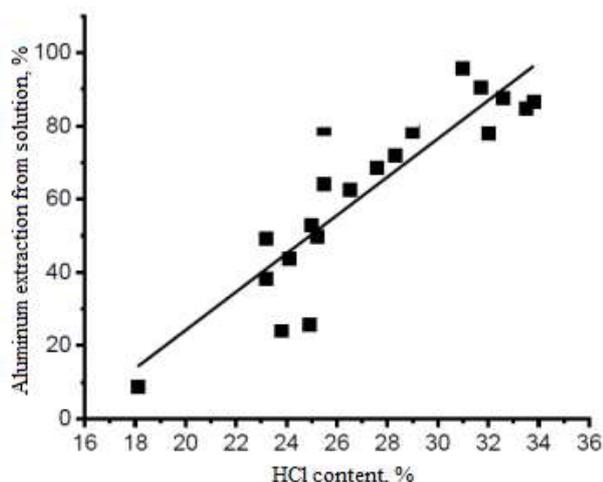


Figure 2 - Dependence of the content of aluminium chloride on the concentration of HCl in solution

Based on the experimental data on the change in the content of aluminium chloride in the solution depending on the concentration of HCl (Fig. 2), the extraction of aluminium from the solution during crystallization was calculated for each experiment. A graphical representation of the dependence of the extraction of aluminium from the solution on the HCl concentration is shown in Fig. 3.



**Figure 3** - Dependence of the extraction of aluminium from the solution on the concentration of HCl in the solution

The extraction of aluminium from the solution increases with an increase in the consumption of hydrochloric acid during crystallization. The highest extraction of aluminium from the solution (~ 95%) is achieved when the HCl concentration in the solution is 32%.

As a result of the mathematical processing of the experimental data shown in Fig. 3 (total array - 21 experiments), a regression equation was constructed, making it possible to predict the extraction of aluminium from the solution depending on the concentration of HCl.

The resulting equation has the following form:

$$\xi = -80.379 + 17.939 \times [\text{HCl}], \quad r = 0.78 \quad (2)$$

where:  $\xi$  - extraction of aluminium from solution, %;

[HCl] - concentration of hydrochloric acid in solution, %;

$r$  - the correlation coefficient.

Based on the quantitative ratios of crystallization products - mother liquor and isolated ACH crystals and the results on the content of impurity metals in them, the distribution of

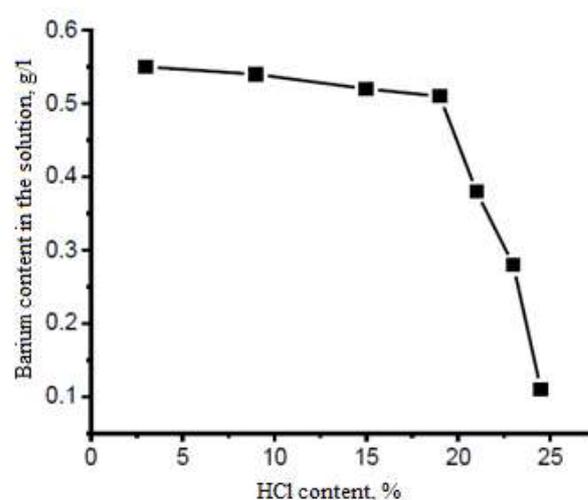
impurity metals between the crystallization products was established. The calculation results for the distribution of impurity metals (average values based on the results of several experiments) are shown in Table 2.

**Table 2** – Distribution of metal impurities between products during crystallization of ACH

Components	Metal distribution, %		
	In mother liquor	Into the solution after washing	Into ACH crystals
Al	2	3	95
Ca	92	7	1
Mg	91	6	3
Fe	92	7	1
Ti	90	9	1
Na	91	7	2
P <sub>2</sub> O <sub>5</sub>	89	8	3
Ba	15	6	79
Cu	97	3	–
Zn	99	1	–
Ni	98	2	–
Sc	97	3	–
Y	97	3	–

It was found that all metal impurities, except for barium, almost wholly pass into the mother liquor. In solutions after washing with hydrochloric acid, their concentrations are insignificant.

The effect of the solution's acidity on its barium content is shown in Fig. 4.



**Figure 4** - Dependence of the barium content in the mother liquor on the HCl concentration in the solution

As shown in Fig. 4, an increase in the concentration of hydrochloric acid up to 20% does

not affect the barium content in the mother liquor: the barium concentration in the solution remains practically constant ~ 0.55 g/l. An increase in the concentration of hydrochloric acid over 20 % leads to a sharp decrease in the barium content. When the concentration of hydrochloric acid in the solution is 26 %, the barium content in the solution reaches its minimum equal to 0.1 g/l.

Several impurity metals, even insignificant (except for barium), are concentrated in the obtained crystals of AlCl<sub>3</sub>·6H<sub>2</sub>O (Table 2). To increase the purity of the obtained crystals, they were subjected to multiple washing with HCl solution (31%), the main meaning was as follows. An initial sample of AlCl<sub>3</sub>·6H<sub>2</sub>O crystals in 200 g was mixed with 400 ml of 30% HCl solution and washed at room temperature. The stirring time was 20 minutes. After a specified time, the resulting mixture was filtered. The solution was used to wash the next set of crystals. The solution and washed crystals were analyzed for the content of aluminium, iron, calcium, and metal impurities. The operation was repeated five times.

The results of analyzes of the solutions obtained after each washing of the AlCl<sub>3</sub>·6H<sub>2</sub>O crystals with hydrochloric acid are shown in Table 3.

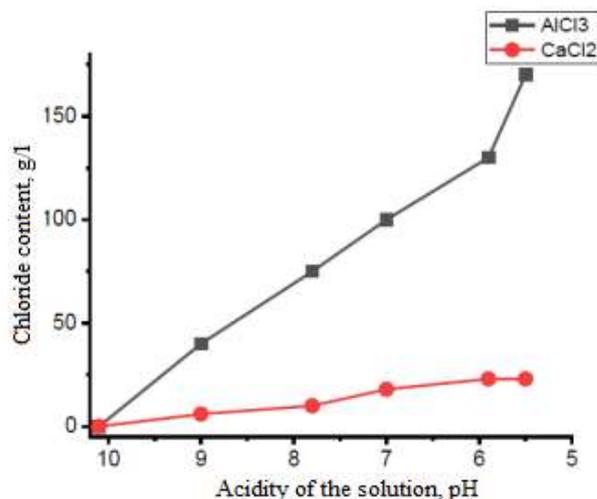
**Table 3** – Compositions of solutions obtained after each wash

Washing	AlCl <sub>3</sub> , g/l	CaCl <sub>2</sub> , g/l	Acidity, pH
Initial solution	-	-	10.1
1	40	6	9.0
2	75	10	7.8
3	100	18	7.0
4	130	23	5.9
5	170	23	5.5

It was found that repeated washing of crystals with a solution of used hydrochloric acid leads to a decrease in the acidity of the washing solution from 10 to 5.5. As a result, partial dissolution of ACH crystals in washing acid with a significant transition of aluminium and calcium into the solution is observed, which is seen in the graphical dependence shown in fig. 5.

The final melt obtained after five times washing of the ACH crystals is sent to the cinder leaching.

The compositions of the crystals obtained after each washing with hydrochloric acid are shown in Table 4.



**Figure 5** - Dependence of the content of AlCl<sub>3</sub> and CaCl<sub>2</sub> in the solution on the acidity of the solution with repeated washing of crystals with acid

**Table 4** – Compositions of the obtained crystals of AlCl<sub>3</sub>·6H<sub>2</sub>O

Washing	Content of metal impurities, ppm					
	Ca	Fe	Mg	Si	Ti	Na
1	6.5	6.2	2.0	45	0.1	1.0
2	6.0	5.0	1.8	2.0	n.d.	1.0
3	5.0	3.5	1.7	n.d.	n.d.	0.7
4	5.3	3.8	2.1	n.d.	n.d.	0.7
5	4.2	2.8	2.0	n.d.	n.d.	0.5

n.d. – not defined

The final average composition of AlCl<sub>3</sub>·6H<sub>2</sub>O crystals obtained after repeated washing with hydrochloric acid contained, ppm: 3-5 Ca, 3-6 Fe, 1-3 Mg, 0.1-0.5 Ti, 1-3 Na, 20-30 P<sub>2</sub>O<sub>5</sub>. The moisture content of the crystals is 4-5%; the particle size is 400-900 microns.

Based on the carried-out studies and the obtained results, the following optimal parameters for the crystallization of ACH from an aluminium chloride solution were selected:

- crystallization temperature of ACH with gaseous HCl – 60 °C;
- HCl gas consumption – 0,5 l/min;
- concentration of HCl in solution – 26-30 %;
- process duration – 60 min;
- ACH crystal washing – repeatable, with hydrochloric acid (32 % HCl).

The crystals of ACH obtained after the crystallization process are sent to a further operation of its thermal decomposition to alumina suitable to produce commercial aluminium.

## Conclusions

1. It is shown that it is possible to obtain ACH crystals ( $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ) from aluminium chloride solutions in one stage. The behavior of impurity metals during the crystallization of an aluminium chloride solution has been studied. The distribution of metal impurities between the products of the crystallization process has been established. It was shown that all metal impurities, except barium, pass into the mother liquor during crystallization up to 98%.

2. It was found that repeated washing of ACH crystals with a solution of hydrochloric acid (32% HCl) increases the extraction of aluminium from the solution into crystals up to 96%. It has been shown that a decrease in the acidity of the washing solution from  $\text{pH} = 10$  to  $\text{pH} = 5.5$  ensures the generation of ACH crystals with a minimum content of impurity metals, ppm: 3-5 Ca; 3-6 Fe; 1-3 Mg; 0.1-0.5 Ti; 1-3 Na; 20-30  $\text{P}_2\text{O}_5$ . The moisture content of the crystals obtained is 4-5%, and the particle

size is 400-900 microns. The recovery of ACH from the solution was 95%.

3. The optimal parameters of the crystallization process of aluminium chloride hexahydrate have been determined:  $T = 60^\circ\text{C}$ , HCl concentration in solution - 26-30%, HCl gas consumption = 0.5 l/min, duration 1 hour.

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

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## $\text{AlCl}_3 - \text{MeCl}_x - \text{HCl} - \text{H}_2\text{O}$ жүйесіндегі $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ кристалдану ерекшеліктері

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### ТҮЙІНДЕМЕ

Тұз қышқылды ерітінділерден алюминий хлориді гексагидратының кристалдану заңдылықтарын зерттеу үшін зертханалық қондырғы жасалды. Бастапқы ерітіндідегі  $\text{AlCl}_3$  құрамының, газ тәріздес HCl шығынының және Қазақстан ЖЭС күлдерін хлорлап күйдіру нәтижесінде алынған құрамында алюминий бар күйіндіні тұзды ерітінділермен шаймалау арқылы алынған қоспалардың ерітінділерінің  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  кристалдануына әсері зерттелді. Алюминий хлориді ерітіндісінің кристалдану процесінде қоспа-металдарының бөліну ерекшелігі зерттелді және олардың кристалдану процесінің өнімдері арасында бөлініп таралуы анықталды. Ерітіндідегі алюминий хлоридінің мөлшері тұз қышқылының шығыны жоғарылағанда төмендейтіні көрсетілді.  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  кристалдану жағдайында барийден басқа барлық қоспалар 98%-ға дейін аналық (кристалдану мен бөліну процестерінен кейінгі қалдық сұйықтық) ерітіндіге өтетіні анықталды. Алынған  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  кристалдарындағы барий мен басқа қоспаларды азайту үшін кристалдарды тұз қышқылымен (32% HCl) бірнеше рет жуу ұсынылады. Жуу ерітіндісінің қышқылдығын  $\text{pH}=10$ -нан  $\text{pH}=5,5$ -ке дейін төмендеткенде қоспа-металдары минималды түрде АГХ кристалдарына шығарылады, ppm: 3-5 Ca; 3-6 Fe; 1-3 Mg; 0,1-0,5 Ti; 1-3 Na; 20-30  $\text{P}_2\text{O}_5$ . Алынған кристалдардың ылғалдылығы 4-5 %, ірілігі 400-900 микронды құрайды. Математикалық өңдеу нәтижесінде тұз қышқылының шығынына тәуелді ерітіндідегі алюминий хлоридінің мөлшерін және оның кристалл гидратына бөлінуін барабар

	болжайтын регрессия теңдеулері құрылды. Кристалдану процесінің оңтайлы параметрлері анықталды: T=60 °C, ерітіндідегі HCl концентрациясы 26-30%, газ шығыны HCl=0,5 л/мин, ұзақтығы, τ=1 сағ. <b>Түйін сөздер:</b> кристалдану, алюминий хлориді гексагидраты, ерітінді, тұз қышқылы, қоспалар, жуу, қышқылдық, экстракция.
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## Особенности кристаллизации $AlCl_3 \cdot 6H_2O$ в системе $AlCl_3 - MeCl_x - HCl - H_2O$

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### АННОТАЦИЯ

Разработана лабораторная установка для исследования закономерностей кристаллизации гексагидрата хлорида алюминия из солянокислых растворов. Изучено влияние содержания  $AlCl_3$  в исходном растворе, расхода газообразного HCl и поведения примесей на кристаллизацию  $AlCl_3 \cdot 6H_2O$  из алюминийсодержащих соляных растворов выщелачивания огарка, полученного в результате хлорирующего обжига золы ТЭЦ Казахстана. Изучено поведение металлов-примесей в процессе кристаллизации раствора хлорида алюминия и установлено их распределение между продуктами процесса кристаллизации. Показано, что содержание хлорида алюминия в растворе снижается с увеличением расхода соляной кислоты. Установлено, что в условиях кристаллизации  $AlCl_3 \cdot 6H_2O$  все примеси, за исключением бария, на 98 % переходят в маточный раствор. Для снижения бария и других примесей в получаемых кристаллах  $AlCl_3 \cdot 6H_2O$  предложено проведение многократной промывки кристаллов соляной кислотой (32 % HCl). Показано, что снижение кислотности промывного раствора с pH=10 до pH=5,5 обеспечивает выделение кристаллов ГХА с минимальным содержанием металлов-примесей, ppm: 3-5 Ca; 3-6 Fe; 1-3 Mg; 0,1-0,5 Ti; 1-3 Na; 20-30  $P_2O_5$ . Влажность полученных кристаллов составляет 4-5 %, крупность – 400-900 микрон. В результате математической обработки построены уравнения регрессии, адекватно прогнозирующие содержание хлорида алюминия в растворе и его извлечение в кристаллогидрат в зависимости от расхода соляной кислоты. Установлены оптимальные параметры процесса кристаллизации: T=60 °C, концентрация HCl в растворе – 26-30 %, расход газа HCl=0,5 л/мин, продолжительность, τ=1 ч.

**Ключевые слова:** кристаллизация, гексагидрат хлорида алюминия, раствор, соляная кислота, примеси, промывка, кислотность, извлечение.

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