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Complex Use of Mineral Resources

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Improving the efficiency of methane extraction from coal seams

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ABSTRACT
This article presents possible reasons for the low productivity of wells for coal methane extraction and ways to resolve them using hydrochloric acid treatment of wells. A common reason for the low productivity of wells is a decrease in the permeability of the bottom-hole formation zone. Starch, calcium carbonate, and drilling rocks, which are part of the drilling mud, change the filtration properties of the layer during the formation of a filtration crust and lead to a decrease in the initial permeability. Hydrochloric acid treatment, during which clay rocks are dissolved, is an effective method of increasing the productivity of wells. It is used to increase pick-up and prevent contamination of the bottom-hole zone of the carbonate formation. The parameters affecting the effectiveness of hydrochloric acid treatments were considered. The results of the experience of the interaction of hydrochloric acid with a clay crust are presented and analyzed using approaches to the mechanics of multiphase media. Dependences of the rate of dissolution of clay rock on the concentration of acid solution are obtained. It is established that the treatment of the productive intermediate layer of the well with hydrochloric acid in a certain concentration, its use increases the technological and economic efficiency of wells. As a result of experimental work, it was found that hydrochloric acid with an HCL concentration above 18% has a negative effect on the internal equipment of the well when processing clay shells.

Keywords: safety, coal mines, colmatation, wells, clay crust, hydrochloric acid.

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Introduction

The issue of creating safe ways of mining in coal mines has always been an important task in the mining industry. Creating a way to intensify the gas supply of coal seams on the basis of a complex set of works may be the answer to the question of how to reduce the number of human casualties and increase the efficiency of drilling and cleaning operations. Therefore, the intensification of gas emissions from coal seams is an urgent scientific and practical task [[1], [2]]. Despite the existence of scientific developments, the results of previous studies still do not solve the problem of increasing the gas release of coal seams under the influence of external forces.

Since 2015, JSC "KazTransGas" has conducted geological exploration for gas production from coal seams in the Karaganda region. For this purpose, the planned work on drilling three core and four experimental-industrial wells were carried out.

The efficiency of well construction is directly related to their productivity, and the latter is to maintain the maximum permeability of reservoirs and the duration of high-performance wells.

In recent years, the urgency of the problem of maintaining the potential productivity of wells has increased significantly, including due to the involvement in the development of complex deposits and fields with low permeability, with high requirements for the quality of their opening [[2], [3]].

The main negative factor in the completion of wells, which significantly impairs the performance of methane coal wells, is the contact of the drilling fluid with the productive formation during drilling [3]. In this case, the proximal part of the formation is clogged with the solid phase of the drilling mud, the conductive area is covered with the filtrate of the drilling mud; physicochemical interaction of the filtrate with both formations of fluids and rocks. The adverse effects of the drilling mud filter entering the formation may vary:

- causes swelling of clay particles in the reservoir layer, resulting in a sharp decrease in the permeability of the lower well area;
- water-oil emulsions are formed, which in some cases significantly reduce the permeability of the lower well area;
- Capillary forces in the porous medium and its partial displacement from the porous channels can only be accompanied by a significant change in pressure, which makes it difficult for methane to move to the bottom of the well, especially with low conductivity reservoirs;
- As a result of the interaction of the drilling mud filter with highly mineralized water, insoluble residues may form in the reservoir pores [4].

The penetration of polymers, starch, and calcium carbonate, which is part of the drilling mud into the productive layer of the drilled rock, changes the filtration properties of the formation during the formation of the filtration crust and leads to a decrease in the initial permeability [5]. To restore it, it can be treated with chemical compounds such as acids and oxidizers.

Experimental part

Hydrochloric acid in different concentrations is used in the productive intervals of the wellbore, to solve this problem. Acid treatment of wells is designed to clean the edges of clay deposits to increase the permeability of coal seams. Under the influence of hydrochloric acid, cavities, cracks, and drainage channels are formed in rocks and coal seams, as a result of which the permeability of the productive layer increases, and, consequently, the productivity of methane-coal wells increases.

Tests for the removal of clay with hydrochloric acid were conducted in the laboratory of drilling mud at Nazarbayev University. The easiest way to remove the filter shell with acid-soluble components is to install acid baths. Limestone, siderite, celestine, etc. react with the acid, effectively destroying the structure of the clay crust, and facilitating its removal from the surface of the collector [6].

Tests were carried out on the drilling mud used during the drilling of wells in the Sherubainura area. Drilling mud is prepared in accordance with the design documentation and consists of the following components such as Bentonite, Carboxymethylcellulose (CMC), Na_2CO_3, polisol, technical salt, POLIPAC UL, POLIPAC R, foam step, Dyovis, DESCO / Burplast. The acid solutions to be tested were prepared from 5 acid compositions with a concentration of 12, 14, 16, 18, and 20%, respectively, as shown in Figure 1.

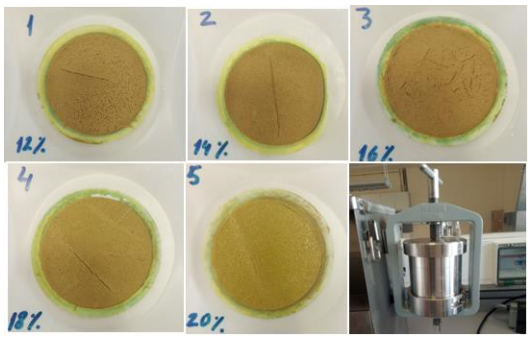

Figure 1. Results of clay samples

Residues of clay suspension were washed with water from the surface of the filtration crust before acid treatment.

Filtration of the acid solution through the clay crust was carried out by the vacuum method (6.9 bar) at a pressure difference.

The first stage is the "latent" phase of the reaction, in which the rate of filtration of the acid through the crust (the volume of the filtrate detected in real-time) is directly proportional.

The second stage is the phase of active interaction of the acid with the filtration crust,

which is characterized by a deviation from the vertical dependence of stage 1.

As the acid concentration increases, the duration of the "latent" phase of the reaction decreases. Thus, in the case of this experiment, the latent reaction time for 20% hydrochloric acid is about 5 minutes. For 12% acid, this period was 31 minutes [7]. According to the 5 tests performed, the diagram of the dependence of the filtration time on the concentration of the acid solution is given (Figure 2) [8].

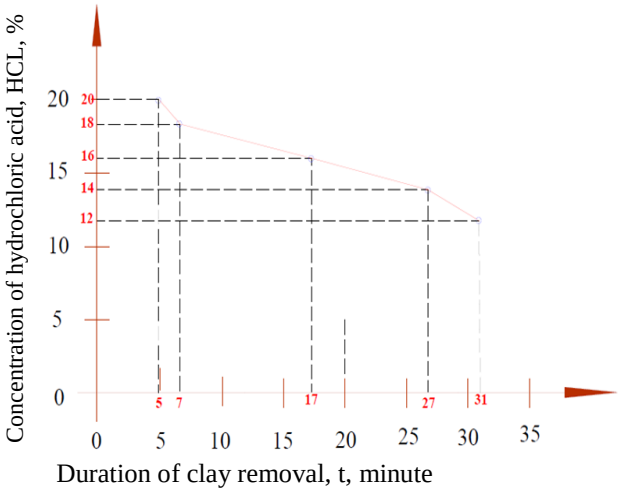

Figure 2. Diagrams of the dependence of the filtration time on the concentration of the acid solution

y - concentration of hydrochloric acid, HCL, %; x time of clay crust removal, t, min - a total of 25 samples were conducted.

The dependence of the start time of the methane production process on the percentage of hydrochloric acid treatment is in the form of cubic regression (Figure 3).

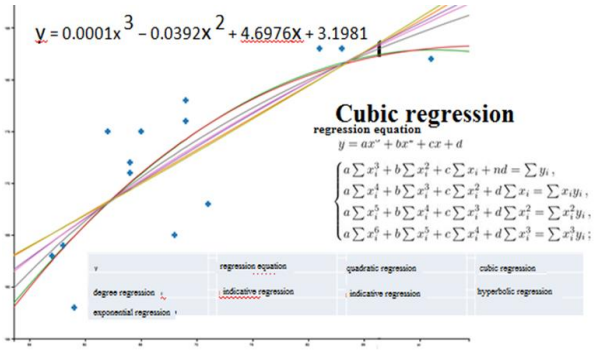

Figure 3. Approximation of a function of a single variable

Thus, an increase in the volumetric concentration of acid increases the permeability of the folds in the filter press, which is a direct indicator of the effectiveness of the destruction of the clay crust [9].

It can be seen that the optimal acid concentration in the processing of clay and effective acid degradation is 18% HCL. Acid concentrations are operatively justified, as low concentrations increase the processing time (more than 17 minutes), while high concentrations have a strong corrosive effect on the equipment inside the well used in drilling and production, especially with a small difference in crust time (2.5 minutes) [10].

One of the main principles of choosing the concentration of acid components in the acid solution is to ensure the maximum amount of soluble clay crust with a minimum amount of acid. Numerous studies and applications show that the optimum concentration of hydrochloric acid is 18% in the main technologies transferred from different regions of the country to the Sherubainura fields [11]. This is convenient because industrial hydrochloric acid contains 37% by weight of the main substance, which allows you to easily prepare the commercially diluted acid solution in half with ordinary water and without any calculations [12].

According to experiments conducted in the laboratory of Nazarbayev University, the melting reaction of the clay crust is intensive at complex concentrations of 12-18%, and when its concentration is less than 12%, the crust does not dissolve in time or does not react at all [13].

The low permeability of coal seams causes low gas release. Therefore, in order to increase the permeability of coal seams during hydraulic fracturing, samples of K3 and K10 coal seams were studied for the effect of 18% hydrochloric acid on the desorption of methane in the laboratory "Methane Energy" in the Mining and Metallurgical Complex of Karaganda Technical University (Figure 4).

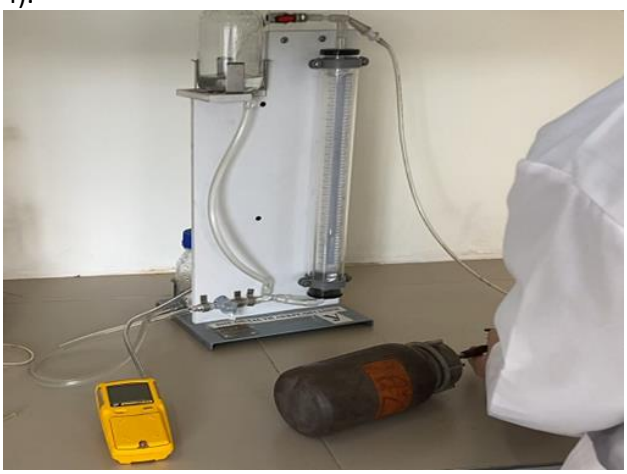

Figure 4. Geokrak desorption unit

The degassed gas from the sampling bottles was degassed.

- The volume of gas released is 140 ml under normal conditions;
- The detector recorded more than 80 levels of methane %;
- 50 g of charcoal was removed and poured 50 ml of water at room temperature;
- After waiting for 10 minutes, the gas medium was surrounded and no traces of methane were found;
- Due to the small volume of coal, the coal was refilled into test vacuum bottles and it was decided to pour 200 ml of 18% hydrochloric acid;
- After waiting for 5 minutes, they turned the valve of the desorption unit and began to correct the gas leak. The volume of gas released at 11 minutes under normal conditions was> 250 ml [14].

The exact concentration of methane in the exhaust gas mixture was determined on an Agilent 7890V gas chromatograph.

According to the chromatograms, the concentration of methane after exposure to 18% of coal was 62%, and the remaining fraction was the concentration of carbon dioxide formed as a result of the decomposition of carbonates in the structure of coal (Figure 5) [[15], [16]].

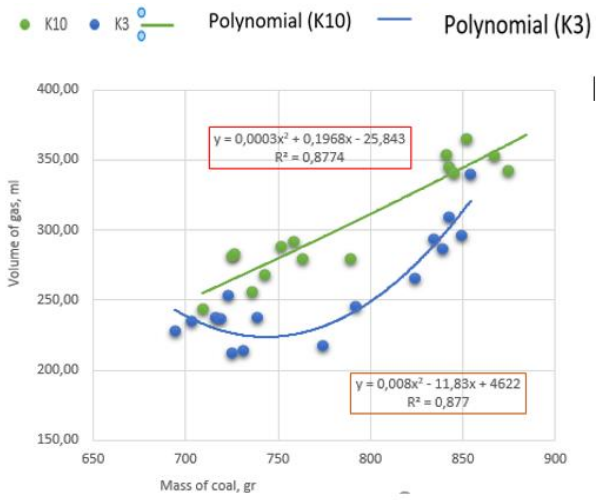

Figure 5. Prediction of methane release by coal mass

Research results and discussion

Thus, the 18% solution increases gas consumption by an average of 17-19% due to the increase in permeability and, consequently, the diffusion of methane in the coal seams [[17], [18]].

Research has been conducted to achieve maximum results in solving the problem of gas emissions from coal seams.

The difference in the proposed work is the intensification of gas release from coal seams on the basis of a fundamental study of the viscosity, strength, and density of the coal mass to identify structural bonds and increase the permeability of coal and methane [[19], [20]].

The result of the fundamental research work was the intensification of gas separation of coal seams by conducting a set of studies, including testing of coal seam samples for viscosity, and permeability of coal seams to identify structural bonds and increase the permeability of coal and methane.

The novelty of the research work:

- increase in gas emissions from coal seams due to the optimal location of methane coal wells in the establishment of regularity;
- intensification of gas release from coal seams under the influence of external forces.

Conclusions

The results of the work will ensure the safety of underground mining in coal mines and reduce the greenhouse effect of methane emissions from coal seams into the atmosphere.

Industrial regions of Kazakhstan, which do not receive enough gas, can be fully self-sufficient through the production of their own methane from coal seams. First of all, we are talking about Karaganda, Akmola, and Pavlodar regions [[21], [22]].

Conflict of interest

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

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ТҮЙІНДЕМЕ

Бұл мақалада көмір қабаттарыннан газ бөлінуін арттыру арқылы көмір шахталарында тау-кен жұмыстарын қауіпсіз жүргізуді қамтамасыз ету мәселелері қаралды. Көмір қабаттарынан газ бөлінуін қарқындату мақсатында бір қатар зерттеулер жүргізілді. Ұңғымалардың төмен өнімділігінің ықтимал себептері және ұңғымаларды тұз қышқылымен өңдеуді қолдану арқылы оларды шешу жолдары келтірілген. Ұңғымалардың төмен өнімділігінің жиі кездесетін себебі – төменгі ұңғыма аймағының өткізгіштігінің төмендеуі. Крахмал, кальций карбонаты, бұрғылау ерітіндісінің құрамына кіретін бұрғылау жыныстары сүзу қыртыстарын түзгенде қабаттың сүзу қасиеттерін өзгертеді және бастапқы өткізгіштіктің төмендеуіне әкеледі. Сазды жыныстарды еритін тұз-қышқылмен өңдеу ұңғымалардың өнімділігін арттырудың тиімді әдісі болып табылады. Тұз қышқылымен өңдеудің тиімділігіне әсер ететін параметрлер қарастырылды. Көп фазалы ортаның механикасы тәсілдерін қолдана отырып талданған тұз қышқылының саз қабығымен өзара әрекеттесу тәжірибесінің нәтижелері келтірілген. Сазды жыныстың еру жылдамдығының қышқыл ерітіндісінің концентрациясына тәуелділігі анықталды. Ұңғыманың өнімді аралық қабатын белгілі бір концентрацияда тұз қышқылымен өңдеу ұңғымалардың технологиялық тиімділігін арттыратыны анықталды. Эксперименттік жұмыстардың нәтижесінде 18% жоғары концентрациясы бар HCL тұз қышқылы сазды қабықтарды өңдеу кезінде ұңғыманың ішіндегі жабдықтарға теріс әсер ететіні анықталды. Зертханалық жағдайда жүргізілген эксперименттердің нәтижесінде қышқылдың өңдеудегі ең оңтайлы концентрациясы және саз қабығының тиімді қышқылдық ыдырауы 18% HCL екендігі анықталды. Эксперимент нәтижелері бойынша 18% ерітінді өткізгіштіктің артуына байланысты газ бөлуді орта есеппен 17%-ға және 19%-ға арттырады.

Түйін сөздер: қауіпсіздік, көмір шахталар, кольматация, ұңғымалар, саз қабығы, тұз қышқылы.

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Повышение эффективности извлечения метана из угольных пластов

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АННОТАЦИЯ

В данной статье рассмотрены вопросы обеспечения безопасного ведения горных работ на угольных шахтах путем повышения газоотдачи угольных пластов. С целью интенсификации газовыделения угольных пластов проведен ряд исследований. Приведены возможные причины низкой производительности скважин и пути их решения с использованием обработки скважин соляной кислотой. Наиболее частой причиной низкой продуктивности скважин является снижение проходимости нижней зоны скважины. Крахмал, карбонат кальция, буровые породы, входящие в состав бурового раствора, изменяют

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фильтрационные свойства пласта при образовании фильтрационной корки и приводят к снижению начальной проницаемости. Обработка глинистых пород растворимой соляной кислотой является эффективным методом повышения продуктивности скважин. Рассмотрены параметры, влияющие на эффективность переработки соляной кислоты. Приведены результаты опыта взаимодействия соляной кислоты с глинистой оболочкой, анализируемого с помощью методов механики многофазных сред. Получена зависимость скорости растворения глинистой породы от концентрации раствора кислоты. Установлено, что обработка продуктивного промежуточного слоя скважины соляной кислотой в определенной концентрации, ее использование повышает технологическую эффективность скважин. В результате экспериментальных работ установлено, что соляная кислота HCL с высокой концентрацией 18% оказывает негативное влияние на внутреннее оборудование скважины при обработке глинистых оболочек. В результате экспериментов, проведенных в лабораторных условиях, было установлено, что наиболее оптимальная концентрация кислоты в обработке и эффективное кислотное разложение глинистой пленки составляет 18% HCL.По результатам эксперимента 18% раствор увеличивает газовыделение в среднем на 17% и 19% за счет увеличения проницаемости.

Ключевые слова: безопасность, угольные шахты, кольматация, скважины, глинистая корка, соляная кислота.

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Earth Sciences

Studies of the influence of the composition of the CHM on the properties of the casting

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ABSTRACT

The quality of the finished casting is largely determined by the quality of the mold. Currently, there are a large number of variations in the composition of CHM (cold hardening mixes), differing both in the nature of the main component and in the nature and ratio of binders and other technological additives. As cleaning dust has a very developed surface due to technological reasons. According to various estimates, the specific surface area of gas cleaning dust is from 8, 000 cm^2/g and higher. In order to verify this assumption, studies were conducted on the effect of the composition of the mixture using SCF (sand-clay forms), on some of its properties. In conclusion, the conducted studies have shown that in order to ensure the maximum performance of the technological properties of CHM, the optimal content of SCF in the mixture should be 2.0 - 10.0 wt.% in the ratio with orthophosphoric acid is not higher than 1.25.

Keywords: CHM, SCF, casting, properties, mixture, strength, surface.

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Introduction

The quality of the finished casting is largely determined by the quality of the mold. In the manufacture of castings from alloys with high hardness, such as Nihard cast iron, such casting quality parameters as surface cleanliness and compliance with geometric dimensions are of particular importance, because the high hardness, wear-resistance, and relative fragility of these alloys complicate the machining of the finished casting. Accordingly, in the manufacture of castings from these alloys, it is necessary to strive for the maximum possible surface cleanliness and accuracy of geometric dimensions.

Casting in sand-clay molds (SCF) does not provide these quality parameters, the use of other casting technologies (investment casting, casting on gasified patterns, coquille casting) is limited due to various reasons: the complexity of the process, high cost, etc. In this case, a good alternative to these methods is the production of casting into molds made using cold-hardening mixtures (CHM).

The essence of the CHM method is the approval of a sand-resin mixture under the influence of a catalyst. The main advantages of this method are high surface cleanliness and accuracy in the geometric dimensions of the castings obtained; the minimum number of casting defects formed; there was the possibility of

regeneration of the molding mixture. In addition, the drying and heating stage of the mold is completely eliminated, which leads to a significant reduction in the time of the mold manufacturing process.

The main disadvantage of using the CHM method is the toxicity of some components of the mixture and in this regard, the need for special conditions for their storage and use [1].

Currently, there are a large number of variations in the composition of CHM, differing both in the nature of the main component and in the nature and ratio of binders and other technological additives [[2], [3], [4]].

For example, in the work of CHM [[5], [6], [7]], a mixture is proposed that contains synthetic resins and inorganic binders: liquid glass, cement, iron scale, iron ore concentrate, magnesite, and chromomagnesite. This CHM includes a refractory filler based on silicon dioxide, a material based on iron oxides, and orthophosphoric acid. Its peculiarity is that in order to reduce crumbling, the mixture contains such a technological additive as aminopropyltriethoxylane. However, the cost of this additive is quite high, in addition, this mixture has fairly low survivability (3 - 15 min) and low compressive strength (0.1-0.49 MPa).

Based on a brief information analysis, it can be concluded that the composition of CHM should be selected based on the optimal cost–property ratio. In turn, this ratio will be determined by the availability and availability of available raw materials.

In this paper, it is proposed to use a mixture as a CHM, which consists of a refractory filler based on SiO_2, a highly dispersed component, and orthophosphoric acid as binders and water. The purpose of introducing a highly dispersed material into the composition of the CHM is to increase the interaction surface between the reagents, which should ensure a rapid reaction and reduce the curing time.

Methods and materials

The composition of CHM is proposed for the manufacture of molds containing a refractory filler, iron oxides, orthophosphoric acid, and bauxite. The disadvantage of such a mixture is the need for preliminary preparation of bauxite before use in CHM [8], namely grinding and drying. In addition, the instability of bauxite in chemical composition significantly affects the possibility and amount of formation of iron phosphate ligaments. The composition of CHM is given [9], including a material based on oxide and iron oxide in the form of waste dust from electric steelmaking, orthophosphoric acid and chromium anhydride. The main disadvantage of this mixture is the presence of a poisonous and carcinogenic substance - chromium anhydride.

It is proposed to use aqueous solutions of phenolic substances reacting with aldehydes and gaseous acetals as a binder. In [[10], [11]], it is proposed to use a mixture containing epoxy resin and furfuryl alcohol as a catalyst.

It should be noted that the variations in the compositions of CHM concern not only binders and technological additives but also the main component – a refractory filler. For example, in [[12], [13], [14]] it is proposed to use a material extracted from rice husks as a refractory filler since it contains a large amount of SiO_2.

As a highly dispersed material, it is proposed to use gas purification dust produced by ferrosilicon (SCF), the average composition is given in Table 1.

Table 1 - Composition of gas purification dust produced by ferrosilicon, %

SiO_2	Fe_2O_3	Al_2O_3	MgO	CaO
80-95	0.2-4.5	1.8-8.6	1.3-1.5	0.4-2.6

It should be noted that gas cleaning dust has a very developed surface due to technological reasons. According to various estimates, the specific surface area of gas cleaning dust is from 8, 000 cm^2/g and higher [[15], [16]]. Such a developed surface provides a high degree of contact between reagents (silicon dioxide and orthophosphoric acid) with the formation of a compound of silicon pyrophosphate and silicophosphate of variable composition of the type x $xSiO_2$ *YP_2O_5. The formation of this compound causes the mixture to harden, which ensures the formation and properties of the mold.

Conducted studies and their results

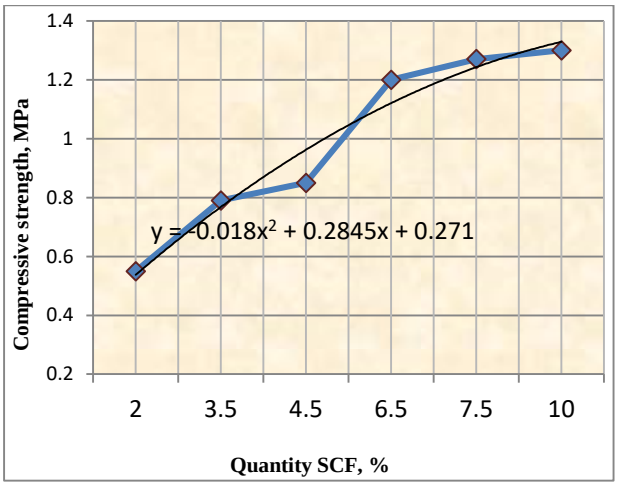
In order to verify this assumption, studies were conducted on the effect of the composition of the mixture using SCF on some of its properties.

The mixture was prepared as follows. Refractory filler (quartz sand) and highly dispersed filler (SCF) were loaded into the paddle mixer and mixed for 5-10 minutes. Then orthophosphoric acid was added, previously diluted with water to a density of 1.5 -1.6 g / cm^3, and mixed for another 5-10 minutes. During the manufacture of the mixture, the number of components varied, the compositions of the mixtures are shown in Table 2.

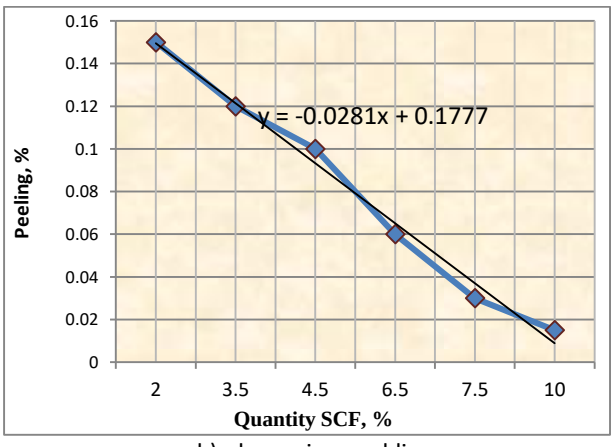
Table 2 - Composition of the studied mixtures, %

Mixture number	Orthophosphoric acid	Highly dispersed filler (SCF)	Water	Quartz sand
1	3	2	4	other
2	4	3.5	4.5	other
3	5	4.5	5	other
4	6	6.0	5.5	other
5	7	7.5	6	other
6	8	10.0	6.5	other

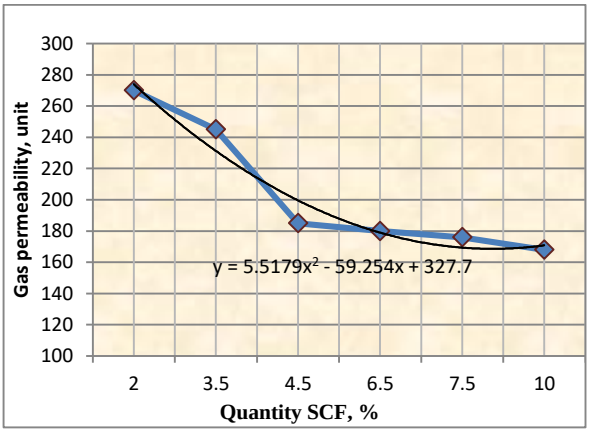
Samples were prepared from the finished mixture to determine compressive strength, survivability, gas permeability and crumblability. Compressive strength was determined on the INSTRON device [17], crumbling on the PP-1100 (02212) device, gas permeability on the P04315-M device according to generally accepted methods. The survivability of the mixture was determined every 30 minutes for 3 hours. In this case, survivability was understood as the minimum time during which the strength drop is more than 30%. The results of the research are shown in Figure 1.



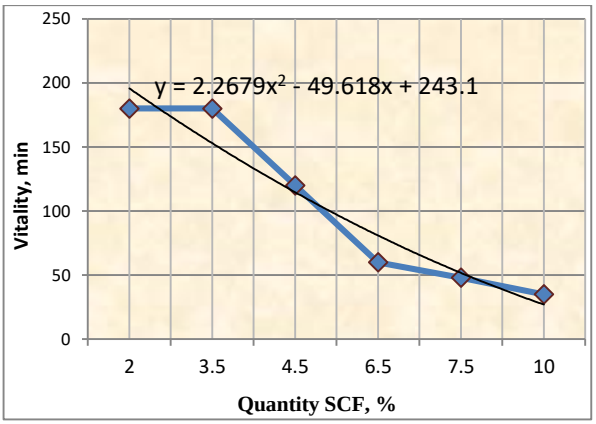
a) change in compressive strength



b) change in crumbling



c) change in gas permeability



d) change in survivability

Figure 1 - Change of properties depending on the amount of PGPF

As can be seen from the above figures, an increase in the amount of SCF in the range of 2-10% has a positive effect on such an indicator as the strength of the mixture, but an increase in the amount of SCF over 6.5% practically does not affect the strength. At the same time, such indicators as survivability, crumbling and gas permeability of the mixture are falling. According to the requirements for the specified parameters, the compressive strength should be at least 0.45 MPa after 1-hour exposure; survivability - at least 10 minutes; gas permeability greater than 150 units; shedding less than 0.3% [[18], [19], [20]].

A comparative analysis of the results obtained with the minimum requirements for the properties imposed on the CHM allows us to draw the following conclusion. The content of SCF in the composition of CHM in the range of 2 - 10% provides the necessary indicators of the mixture within the norm.

A further increase in the amount of SCF in the mixture is impractical since an increase of more than 7-8% practically does not affect the strength. However, at the same time significantly reduces such indicators as survivability, gas permeability and crumbling, which leads to an increase in the cost of the mixture and is

economically impractical. A decrease in the amount of SCF below the lower limit (3.0%) is also undesirable since the contact surface created will not be sufficient for active interaction of reagents, which leads to a deterioration in strength indicators.

As can be seen from the data in Table 2, the content of orthophosphoric acid increased with the content of SCF. This is necessary in order to ensure the completeness of the curing reaction and the formation of the complex compound $xSiO_2 * YP_2O_5$. Figure 2 shows the effect of the ratio of the amount of SCF and orthophosphoric acid (OPA) on the strength of the mixture.

As can be seen from Figure 2, with an increase in the ratio of SCF / OPA, the strength of the mixture increases, but then when the ratio is reached equal to 1.25, the strength of the mixture begins to fall. This indicates that with an increase in the proportion of PGPF relative to orthophosphoric acid in the mixture above 1.25, the formation reaction of silicon silicophosphate practically does not proceed, and the curing process does not develop further. Accordingly, it is impractical to exceed the specified ratio.

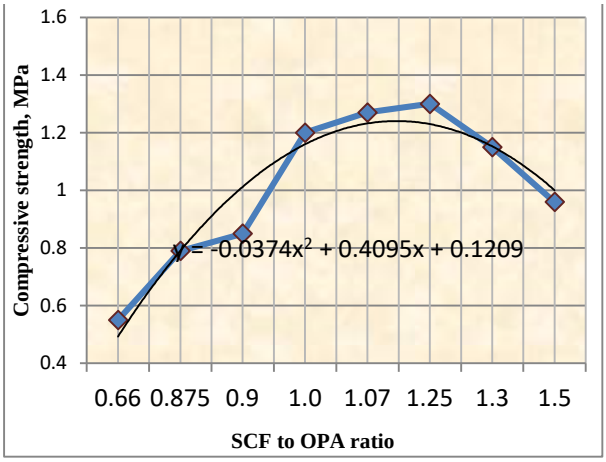


Figure 2 - The effect of the ratio of SCF to OPA on the strength of the mixture

Conclusion

Thus, the conducted studies have shown that in order to ensure the maximum performance of the technological properties of CHM, the optimal content of SCF in the mixture should be 2.0 - 10.0 wt.% in the ratio with orthophosphoric acid is not higher than 1.25. A further increase in the ratio of SCF / OPA in the composition of the mixture leads to a drop in the strength of the mixture.

The proposed mixture has a high survivability (35 - 180 minutes), low crumbling (0.03 - 0.1%) and a wide range of strength from 0.55 to 1.3 MPa with a required minimum of 0.45 MPa, depending on the ratio of SCF / OPA, and the content of SCF should be organic to the specified limits. Consequently, by changing the amount and ratio of SCF and orthophosphoric acid, under other equal conditions, it is possible to regulate the technological properties of the proposed CHM in a wide range.

The studied mixture can be used for the production of small, medium, and large molds and the manufacture of rods of all five complexity classes in conditions of both small-scale production and serial and mass production. The preparation of the mixture can be carried out on standard equipment, which does not require additional costs for the purchase of specialized equipment. The most important advantage of the composition of this mixture is the use of waste from metallurgical production, which contributes to the solution of two tasks: reducing the cost of molds and rods and solid waste disposal and, consequently, improving the environmental situation of the region.

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Суықтай беріктенетін қоспа құрамының құйма қасиеттеріне әсері

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ТҮЙІНДЕМЕ

Дайын құйманың сапасы көбінесе қалыптың сапасымен анықталады. Қазіргі уақытта негізгі компоненттің табиғаты бойынша да, байланыстырғыштар мен басқа да технологиялық қоспалардың табиғаты мен қатынасы бойынша да ерекшеленетін СҚҚ (суықтай қатаятын

Мақала келді: *18 наурыз, 2022*
Сараптамадан өтті: *8 мамыр 2022*
Қабылданды: *05 шілде 2022*

қоспалар) құрамында көптеген вариациялар бар. Тазалаған кезде шаңның технологиялық себептерге байланысты өте дамыған беті болады. Әртүрлі бағалаулар бойынша газ тазартатын шаңның үлестік ауданы 8000 см^2/г және одан да көп. Бұл болжамды тексеру үшін ҚСҚ (құмды-сазды қалыптар) көмегімен қоспа құрамының кейбір қасиеттеріне әсеріне зерттеулер жүргізілді. Қорытындылай келе, зерттеулер көрсеткендей, СҚҚ (суықтай қатаятын қоспалар) технологиялық қасиеттерінің максималды өнімділігін қамтамасыз ету үшін қоспадағы ҚСҚ-ның, оңтайлы мөлшері фосфор қышқылымен 1,25 жоғары емес қатынасында 2,0 – 10,0 масс. % болуы керек..

Түйін сөздер: СҚҚ, ҚСҚ, құйма, қасиеттер, қоспа, беріктік, бет.

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Исследования влияния состава ХТС на свойства отливки

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Аннотация

Качество готовой отливки во многом определяется качеством формы. В настоящее время существует большое количество вариаций состава ХТС (холодно-твердеющие смеси) различающихся как по природе основного компонента, так и по характеру и соотношению вяжущих и других технологических добавок. При очистке пыль имеет очень развитую поверхность по технологическим причинам. По разным оценкам удельная поверхность пыли газоочистки составляет от 8000 см^2/г и выше. Для проверки этого предположения были проведены исследования влияния состава смеси с использованием ПГФ (песчано-глинистых форм) на некоторые ее свойства. В заключение проведенные исследования показали, что для обеспечения максимальных показателей технологических свойств ХТС оптимальное содержание ПГФ в смеси должно составлять 2,0 - 10,0 мас.% в соотношении с ортофосфорной кислотой не выше 1,25.

Ключевые слова: ХТС, СКФ, литье, свойства, смесь, прочность, поверхность.

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Earth Sciences

Justification of the stress-strain state's parameters of the mine workings contours depending on the influencing factors

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ABSTRACT

The complication of mining and geological conditions is associated with the involvement in the development of areas and entire deposits with complex tectonics, an increase in the depth of development, the manifestation of dangerous dynamic effects of rock pressure, which necessitates the improvement of methods, systems, methods and means of supporting mine workings, as well as improving the quality of materials used for support. Mining and geological factors affecting the use of mining support include: the depth of occurrence, which determines the magnitude of the vertical and horizontal components of the rock pressure; layer thickness, developed deposit; bed angle; properties of the host rocks, structure and physical and mechanical properties of rocks and minerals. The paper presents the conduction of the analytical modelling of the rock mass stress-strain state around the active mine workings using the ANSYS software with the assessment of the influence of its cross-section shape and the angle of the coal seam fall on the value of the maximum stresses arising in the rock mass when the workings are supported with the anchoring support depending on the thickness of the easily collapsible rock layer at different lengths of anchoring.

Keywords: massif, mine development, stress-strain state, stress, anchoring.

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Introduction

Due to the high rate of drifting faces' advance and the strategy of mining operations' development, two mining areas require accelerated and timely development of mine workings with intensive technology of preparation workings.

The increase in the volume of underground coal mining is possible only with the highly efficient technology of carrying out and maintaining preparatory mine workings.

As the level of mining depth increases, one of the problems is to ensure the stability of mine workings. Metal compliant support of arch type and anchoring is used to maintain mine workings in the mines of the Karaganda basin. The cost of money is more than one thousand dollars at the expense of metal-roll to conduct and fix 1 meter of mine workings using arch support. The maintenance cost is at least 10-15 % of the cost of mine workings. The development of 5.0-5.5 km of mine workings is required for 1 million tons of coal accepted in practice systems, which defines essential expenses for preparing mine workings.

More than 10 % of underground workers are engaged in the repair of mine workings [[1], [2], [3], [4], [5]]. Loss of the cross-sectional area of reservoir workings reaches 60-70%. This leads to 20% of mine workings being repaired and refastened annually. The share of expenses on carrying out, fastening and maintenance of mine workings reaches 15-20 % of the cost price of coal mining.

The use of more significant profiles and increased density of frame support considerably increases the metal intensity of workings and labor intensity of erection. Its operation has several

serious drawbacks, which lead to significant deformations of excavations: flattening of tops, extrusion into the section cavity of lateral legs, and failure of locking joints.

Improving the efficiency of maintaining the mine workings' stability can be achieved using progressive anchoring technology.

The behavior of rocks of the coal seams' roof in the Karaganda basin is determined by their composition, physical and chemical properties, stratification and fracturing. The immediate roof of the coal seams is most often represented by mudstones, more rarely siltstones and by sandstones in isolated cases; the main roof is usually composed of sandstones. Argillites predominate in the soil of coal seams [[6], [7], [8], [9], [10]].

The value of using the technology of anchoring mine workings in 2021 in the mines of the Karaganda basin reached 25%, and with the combined (metal-anchored underlay and anchoring) - 48%. To increase the volumes of using the anchoring technology, it is necessary to estimate its application depending on operating conditions and develop typical effective driving and supporting workings technologies [[11], [12], [13], [14]].

An urgent task of mining production is the study of rock mass deformation peculiarities around preparatory workings with anchoring at different dip angles and anchoring depths, justification of anchoring parameters and determination of the rational area of its use [[15], [16], [17], [18]].

The experimental part

The research aims to develop effective technology for supporting the contour rock mass based on studying the technogenic stress-strain state (TSSS). To implement it, a technology of intensive and safe conduct of mine workings based on the identified patterns of behavior of host rock massifs adjacent to them, optimization of parameters of technological schemes of preparatory works was created.

One of the main directions of technical progress in anchoring and maintenance of mine workings is the use of resource-saving technology of preparatory workings with the use of anchoring, including in combination with metal arch support.

Thus, the urgent task of mining production is the study of the deformation features of the rock mass around preparatory mine workings with anchoring at different angles of bed dip and anchoring depths, justification of the anchoring parameters and determination of the rational area of its use.

The excavation disturbs the equilibrium state of rocks. It leads to the redistribution of stresses in the surrounding massif, and the intensity of stresses on the excavation contour is much higher than in the disturbed massif. Increased stresses on the mine workings lead to a zone of inelastic deformations around them. The structure of the zone and the nature of rock deformation depend on the excavation depth, physical, mechanical and technological properties of rocks, the size of the excavation, the type and characteristics of the mount, and the angle of the enclosing rocks.

The diversity of mining and geological and mining conditions and the related mechanism of interaction between rocks and supports have led to various geomechanical mathematical models of the rock mass state around mine workings.

Modelling is executed using the numerical method of finite elements, the stress-strain state of the massif around the active mine working. The solution is carried out in the elastic statement due to a comparatively short time of rock deformation in the vicinity of the preparatory face during its movement. In contrast to the known approaches, the dimensions of the deformation propagation zones are specified with the analysis of their parameters [[19], [20], [21]].

Using the ANSYS software package, the influence of the shape of the mine cross-section and the dip angle of the coal seam on the value of the arising maximum stresses in the rock massif when securing the mine with the anchor support is evaluated.

Figure 2 (for reservoir conditions of 4.0 m) shows calculations of stress components: σ_y is normal, σ_x is the longitudinal component of supports. Vertical (Figure 1a), longitudinal (Figure 1 b), and tangential (Figure 1c) components increase with formation dip angle, within its component change from 100 to 400. For all cross-sectional forms, the values of σ_x and σ_{xy} are an order of magnitude higher than σu for the same x, with high σ_x, σ_y characteristic of the arch form, the same for σ_{xy} (the tangential stress component).

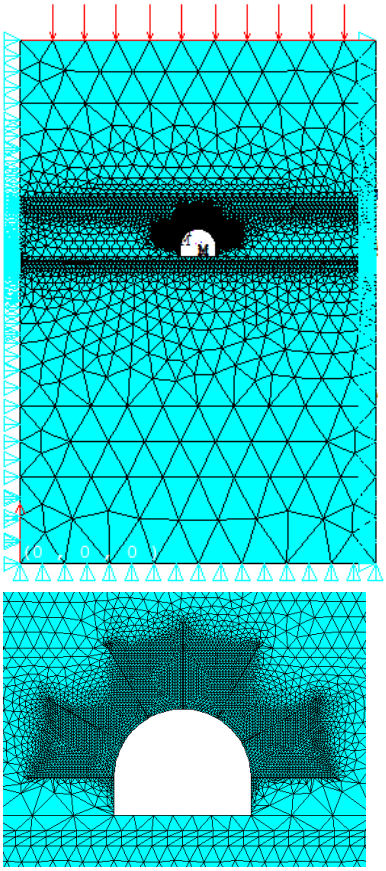


Figure 1 - Calculation scheme of the problem

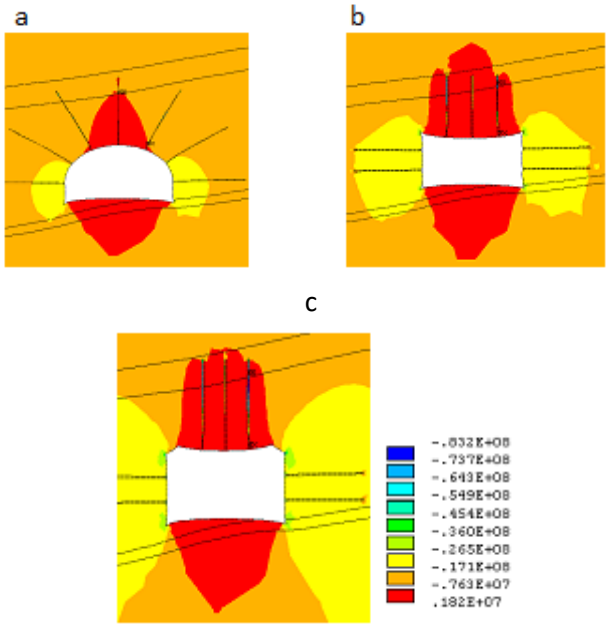


Figure 2 - Diagrams (at α = 100) of the maximum normal stresses in the areas surrounding the mine workings of the arch (a), rectangular (b) and polygonal (c) cross-sectional forms

Figure 3 shows plots of maximum normal (a), longitudinal (b), and shear (c) stresses in rock mass at anchoring of arch (1), rectangular (2) and polygonal mine workings with formation dip angle.

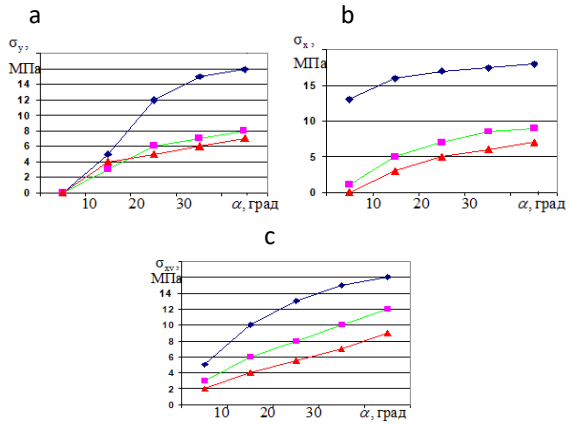


Figure 3 - Plots of maximum normal (a), longitudinal (b) and tangential (c) stresses in rock mass at anchoring of arch-shaped (1), rectangular (2) and polygonal (3) workings on the dip angle

The stress-strain state of the host rock layers depending on the thickness of the easy-rock layer is studied at different anchoring lengths. We investigated the character of changes and distribution of stresses in the roof, the ground and the sides of the mine workings by the example of a trapezoidal excavation of a cross-sectional form with the following parameters of the claim scheme: the dip angle of the formation is 15°; its thickness is 4,0 m; the depth of development is 500 m; the working cross-section is 15.5 m^2; the anchor diameter is 0.022 m.

The conducted research allowed us to establish the following character of the behavior of lateral rocks by zones of their location (Fig. 4, a and b).

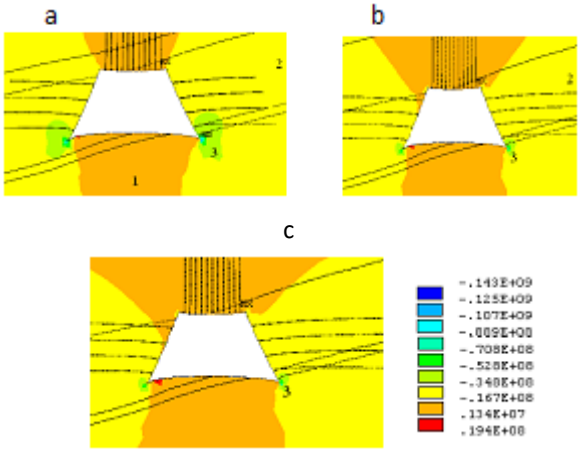


Figure 4 - Distribution diagram (a) and dependences of changes in normal stresses (b) in the host rock with a thickness of argillite layer 1 - 1 m; 2 - 3,5 m; 3 - 5 m, on the depth of their anchoring at the anchor length of 3,5 m.

The influence of the roof rocks (with increasing the layer of easily collapsing argillite) at the

trapezoidal form of the excavation cross-section is studied. Parameters of the rated scheme: dip angle 15°, its thickness 3.8 m; excavation depth 400 m; working cross-section 15.5 m^2; anchor length 3.0 m, its diameter 0.05 m.

Figure 5 shows the distribution of longitudinal stresses around the trapezoidal excavation with a claystone layer of 1 m along the length of the boreholes. Significant stresses are subjected only to the area of rocks at the extremities in the roof of the boreholes, which requires increasing their density in this area [4].

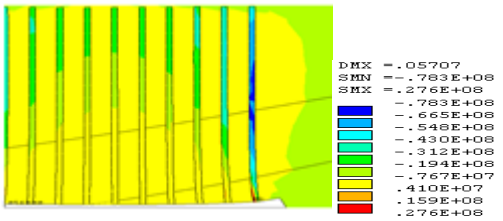
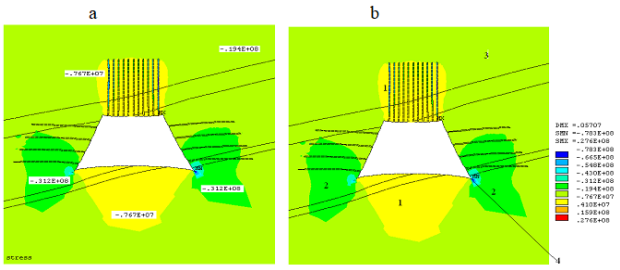


Figure 5 - Distribution of longitudinal stresses around the trapezoidal excavation with a layer of argillite 1 m on the length of the boreholes

Figure 6 shows the distribution of normal and longitudinal stresses at the argillite layer of 7.5 m along the contour of the mine workings.

Analysis of the stress distribution shows that zones of unstable rock formations occur around the excavation. The analysis of the stress distribution shows that there are zones of unstable rock around the excavation. The maximum value of normal stresses is in the anchor, located on the top of the excavation, in the rightmost anchor of the securing point. The maximum value of longitudinal stress occurs in the anchor on the right side surface of the excavation (first from the bottom).



1 - zone of very unstable; 2 - zone of unstable; 3 - zone of unstable; 4 - zone of medium stability; at the minimum point - zone of stable

Figure 6 - Distribution of normal (a) and longitudinal (b) stresses at argillite layer equal to 7.5 m

Conclusions

The revealed patterns of change in the stress-strain state of coal massifs (displacements, stresses, fracture zones) depending on the main mining-geological and mining-technical factors make it possible to set the optimal parameters anchorage to increase the stability of preparatory mine workings under particular operating conditions. This will allow the development of new and improved technologies for effective and safe anchoring of near-surface rocks when conducting mine workings on flat and inclined coal seams, adaptive to changing mining-geological and mining-technical conditions of operation.

Conflicts of interest

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

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Әсер етуші факторларға байланысты тау-кен қазбалары контурларының кернеулі-деформацияланған жай-күйінің параметрлерін негіздеу

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Қабылданды: *11 шілде 2022*

ТҮЙІНДЕМЕ

Тау-кен-геологиялық жағдайлардың күрделенуі кен қазбаларын бекіту әдістерін, жүйелерін, тәсілдері мен құралдарын жетілдіруді, сондай-ақ бекіту кезінде пайдаланылатын материалдардың сапасын жақсартуды қажет ететін күрделі тектоникасы бар учаскелер мен тұтас кен орындарын игеруге тартумен, игеру тереңдігінің ұлғаюымен, тау-кен қысымының қауіпті динамикалық әсерінің көрінуімен байланысты.Тау бекітпесін пайдалануға әсер ететін тау-геологиялық факторларға мыналар жатады: тау қысымының тік және көлденең құраушыларының шамасын анықтайтын тереңдік; кен шоғырының игерілетін қабатының қуаты; қабаттың жату бұрышы; негізгі тау жыныстарының қасиеттері, жыныстар мен пайдалы қазбалардың құрылымы мен физикалық-механикалық қасиеттері. ANSYS бағдарламалық кешенін қолдана отырып, жұмыс істеп тұрған қазба айналасындағы массивтің кернеулі-деформацияланған күйін аналитикалық модельдеу, оның көлденең қимасының пішіні мен көмір қабатының құлау бұрышының әр түрлі анкер ұзындығы бар оңай бұзылатын жыныстар қабатының қуатына байланысты қазбаларды анкермен бекіту кезінде тау жыныстарының массивінде пайда болатын максималды кернеулерге әсерін бағалай отырып жүргізілді.

Түйін сөздер: массив, қазба, кернеулі-деформацияланған күй, кернеу, анкерлік қолдау.

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Обоснование параметров напряженно-деформированного состояния контуров горной выработки в зависимости от влияющих факторов

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АННОТАЦИЯ

Усложнение горно-геологических условий связано с вовлечение в отработку участков и целых месторождений со сложной тектоникой, увеличением глубины разработки, проявления опасных динамических воздействий горного давления, что обуславливает необходимость совершенствования методов, систем, способов и средств крепления горных выработок, а также улучшать качество материалов, используемых при креплении**.** К горно-геологическим факторам, влияющим на использование горной крепи, относятся: глубина залегания, что определяет величину вертикальной и горизонтальной составляющих горного давления; мощность пласта, разрабатываемой залежи; угол залегания пласта; свойства вмещающих пород, структура и физико-механические свойства пород и полезного ископаемого. Выполнено аналитическое моделирование напряженно-деформированное состояние массива вокруг действующей выемочной выработки с использованием программного комплекса ANSYS с оценкой влияния формы ее сечения и угла падения угольного пласта на величину возникающих максимальных напряжений в массиве горных пород при креплении выработки анкерной крепью в зависимости от мощности слоя легкообрушающихся пород при разной длине ее анкерования.

Ключевые слова: массив, горная выработка, напряженно-деформированное состояние, напряжение, анкерная крепь.

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Earth Sciences

Ways of Rare Earth Elements Migration and Transportation to the coals of the Shubarkol Deposit

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ABSTRACT

The article presents the results of studying the mineralogical and geochemical features of coals and clay interlayers of the Shubarkol deposit. There were analyzed 71 samples of clay layers and 49 samples of coal using the instrumental neutron activation analysis (INAA), powder X-ray diffractometry, and scanning electron microscopy. A comprehensive analysis of the geochemical and mineralogical characteristics of coals and their enclosing clay interlayers was carried out. A variety of geochemical criteria made it possible to establish the facts of the rare earth elements (REE) migration, and the latest data of mineralogy made it possible to establish the ways of their transportation to the paleobasin in the syn- and epigenetic periods of the Shubarkol deposit formation. The data of the paleoclimate and water composition of the paleobasin of peat formation are presented for the first time. Among other things, the analysis made it possible to identify a number of independent sources and various mechanisms of REE accumulation in the sediments of the Shubarkol deposit. The main patterns of the REE distribution that are expressed in the predominance of light lanthanides over heavy lanthanides, were established, and the role and composition of the rocks surrounding coal deposits in the concentration of REE were considered. Aluminosilicates, sulfides, and sulfates with inclusions of microparticles of rare and rare-earth REE elements were found in coals and clay interlayers.

Keywords: coal, Shubarkol, rare earth elements, mineralogy, geochemistry.

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Introduction

In recent years, the issue of the nature of impurity element accumulation in coal deposits has been increasingly raised. Understanding the patterns of accumulation of certain elements, and dispersion of others is important for predicting mineralization in coals formed in different blocks of the earth's crust. To these issues, scientists have already formulated theories that explain the anomalous concentrations of various components, the main sources of which are considered to be the rocks of the feeding area of the coal accumulation basin; volcanic-clastogenic inflow of pyroclastic material into the paleopeat bog; hydrothermal introduction of impurity elements into the paleopeat bog or coal seam; hydrological factor, etc [1].

Studying impurity elements, including rare earth elements (REE) in coals and clay interlayers, is

of scientific importance due to their static geochemical characteristics, and are studied indicators of the origination of coal [[2], [3], [4], [5]].

But at present, there is not yet sufficient geological information on accumulation and forms of REE occurrence, as well as the mechanisms of their concentration in the coals of Kazakhstan. The Shubarkol deposit is one of the objects, where, alongside a low ash content and a lower sulphur, which makes the coal of the deposit a valuable fuel, there are high contents of impurity elements that often reach industrial significance.

The relevance of the work is due to the need to determine the nature and accumulation of impurity elements in order to obtain comprehensive information necessary for the development of predictive criteria in the future.

In order to elucidate the ways of migration and the mechanism of concentration of impurity elements in the Shubarkol deposit coals, clay interlayers, and coals containing them were tried and explored in detail.

A comprehensive analysis of the geochemical and mineralogical characteristics of coals and their enclosing clay interlayers was carried out. A variety of geochemical criteria made it possible to establish the facts of the rare earth elements (REE) migration, and the latest data of mineralogy made it possible to establish the ways of their transportation to the paleobasin in the syn- and epigenetic periods of the Shubarkol deposit formation. The data of the paleoclimate and water composition of the paleobasin of peat formation is presented for the first time.

Experimental part

The basis for this work is the results of analyzing impurity elements of 49 coal samples and 71 samples of coal-bearing rocks of the Shubarkol deposit. The samples for studying were taken at the Western and Central sections of the Shubarkol deposit, in coal seams 2B, 1B1, 1B2, in sections 1-6 (sections 1 and 2 are located within the Western section, sections 3-6 within the Center section) (Figure 1). The sampling distance in the plots was within 30-35 m. The composite samples weighing 200 g were made using the basic samples. In entire, the group composition of 120 samples was explored.

The samples were studied by the instrumental neutron activation analysis (INAA) to determine the average contents of 28 elements in the nuclear geochemical laboratory of the Geoecology and Geochemistry Department at National Research Tomsk Polytechnic University (TPU) (analyst A.F. Sudyko). To determine the mineral composition of the samples of coal-bearing rocks and coals there was used X-ray powder diffractometry, and scanning electron microscopy.

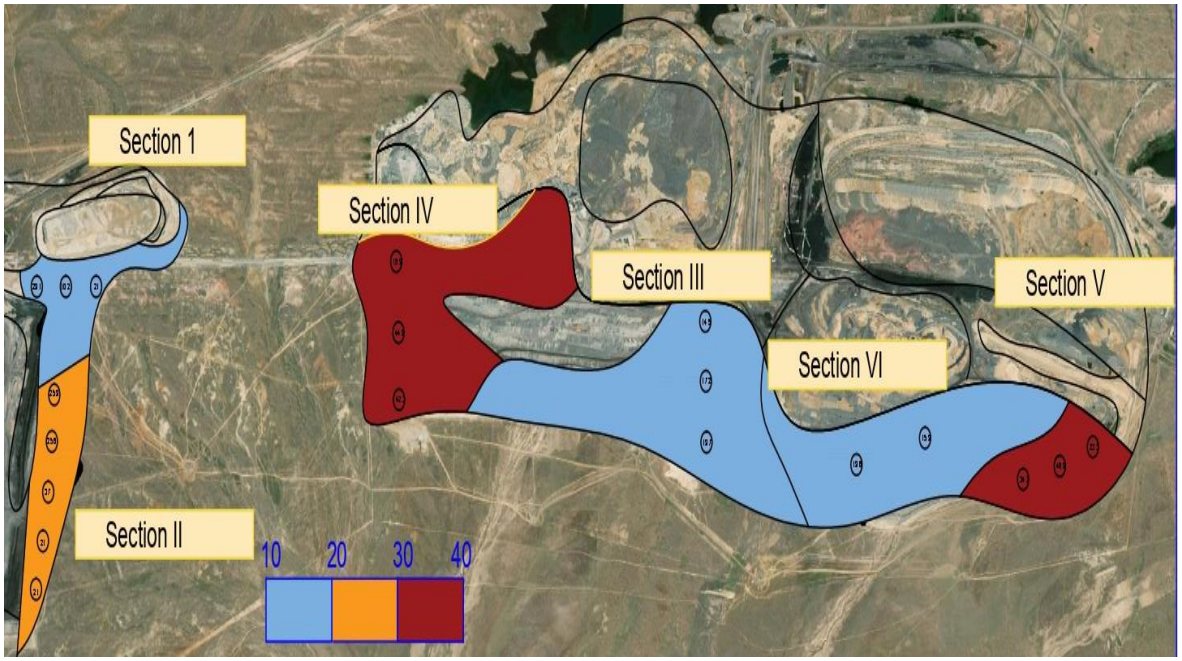

Figure 1 – Total REE distribution (La, Ce, Sm, Eu, Tb, Yb, Lu, Nd) in the Shubarkol deposit coals

Discussion of the results

Compared with the REE content in the UCC (upper part of the continental crust [6]), three types of enrichment are distinguished: L-type ($La_N/Lu_N>1$), M-type ($La_N/Sm_N<1$,) and H-type ($La_N/Lu_N<1$).

In this work, the La_N/Lu_N ratios of coal can be seen as ranging from 0.44 to 14 (Table 1), which indicates the characteristic predominance of light lanthanides over heavy lanthanides in the coals of the deposit.

The deposit-averaged value of the La/Yb ratio significantly exceeds a unit. REE in coals has low concentrations and is characterized by the distinct L-type enrichment, the formation of which is associated with the REE introduction into the coal accumulation basins, mainly in the composition of clay minerals and LREE-phosphates (Table 1).

Oxidized coal exhibits the H-type distribution of rare earth elements. The normalized La/Yb ratio in the roof coals: 13.8; 15.8; 5.8 - demonstrate a strong relationship between rare earth elements and inorganic matter, since high values of the La/Yb ratio reflect the contribution of the terrigenous (inorganic) component to the light rare earth elements accumulation, as evidenced by significant barium enrichment [7].

The results of the data obtained indicates the existence of a series of unrelated sources and different mechanisms of REE accumulation in the sediments of the Shubarkol deposit.

Table 1 – Geochemical parameters of rare earth elements in the samples of coal and clay interlayers of the Shubarkol deposit

Coal seam	Sample	∑REE	La_n/Lu_n	La_n/Yb_n	δEu	δCe	Enrichment type	Sample	∑REE	La_n/Yb_n	δEu	δCe
	In coals							In clay interlayers				
2B	6	11.14	10.95	13.84	0.8	0.3	L type	7	23.4	5.35	0.82	0.67
	10	9.27	14.05	15.80	0.6	0.3	L type	8	26.1	5.39	0.87	0.80
	41	11.11	1.20	1.34	1.2	0.7	L type	9	14.5	5.83	0.68	0.46
	50	17.01	4.38	5.39	0.9	0.5	L type	42	66.2	1.61	0.74	0.93
	59	19.81	4.68	5.84	0.8	0.5	L type	43	133.9	1.37	0.81	0.92
1B2	68	20.16	4.55	5.01	0.8	0.6	L type	69	40.5	4.18	0.74	1.06
	72	22.88	2.73	3.17	0.8	0.9	L type	70	40.5	4.13	0.76	0.99
	76	13.59	2.42	2.88	1.0	0.5	L type	71	48.7	1.98	0.85	1.17
	85	56.77	1.88	2.04	0.8	0.8	L type	83	48.8	6.42	0.77	0.83
	86	87.06	0.44	0.51	0.8	1.1	H type	88	55.8	5.80	0.80	0.79
	100	43.42	1.47	1.69	0.9	0.9	L type	89	40.0	4.76	0.84	0.91
	104	50.39	1.08	1.14	1.0	1.1	L type	91	38.3	4.83	0.89	0.93
	105	36.29	2.46	2.46	0.8	1.0	L type	92	49.4	4.67	0.73	0.77
	109	32.09	2.26	2.24	0.9	1.0	L type	93	38.2	3.91	0.75	1.01
1B1	115	14.21	4.11	4.75	0.9	0.7	L type	-	-	-	-	-
	116	17.98	6.13	6.88	0.8	0.6	L type	-	-	-	-	-
	117	12.03	8.18	9.87	1.0	0.5	L type	-	-	-	-	-
	118	18.00	4.23	4.68	0.9	0.5	L type	-	-	-	-	-
	119	17.87	5.61	6.08	0.8	0.7	L type	-	-	-	-	-
	120	15.47	5.88	6.45	0.8	0.7	L type	-	-	-	-	-

Note. Alternation of: ∑REY = La + Ce + Nd + Sm + Eu + Tb + Yb + Lu; $\delta Eu = Eu_N/Eu_N^* = Eu_N/[(Sm_N \times 0{,}67)+ (Tb_N \times 0{,}33)]$, $\delta Ce = Ce_N/Ce_N^* = Ce_N/[(La_N \times 0{,}67 + Nd_N \times 0{,}33)]$.

This can be explained by the strong enrichment of the peat deposit with terrigenous suspension within the period of transgression (of the reservoir) [8].

Granitoids could be a source of rare-earth. A certain contribution of acidic solutions enriched in rare earth elements is also assumed.

Enrichment of peat with piles of earth could occur during the acidic natural waters infiltration within the epigenetic period, as evidenced by a positive cerium anomaly. It is known that cerium migrates well in acidic waters and precipitates in an alkalized medium [9].

Table 1 also shows the appearance of a negative cerium anomaly in layers 2B and 1B1 (which fluctuate between 0.3-0.8), which is explained by the presence of authigenic minerals [7].

The Eu/Eu* value in clayey shales, silty mudstones, and mudstones is also an indicator of the composition of rock complexes eroded in paleowatersheds. In our case, the samples have moderate negative Eu anomalies (Eu/Eu*, the average value is 0.85-0.9), which indicates the predominance of Archean crystalline rocks or rocks formed by juvenile material that has not undergone significant transformation in the continental crust [10].

The authors revealed the principal regularities and features of the REE concentration in the Shubarkol deposit.

Based on Figure 2 and Table 1, it can be concluded that the elevated concentrations of all the REEs are characteristic of clay interlayers and oxidised coals. On this illustration, the La/Yb reciprocality escalations up the section, indicating a preponderantly clastogenic mechanism of REE supply to coals. This REE distribution is explained by the different sorption capacities of clay minerals.

The analysis of the lateral distribution of lanthanides in coals (Figure 3) showed that the contents clearly decreased from the periphery to the center of the deposit; this fact indicates a certain role of aqueous solutions in the accumulation of REE in coals [11]. A similar pattern of distribution is characteristic of carbonophilic elements.

The content of impurity elements in the coals of seams 2B, 1B2, and 1B1 of the Shubarkol deposit is shown in Table 2. The degree of enrichment with impurity elements of the Jurassic deposits of the Shubarkol deposit is estimated respectively compared with the clarke values for hard coals [12].

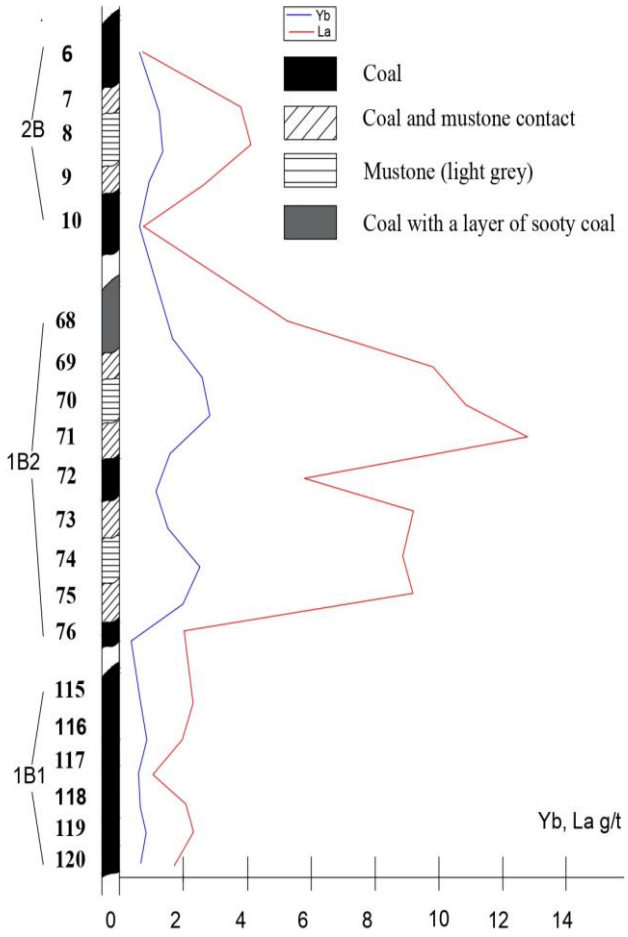

Figure 2 – La and Yb vertical distribution in the section of the Shubarkol deposit coal seams

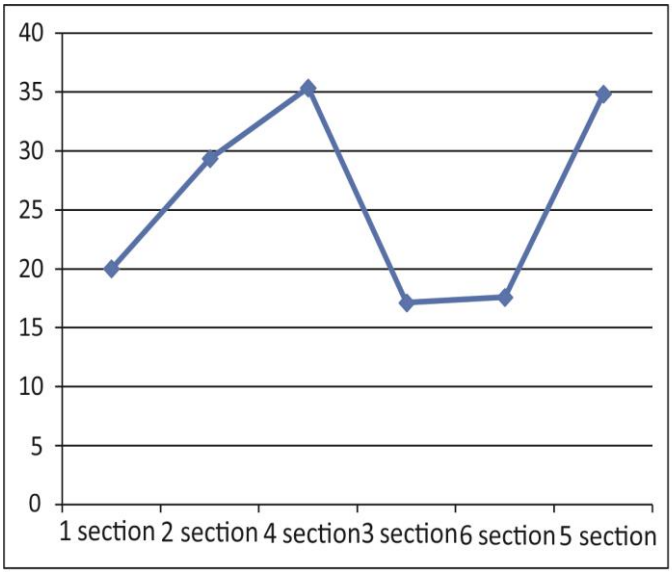

Figure 3 – Graph of lateral variability of rare earth elements from the 1st to the 6th sections of the Shubarkol deposit

The elements with the highest enrichment are Sr and Ba (ionic lithophiles) with the values of 10.1 and 21.7 (10<CC<100); slightly enriched are Th, Cr, As, Br, Rb, Zn, Ta (transit) (CC<0.5). The concentrations of other trace elements are close to the average values for global coals (0.5 < KK < 2) (Figure 4).

Apatite associations that can be obtained from bauxites on a weathered basement in the area of the sediment source have elevated contents of Sr and Ba. In addition, REE enrichment was found to be controlled by both groundwater and acidic hydrothermal fluids based on REE genetic types [13].

In this paper, the indicators of sensitive elements were studied for an attempt to reconstruct the paleoclimate.

The Sr/Ba ratio is one of the most widely used indicators for sedimentary rocks and coals [14], which indicates paleolonetzicity and paleoclimate, respectively.

Sr/Ba values > 1 and < 1 indicate, as a rule, arid and humid climatic conditions, respectively [14]. The values of this ratio in the studied area range from 0.3 to 2.4.

The formation of the Jurassic terrigenous system took place under essentially constant climatic and tectonic conditions, more precisely, the one changing within a very narrow framework. The climate, being generally humid, experienced some shift towards aridization at the very end of the system accumulation. This is evidenced by the Sr/Ba values, as well as the appearance of red-colored rocks and a slight increase in carbonate content [15].

Table 2 – Impurity elements content in the Shubarkol deposit coal samples

No.	Sm	Ce	Lu	U	Th	Cr	Yb	Hf	Ba	Sr	Nd	As	Ag	Br	Cs	Tb	Sc	Rb	Zn	Ta	Co	Eu	La	Sb
2B	1.2	8.7	0.1	0.4	0.6	6.0	0.7	0.2	29.1	39.0	3.9	0.9	0.4	0.7	0.2	0.2	4.1	0.8	7.4	0.0	8.3	0.3	1.9	0.3
1B2	3.4	39.7	0.1	1.0	1.3	5.1	0.7	0.9	3258.3	1010.9	21.2	1.1	0.4	0.8	0.7	0.4	7.1	2.9	8.7	0.0	2.4	0.9	20.6	0.2
1B1	0.8	5.9	0.1	0.2	0.1	1.8	0.7	0.1	7.1	39.0	3.0	0.9	0.4	1.5	0.0	0.3	2.9	3.0	5.7	0.0	10.1	0.2	1.1	0.2
W.C.	2.2	23	0.2	1.9	3.2	17	1	1.2	150.0	100	12	9	0.1	6	1.1	0.31	3.7	18	28	0.3	6.00	0.43	11	1

Note. W.C. – world coal, according to [12].

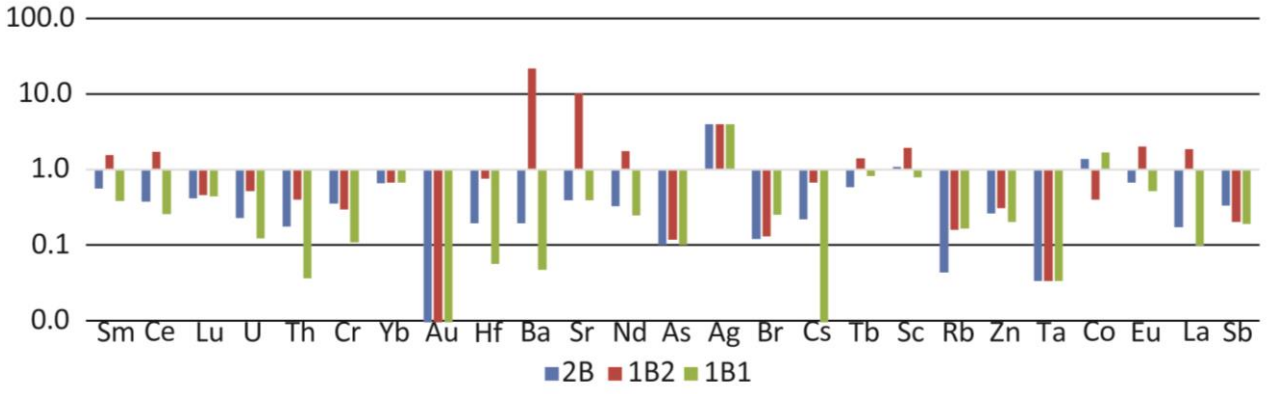

Figure 4 – Element concentration coefficients (CC) in coals that are normalized based on the average concentrations of microelements in hard world coals [12] and based on the classification of microelement enrichment

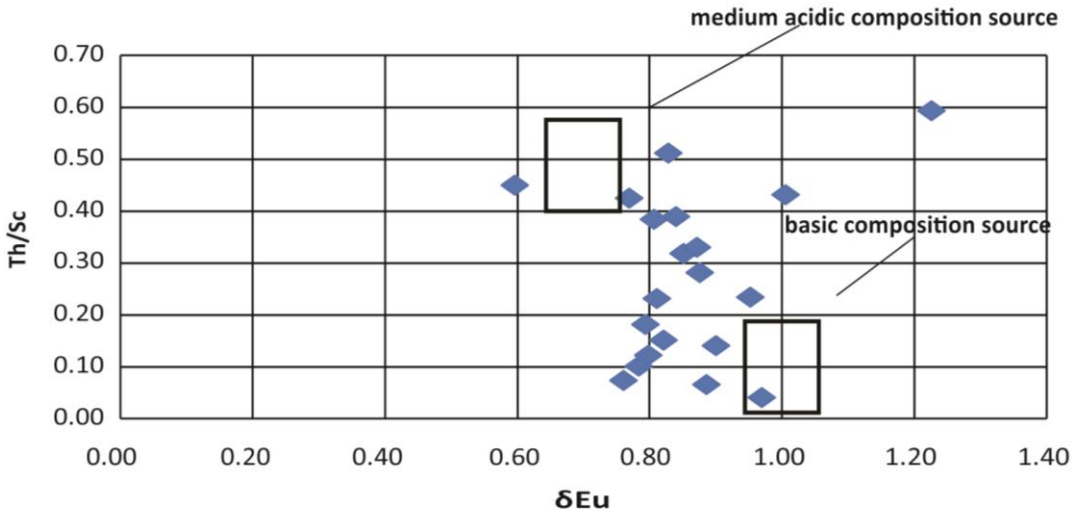

Figure 5 - The position of figurative points of the compositions on the discrimination diagram [17]

Based on the lithochemical features of clay shales, the climate was defined as arid-humid. The systematics of Sr, Ba, and Zr in clayey rocks according to the data of the reference [16] made it possible to establish that the sedimentation basin was freshwater.

The ratios of a number of indicator elements (Sc, Th, Eu) were also used to reconstruct the features of the composition of rocks in the feeding areas and a corresponding graph was built. The sources of rare earth elements for the studied rocks were both sufficiently mature rocks (presence of clay minerals in the initial sediments) and less altered petrogenic material of acidic composition (enrichment of the K-feldspar protolith). Elevated contents of Ba and Rb in the rocks are also indirect evidence of the presence of K-feldspar.

The diagram (Figure 5) used to determine the composition of rocks in the recharge areas shows that the sources of impurity elements for most of the studied samples were sedimentary formations enriched in quartz, as well as igneous rocks of medium acidic and basic composition.

Studying the REE occurrence forms plays an important role in obtaining data on the ways of their migration and concentration in coals and clay interlayers, and they are also significant geochemical indicators that make it possible to assess the nature of REE accumulation in coals, to consider the evolution of matter in the process of coalification and other epigenetic transformations.

According to the studies carried out, it was revealed that the mineral forms of finding rare, rare earth elements in coals and rocks had uneven distribution and differed in composition in the deposit. At the same time, many of the identified minerals were confined to areas of enrichment with organic matter: at the contact of enclosing rocks and coals, or in the coals themselves.

In coals, the bulk of the mineral matter is represented by kaolinite which contributes to the concentration of light REE. With kaolinite, the supply of REE within the peat stage in the composition of water and mineral nutrition should be associated.

Quartz predominates in the composition of petrogenic elements in coal seams in the studied area, which indicates that the source of the material can be mainly terrigenous fragments. Since most of the quartz in coal is terrigenous, it is transported by geological processes such as water or wind to peat bogs and stored in coal seams [18].

Based on the results of microscopic studies of the sample, there were found numerous inclusions of barite ($BaSO_4$) that had angular grains of irregular shape in the form of plates (Figure 6a), inclusions of sphalerite (Figure 6b) of a roundish shape on the microcrack of the sample, well-cut crystals of baddeleyite (Figure 6c) and zircon (Figure 6d).

Fragments of zircon crystals, as well as prismatic crystals, were found in the rocks. Individual zircon grains are irregularly shaped; they look either as rounded intergrown crystals or as neoformations. Baddeleyite is rarer than zircon. The shape of the grains is similar to zircon: prismatic, or grains of irregular shape.

The forms of occurrence of rare earth elements in coals in the form of aggregates of lamellar, foliar, columnar crystals, and fragments of prismatic crystals suggest the authigenic nature of their formation.

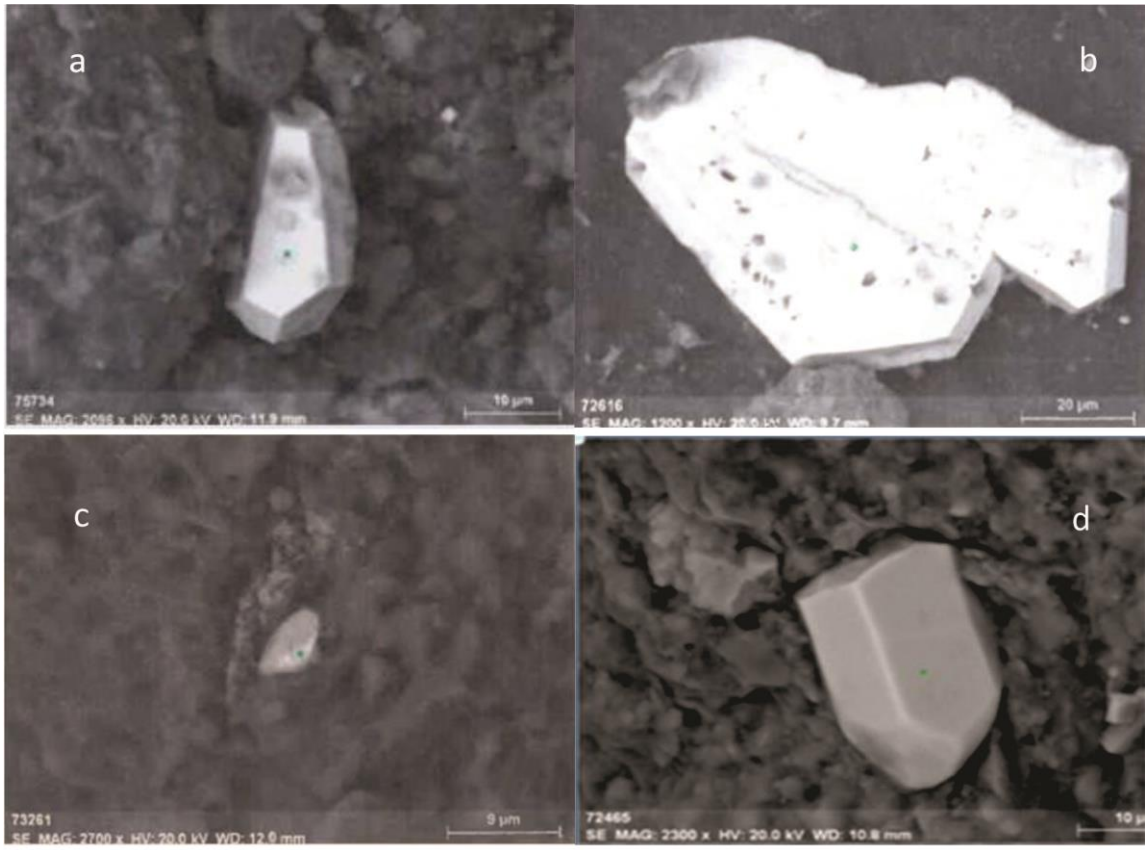

Figure 6 – Barite (a), sphalerite (b), baddeleyite (c), and zircon (d) crystals

Rare earth minerals in rocks are often found in or near organic matter. These minerals are less common in mudstone samples. Oxides form needle-shaped crystals, their aggregates, plates, and grains of irregular shape. This is turn points to various ways of REE migration into coals and coal-bearing rocks of the deposit.

Determining the degree of roundness of detrital grains is important when assessing the porosity and permeability of rocks since increasing the roundness of fragments (in cases of low cement content) contributes to the formation of pores with smooth walls, which in turn facilitates the migration of hydrocarbons. The very fact of roundness indicates that the mineral samples were redeposited, but the range of transfer judging by the poor processing, is small, or such a character indicates that the material was not transported by water flows.

The impurity element migration occurred with capturing denudation plains, stable processes of peat accumulation, and localization of useful components in watercourses adjacent to the plains [19].

Coal swamps/basins are generally low-energy environments not subject to heavy input of clastic materials.

Periodic cycles of geological transgression/regression (cyclic rise/fall of sea level relative to land) can introduce clastic materials into the basin between the coal layers. Finally, diapiric emplacement (upward movement of igneous material through the rock underlying the basin) can introduce REE materials into the region of the basin, where bound hydrothermal fluids can mobilize REE until they find a suitable receptor material such as kaolinite [20].

The weathering of rocks in the conditions of the warm humid Jurassic climate in the territory of Central Kazakhstan also entailed the movement of elements into the dissolved state and their transfer into water solutions. Carbonate rocks in the frame structures led to the organization of alkaline and subalkaline carbonate and hydrocarbonate waters.

Conclusions

The analysis of the obtained complex geochemical and mineralogical data made it possible to identify various ways of REE migration into coals and clay interlayers within the syngenetic and epigenetic periods of the Shubarkol deposit formation. It was established that peat accumulation occurred under essentially constant climatic and tectonic conditions, the climate was generally humid, experienced some shift towards aridization at the very end of formation accumulation, and the sedimentation basin was freshwater.

It was revealed that the impurity element migration occurred on denudation plains and in watercourses associated with plains in stable processes of peat accumulation. Clastogenic transportation took place by alkaline and sub-alkaline carbonate and hydrocarbonate waters from nearby rocks of the framing: sedimentary rocks enriched in quartz, terrigenous rocks, the initial ones that were basic, medium-acid igneous rocks, including granitoid. The addition also occurred with clay minerals.

Conflict of interests

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

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Шұбаркөл кен орнының көміріне сирек жер элементтерінің миграциясы және тасымалдану жолдары

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Мақала келді: *16 мамыр 2022*
Сараптамадан өтті: *30 маусым 2022*
Қабылданды: *12 шілде 2022*

ТҮЙІНДЕМЕ

Мақалада Шұбаркөл кен орнының көмір және саз аралық қабаттарының минералогиялық және геохимиялық ерекшеліктерін зерттеу нәтижелері берілген. Сазды қабаттардың 71 үлгісі және көмірдің 49 үлгісі аспаптық нейтронды белсендіру талдауы (INAA), ұнтақ рентгендік дифрактометрия және сканерлеуші электронды микроскопия арқылы талданды. Көмірлердің геохимиялық және минералогиялық сипаттамаларына және оларды қоршайтын саз аралық қабаттарына кешенді талдау жүргізілді. Әртүрлі геохимиялық критерийлер СЖЭ-нің көші-қоны туралы фактілерді анықтауға мүмкіндік берді, ал минералогияның соңғы деректері Шұбаркөл кен орнының қалыптасуының син- және эпигенетикалық кезеңдерінде олардың палеобассейнге тасымалдану жолдарын анықтауға мүмкіндік берді. Торфтың түзілу палеобассейннің палеоклиматы мен су құрамы туралы мәліметтер алғаш рет берілген. Сонымен қатар, талдау Шұбаркөл кен орнының шөгінділерінде сирек жер элементтерінің жинақталуының бірқатар тәуелсіз көздері мен әртүрлі механизмдерін анықтауға мүмкіндік берді. Жеңіл лантанидтердің ауыр лантанидтерден басым болуымен ерекшеленетін сирек жер элементтерінің (СЖЭ) таралуының негізгі заңдылықтары белгіленді, көмір кен орындарын қоршап тұрған тау жыныстарының СЖЭ шоғырлануындағы рөлі мен құрамы қарастырылды. Көмірлер мен саз аралық қабаттарда сирек және сирек жер элементтерінің микробөлшектерінің қосындылары бар алюмосиликаттар, сульфидтер және сульфаттар табылды.

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Пути миграции и транспортировки РЗЭ в угли месторождения Шубарколь

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АННОТАЦИЯ

В статье представлены результаты исследования минералого-геохимических особенностей углей и глинистых прослоев месторождения Шубарколь. Проанализированы 71 проба глинистых прослоев и 49 проб угля методами инструментального нейтронно-активационного анализа (ИНАА), порошковой рентгеновской дифрактометрии, а также сканирующей электронной микроскопии. Проведен комплексный анализ геохимических и минералогических характеристик углей и вмещающих их глинистых прослоев. Разнообразные геохимические критерии позволили установить факты о миграции РЗЭ, а приведенные новейшие данные о минералогии позволили установить пути их транспортировки в палеобассейн в син- и эпигенетические периоды формирования месторождения Шубарколь. Впервые приведены данные о палеоклимате и водном составе палеобассейна торфообразования. В том числе проведенный анализ помог определить ряд независимых источников и различных механизмов накопления РЗЭ в отложениях месторождения Шубарколь. Установлены основные закономерности распределения редкоземельных элементов (РЗЭ), которые выражены в преобладании легких лантаноидов над тяжелыми, рассмотрена роль и вывлен состав пород обрамления угольных залежей в концентрации РЗЭ. Обнаружены алюмосиликаты, сульфиды и сульфаты с включениями микрочастиц редких и редкоземельных элементов РЗЭ в углях и глинистых прослоях.

***Ключевые слова*:** уголь, Шубарколь, редкоземельные элементы, минералогия, геохимия.

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Metallurgy

Flotation processing of copper-containing technogenic raw materials using a composite flotation reagent

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ABSTRACT

The article presents the results of laboratory research on the possibility of flotation processing of copper-containing technogenic raw materials. Studies were performed using a sample of copper-containing tailings obtained after the processing of copper ore from the Kazakhstan deposit and a composite flotation reagent. The application of a combination of various collectors allows for raising technological indicators of flotation. The purpose of the research is the increase extraction of copper at flotation of copper-containing technogenic raw materials with the application of a composite reagent. The studied sample of tailings contains 0.23% of copper. A mixture of sodium butyl xanthate and thionocarbamate in the ratio of 1:1 was used as a composite flotation reagent. Parameters of flotation of copper-containing tailings were worked out: degree of regrinding, charges of sodium butyl xanthate, blowing agent T-92, and a composite reagent. Composite flotation reagent was fed into the flotation process of copper-containing tailings in the form of emulsion produced in a T 18 digital ULTRA-TURRAX dispersant. The optimal emulsification time of the composite flotation reagent was 1 min. Without emulsification in the composite reagent the percentage of particles smaller than 1.192 µm is 55.047%. After emulsification of the composite reagent for 1 minute, the percentage of particles smaller than 1.192 µm is 91.134%. In optimum basic mode the rough copper concentrate with a copper content of 4.2% was obtained with the extraction of 61.56%. With the use of a composite reagent, a blister copper concentrate with a copper content of 4.5% and a recovery of 66.54% was obtained. Extraction of copper increases by 4,98%.

Keywords: copper-containing tails, flotation, flotation agent, emulsion, concentrate, recovery.

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Introduction

Technogenic wastes from mining and processing plants, metallurgical plants, oil refineries, and enterprises to process the natural minerals contain millions of tons of valuable metals in sufficiently high concentrations suitable for their highly profitable processing and use as secondary raw materials.

Due to the depletion of the mineral resource base, it is necessary to develop new and optimize existing methods of extraction of valuable components from ore materials [[1], [2], [3], [4]]. In recent years the task of localization and

neutralization of technogenic and natural-technogenic objects especially saturated with harmful substances (mercury, radionuclides, oil products, flotation reagents, etc.) has become extremely acute. Such objects include tailing dumps, sludge storages and waste dumps. Anthropogenic formations may serve and have served as sources of raw materials for the industry. Being an important reserve for replenishing the volume of mineral raw materials, technogenic deposits or formations have a very aggressive impact on the natural environment. Therefore, the interest in their processing is caused not only by commercial calculations but also by increased environmental requirements [[5], [6], [7], [8]]. The concentration of technogenic formations in areas with a developed infrastructure and communication network in the absence of the need for stripping works serves as an additional factor in reducing the energy and material charges of mining. It is necessary to develop highly efficient, fast-payback technological schemes for complex processing, ensuring the creation of low-waste and non-waste production, the implementation of which will significantly expand the mineral resource base without disturbing the subsoil and land [[9], [10], [11], [12]].

Enrichment wastes are generated in the processes of the same name, which are usually intermediate between mining technologies and their deep physical and chemical processing. A significant part of them, about 80 percent, is used for backfilling of mines and quarries as part of the execution of industrial mining technologies. The rest part of them, also considerable, is accumulated in the tailing dumps of beneficiation plants.

The main difficulties are related to the processing of the slurry part of the tailings, which is to a great extent enriched with non-ferrous, rare and precious metals [[13], [14], [15], [16], [17]].

In this regard, the use of modern approaches, new flotation reagents and modernized equipment for the beneficiation of technogenic raw materials is important in creating promising innovative technologies [[18], [19], [20], [21]].

The purpose of the research presented in this article is to increase copper recovery during flotation of copper-containing technogenic raw materials with the use of a composite reagent/

Experimental part

Researches on studying the possibility of flotation processing of copper-containing technogenic raw materials with application of a composite reagent were performed.

Researches were performed with use of the sample of copper-containing tailings received after processing the copper ore of the Kazakhstan deposit and a composite flotation reagent representing a mix of sodium butyl xanthate and thionocarbamate (non-ionogenic collector with thioamide group).

In the process of conducting research, various methods were used using modern technological and analytical equipment such as mineralogical and dispersion analysis, X-ray phase, X-ray fluorescence, electron-probe, particle size analysis, chemical analysis, flotation.

For analysis, a Venus 200 PANalyical B.V. spectrometer, a D8 ADVANCE X-ray diffractometer, and a JEOL JXA-8230 scanning electron microscope were used. Chemical analysis was performed using an Optima 2000 DV optical emission spectrometer.

The initial tailings were regrind in a ball mill 40ML-000PS (40МЛ-000ПС) to perform the studies. Flotation was carried out on laboratory flotation machines in open and closed cycles. The sample weight for flotation was 0.5 kg. The scheme of flotation included regrinding, rougher floatation, control and three retreatment operations of the rough copper concentrate.

Sodium sulfide was fed into the regrinding process to sulfidize oxidized minerals. The rougher floatation was performed for 15 min, the control flotation for 10 min, and the refining operations for 6-8 min. In the basic mode the following reagents were used as a collector - sodium butyl xanthate; foaming agent - T-92.

Total consumption of basic reagents: sodium sulfide (sulfideizer) - 400 g/t; sodium butyl xanthate (collector) - 240 g/t; T-92 (blowing agent) - 120 g/t. Sodium sulfide was fed into the grinding process in a ball mill. Sodium butyl xanthate and T-92 were fed into the flotation operation. The reclamation operations were performed without addition of reagents.

In flotation of tailings using the composite flotation reagent it was fed to the rougher and control flotations instead of the basic collector sodium butyl xanthate. Composite flotation reagent was a mixture of sodium butyl xanthate and thionocarbamate in the ratio 1:1. Before flotation the composite flotation reagent for reception of a microemulsion was passed through the disperser T 18 digital ULTRA-TURRAX. The optimum particle size of microemulsion for flotation of tailings was

selected. The particle size was determined on a laser particle analyzer Winner2000E.

After regrinding in a ball mill in the presence of sodium sulfide, the mineral slurry was placed in the chamber of the flotation machine. Then sodium butyl xanthate (or composite flotation reagent) and foaming agent T-92 were added to the flotation machine. The mineral slurry was stirred for 0.5 minutes without air supply at a rotor speed of 1,300 rpm. After atmospheric air supply (3.5 dm^3/min) pulp flotation was performed according to the scheme of tailings processing. Foam product of the rougher floatation was subjected to three refinements with receiving the draft copper-containing concentrate.

Discussion of results

The use of a mixture of various flotation reagents makes it possible to increase the technological parameters of flotation. Combination of reagents, their dispersion and optimization of composition (increase or reduction of length of a hydrocarbon radical and its branching, introduction of an additional component) leads to improvement of foaming, collecting and other properties of used flotation reagents [[9], [10], [11], [12], [13]].

In the present work efficiency of application of sodium butyl xanthate and thionocarbamate composition for flotation processing of copper-containing technogenic raw materials is shown. The combination of these reagents will not only improve the quality of the resulting concentrates due to the action of thionocarbamate, but also increase the recovery of copper by improving the flotation of slurry particles of sulfide minerals.

Mineralogical analysis of the initial tailings showed that copper minerals are represented mainly by chalcopyrite; secondary sulfides and copper oxides account for about 15%. Tailings contain about 20% of zinc oxide compounds. The main amount of sulfides is open, about 15-20% of copper and zinc minerals are present in the form of intergrowths with pyrite and rock-forming minerals. The surface of the sulfides is partially oxidized and covered with iron oxide films.

The X-ray phase analysis has shown that the main part of the initial sample of copper-containing tailings of the beneficiation plant is represented by rock-forming minerals, such as quartz (72.2%), illite (11.2%), clinoferrosilite (5.9%), albite (4.3%), muscovite (3.2%), microcline (1.9%), clinochlor (1.3%) (Table 1).

Table 1 - Results of X-ray phase analysis of the initial sample of copper-containing tailings

Compound Name, Formula	S-Q
Quartz, syn, SiO_2	72.2
Illite, $KAl_2Si_3AlO_{10}(OH)_2$	11.2
Clinoferrosilite, syn, $Fe(SiO_3)$	5.9
Albite, low, $Na(AlSi_3O_8)$	4.3
Muscovite-2M1, $KAl_2(Si,Al)_4O_{10}(OH)_2$	3.2
Microcline, intermediate, $KAlSi_3O_8$	1.9
Clinochlore (IIb-4), $Mg_{4.882}Fe_{0.22}Al_{1.881}Si_{2.96}O_{10}(OH)_8$	1.3

According to the results of chemical analysis, the analyzed sample of tailings contains 0.23% copper. The results of X-ray fluorescence analysis are presented in the table 2.

Table 2 - Results of X-ray fluorescence analysis of the initial sample of copper-containing tailings

Item name	Contents,%
O	51.468
Na	0.412
Mg	0.650
Al	6.621
Si	27.020
P	0.046
S	0.137
Cl	0.012
к	1.146
Ca	2.810
Ti	0.393
V	0.006
Cr	0.020
Mn	0.050
Fe	4.473
Cu	0.230
Zn	0.215
As	0.016
Rb	0.006
Sr	0.012
Zr	0.010
Mo	0.007
Pb	0.071

According to the results of X-ray fluorescence analysis in the initial sample of copper-containing tailings of the beneficiation plant, the content of copper is 0.23%, molybdenum 0.007%. The main mass is composed of silicon - 27.02%, oxygen - 51.468%, aluminum - 6.621%, iron - 4.473%, calcium - 2.81% etc.

A sample of the original tailings was analyzed on a JXA-8230 electron probe microanalyzer (Figure 1).

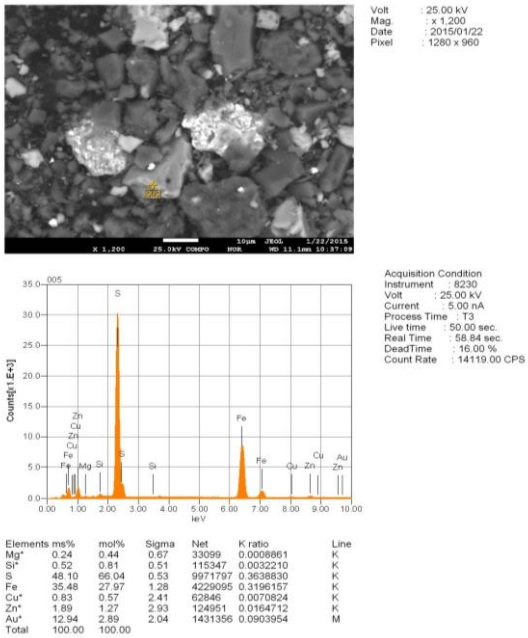

Figure 1 - Analysis of initial copper-containing tailings on electron-probe microanalyzer JXA-8230 by JEOL (chalcopyrite)

As a result of studies on a microanalyzer, it was shown that copper is presented mainly in the form of chalcopyrite and its content is less than one percent. They are most often found as inclusions in non-metallic minerals.

The grain-size composition of copper-containing tailings with distribution of copper by grain-size classes using sieve method was determined. The results are given in table 3. The results of the grain-size analysis showed that 68.94% of copper is in the class larger than 0.071 mm. This shows that it is necessary to include a regrinding operation into the scheme of tailings processing.

Table 3 - Grain size composition and grain-size classes distribution of copper in source copper-containing tailings

Grain-size class, µm	Yield %	Cu Content,%	Cu extraction,%
+0.4	6.96	0.23	7.38
-0.4+ 0.2	29.93	0.21	29.62
-0.2 + 0.1	30.33	0.19	26.90
-0.1 + 0.071	8.3	0.13	5.04
-0.071+ 0.05	6.88	0.20	6.44
-0.05+ 0	17.58	0.30	24.62
Initial Tails	100.0	0.21	100.0

Dispersion analysis of the initial sample of tailings was carried out on the FSH-6K photometric sedimentometer, the results of which are shown in Figure 2.

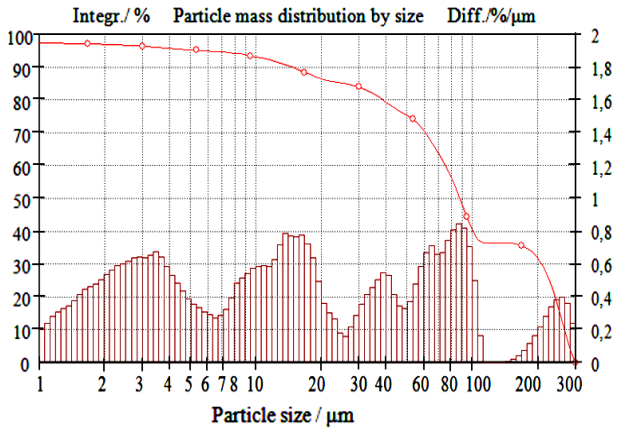

Figure 2- Dispersion analysis of initial copper-containing ore tailings on FSKh-6K

The dispersion analysis results show that in the initial sample of tailings the grain-size classes in the area of 70-80 µm make up 40-45%, the fine grain classes of 3-5 µm make up 30-35%. Up to 20-25% are the grain-size classes of 100-300 µm.

Thus, the results of mineralogical, granulometric, chemical and phase analyses of copper-containing tailings of the beneficiation plant indicate that part of the valuable components is concentrated in coarse grain classes and is in the form of aggregates. The regrinding process in the technological scheme of tailings processing shall be included to open such aggregates.

The initial coarseness of the flotation tailings of the beneficiation plant by the class -0.071 mm was 31%. Studies to determine the optimal degree of regrinding of the initial tailings lot were performed. Regrinding of initial tailings in a ball mill 40МЛ-000ПС was performed from 10 to 30 minutes, which corresponded to the degree of grinding 66.04-96.82% of class -0.071 mm.

It is shown that the best results were achieved when tails were regrind up to 95% of class -0.074 mm (table 4).

A rough copper-containing concentrate containing 2.60% of copper with the extraction of 30.05% was obtained without regrinding. At the optimum degree of regrinding of 95% of class -0.071 mm a copper-containing concentrate containing 3.23% of copper was obtained with the extraction of 48.75%.

The research results show that regrinding of copper-containing flotation tailings of the

beneficiation plant allows to increase in the extraction degree of copper in the rough copper concentrate by 18.7%.

Table 4 – Results of flotation of copper-containing tailings using regrind

Product name	Yield %	Cu content,%	Cu extraction, %
Without regrind			
Rough Cu conc.	2.46	2.60	30.05
Intermediate product 1	3.14	0.37	5.44
Intermediate product 2	1.2	0.71	4.00
Intermediate product 3	0.66	0.88	2.72
Cont. fl. conc.	2.38	0.59	6.60
Final tails	90.16	0.12	51.19
Initial Tails	100.0	0.21	100.0
With regrind			
Rough Cu conc.	3.10	3.23	48.75
Intermediate product 1	4.34	0.20	4.26
Intermediate product 2	2.24	0.33	3.57
Intermediate product 3	1.14	0.48	2.65
Cont. fl. conc.	2.52	0.37	4.54
Final tails	86.66	0.08	36.23
Initial Tails	100.0	0.21	100.0

For the flotation process, the optimal costs of sodium butyl xanthate, foaming agent T-92, and composite reagent were selected.

Optimal flotation conditions in the basic mode with the use of sodium butyl xanthate as collector are: regrinding of tailings to 95% of class -0.071 mm, Na_2S - 400 g/t; charge of butyl xanthate in the rougher floatation is 160 g/t, T-92 is 80 g/t; charge of butyl xanthate in the control flotation is 80 g/t; T-92 is 40 g/t. In optimum basic mode in an open cycle the rough copper concentrate with copper content of 4,03% at extraction 51,9%.

The reagent mode of flotation of copper-containing tailings using a composite reagent which is a mixture of sodium butyl xanthate and thionocarbamate in the ratio of 1:1 was proccessed.

The composite flotation reagent was fed into the process of flotation of copper-containing tailings in the form of an emulsion generated in a T 18 digital ULTRA-TURRAX dispersant. The consumption rate of the composite reagent in the rougher copper flotation was 120 g/t, in the control flotation - 60 g/t. Optimal time of emulsification of composite flotation reagent was 1 minute.

Composite reagent without emulsification and after emulsification studied on a laser particle size analyzer Winner2000E (Figure 3-4).

The results showed that without emulsification in the composite reagent the percentage of particles smaller than 1.192 µm is 55.047% (Figure 3). After emulsification of the composite reagent for 1 minute, the percentage of particles smaller than 1.192 µm is 91.134% (Figure 4).

The study of the particle distribution of the proposed flotation reagent on a Winner2000E laser particle size analyzer shows the need to obtain a reagent in the form of an emulsion for its more effective action during flotation. The flotation agent emulsion enhances the hydrophobization of fine copper mineral particles, contributing to an increase in flotation performance.

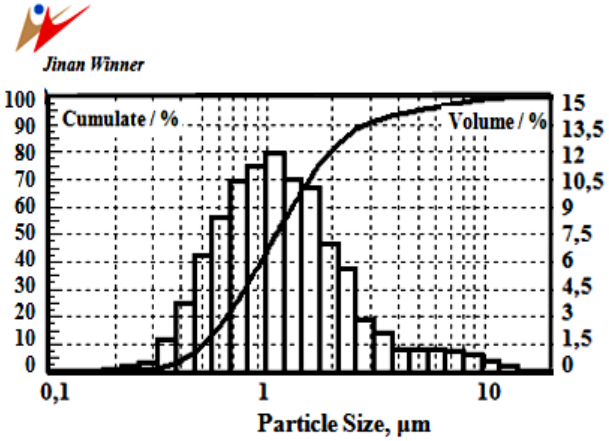

Figure 3 - Composite reagent particle distribution obtained on the Winner 2000E without emulsification

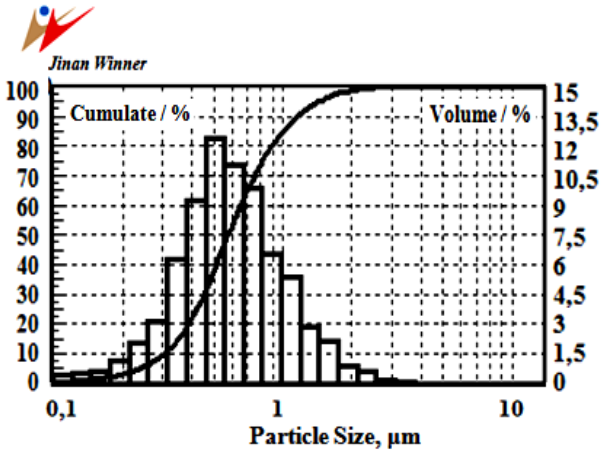

Figure 4 - Distribution of composite reagent particles obtained on Winner 2000E after emulsification

Studies on the processing of copper-containing technogenic raw materials using the proposed composite flotation reagent were carried out in comparison with basic flotation reagents.

According to the basic mode with application of sodium butyl xanthate, the rough copper concentrate with copper content 4.2% with copper extraction of 61.56% was obtained. Rough copper concentrate with copper content of 4.5% and extraction of 66.54% was obtained using a composite reagent. Extraction of copper increases by 4,98%.

The dispersion analysis of flotation tails of the basic mode and the optimal mode of flotation with the dispersed microemulsion of composite flotation reagent was conducted in order to establish the dependence of the degree of dispersion of the emulsion of composite flotation reagent on the extraction degree of slime particles of copper-bearing minerals. Results of dispersion analysis are given in the table 5.

Table 5 – Results of dispersion analysis of flotation tailings of basic mode and with dispersed emulsion of composite reagent

Product name	Yield %	Cu contents, %	Cu distributio n,%
Flotation tailings in basic mode			
-0.071+0.050	24.55	0.084	27.07
-0.050+0.030	17.9	0.060	14.10
-0.030+0.020	12.85	0.052	8.77
-0.020+0.010	26.9	0.067	23.66
-0.010+0	17.8	0.113	26.40
Initial Tails	100.0	0.076	100.0
Flotation tailings with a composite reagent			
-0.071+0.050	28.95	0.083	33.29
-0.050+0.030	19.45	0.058	15.63
-0.030+0.020	10.25	0.031	4.40
-0.020+0.010	26.45	0.062	22.72
-0.010+0	14.9	0.116	23.95
Initial Tails	100.0	0.072	100.0

The dispersion analysis of flotation tails showed that the use of dispersed emulsion of composite reagent allows to increase the extraction degree of slam particles of copper-containing minerals in the rough copper concentrate. The flotation tailings received in the basic mode contain 58.83% of copper in the grain-size classes less than 30 μm. The flotation tailings received with the use of the composite reagent contain 51,07% of copper in the grain-size classes less than 30 μm. The content of copper in sludge classes (less than 30 μm) in the final flotation tailings is reduced by 7.76% when using a composite flotation reagent.

Thus, results of researches show perspectivity of application of a composite reagent to process the copper-containing technogenic raw materials.

Conclusions

The influence of the composite flotation reagent on flotation of copper-containing technogenic raw materials was studied. As object of researches the sample of mature tailings of flotation of one of Kazakhstan beneficiation plants with the contents of copper 0.23% was taken.

Composite reagent is a mixture of sodium butyl xanthate and thionocarbamate in a ratio of 1:1. Composite reagent in the process of flotation was fed in the form of dispersed microemulsion. Optimal dispersion time of the composite flotation reagent was 1 min.

Microemulsion of a composite flotation reagent allows to strengthen hydrophobization of slurry particles of copper minerals, thereby to improve their flotation and to increase technological parameters of flotation.

The percentage of particles with a size less than 1.192 μm in the emulsion is 91.134% at optimum dispersion time as defined on the laser particle size analyzer Winner2000E.

In optimum basic mode in a closed cycle rough copper concentrate with copper content of 4.2% was received at extraction of 61.56%. Rough copper concentrate with copper content of 4.5% and extraction of 66.54% was obtained with application of composite reagent. Extraction of copper increases by 4.98%.

Dispersion analysis of flotation tailings showed that the use of dispersed emulsion of composite reagent allows to increase the extraction degree of slime particles of copper-containing minerals in the rough copper concentrate.

The results of the research can be used at beneficiation plants in the development of flotation technology to process the thin-rocked technogenic waste using microemulsion of flotation reagents.

Conflict of interest

The corresponding author, on behalf of the authors of this study, declares that there is no conflict of interest.

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Комбинирленген флотореагентті қолдана отырып, мысқұрамды техногендік шикізатты флотациялық өңдеу

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ТҮЙІНДЕМЕ

Мақалада мысқұрамды техногендік шикізатты флотациялық өңдеу мүмкіндігі бойынша зертханалық зерттеулердің нәтижелері ұсынылған. Зерттеулер Қазақстан кенорнындағы мыс кенін өңдеуде алынған мысқұрамды қалдықтардың сынамасын және композиттік флотациялық реагентті қолдану арқылы жүргізілді. Әр түрлі жинағыштардың қоспасын қолдану флотацияның технологиялық көрсеткіштерін жақсартуға мүмкіндік береді. Зерттеудің мақсаты комбинирленген реагентті қолдана отырып, мысқұрамды техногендік шикізатты флотациялауда мыстың бөліп алу дәрежесін арттыру болып табылады. Зерттелетін қалдықтардың сынамасында мыстың үлесі 0,23% құрайды. Комбинирленген флотореагент ретінде 1:1 қатынасында натрий бутил ксантогенаты мен тионокарбамат қоспасы қолданылды. Мысқұрамды қалдықтарды флотациялау параметрлері анықталды: қайта ұсақтау дәрежесі, натрий бутил ксантогенатының, Т-92 көбіктендіргіштің, комбинирленген реагенттің шығындары. Комбинирленген флотациялық реагент мыс қалдықтарын флотациялау процесіне эмульсия түрінде жіберілді, эмульсия Т 18 сандық ULTRA-TURRAX диспергаторында алынған. Комбинирленген флотореагентті эмульсиялаудың оңтайлы уақыты 1 минутты құрады. Эмульсияға айналмағанда, комбинирленген реагентте 1,192 мкм-ден кем бөлшектердің пайыздық мөлшері 55,047 % құрайды. Комбинирленген реагентті 1 минут эмульгирлеуден кейін 1,192 мкм-ден кем бөлшектердің пайыздық мөлшері 91,134% құрайды. Оңтайлы базалық режимде өрескел мыс концентраты алынды, ондағы мыстың үлесі 4,2%, бөліп алу дәрежесі 61,56 % құрайды.Комбинирленген реагентті қолдану барысында мыстың үлесі 4,5 %, бөліп алу дәрежесі 66,54 % құрайтын өрескел мыс концентраты алынды. Мыстың бөліп алу дәрежесі 4,98 % - ға артады.

Түйін сөздер: мысқұрамды қалдықтар, флотация, флотациялық реагент, эмульсия, концентрат, бөліп алу.

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Флотационная переработка медьсодержащего техногенного сырья с применением композиционного флотореагента

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АННОТАЦИЯ

В статье представлены результаты лабораторных исследований по возможности флотационной переработки медьсодержащего техногенного сырья. Исследования проведены с использованием пробы медьсодержащих хвостов, полученных после переработки медной руды казахстанского месторождения, и композиционного флотационного реагента. Прменение сочетания различных собирателей позволяет повысить технологические показатели флотации. Целью исследований является повышение извлечения меди при флотации медьсодержащего техногенного сырья с применением композиционного реагента. В исследуемой пробе хвостов содержится 0,23 % меди. В качестве композиционного флотореагента применена смесь бутилового ксантогената натрия и тионокарбамата в соотношении 1:1. Отработаны параметры флотации медьсодержащих хвостов: степень доизмельчения, расходы бутилового ксантогената натрия, пенообразователя Т-92, композиционного реагента. Композиционный флотореагент подавался в процесс флотации медьсодержащих хвостов в виде эмульсии, полученной в диспергаторе T 18 digital ULTRA-TURRAX. Оптимальное время эмульгирования композицинного флотореагента составило 1 мин. Без эмульгации в композиционном реагенте процентное содержание частиц крупностью менее 1,192 мкм составляет 55,047 %. После эмульгации композиционного реагента в течение 1 минуты процентное содержание частиц крупностью менее 1,192 мкм составляет 91,134 %. В оптимальном базовом режиме получен черновой медный концентрат с содержанием меди 4,2 % при извлечении 61,56 %. С применением композиционного реагента получен черновой медный концентрат с содержанием меди 4,5 % при извлечении 66,54 %. Извлечение меди повышается на 4,98 %.

Ключевые слова: медьсодержащие хвосты, флотация, флотореагент, эмульсия, концентрат, извлечение.

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Metallurgy

Testing of the optimum extragent for solvent-extraction of Almaly deposit copper

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ABSTRACT

For the solvent extraction of copper from pregnant leach solutions, (PLS) a wide range of modern extractants is currently offered on the market, and its choice is a very important issue in the production of copper using the SX-EW (Solvent Extraction and Electrowinning) technology. The purpose of this work was to determine the optimal copper extractant for processing productive solutions of the Almaly deposit using the SX-EW. The studies were carried out with a productive solution obtained by leaching copper ores from the Almaly deposit of composition, g/dm3: 1) Cu–0.262, Fe–17.97, SiO2–0.36. The results of copper extraction from model solutions showed that the maximum extraction of copper (94%) is observed when using the extractant 5% Acorga 5640, while the other extractants did not provide a high degree of extraction of 10% Lix984 - 93%; 10% Acorga 5640 - 91%; 10% Acorga 5910 and 10% Acorga 5747 - 85% each. According to the results of the retraction process, a high degree of copper extraction from the organic phase (90.2 and more) was ensured when using extractants of 5% Acorga 5640, 10% Lix984, and 10% Acorga 5640, the minimum - at 10% Acorga 5910 (88.2%). For the extraction of copper from the productive solution of the Almaly deposit 5% Acorga 5640 was chosen as the optimal extractant.

Keywords: copper, SX-EW technology, Acorga 5640, extraction, selectivity.

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Introduction

In recent years, in the production of copper from poor refractory oxidized and transit copper ores, dumps and tailings of concentrating plants, the SX-EW technology, which consists of the stages of leaching, extraction and stripping, and electrowinning, has been increasingly used. The share of copper produced using SX-EW technology in the world has already reached 30% of the total copper production, and this is due to numerous developments in the field of synthesis of selective extractants for copper [[1], [2]].

Currently, the development of the copper ore base in the Republic is associated not only with the commissioning of new rich deposits, but, first of all, with the involvement in the processing of previously unprocessed poor oxidized ores, dumps of substandard ores, overburden mineralized rocks, enrichment tailings, waste from metallurgical production etc. using cost effective SX-EW technology. A typical example of

refractory oxidized copper ores is the Almaly porphyry copper deposit.

As the practice of operating plants using SX-EW technology shows, productive solutions obtained by leaching copper ores contain a number of elements, compounds and suspended solids, some of which can create problems during extraction [[3], [4]] and electrolysis [[5], [6]]. The main constituents to be constantly monitored are Cu2+, Fe3+ and/or pH [[7], [8]]. The main undesirable impurities in the productive solution are ions of iron, manganese [[9], [10]], silica [10].

Currently, a number of extractants are offered on the market that meets the highest technological requirements [11], but in each specific case, they must be selected on the basis of preliminary studies. For the extraction recovery of copper at each enterprise of a particular deposit, depending on the composition of the productive solution [[12], [13], [14]], it is first necessary to select the appropriate extractant with high selectivity to copper [[15], [16], [17]]. The purpose of this work was to study the extraction properties of a number of reagents that can be used for the efficient extraction of copper from the productive solutions of the Almaly deposit for the subsequent development of the SX-EW technology.

Experimental part

Studies to determine the selectivity of reagents were carried out with modified extractants of the Acorga series (5747, 5910, 5640) and unmodified Lix 984N reagent. Lighting kerosene brand KO-30 was used as a diluent. Productive solutions of copper ores of the Almaly deposit were obtained by multi-stage non-oxidizing sulfuric acid leaching.

In order to determine the selectivity of each type of extractant, as well as a sample for comparing the duration of phase separation, in addition to the productive solution from the field, a model solution was used. The specified concentration of copper in the model solution was 1 g/l, total iron was 2.4 g/l (Fe2+: Fe3+ ≈ 1:1), the pH was adjusted to 1.7 with sulfuric acid (according to pH = 1.7 in a productive solution). To prepare a model solution, copper sulfate $CuSO4 \cdot 5H_2O$ was used in terms of the molecular fraction of copper (25%) - 4 g/l of copper sulfate to achieve 1 g/l of Cu2+ ions. Iron salts were dissolved in a similar way to achieve the specified concentration of Fe^{2+}/Fe^{3+} ions = 2.4 g/l. Sulfuric acid and sodium hydroxide solutions were used to adjust the pH of the solution. All reagents used to prepare the model solutions were analytical grade. or "h.ch.".'

The content of copper in the solution was determined by iodometric titration, iron - photocolorimetrically. The extraction of metals was calculated from the balance of the distribution of metals between the organic and aqueous phases. To determine the dependence of copper extraction on various parameters, 25 cm3 of a freshly prepared solution of copper sulfate with a concentration of 4 g/dm3 were mixed for 5 minutes with 10% extractants dissolved in kerosene [[18], [19], [20]].

Discussion of the results

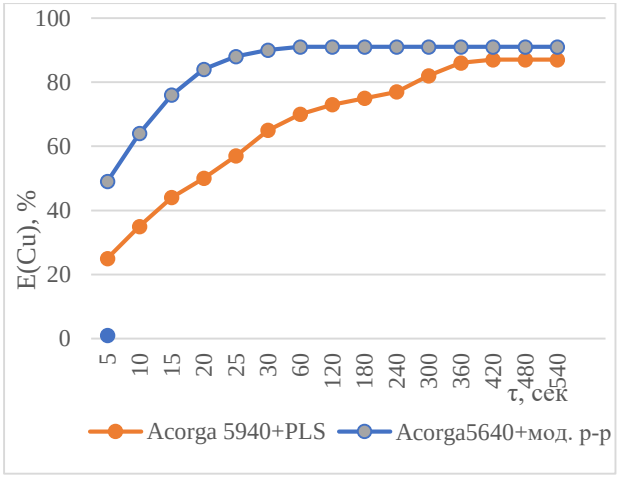
Effect of phase separation time on copper extraction one of the main stages of solvent extraction is the separation or separation of phases into an extract and refined [12]. Depending on the composition of the extractant, the duration of separation of the organic and aqueous phases may be different. The larger it is, the more it can lead to a decrease in the efficiency of the process. It is recommended that for hydrometallurgical production of cathode copper using SX-EW technology, the phase separation time should not exceed 30 seconds. This test, under production conditions, is carried out by taking a sample of a mixture of organic matter and an aqueous phase from the mixer chamber, followed by fixing the moment of complete separation. The research results are shown in Figures 1 and 2.

Studies on the extraction of copper were carried out under the following conditions: the concentration of extractants was 10%, the ratio of the aqueous and organic phases O/W=1:1, the duration of mixing of the organic and aqueous phases was 5 minutes, the temperature was 20 °C, pH was 1.7.

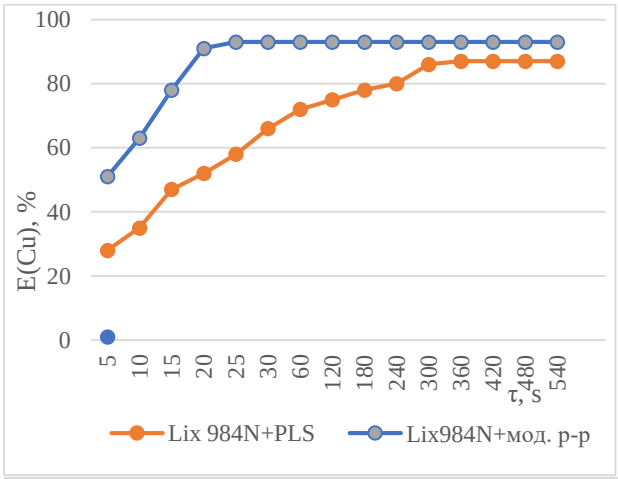
1a - productive solution

1b - model solution

Figure 1 - Separation of organic and aqueous phases, productive and model solutions in a separating funnel



a - the dependence of the degree of extraction of copper on the duration of phase separation during the extraction of copper Acorga 5640



b - Dependence of the degree of extraction of copper on the duration of phase separation during the extraction of copper Lix984N

Figure 2 - Results of copper extraction with Acorga 5640 and Lix984N extractants

The studies carried out to determine the duration of phase separation after extraction led to the following results: the complete separation of the aqueous and organic phases in productive solutions (Fig. 1a) took a longer time (after more than 5-7 minutes), while the complete separation of phases for model solution was reached in 20 seconds (Fig. 1b). In addition to a long phase separation, in the productive solutions, the fuzziness of the interfacial separation was also observed - in the upper layer of the aqueous phase, there were noticeable traces of the third phase, i.e. interfacial suspension "crud".

During the subsequent stripping of the organic phase with a solution of sulfuric acid with a concentration of 200 g/dm^3 and regeneration of the electrolyte by washing the organics with a 20% solution of sulfuric acid, phase separation occurred within the required duration of no more than 30 seconds. At the same time, the electrolyte obtained by washing the organics after the extraction of the productive solution differed markedly in color from the electrolytes obtained by processing the model solutions.

As you know, one of the main parameters affecting the extraction performance is the concentration of the extractant. Often, 10% extractants in various diluents are used as organic phases in production. Most 10% organic extractants are able to accumulate more than 10 g/l of copper and this leads to an increase in the viscosity of the organic phase. Therefore, saturation of the organic phase with copper is desirable not to produce more than 5 g/l. As noted earlier, after stripping, washing, a certain amount of metal will continue to be constantly on the balance in the organic matter. The results of solvent extraction experiments are shown in table 1

Table 1 - Results of copper extraction with various extractants

Extractant name	C(Cu) in ., g/l	C_{Cu} in el. ., g/l	$V_{эл-та}$, l	E_{Cu}, % l	E_{Cu}, % (main)
Acorga 5910 - 10%	2.55	4.5	0.1	88.2	75.0
Acorga 5747 - 10%	2.55	4.6	0.1	90.2	76.7
Acorga 5640 - 10%	2.73	5.0	0.1	91.6	83.3
Acorga 5640 - 5%	2.82	5.25	0.1	93.1	87.5
Lix984 - 10%	2.79	5.14	0.1	92.1	85.7

As the results of copper extraction from the model solution show, the maximum extraction of copper (94%) is observed when using the extractant 5% Acorga 5640, while the extractants 10% Acorga 5910 and 10% Acorga 5747 did not provide a high degree of extraction - the extraction of copper does not exceed 85% in both cases. 10% Acorga 5640 and 10% Lix984 showed relatively high copper recovery of 91% and 93% respectively.

Stripping results

After each extraction stage, the process of copper stripping from the organic phase followed with a sulfuric acid solution with a concentration of 200 g/dm^3 at a ratio of O:B=1:2, the total number of stripping stages was 3. The results of experiments on copper stripping are shown in Table 2.

Table 2 - Results of copper stripping from various organic phases

Extractant name	C_{Cu} in ., g/l	C_{Cu} in ., g/l	E_{Cu}, % during re-extraction	E_{Cu}, % through
Acorga 5910 - 10%	2.55	4.50	88.2	75.0
Acorga 5747 - 10%	2.55	4.60	90.2	76.7
Acorga 5640 - 10%	2.73	5.00	91.6	83.3
Acorga 5640 - 5%	2.82	5.25	93.1	87.5
Lix984 - 10%	2.79	5.14	92.1	85.7

As the results of the retraction process show, a high degree of copper extraction from the organic phase (90.2% or more) was ensured when using extractants 5% Acorga 5640, 10% Lix984 and 10% Acorga 5640, the minimum - with 10% Acorga 5910 (88.2%). To select the optimal extractant, we calculated the residual concentration in various organic phases (Table 3).

Table 3 - Residual concentration of copper in the organic phase after extraction and stripping processes

Residual Cu in org. Phase g/l	Acorga 5910 10 %	Acorga 5747 - 10 %	Acorga 5640 - 10%	Acorga 5640 – 5%	Lix984 - 10%
	0.3	0.25	0.23	0.195	0.22

The data in tables 1, 2, and 3 demonstrate the highest efficiency when using 5% Acorga 5640 extractant - the final transfer of copper from the productive solution to the electrolyte is 87.5%, and at the extraction stage, the extraction of copper into the organic phase is 94%, during stripping - 93.1. For a productive solution with a copper concentration of 1 g/l, the concentration of Acorga 5640 extractant equal to 5% is the best in comparison with 10%, which is due to the transfer mechanism.

Large-scale laboratory studies Studies on the extraction of copper from a productive solution of the composition, g/dm^3: Cu-2.62, Fe-17.97, SiO_2-0.36, were carried out using the extractant 5% Acorga 5640 in kerosene. The composition of the productive solution included the following components, g/dm^3: copper - 0.262; total iron - 17.97, colloidal insoluble silicates - 0.36. The total volume of the solution supplied for extraction was 5000 ml. The ratio O:B=1:1 was set using flows, the number of extraction stages was 3, the pH of the solution was 1.7. The results of the extraction experiments are shown in Table 4.

Table 4 - Results of extraction of the components of the productive solution of the Almaly deposit with 5% extractant Acorga 5640.

Element	C_{Cu2+} in PLS solution , g/l	$C_{Fe\ в}$ Raffinate , g/l	E, %	D	β
Cu^{2+}	0.26	0.006	97.7	43.33	-
$Fe^{3+/2+}$	17.97	15.7	12.6	1.14	Cu/Fe – 37.86
SiO_2	0.36	0.26	27.8	1.38	Cu/SiO_2 - 31.30

The results of extraction studies showed a rather high transition of iron ions and silicate compounds into the organic phase. Despite the high copper extractability of 97.7%, 12.6% of iron and 27.8% of silicate compounds passed into the organic phase from the productive solution.

Comparison of distribution coefficients shows that the extractant has a sufficiently high selectivity, the distribution coefficient of copper ions is high and is 43, compared with iron and silicon (1.14 and 1.38, respectively). Separation factors β (Cu/Fe) = 38 and β (Cu/SiO_2) = 31.

At the stage of stripping from the organic phase, 64% of iron passed into the electrolyte, with an iron concentration of 7.26%. At the same time, the residual concentration of iron in the organic matter was 4.09 g/l. The silicate compounds extracted from the productive solution subsequently also passed into the electrolyte (38%), the rest (62%) polluted the organic phase, forming an interfacial suspension - krad. The residual content of silicate compounds in organic matter was 0.31 g/l.

In addition to the accumulation of crud, an incomplete transition of copper into the electrolyte was also observed at the stage of stripping. This may be due to the fact that part of the copper, along with silicate and iron compounds, entered the formed thief [13], the prevention and removal of which will be studied by us further.

Conclusions

For the processing of productive solutions obtained by leaching of refractory oxidized ores of the Almaly deposit, the SX-EW technology is the most suitable.

Effective extractants of copper from sulfate solutions are the modified extractant Acorga 5640 and unmodified Lix984, from the productive solution

of the Almaly deposit composition, g/l: Cu 2, 62; Fe 17.97; SiO2 0.36 - 5% Acorga 5640 extractant.

The best selectivity for Cu2+/(Fe3+/Fe2+) ions is shown by estragents of the Lix984 and Acorga 5640 series (5 and 10%). The use of the extractant - 5% Acorga 5640 allows up to 93.1% to extract copper into the organic phase and avoid the accumulation of iron in it. As a result of 3-stage extraction and stripping of copper from the productive solution with 5% Acorga 5640 extractant, a more concentrated electrolyte was obtained with a copper content of 9.12 g/l.

To prevent and remove the formation of the third phase - steal, it is recommended to add various modifiers, flocculants and additives, the effects of which will be studied in the future.

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Алмалы кенорнындағы мыстың сұйық экстракциясы үшін тиімді экстрагентті анықтау бойынша зерттеулер

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ТҮЙІНДЕМЕ

Мысты шаймалау ерітінділерінен бөліп алу үшін қазіргі уақытта нарықта заманауи экстрагенттердің кең спектрі ұсынылған және оны таңдау мысты SX-EW (Solvent Extraxtion and Electrowinning, Сұйықтық экстракция және электролиз) технологиясымен жұмыс жасайтын өндіру орындарында өте маңызды мәселе болып табылады. Бұл зерттеудің мақсаты Алмалы кенорнының өнімді ерітінділерін сұйықтық экстракция технологиясымен өңдеу үшін оңтайлы мыс экстрагентін анықтау болып табылды. Өнімді ерітінді ретінде Алмалы мыс кендерін концентрациясы 25 г/л күкірт қышқылы ерітіндісімен тотықтырусыз шаймалау нәтижесінде алынған құрамы келесідей ерітінді алынды, г/дм^3: 1) Cu – 0,262 , Fe– 17,97, SiO2 – 0,36. Модельді ерітіндіден мысты бөліп алу нәтижелері келесідей болды: мысты бөліп алу дәрежесі 5% Acorga 5640 экстрагентін пайдаланған кезде максималды болатыны (94%), ал басқа экстрагенттер экстракцияның жоғары дәрежесін қамтамасыз етпейтінін көрсетті: 10% Lix984 - 93%; 10% Acorga 5640 - 91%; 10% Acorga 5910 және 10% Acorga 5747 - әрқайсысында 85%. Реэкстракция процесінің нәтижелері бойынша 5% Acorga 5640, 10% Lix984 және 10% Acorga 5640 экстрагенттерін пайдаланған кезде органикалық фазадан мысты бөліп алудың жоғары дәрежесі (90,2 және одан да көп) қамтамасыз етілді, ал 10% Acorga 5910 жағдайында бұл көрсеткіш минималды (88,2%) болды. Алмалы кенорнының өнімді ерітіндісінен мысты экстракциямен бөліп алу үшін тиімді экстрагент ретінде 5% Acorga 5640 таңдалды.

Түйін сөздер: мыс, SX-EW технологиясы, Acorga 5640, экстракция, селективтілік

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Исследования по определению оптимального экстрагента для жидкостной экстракции меди месторождения Алмалы

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АННОТАЦИЯ

Для экстракции меди из растворов выщелачивания в настоящее время на рынке предлагается большой ассортимент современных экстрагентов и его выбор является весьма важной проблемой в производстве меди по технологии SX-EW (Solvent Extraxtion and Electrowinning; Жидкостная экстракция и Электролиз). Целью настоящей работы явилось определение оптимального экстрагента меди для переработки продуктивных растворов месторождения Алмалы. Исследования проводились продуктивным раствором, полученный выщелачиванием медных руд месторождения Алмалы состава, г/дм3: 1) Cu – 0,262, Fe –17,97, SiO2 – 0,36. Результаты экстракции меди из модельных растворов показали, что максимальное извлечение меди (94%) наблюдается при использовании экстрагента 5% Acorga 5640, тогда как остальные экстрагенты не обеспечили высокую степень экстракции: 10% Lix984 - 93%; 10% Acorga 5640 - 91%;10% Acorga 5910 и 10% Acorga 5747 – по 85%. По результатам процесса рекстракции высокая степень извлечения меди из органической фазы обеспечивалась при использовании экстрагентов 5% Acorga 5640, 10% Lix984 и 10% Acorga 5640, минимальное – при 10%Acorga 5910. Для экстракции меди из продуктивного раствора месторождения Алмалы в качестве оптимального экстрагента был выбран 5 % Acorga 5640, показавший лучшие показатели.

Ключевые слова: медь, технология SX-EW, Acorga 5640, экстракция, селективность

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Metallurgy

Electrothermal production of ferroalloy from tripoli

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ABSTRACT
The article presents the research results on the electrothermal production of a ferroalloy from an amorphous sedimentary rock tripoli. The studies were carried out by electric melting in a single-electrode arc furnace using the second-order rotatable experiment planning (Box-Hunter plan). The influence of the amount of coke and steel chips on the degree of extraction of silicon into the alloy and the content of silicon in it is determined. It was found that silicon from tripoli to ferroalloy passes by 49-90.6%, and the silicon content in the alloy is 28-48%. Ferrosilicon grade FS25 (23.0-29% Si) is formed in the presence of 30-33.6% coke and 40.6-45.0% steel chips, grade FS45 (41-46.6% Si) with 32.1-40.9% coke and 26.2-37.0% steel chips. The maximum degree of silicon extraction (90.0-90.3%) in FS45 grade ferrosilicon (42.6-43.5% Si) is observed in a small coke range (36.0-37.3%) and steel chips (33.0-35.2%). Using tripoli instead of quartzite in the charge makes it possible to reduce the duration of the process by 1.2 times.
Keywords: tripoli, electric melting, thermodynamics, ferroalloys, ferrosilicon

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Introduction

According to [1], the world reserves of tripoli, a sedimentary rock containing up to 86% SiO_2, are > 1.1 billion tons. The main part of tripoli consists of opal-like silica and a small number of shells of diatomaceous algae [[2], [3]]. Therefore, silica in tripoli is mainly in an amorphous state, a characteristic feature of which is an increased reactivity in comparison with the crystal form [4]. Using this property of amorphous silica, in contrast to the known methods of its application [[5], [6], [7], [8], [9], [10]], it was proposed to use tripol as a silicon-containing raw material to produce a siliceous ferroalloy [11] for the smelting of which quartzite is used [[12], [13], [14], [15]]. The article presents the results of studies to determine the optimal parameters for the electrothermal production of silicon ferroalloy from tripoli.

Experimental part

The studies were carried out on the setup shown in Figure 1.

The main components of the installation include an arc single-electrode electric furnace, transformer, and short circuit. An electric furnace is a unit lined with chrome-magnesite bricks. The hearth of the furnace is made of a carbon-graphite block, which served as the lower conductor. A graphite electrode with an internal diameter of 9 cm and a height of 20 cm was installed on the hearth. The space between the crucible and the lining was filled with graphite chips with a particle size of 0.1–0.3 cm. The upper current conductor was made of a graphite electrode with a diameter of 5 cm.

I

II

I - General view, II - Electric melting

Figure 1- Installation for electric melting of tripoli

The furnace was equipped with a mechanical device for moving the electrode. The installation used a single-phase furnace transformer brand TDZhF-1002. The transformer was equipped with a thyristor power regulator. Maximum power 56kV·A. The short net was made of aluminum tires. An aluminum bus was connected to a graphite hearth using three copper studs. The upper electrode is connected to the aluminum bus by a flexible copper cable 2 cm in diameter. In the upper part, a detachable refractory cover 7 cm thick was installed on the lining.

Before melting, tripoli was ground in a ball mill to fractions <0.1 m and pelletized in the presence of bentonite clay on a bowl granulator. Dried granules 1-1.5 cm in size were mixed with coke and steel shavings. The charge was melted in portions (300-500 g each) in an arc furnace at a voltage of 20-50 V and a current of 400-500 A. The melting time of the last charge was 30 minutes. After melting, the crucible with the charge was removed from the furnace and cooled for 4-5 hours. Then the crucible was broken. Alloy and slag were weighed. The content of metals in the alloy was determined using Scanning electron microscopy. In addition, the density of the alloys was determined by the pycnometric method (P, g/cm^3), using which the silicon content in the alloy was determined from the expression [16]:

$$CSi=690.679-545.783\cdot P+166.151\cdot P^2-17.467\cdot P^3 \quad (1)$$

The degree of extraction of silicon into the alloy (αSi, %) was determined from the ratio of the mass and metal in the alloy to the mass of metal in the charge.

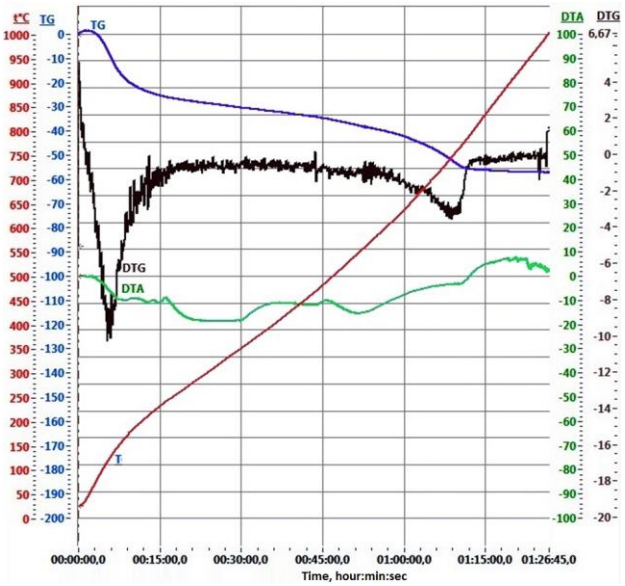
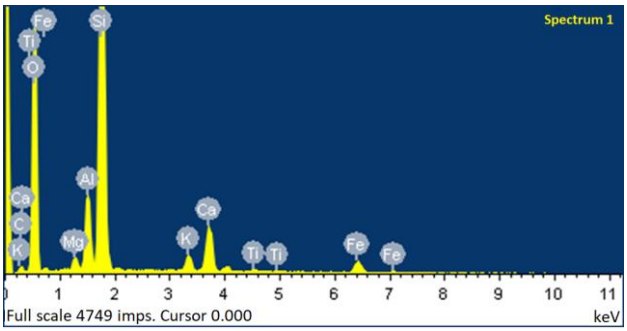


Figure 2- DTA analysis

Figure 2 shows a tripoli derivatogram, which shows that the heating of tripoli was accompanied by two endothermic effects. The first at 50-220 °C and the second at 600-830 °C. The first effect is associated with the decomposition of magnesium and calcium carbonates. The weight loss of tripoli was 13.52%. Figure 3 shows the SEM analysis of tripoli dried at 200-230 °C for 30 minutes.

I



II

Element	C	O	Mg	Al	Si	K	Ca
Weight, %	2.63	53.93	0.85	4.41	28.3	1.6	4.9

I- electronic image, II- elemental composition

Figure 3-SEM analysis of tripoli

It can be seen that in the original tripoli the Si concentration is -28.3%, Al-4.4%, O-53.93%. After burning at 800 °C the tripoli contained mass %: 71.6% SiO_2, 9.2% Al_2O_3, 7.5%CaO, 1.5% MgO, 2.1% K_2O, 4.9% Fe_2O_3, 0.2% TiO_2, 2.8% CO_2, and coke, mass %: 5.1% SiO_2, 2.0% Fe_2O_3, 1.8% Al_2O_3, 1.5% CaO, 0.4% MgO, 0.8% S, 1.2% H_2O, 85.8% C, 1.4% others. In steel chips, Fe was -96.9%, C -1.5%, Si-0.2%, Mn 0.3%, others (Ni, Cr, Cu) – 1.1%.

The studies were carried out by the method of planning experiments using a rotatable plan of the second order (the Box-Hunter plan) [17]. Regression equations for the influence of technological parameters on the degree of silicon extraction into the alloy and the silicon content in it, as well as a graphical representation of the parameters for optimizing the determination, respectively, according to the methods [[18], [19]]. As independent variables using the amount of coke (C) and steel chips (St), % of the mass of tripoli. The intervals of variation of independent variables are shown in Table 1, and the matrix of experiment planning and their results are shown in Table 2.

Table 1-Variable intervals

Level	Coded look		Natural look	
	Coke	***Steel shavings***	***Coke***	***Steel shavings***
	X1	***X2***	***C, %***	***St., %***
Zero level	0	0	38	35
Lower level	-1	-1	32.4	28
Upper level	+1	+1	43.6	42
Upper star shoulder	+1.414	+1.414	46	45
Lower Star Shoulder	-1.414	-1.414	30	25

Using the method described in [18,] and the data in Table 2, the following regression equations were obtained:

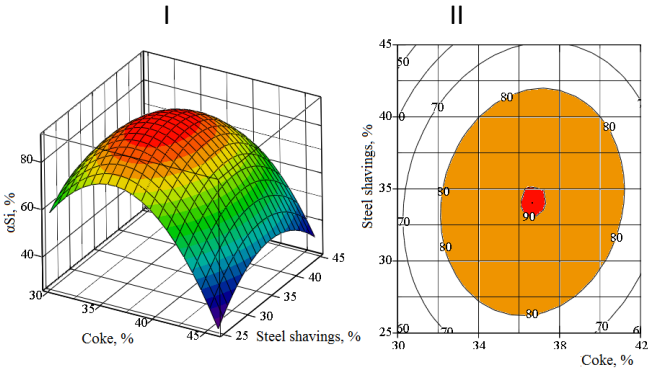
$$\alpha Si=-696.16+34.52\cdot C+9.012\cdot St-0.503\cdot C^2-0.166\cdot St^2+0.063\cdot C\cdot St; \quad (2)$$

$$CSi=-179.25+11.92\cdot C+0.96St-0.173\cdot C^2-0.036\cdot St^2+0.021\cdot C\cdot St. \quad (3)$$

Table 2-Experiment design matrix and results

№ of experiment	Variables				Technological optimization parameters			
	Coded		Natural					
	X_1	X_2	C, %	St., %	α_{Si} (exp), %	α_{Si} (distr), %	C_{Si} (exp), %	C_{Si} (distr), %
1	-1	-1	32.4	28	73.6	76.7	42.2	43.8
2	+1	-1	43.6	28	53.8	57.3	35.5	36.8
3	-1	+1	32.4	42	69.2	68.7	32.4	32.0
4	+1	+1	43.6	42	59.3	59.2	29.1	28.4
5	+ 1.414	0	46.0	35	49.5	47.7	28.0	27.8
6	- 1.414	0	30.0	35	69.3	68.1	36.0	35.3
7	0	+ 1.414	38	45	69.8	70.8	30.8	31.8
8	0	- 1.414	38	25	79.2	75.2	47.9	46.0
9	0	0	38	35	88.8	89.3	42.0	42.4
10	0	0	38	35	89.9	89.3	41.5	42.4
11	0	0	38	35	89.0	89.3	42.8	42.4
12	0	0	38	35	88.0	89.3	42.6	42.4
13	0	0	38	35	89.3	89.3	43.2	42.4

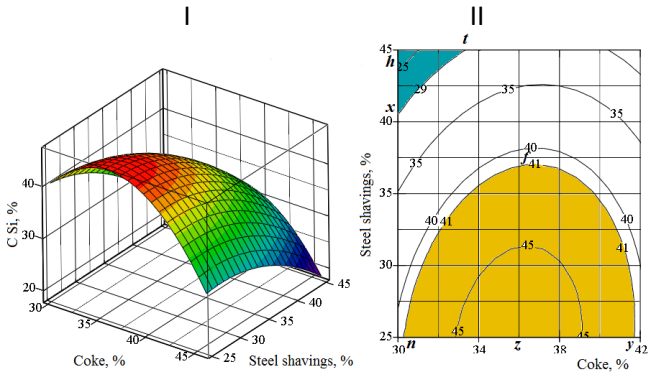
Figures 4 and 5 show volumetric and planar images constructed in accordance with [19] of the effect of coke and steel chips on the degree of silicon extraction into the alloy and the concentration of silicon in it.



I- volumetric image, II- planar image

Figure 4-Influence of coke and steel chips on the extraction of silicon into an alloy

Figure 4 shows that the degree of extraction of silicon into the alloy from 80 to 90% is observed at 32.1-41.2% of coke and 25.9-41.8% of steel chips (shaded area in the figure), and from 90.0 up to 90.6% at 36.0-37.3% coke and 33.2-35.0% steel chips (shaded area of Figure 4).



I - volumetric image, II - planar image

Figure 5- Effect of coke and steel chips on the silicon content of the alloy

A ferroalloy containing from 41 to 47% silicon (ferrosilicon grade FS45 [20]) is formed in the ***nfyz*** region (Figure 5), in which the amount of coke is from 30.3 to 41.6%, steel chips - from 25 to 37%. Low-silicon ferrosilicon (FS25) is formed in the ***xht*** region in the presence of 30.0-33.3% coke and 40.6-45% steel chips. Figure 6 shows combined information on the effect of coke, and steel chips on αSi and CSi.

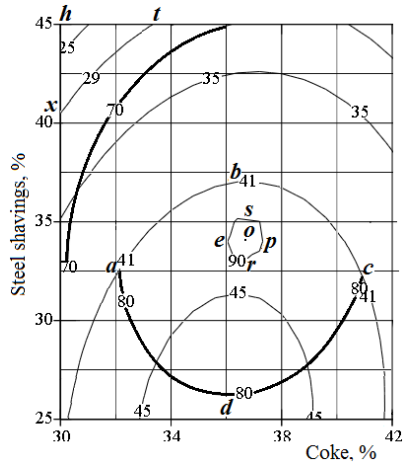


Figure 6 - Combined information on the effect of coke and steel chips on the extraction of silicon into the alloy and the content of silicon in it

The choice of optimal conditions for obtaining a ferroalloy from tripoli was determined based on the accepted conditions: αSi ≥80% and CSi>41%. The region ***abcd*** meets these conditions. Table 3 shows the boundary parameters of the three regions in Figure 6.

Table 3 - Boundary values of technological parameters in the production of ferroalloys from Tripoli

Point in the figure	Technological parameters			
	Coke, %	Steel chips, %	C Si, %	αSi, %
a	32.1	32.5	41.0	80.0
b	37.0	37.0	41.0	88.9
c	40.9	32.2	41.0	80.0
d	36.3	26.2	46.6	80.0
x	30.0	40.6	29.0	58.3
h	30.0	45.0	23.0	47.7
t	33.3	45.0	29.0	62.5
o	36.6	34.0	43.5	90.3
e	36.0	34.5	43.0	90.0
s	37.0	35.2	42.6	90.0
p	37.3	34.5	43.0	90.0
r	37.0	33.0	44.0	90.0

Table 6 shows that ferrosilicon grade FS45 is formed from tripoli in the presence of 32.1-40.9% coke and 26.2-37.0% steel chips. The degree of extraction of silicon into the alloy is 80-90.6%. Ferrosilicon grade FS25 is formed with a large number of steel chips - 40.6-45.0% and less coke - 30.0-33.3%. However, the extraction of silicon into the alloy, in this case, is only 47.7–62.5%. It is necessary to dwell on the region ***espr***, in which αSi is 90.0-90.3%, and the concentration of Si in the alloy is 42.6-43.5%. Such indicators are achieved with 36-37.3% coke and 33.0-35.2% steel chips.

Figure 7 shows photographs of ferroalloys obtained with various amounts of coke and steel chips.

The numbers in the photographs correspond to the melting numbers according to table 3
I- ferrosilicon FS25 (Si=29-32%), II- ferrosilicon FS45 (Si=41.5-43.2%)

Figure 7-Photos of some ferroalloys obtained from tripoli

It should be noted that in comparison with the conventional charge, which uses quartzite, the smelting of ferrosilicon from tripoli is more intensive. So, for experiment No.14, the duration of melting of the last portion of the charge decreases from 30 to 25 minutes, i.e. 1.2 times.

Conclusions

Based on the studies carried out on the production of ferroalloys by electric melting of tripoli, the following conclusions can be drawn:

- silicon from tripoli into ferroalloy is extracted by 49-90.6%, and the silicon content in the alloy was 28-48%;

- ferrosilicon grade FS25 (23.0-29% Si) is formed in the presence of 30-33.3% coke and 40.6-45.0% steel chips, grade FS45 (41-46.6% Si) with 32.1-40.9% coke and 26.2-37 % steel chips;

- the maximum degree of extraction of silicon (90.0-90.3%) in ferrosilicon FS45 (42.6-43.5% Si) is observed in a small range of coke (36.0-37.3%) and steel chips (33.0-35.2%);

- in comparison with the standard charge, the duration of the smelting of ferrosilicon from tripoli is reduced by 1.2 times.

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ТҮЙІНДЕМЕ

Мақалада аморфты шөгінді тау жыныстарынан - трепелден ферроқорытпаны электротермиялық өндіруді зерттеу нәтижелері келтірілген. Зерттеулер екінші ретті экспериментті рототабельді жоспарлау әдісін (Бокс-Хантер жоспары) қолдана отырып, бір электродты доғалы пеште электрмен балқыту арқылы жүргізілді. Кокс пен болат жоңқаларының мөлшері кремнийдің қорытпаға шығарылу дәрежесіне және ондағы кремнийдің құрамына әсері анықталды. Трепелден ферросплавқа кремний 49-90.6% - ға ауысады, ал қорытпадағы кремний мөлшері 28-48% - ды құрайды. Кокс 30-36.3% және болат жоңқалар 40.6-45.0% қатысуымен ферросилиций маркалы ФС25 (23-29% Si) құрылады, Кокс 32.1-40.9% және болат жоңқалар 26.2-37% кезінде ферросилиций маркалы ФС45 (41-46.6% Si) түзіледі. Фс45 (42.6-43.5% Si) маркалы ферросилицийде кремнийді алудың ең жоғары дәрежесі (90.0-90.3%) шағын Кокс интервалында (36.0-37.3%) және болат жоңқасында (33.0-35.2%) байқалады. Кварциттің орнына трепелді қолдану процестің жалғасуын 1,2 есе азайтады.

Түйін сөздер: Трепел, электрлік балқыту, термодинамика, ферроқорытпа, ферросилиций

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Электротермическое получение ферросплава из трепела

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АННОТАЦИЯ

В статье приводятся результаты исследований электротермического получения ферросплава из аморфной осадочной породы-трепела. Исследования приводились электроплавкой в дуговой одноэлектродной печи с использованием метода рототабельного планирования эксперимента второго порядка (план Бокса-Хантера). Определено влияние количество кокса и стальной стружки на степень извлечения кремния в сплав и содержание в нем кремния. Найдено, что кремний из трепела в ферросплав извлекается на 49-90.6%, а содержание кремния в сплаве составило 28-48%; ферросилиций марки ФС25 (23-29% Si) образуется в присутствии 30-33.3% кокса и 40,6-45.0% стальной стружки, марки ФС45 (41-46.6% Si) при 32.1-40.9% кокса и 26.2-37% стальной стружки; максимальная степень извлечения кремния (90.0-90.3%) в ферросилиций ФС45 (42.6-43..5% Si) отмечается в небольшом интервале кокса (36.0-37.3%) и стальной стружки (33.0-35.2%). В сравнении со стандартной шихтой продолжительность выплавки ферросилиция из трепела сокращается в 1,2раза.

Ключевые слова: трепел, электроплавка, термодинамика, ферросплавы, ферросилиций

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Metallurgy

Vacuum sublimators with a rheological displacement of the dispersed medium

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ABSTRACT

Based on the analysis of designs and technological processes carried out in vacuum electric furnaces developed to date for the processing of dispersed materials by sublimation of volatile components from them, and problems associated with technological processes, technical solutions are proposed in the present work in which the movement of concentrate is carried out due to rheological properties with direct heating by radiation from the heater to the surface of the transported and mixing raw materials. During the development of the equipment, a concept was adopted in which the movement of material in the sublimation zone of the furnace is ensured due to rheological properties, which opens up the possibility of using materials inert to the sulfide atmosphere and realizing heat transfer by radiation to open areas of dispersed material. Technological tests on the sublimation of arsenic sulfide compounds from granulated concentrates of Nezhdaninsky and Bakyrchik deposits have confirmed the prospects of such a constructive design of sublimation processes. The application of the developed equipment in practice will ensure the technical and economic efficiency of production in compliance with all environmental requirements with minimal impact on the environment, which is currently a fundamental indicator when choosing a particular technology.

Keywords: Rheology, dispersed material, electric furnace, heating, dearsenation.

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Introduction

Currently, there is a large number of deposits of polymetallic sulfide ores and concentrate productions that contain arsenic, antimony, and mercury in the form of sulfides or other compounds [[1], [2], [3], [4], [5]]. Extraction of valuable components from these types of raw materials with the help of classical methods is not safe from an environmental point of view due to the significant toxicity of accompanying elements [[6], [7], [8]].

The analysis of the studies performed in the field of arsenic extraction technologies corresponding to the current requirements enables us to make the following conclusion. The arrangement of the preliminary stage of arsenic extraction allows

excluding its circulation in the processed products, which, in its turn, contributes to the improvement of the quality of the finished product. That is why the most promising technologies are those which provide for preliminary extraction of arsenic in the form of low-toxic and low-soluble compounds [[9], [10]].

For example, these methods include oxidation-sulfiding roasting of granulated concentrate with arsenic removal in a low-toxic form [[11], [12]], and heating of arsenopyrite-pyrite-containing concentrates in reducing or sulfur-containing media with arsenic conversion to sulfide sublimates [[13], [14]]. However, these methods have not found industrial application due to the complexity of strict control over the oxidative and sulfur potential of the gas phase. This problem can be solved using a vacuum-thermal method of arsenic removal [15] in combination with traditional methods of extraction of noble metals from the obtained cinders [16]. It should be noted that the implementation of the process in a vacuum, among other things, enables to reduce the process temperature, and improve the working conditions of the personnel of the enterprise and the environmental situation in the region as a whole.

The employees of the laboratory of vacuum processes in the Institute of Metallurgy and Ore Beneficiation JSC are engaged in the development of vacuum-thermal and vacuum-distillation equipment for the processing of various types of raw materials for several decades [17].

To date, the movement of bulk solids in vacuum apparatuses is provided forced, mainly by fluidization of the directed vibration [18] and sucking of gas flow through a dispersed material layer [19].

Vibro-vacuum electric furnaces are the most advanced design of disperse material processing by fluidization. They have been validated by a pilot and industrial tests in the processing of gold-arsenic concentrates [17]. The material is moved and heated on a screw vibrating conveyor having an internal cavity that is not communicated with the vacuum furnace space. A furnace heater is placed in the inner cavity of the vibrating conveyor.

The main disadvantage of this equipment type is the process of heat transfer to the dispersed material through the central steel tube of the vibrating conveyor resulting in severe overheating from the heater and residual deformations in it.

Analyzing the technical design of sublimation processes during the vacuum processing of dispersed raw materials, we can highlight some of the difficulties affecting the quality of the resulting product and the operating time of the equipment. They include the following drawbacks:

- pressure reductions inherent for the vacuum sublimation layer;
- increase in the process temperature during heat transfer to the processed material;
- thermal and corrosion resistance of special steels in vacuum vibro-vacuum furnaces.

It is required to conduct research in the field of new, modern, effective, and environmentally safe equipment for the dearsenation of mineral and man-made materials by vacuum method to solve these problems which is the purpose of this work.

Experimental part

In this regard, we have developed two equipment designs where the movement of bulk materials in the sublimation zone of the furnace is provided by rheological properties. This method of movement opens up the possibility to use materials that are inert in relation to the sulfide atmosphere and to realize the transfer of heat by radiation to the exposed areas of the dispersed material.

The scheme of the first version of the sublimation unit intended to process dispersed materials and the principle of its operation are considered and given by us in [20]. Further design developments were aimed to simplify the manufacturing process of inclined surfaces, where the processed material descends, their placement, and mounting of the column in the sublimator volume. In the first version, the inclined surfaces were made in the form of a column of truncated conical shells facing upwards with a large base. The inclined surfaces in the new version are made in the form of polyhedral truncated pyramids or inclined plates assembled with inclined grooves in the form of a vertical shaft (Figure 1).

The vacuum sublimator scheme with these inclined surfaces is shown in Figure 2. The unit is a sublimator (1) heated by an electric furnace (2), inside which a shaft formed by truncated pyramids (3) is placed. The pyramids are located with their larger bases upwards with a slope angle of 60° that significantly exceeds the natural slope angle of almost all types of bulk materials.

The truncated pyramids are turned on half of the face one relative to the other, and the larger base

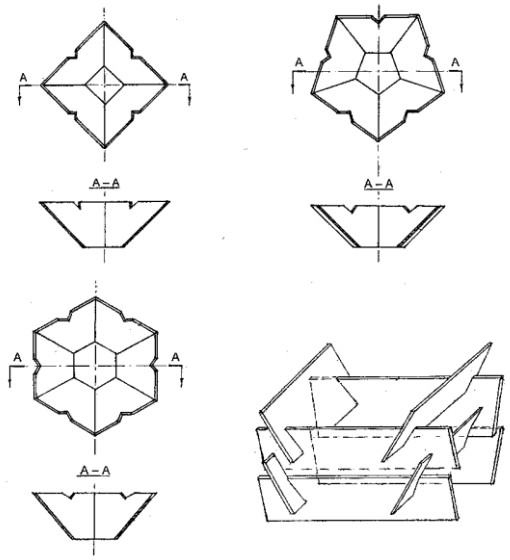
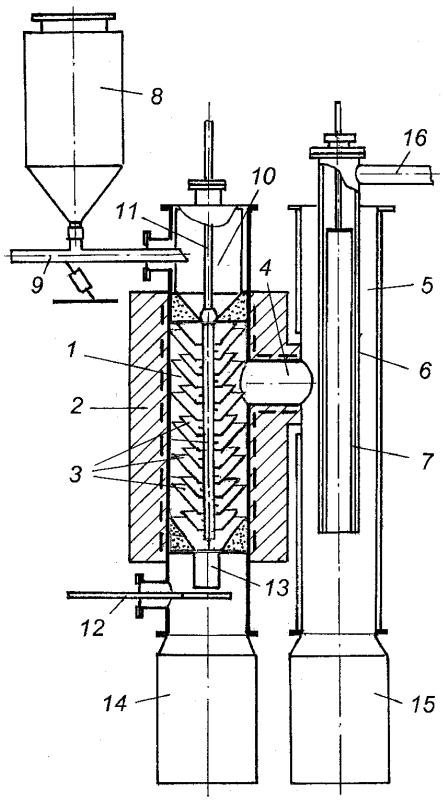


Figure 1 – Type of inclined surfaces in the form of truncated pyramids or plates, forming a shaft in the sublimator



1 – sublimator; 2 – electric furnace; 3 – inclined surface; 4 – steam pipeline; 5 – condenser; 6 – pipe; 7 – fabric filter; 8 – hopper for raw materials; 9 – vibrating loader; 10 – intermediate vessel; 11 – a rod with cone shutters; 12 – vibrating unloader; 13 – mouth; 14 – receiving hopper residue; 15 – receiving hopper condensate; 16 – vacuum wire.

Figure 2 – Schematic diagram of a vacuum sublimation unit with a rheological displacement of dispersed materials

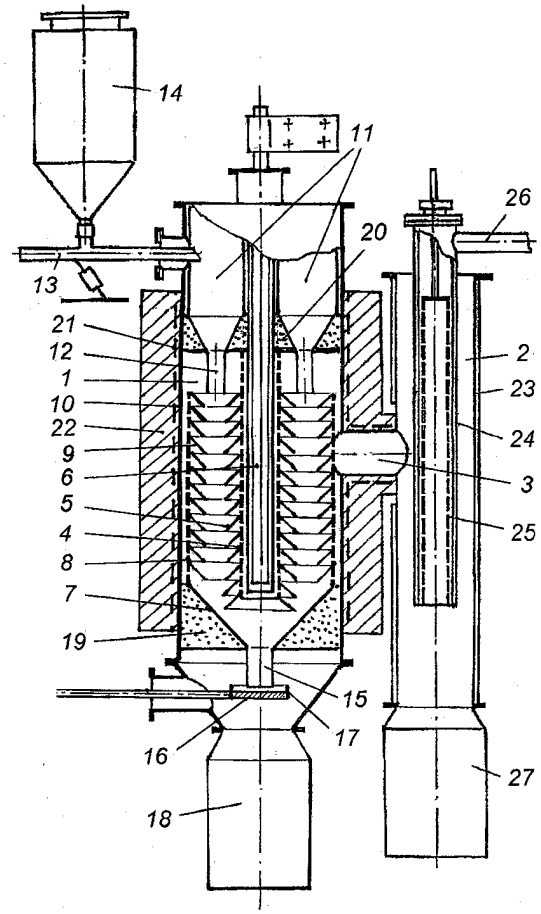
corners touch the sublimator body that ensuring their fixation in the column. The gaps are correlated so that the material pouring out of the upper pyramid or shell plate at the natural slope angle does not "overflow" the upper edge of the larger base below the pyramid or plate. The sublimator is connected by a heated steam line (4) to a water-cooled condenser (5). There is a water - cooled coaxially mounted tube (6) inside the condenser inside which a fabric filter for catching fine condensate (7) is placed. The apparatus is equipped with a hopper for raw materials (8) and a vibrating feeder (9) for feeding the latter to an intermediate vessel (10). The intermediate vessel is separated from the sublimator space by a movable hollow rod with a cone gate (11), inside which the thermocouple is placed. A vibrating unloader (12) is placed below the sublimator, which together with the bulk material in the mouth (13) forms a gate that separates the receiving hopper of the residue from the processing (14) from the sublimator (1). Arsenic sulfides crumbling from the walls of the condenser accumulate in the hopper (15). The gases are evacuated from the apparatus through a vacuum conduit.

Technological tests of the unit were performed on the model material. When they have performed the dispersed material from the bunker for initial raw materials was fed by means of the vibrating feeder into the intermediate vessel above a sublimator, from where they filled the internal cavity of the shaft formed by truncated pyramids or plates. The treated material was heated by radiation on the exposed surface areas. Such areas are formed by dispersed material due to natural oversaturation and face the external heater.

The processing time of the bulk material (staying in the sublimator) was regulated by the productivity of the vibrating unloader, the plane of which is located with a gap relative to the mouth. Dispersed material in the mouth and on the unloader with sides formed a gate, separating the sublimation volume from the bunker space, which prevented penetration and condensation of the sulfide vapor phase in the latter. The vapor phase from the sublimator through a steam pipeline was directed to the solid-phase condensation of arsenic sulfides in a cyclone-type condenser. The design shown in Figure 3 was developed to increase the performance of the sublimator.

The technology for processing dispersed raw materials containing volatile components is similar to that for the sublimator presented in Figure 2. The

difference is that the dispersed material in the sublimator is located in a tube-shaped shaft formed by an inner column of shells of smaller diameter, with the slope of the formation downward, and the outer column of shells of larger diameter, facing upward with their large bases. The sublimated steam exits inside the perforated tube where the heater is located, and outside through the perforated screen into the gap between the shell and the screen, and then through the steam line to the condenser. The external heater prevents the condensation of steam on the sublimator body.



1 – sublimator; 2 – condenser; 3 – steam pipeline; 4 – perforated tube; 5 – shells turned downward; 6 – heater; 7 – collapsible cone; 8 – perforated screen; 9 – shells with the larger base upward; 10 – the body of sublimator; 11 – receiving hopper; 12 – mouth of the receiving hopper; 13 – vibrating loader; 14 – hopper of raw materials; 15 – mouth of collecting cone; 16 – shaker; 17 – sides of the vibration discharger plane; 18 – hopper of the rest; 19, 20, 22 – heat-insulation; 21 – outdoor heater; 23 – cooled condenser housing; 24 – cooled pipe; 25 – fabric filter; 26 - vacuum-pipe; 27 – receiving condensate hopper.

Figure 3 – Scheme of the sublimator with a rheological displacement of increased productivity material

Discussion of results

Technological tests of the equipment on the model material showed the fundamental possibility of abandoning the forced movement of bulk materials in the reaction zone of the sublimator by imposing directional vibrations with the achievement of high raw material dearsenation parameters [[15], [16]].

The tests were conducted at temperatures in the sublimator reaction zone of 600-700 °C. The residual pressure in the system was 0.13 kPa. The residence time of the material in the isothermal zone of the furnace was regulated by changing current loads on the electromagnet windings of the vibration unloader, which, in turn, determined the material unloading rate, and thus the volume of a new portion of the material fed into the reaction space. It was determined that the time when the material was in the reaction zone of the furnace could vary from 5 to 18 minutes. It should be noted that no dust escape was observed in the used design of the sublimation electric furnace with the model material work which, in turn, excludes the additional design of a heated system for rough cleaning of the gas flow from the sublimator against fine dust.

The proposed rheological movement of the dispersed material in the sublimation zone of arsenic sulfides in combination with direct radiation heating of the open surface of the treated material confirmed the prospects of such a design of the technological process. Sublimators of such design can be used for processing both arsenic- and mercury- and antimony-containing raw materials.

Conclusions

Several variants of equipment designs with the rheological movement of the processed material designed to process dispersed arsenic-containing concentrates are proposed as a result of research and design developments.

For practical use of research results, the authors proposed a variant of design with external heating of the sublimator body and the use of inclined planes to transfer the material in the form of plates with grooves, assembled in pairs in a certain way in the form of a vertical shaft.

This sublimation electric furnace design provides a more efficient transfer of heat to the material from

the heated surfaces of the furnace, eliminating mechanical stress on the elements of the furnace, resulting from the imposition of directional vibrational motions occurring in the vibration-vacuum apparatus.

The main advantage of the proposed sublimation electric furnace design is its simplicity which is one of the most important aspects when the equipment is used on an industrial scale.

Conflict of interest

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

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Дисперсті ортаның реологиялық орнын ауыстыратын вакуумдық сублиматорлар

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ТҮЙІНДЕМЕ

Дисперсті материалдарды олардан Ұшпа құрауыштарды сублимациялау арқылы өңдеу үшін қазіргі уақытта әзірленген вакуумдық электр пештерінде жүзеге асырылатын конструкциялар мен технологиялық процестерді талдау және технологиялық процестермен байланысты проблемалар негізінде ұсынылған жұмыста концентраттың орын ауыстыруы жылытқыштан орын ауыстырылатын және тасымалданатын жер бетіне тікелей сәулеленумен реологиялық қасиеттер есебінен жүзеге асырылатын техникалық шешімдер ұсынылған аралас шикізат. Жабдықты әзірлеу кезінде тұжырымдама қабылданды, онда пештің сублимациялық аймағында материалдың қозғалысы реологиялық қасиеттерге байланысты қамтамасыз етіледі, бұл сульфидті атмосфераға қатысты инертті материалдарды қолдануға және дисперсті материалдың ашық жерлеріне сәуле арқылы жылу беруді жүзеге асыруға мүмкіндік береді. Нежданинск және Бақыршық кен орындарының түйіршіктелген концентраттарынан мышьяк сульфидті қосылыстарын сублимациялау бойынша технологиялық сынақтар сублимациялық процестердің осындай құрылымдық дизайнының болашағын растады. Әзірленіп жатқан жабдықты практикада қолдану қоршаған ортаға ең аз әсер ете отырып, барлық экологиялық талаптарды сақтай отырып, өндірістің техникалық-экономикалық тиімділігін қамтамасыз етеді, бұл қазіргі уақытта қандай да бір технологияны таңдау кезінде негізгі көрсеткіш болып табылады.

Түйін сөздер: Реология, дисперсті материал, электр пеші, қыздыру, деарсенация.

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АННОТАЦИЯ

На основании анализа конструкций и технологических процессов, осуществляемых в разработанных к настоящему времени вакуумных электропечах для переработки дисперсных материалов сублимацией из них летучих составляющих, и проблем, связанных с технологическими процессами, в представленной работе предложены технические решения, в которых перемещение концентрата осуществляется за счет реологических свойств с прямым нагревом излучением от нагревателя к поверхности перемещаемого и перемешивающегося сырья. При разработке оборудования принята концепция, в которой перемещение материала в сублимационной зоне печи обеспечивается за счет реологических свойств, что открывает возможность использовать инертные по отношению к сульфидной атмосфере материалы и реализовать передачу тепла излучением на открытые участки дисперсного материала. Технологические испытания по сублимации сульфидных соединений мышьяка из гранулированных концентратов Нежданинского и Бакырчикского месторождений подтвердили перспективность подобного конструктивного оформления сублимационных процессов. Применение разрабатываемого оборудования на практике обеспечит технико-экономическую эффективность производства с соблюдением всех экологических требований с минимальным воздействием на окружающую среду, что в настоящее время является основополагающим показателем при выборе той или иной технологии.

Ключевые слова: Реология, дисперсный материал, электропечь, нагрев, деарсенация.

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Engineering and technology

Synthesis and application of nonionic graft copolymers P(mPEG-g-MMA)

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ABSTRACT

The goal of this research is to prepare novel amphiphilic graft copolymers (nonionic) based on hydrophilic poly (ethylene glycol) methyl ether (mPEG) and hydrophobic methyl methacrylate (MMA) at room temperature and pressure. To generate P(mPEG-g-MMA) grafts, poly (ethylene glycol) methyl ether (mPEG) was synthesized and grafted with varied ratios of methyl methacrylate (MMA) in the existence of benzoyl peroxide as an initiator utilizing a macro-free radical initiator procedure under the effect of heating in toluene. The research discussed in this paper looked at the possibility of using the synthesized graft copolymer P(mPEG-g-MMA) as a nonionic demulsifier in Petroleum Crude Oil Emulsions. The produced nonionic surfactants were assessed as water demulsifiers in oil emulsions that were noticeable at varying oil: water ratios at 60°C. According to the demulsifier chemical compositions as well as concentrations, the testing findings revealed that the dehydration rate of the prepared demulsifiers reached 100%. The optimal demulsifier dose was 300 ppm.

Keywords: Methyl methacrylate, Polyethylene glycol methyl ether, free radical polymerization, demulsifier, catalyst.

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Introduction

The existence of higher than 80% water throughout the production process on gas and oil platforms is a major topic of concern for the industry. This water originates from two natural sources such as the injection and reservoir during the extraction of the hydrocarbon [1].

Emulsified water mineralization and pH. The mineralization and salt content of the aqueous phase surely have an impact on the stability and kind of oil emulsions. However, two characteristics should be highlighted: This impact is indirect, because of the production of chemical compounds with polar oil components. Oil naphthenic acids, for example, have strong surface-active characteristics and can interact with ions such as Na^+, K^+, Mg^{2+}, Fe^{3+}, and Al^{3+} that are present in formation water. At the same time, because naphthenates K and Na are readily soluble in water, they contribute to the production of oil/water (O/W) emulsions and impair the stability of water/oil emulsions stabilized by Resinous Asphaltene substances.

Unlike Na and K salts, Mg-, Fe-, and Al- salts of naphthenic acids are more soluble in oil and can stabilize the reverse kind of Water/Oil emulsion. However, when combined with a resinous-asphaltene natural emulsifier, its impact is

weakened, most likely due to a reduction in the forces of intermolecular contact between resinous-asphaltene molecules.

As a result, all these compounds lead to considerable problems in petroleum refineries, such as corrosion in equipment and pipelines, fouling, and catalyst toxicity in the upstream facility [[2], [3]]. Water-in-oil crude oil emulsions can be found at any level of the petroleum production and processing business. They are frequently undesirable in the presence of water because they might result in high pumping costs, pipeline damage, and higher transportation costs [4].

As a result, emulsions should be separated into two phases such as water and oil [5]. Crude oil comprises aromatic molecules, alkenes, carboxylic acids, phenols, naphthenes, and other hydrocarbon chemicals. Asphaltenes are the mixture's heaviest ingredients. Asphaltenes provide a protective layer on the interfacial phase between the water and oil phases, improving the stability of the interfacial film [6].

Chemical flooding has been demonstrated to improve oil recovery, and the injection of chemicals such as surfactants helps with emulsion production [[7], [8], [9]].

As a result, emulsion formation is a difficult task for the petroleum industry. For O/W separation, many demulsifiers, such as polymeric surfactants, ionic liquids, and nanoparticles, have been produced [10].

It is well understood that oil type and salinity have a significant impact on the effectiveness of surfactants used in the industry. The authors of publications [[11], [12]] studied the influence of oil type on the performance of mixed surfactants. The synergism of combinations of anionic, nonionic, and cationic surfactants in various types of oil was examined.

Natural surfactants (asphaltenes & resins) present in the oil contribute to the stability of water-in-crude oil emulsions. These components are recognized as natural stabilizers of crude oil emulsions because they adsorb spontaneously at the water-oil interface and form an adsorption layer. Because of their interfacial activity, asphaltenes and resins are high molecular oil components that provide a large structural-mechanical barrier at the oil-water interface [[13], [14]].

Emulsion stability is the uniformity of emulsion qualities throughout time. Simultaneously, the emulsion is considered an unstable system from a thermodynamic, and emulsion features fluctuate slowly, as do several processes that occur during emulsion property change, such as creaming, flocculation, and Ostwald ripening, coalescence, and so on. These instances, however, can occur in groups or separately [15].

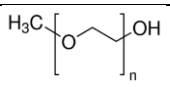
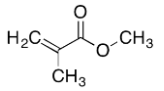
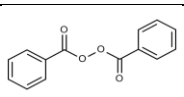
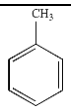
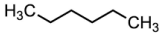
To create effective and relevant techniques for oil separation, the stability of O/W emulsions has been explored in several petroleum oil research studies [16].

Already in our earlier work [17], the grafted copolymer P(mPEG-g-MMA) so produced was studied by ^{1}H NMR, ^{13}C NMR, FT-IR, DSC, TGA, and SEM methods.

Experimental technique

Research materials. Toluene (ACS reagent, reagent ISO, >99.7%) and hexane (HPLC grade) were purchased from Sigma Aldrich. Methyl methacrylate (MMA) (which contains 30 ppm of hydroquinone monomethyl ether (MEHQ) as an inhibitor (99%). Alfa Aesar supplied 97% (dry weight) dibenzoyl peroxide, wet with 25% water. In the experimental part, chemicals from table 1 were employed without purification.

Table 1 – Chemicals used in the synthesis

Name	Structure	Source
Polyethylene glycol methyl ether		Sigma Aldrich
Methyl methacrylate		Sigma Aldrich
Benzoyl peroxide		Alfa Aesar
Toluene		Sigma Aldrich
Hexane		Sigma Aldrich

The preparation of grafted copolymer P(mPEG-g-MMA). The synthesis of the grafted copolymer was carried out in accordance with the mechanism reported in the reference [18].

The grafted copolymers in various ratios were synthesized in a 500 ml Syrris Globe reactor with a condenser and constant stirring.

Figure 1 – Syrris Globe reactor used for synthesis with doser

The first step was to dissolve mPEG in toluene, followed by the addition of a catalyst (0.1% weight of monomer). In free radical polymerization, benzoyl peroxide was utilized as a catalyst. Benzoyl peroxide was recrystallized, then dried in an oven at temperature of less than 400°C and later in a desiccator over silica gel to get rid of the water content. The monomer (MMA) was injected into the solution drop by drop in the second stage, and the temperature was increased to 700°C for one hour. Polymerization of mPEG with methyl methacrylate in various ratios, such as 10:90, 20:80, and 30:70, was carried out. A thermometer was used to record the temperature, and the stirring speed was set at around 100 rpm. For the last stage, the temperature was raised to 850°C for 1 hour. The reaction product was then precipitated out using hexane. The precipitated copolymer was filtered and then dried overnight at room temperature. The final dry products were powders.

Table 2 – Composition of grafted copolymers

Name	Sample 1, g	Sample 2, g	Sample 3, g
PGME	5	10	15
MMA	45	40	35
Catalyst	0.05	0.1	0.15
Toluene	100	100	100
Hexane	100	100	100

Figure 2 – Synthesized P(mPEG-g-MMA) copolymers

Preparation of Water/Oil Emulsions. All the emulsions were made in a total volume of 100 ml. The crude oil-to-aqueous phase (sea water) ratio was raised from 10-50%. (Vol.%). The emulsions were made by combining them with an IKA T25 digital ULTRA-TURRAX homogenizer. The speed was set to 1500 rpm for one hour.

The prepared emulsion was put into graduated 100 ml beakers. Starting with the second test flask, the determined amount of demulsifier was added and the emulsion was agitated for 1 minute. The emulsion was then allowed to stand for 30 minutes at the demulsifier's operating temperatures. The water, in the first test flask, was allowed to stand without any demulsifier. After that, the amount of water was measured with an accuracy of 0.1 ml. The demulsifier's effectiveness was determined by dividing the volume of water released by the total amount of water in the emulsion.

In this regard, the crude oil was stirred in a 100 mL beaker at 350°C (1500 rpm) while water was slowly combined with the oil until the two phases were completely homogeneous. At various oil :water ratios, the emulsions were noticeable (90 :10, 80 :20, 70 :30, and 50 :50).

Figure 3 – Emulsion prepared in different ratios of oil and water

Methods and techniques for characterization of emulsifier efficiency

The international standard "Bottle-Test" was used to assess the efficiency of new grafted copolymer reagent-demulsifiers. The bottle test technique is utilized in the production site to identify demulsifiers by calculating water separation performance on crude oil emulsions [19].

The tests involve determining the dynamics of oil-water emulsion stratification in time as a result of reagent-demulsifier and temperature action, followed by determining the residual water and chloride salts content.

At the dehydration step, we placed 70ml of oil in a 100ml graduated test tube, carefully capped with a cork, and placed in the thermostat for 5-7 minutes to heat up to 60°C.

Adding reagent-demulsifier in the required dosage (ppm), shaking vigorously for 1.5 minutes, and placing in thermostat to determine the dynamics of oil-water emulsion stratification in time -0.5, 1, and 2 hours at 60°C: the volume of the stratified water phase was measured in time.

After 60 minutes, the bottle test produced approximately 50% water separation at a demulsifier dosage of 300 ppm.

The method [20] was used to determine the residual water content of an oil phase sample.

The full volume of the aqueous phase was separated and discarded for the next step of testing.

Research Characterization

Differential scanning calorimetry (DSC), thermal gravimetric analyses (TGA), scanning electron microscopy (SEM), nuclear magnetic resonance (^{1}H NMR & ^{13}C NMR), and Fourier transform infrared FT-IR spectroscopies are used to evaluate the graft copolymers P(mPEG-g-MMA).

Research Results and Discussion

The grafted copolymer P(mPEG-g-MMA) was effectively made by free radical polymerization utilizing benzoyl peroxide as an initiator. SEM, FT-IR, ^{1}H NMR, ^{13}C NMR, TGA, and DSC were all used to characterize the samples. NMR analysis revealed the presence of all groups in the copolymers. According to the thermal stability investigations, the grafted copolymer has outstanding thermal stability and may be employed in a variety of applications. Furthermore, grafting and polymerization of the grafted samples greatly enhance the rate of breakdown. As a result, this copolymer has a wide range of uses, including surfactants in chemical technology.

Table 3 – Effectiveness of demulsifiers on needed time to separate oil from water at room temperature

Name	Amount, ppm	Time, min
P(MPEG-g-MMA) 10:90	100	18
P(MPEG-g-MMA) 10:90	200	14
P(MPEG-g-MMA) 10:90	300	9
P(MPEG-g-MMA) 10:90	400	8
P(MPEG-g-MMA) 10:90	500	5

Figure 4 – End of oil-water emulsion demulsification process by grafted copolymer

Three different demulsifier ratios were examined for the performance of water separation at 30°C using the bottle-test experiment methods outlined in the preceding section. The oil :water ratio was chosen such as the emulsion sample, 70 :30, and P(MPEG-g-MMA) was chosen as the reagent demulsifier, 10 :90. The results were collected for a 100 mL emulsion at 250°C and atmospheric pressure. The maximum demulsifier dose is established by the tests with the purpose of the optimizing demulsifier dosage to optimize water separation. As indicated in table 3, the reagent-demulsifier with a concentration of 300 ppm produced the best results compared to the others. All three demulsifiers produced excellent water, with no oil droplets on the bottle/tube wall and clear, colorless water.

Conclusions

The grafted copolymer P(mPEG-g-MMA) was effectively produced by free radical polymerization utilizing benzoyl peroxide as an initiator. SEM, FT-IR, nuclear magnetic resonance (^{13}C NMR & ^{1}H NMR), TGA, and DSC were all used to characterize the samples. NMR analysis revealed the presence of all groups in the copolymers. Based on the thermal stability outcomes, the grafted copolymer has good thermal stability and thus might be used as a surfactant-demulsifier in the Crude Oil Petroleum business. It has been established that the proper dose will have an economic effect.

Conflict of interest. All authors declare that there is no conflict of interest.

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P(mPEG-g-MMA) иондық емес егілген сополимерлердің синтезі және қолданылуы

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ТҮЙІНДЕМЕ

Бұл жұмыстың мақсаты қоршаған орта температурасында және қалыпты атмосфералық қысымда гидрофильді поли(этиленгликоль) метил эфирі (MPEG) және гидрофобты метилметакрилат (MMA) негізіндегі жаңа иондық емес амфифильді сополимерлерін алу болып табылады. Поли(этиленгликоль) метил эфирі (mPEG) әртүрлі қатынаста 10:90, 20:80, 30:70 метилметакрилат (MMA) дайындалды және инициатор ретінде бензоил асқын тотығының қатысуымен жылу астында макробосрадикалды инициатор әдісімен егілді. P(mPEG-g-MMA) сополимерлерін алу үшін толуолда. Осы жұмыста ұсынылған зерттеулер мұнай эмульсиялары үшін иондық емес деэмульгатор ретінде синтезделген трансплантаттық сополимер P(mPEG-g-MMA) мүмкін пайдалану мақсатында жүргізілді. Дайындалған ионды емес беттік белсенді заттар 60°C температурада әртүрлі мұнай: су

	қатынасында көрсетілген майдағы су эмульсиялары үшін деэмульгаторлар ретінде бағаланды. Тәжірибе нәтижесі дайындаған деэмульгаторлардың сусыздану жылдамдығы деэмульгаторлардың химиялық құрамы мен концентрациясына байланысты 100%-ға жететінін көрсетті. Деэмульгатордың оңтайлы дозасы 300 ppm болды. ***Түйін сөздер:*** полиэтиленгликоль метил эфирі, метилметакрилат, бос радикалды полимерлеу, катализатор, деэмульгатор.
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Синтез и применение неионогенных прививочных сополимеров P(mPEG-g-MMA)

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АННОТАЦИЯ

Цель данной работы - получение новых неионогенных амфифильных прививочных сополимеров на основе гидрофильного поли(этиленгликоль) метилового эфира (МПЭГ) и гидрофобного метилметакрилата (ММА) при температуре окружающей среды и нормальном атмосферном давлении. Поли(этиленгликоль) метиловый эфир (mPEG) был подготовлен и привит с различными соотношениями 10:90, 20:80, 30:70 метилметакрилата (ММА) в присутствии пероксида бензоила в качестве инициатора с использованием метода макросвободнорадикального инициатора под воздействием нагревания в толуоле для получения сополимеров P(mPEG-g-MMA). Исследования, представленные в данной работе, проводились с целью возможного применения синтезированного прививочного сополимера P(mPEG-g-MMA) в качестве неионогенного деэмульгатора для нефтяных эмульсий. Приготовленные неионогенные ПАВ были оценены как деэмульгаторы для эмульсий "вода в нефти", которые были выражены при различных соотношениях нефть: вода при температуре 60°C. Результаты эксперимента показали, что скорость дегидратации приготовленных деэмульгаторов достигает 100% в зависимости от химического состава и концентрации деэмульгаторов. Оптимальная дозировка деэмульгатора составила 300 ppm.

Ключевые слова: метиловый эфир полиэтиленгликоля, метилметакрилат, свободнорадикальная полимеризация, катализатор, деэмульгатор.

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Engineering and Technology

Ceramic molds based on yttrium oxide for the casting of titanium alloys

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ABSTRACT
The effect of various binding agents based on aqueous solutions of nitric acid, yttrium nitrate and orthophosphoric acid and yttrium hydroxide gel on the physical and mechanical properties of casting molds based on Y_2O_3 has been studied. It is shown that the most promising binding agent for yttrium oxide casting molds is a phosphate bond. The data describing the curing mechanism of phosphate-bonded molding mass is presented. The influence of the concentration of binding agent solutions on the strength characteristics of molding materials after curing and heat treatment is shown. Information about the interaction of yttrium oxide powder molds with phosphate-binding with titanium melt of VT1-0 and VT6 grades is presented. The obtained data allowed us to describe the advantages and disadvantages of the developed molding compound. A method for producing casting molds based on yttrium oxide powder with a yttrium phosphate-binding agent was developed based on this research.

Keywords: molding mixture, yttrium oxide, binding agent, casting mold, titanium alloy

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Introduction

Investment casting is one of the most efficient and cost-effective manufacturing methods for titanium alloys of various complexity and with weights ranging from a few grams to tens of kilograms. The manufacture of high-quality titanium products with a minimum of surface defects is possible only when using casting molds obtained from refractory materials inert concerning titanium melts. This requirement and the high melting point of titanium alloys do not allow the use of most materials traditionally used in the foundry of non-ferrous and ferrous metals.

Forming material or its components, if they are not sufficiently resistant to titanium melts, will develop physical and chemical processes between them, leading to the dissolution of the mold elements, redox reactions, and wetting and capillary phenomena when receiving the castings. These processes lead to defects in the castings: burning, formation of an alpha layer, porosity, and poor filling of narrow channels with melt. This contributes to higher machining costs and higher rejection rates and makes it impossible to produce thin-walled castings. A gas-saturated layer can lead to the emergence and spreading of cracks, which reduces the operational reliability of the titanium casting. For this purpose, the initial refractory molding and binder materials that are inert with respect to the titanium melt should be used for casting.

Mixtures based on fused aluminum oxide (electrocorundum), magnesite, zirconium dioxide, and graphite have been used in the industry for casting titanium alloys. The low chemical activity or inertness of refractory oxides MgO, ZrO_2, Al_2O_3, CaO, and Y_2O_3 for titanium melts and titanium alloys has been shown in the works of of [[1], [2], [3], [4], [5], [6], [7], [8], [9], [10], [11], [12], [13]]. However, such oxides react in varying degrees with the titanium melt [14], which can cause burn-in and limit the wall thickness of the castings. Y_2O_3 interacts with the titanium melt to a lesser degree than the above oxides, and this can be explained by the fact that their contact, due to the reduction of the titanium oxide, produces metallic yttrium, which is extremely insoluble in the melt. A barrier layer is formed, reducing the rate of interaction between them.

REMET® UK offers a water-dispersed aluminum oxide binder, Remal20, which has solution stability in a certain pH range, to form the face layer of the refractory shell for casting titanium alloys. It is known that aluminum oxide interacts very actively with the titanium melt, which will prevent the melt from filling the thin channels. In addition, ceramic layers obtained from zirconium oxide with Remal20 bonding are characterized by relatively low strength and crack formation [15]. Tetsui et al. and Zhao et al. (reference) found in experiments on casting titanium alloys into molds made of various refractory materials that the least oxygen enrichment in titanium parts occurs when Y_2O_3 is used as the face layer [1]. Contamination studies of directionally solidified alloy Ti46Al8Nb and other titanium alloys in Al_2O_3, Y_2O_3, and CaO crucibles were performed [[16], [17], [18], [19], [20]].

Electrocorundum molds are widely used in the aircraft industry to manufacture castings, which are produced by investment models on an ethyl silicate binder. However, this technology also produces a surface layer on the surface of the titanium castings that is saturated with impurities and negatively affects the characteristics of the castings (alpha layer). In addition, a significant disadvantage of these binding agents is their high cost, low eco-friendliness, and low survivability, which limits their use for large castings from titanium alloys [20], [21]. One of the main problems in producing Y_2O_3 casting molds is the inability to use binding agents based on silicon dioxide and aluminosilicates, which cause a reaction with titanium alloys with the formation of cracks on the casting surface and a very hard alpha layer of 0.3-0.6 mm thickness [22]. The work [23] shows the formation of an alpha layer with a width of 0.45-0.55 mm, when used as the first layer of ceramic shells of calcium oxide stabilized with zirconium oxide or yttrium oxide stabilized with zirconium oxide. This surface layer results from the reaction of Ti with metal oxides of the ceramic shells, which consists of brittle intermetallic compounds that significantly impair the mechanical properties of the castings. [24]. To overcome this problem, titanium alloys should be embedded in special ceramic casings that prevent or significantly reduce this reaction.

Further research on the selection of a binding agent for the production of ceramic molds from Y_2O_3 for the manufacture of castings from titanium and titanium-based alloys is necessary in this regard. Reducing the thickness of the alpha layer when producing castings from titanium alloys can only be achieved by casting in molds made entirely or partially (face layer) of materials that are inert in relation to titanium. The development of such materials will provide the required quality of the casting surface, which will make it possible to produce titanium castings with a relief surface. The lack of research on the development of binding agents inert to titanium melts for molds based on yttrium oxide hinders the development of technologies for casting titanium alloys. In this regard, studies were performed to find binding agents for the production of Y_2O_3 casting molds by the method of investment casting. The results of these studies are given in this article.

Experimental part

It is necessary to develop molding materials characterized by good fluidity, harden after model pouring, and do not interact with titanium melts, and provide high mold strength to obtain complex configuration castings from titanium alloys using wax models, including those made by additive technologies.

We set the following requirements when developing binding agents for Y_2O_3 powders:

- the binding agent must be stable up to the casting temperature of the titanium alloy, or at decomposition, it must provide high strength to the casting molds;
- the binding agent must interact weakly with the titanium melt;
- the binding agent should be based on yttrium compounds. Curing the molding mixture from Y_2O_3

powders should occur within an acceptable time interval (from 0.25 to 24 hours).

The possibility of using compounds as binders is considered:

- formed by the interaction of Y_2O_3 with solutions HNO_3 and $Y(NO_3)_3$

- forming yttrium hydroxide $Y(OH)_3$ - yttrium acetate $Y(CH_3COO)_3$

- not decomposing when heated - yttrium phosphate YPO_4.

Recrystallization of yttrium oxide powders increases their chemical resistance to both yttrium nitrate and orthophosphoric acid solutions, and titanium melts due to a decrease in surface energy. The initial yttrium oxide used as a filler of the molding material was subjected to heat treatment in a tubular furnace in an argon flow to remove hydrated water and decompose yttrium carbonate which recrystallization of the powder developed. It was found that the minimum temperature at which recrystallization of chemically deposited yttrium oxide powders begins is 1300 ^oC, this process actively proceeds above 1500 ^oC, above 1700 ^oC their sintering develops (Figure 1).

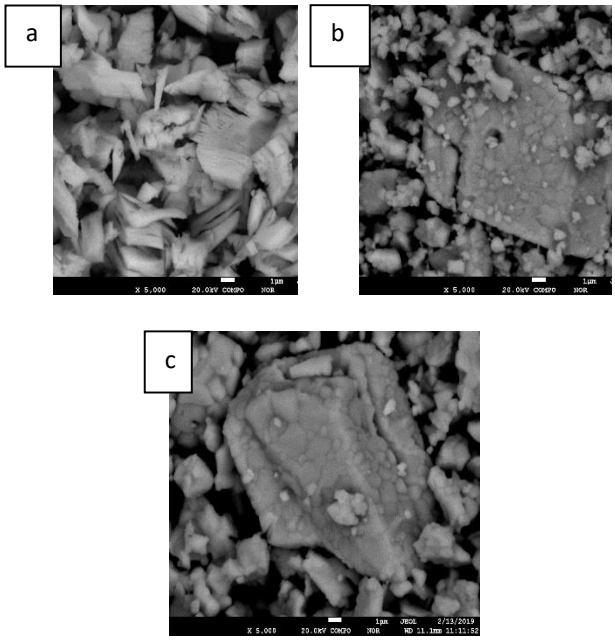


Figure 1 – Recrystallization of yttrium oxide powder during annealing: (a) initial state; (b) 1500 ^oC, 2 hours; (c) 1650 ^oC, 2 hours

Evaluation of the possibility of using solutions of HNO_3 and Y $(NO_3)_3$. The conducted research has shown that when Y_2O_3 powder is mixed with an aqueous nitric acid solution with a concentration of 0.5-2 mol/l or with an aqueous $Y(NO_3)_3$ solution with a concentration of 2-10 mol/l at a T/L ratio of 2:1, an interaction develops between them, which leads to the solidification of the mixture. The curing speed improves from 10 to 2 minutes with an increase in solution concentration in the specified interval. The hardened mixture at room temperature is characterized by high strength, however, when heated above 400 ^oC, such materials lose strength and crumble. This makes it impossible to use HNO_3 and $Y(NO_3)_3$ solutions as binding agents in the production of casting molds based on Y_2O_3 powders.

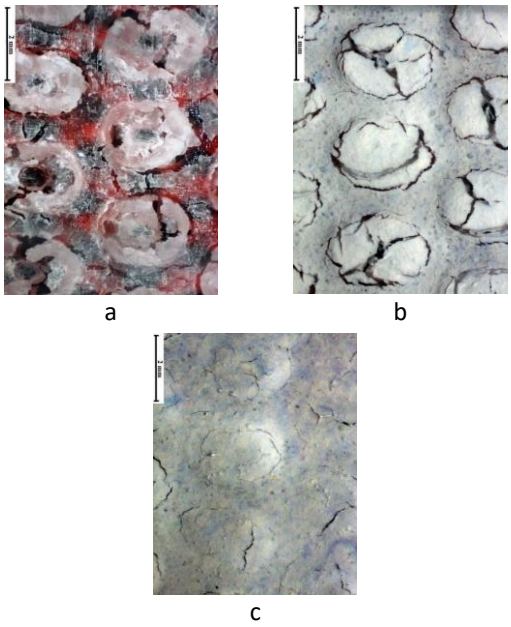
Evaluation of the possibility of using yttrium hydroxide $Y(OH)_3$ as a binding agent in the production of Y_2O_3-based molds. It is known that the precipitation of yttrium hydroxide from aqueous solutions of yttrium acetate $Y(CH_3COO)_3$ forms a gel. Separation of the gel and ammonium acetate solution was performed by dilution with water in a ratio of 1/1, stirring and subsequent centrifugation at a centrifuge spindle speed of 2500 rpm for 10 min with the separation of the gel from the solution. It was found that the water content in it is 73%, when drying yttrium hydroxide gel at 180 ^oC for 1 hour. Only 10% yttrium oxide remained of the initial gel mass after calcination of the remaining material at 900 ^oC.

Three layers of yttrium hydroxide gel and yttrium oxide gel were applied to the surface of molding models in the amounts of 25 and 50 wt% to evaluate the possibility of using yttrium hydroxide gel as a binding agent for the first and subsequent layers of molding materials. The model was dried for 1 day after applying each layer, and then the surface was photographed. Figure 2 shows the structure of the obtained shells on the surface of the models after the application of 3 layers of the mixture.

High water content during drying causes cracking of even thin gel films up to 0.2 mm, applied to both smooth and rough surfaces of the model (Figure. 2a). Mixtures of gel with yttrium oxide powder in amounts of 50 and 75 wt% also crack when dried (Figures 2 b-c). However, the number and width of cracks decrease as the proportion of yttrium oxide increases. But the high viscosity of such mixtures requires their mechanical application to the surface of the model and excludes the possibility of spraying. High shrinkage with crack

formation makes it impossible to use $Y(OH)_3$ gel as a bond for yttrium oxide-based molding materials.

Using as a concentrated binding solution (10%) yttrium acetate does not provide the required level of strength of the mixture with Y_2O_3 in the ratio W/T 1:2 after drying. The layer of such material on the model surface increases in thickness by at least 40% due to $Y(OH)_3$ gel formation during subsequent ammonia drying. This causes the face layer to crack and chip off the surface of the model during subsequent drying, which makes the use of yttrium acetate solution as a binding agent useless.



a b c

Figure 2 – Crack formation in hydroxide-based shells: (a) $Y(OH)_3$ gel; (b) 50% $Y(OH)_3$ gel +50% Y_2O_3; (c) 2nd layer 25% $Y(OH)_3$ gel+75% Y_2O_3

Study of the possibility of using yttrium phosphate as a binding agent. It is known that yttrium phosphate is formed by the interaction of yttrium nitrate and phosphoric acid in an ammonia atmosphere in the following reaction:

$$Y(NO_3)_3+H_3PO_4+3NH_3*H_2O \rightarrow YPO_4+3NH_4NO_3+3H_2O \quad (1)$$

We used chemically precipitated yttrium oxide powder with a dispersion of fewer than 10 µm, an aqueous solution of yttrium nitrate, and orthophosphoric acid as the initial raw materials in the experiments. It was found during preliminary experiments that mixing yttrium oxide powders with a mixture of yttrium nitrate and orthophosphoric acid in a short time (up to 5 minutes) resulted in the curing of the molding mixture, which did not allow to fill the flask with the model and remove air bubbles from it. The solution to this problem was to pretreat the mixture of yttrium nitrate and phosphoric acid solutions for at least 24 hours at room temperature. The curing of mixtures of Y_2O_3 with $Y(NO_3)_3+H_3PO_4$ solution followed from 10 minutes to 8 hours, depending on the concentration of the solution. The temperature of preliminary annealing of Y_2O_3, in this case, did not have a significant effect on the curing rate of the molding mixture.

Cylindrical samples with a mixture of pre-baked yttrium oxide powder at 1300-1700 ^oC and an aqueous solution of yttrium nitrate with a concentration from 80 g/l to 333.3 g/l and orthophosphoric acid from 14 g/l to 52 g/l were prepared to determine the effect of the concentration of yttrium nitrate and orthophosphoric acid on the structure and strength of the molding materials. We took a stoichiometric ratio of $Y(NO_3)_3$ and H_3PO_4 according to the reaction equation (1). The ratio W/T was taken no more than 1:2. The mold with the samples was left at room temperature for 24 hours to cure the mixture, then the samples were removed from the mold and dried in ammonia medium at room temperature for 1 day and then in a normal atmosphere at 90-95 ^oC for 0.4 days. The ceramic forms were calcined in a resistance shaft furnace at 600 ^oC and 900 ^oC for 3 hours. Heating to the target temperature was performed at a rate of 3 deg/min. The purpose of the heat treatment was to remove crystalline moisture, decompose ammonium nitrate and yttrium nitrate that did not interact.

Cylindrical samples made of yttrium oxide molding mixture were tested in compression on a Shimadzu AG 100kNx electromechanical testing machine with a 1 mm/min loading speed.

Casting into ceramic molds was performed using titanium alloys VT1-0 and VT6 in a UIPV-0.001 vacuum induction furnace with melt discharge through the bottom.

We investigated the structure of the near-surface and alpha layers of molding materials and cylindrical castings obtained using the developed molding materials by optical and scanning electron microscopy (SEM) and microprobe analysis using a JEOL JXA-8230 microprobe analyzer. The structure was studied using the backscattered electron mode (COMPO). The thickness of the alpha layer was determined by measuring the microhardness from the surface to the center of the casting using a PMT-3 microhardness tester at a load of 50 g.

Research Results and Discussion

The molding mixture had the consistency of thick sour cream when the ratio of a yttrium oxide powder to an aqueous solution by weight is 2:1, and, when vibrations were applied, well filled the flask with a model installed in it to obtain a shape with the required wall thickness and surface relief. In this case, air bubbles were well removed from the mold cavity. The introduction of orthophosphoric acid with a concentration of 21.5 g/l to 43.0 g/l into the composition of an aqueous solution of yttrium nitrate with 125 to 250 g/l provided a solidification period of the mixture from 2 hours to 15 minutes. Increasing the concentration of binders $Y(NO_3)_3$ and H_3PO_4 more than 250 g/l and 43 g/l, respectively, led to self-heating of the mixture and its rapid hardening, which did not allow to complete the molding process.

A graph of the dependence of the strength limit of the molding compound on the concentration of the binder $Y(NO_3)_3$ and H_3PO_4 was drawn according to the results of tests of the obtained cylindrical samples. The analysis of the graph (Figure 3) shows that with increasing binder concentrations of $Y(NO_3)_3$ and H_3PO_4 from 80 and 14 g/l to 167 and 28.7 g/l respectively, the strength of the molding compound increases, and decreases with further increase. This may be due to the fact that as the concentration of these substances increases, the proportion of binding agents formed becomes higher. Curing time is shortened to a few minutes if the concentration is above a certain value and air bubbles are not effectively removed from the mixture during vibration. This reduces the strength of the material. The strength of the molding material decreases after ammonia drying and heat treatment at 600 and 900 °C. At the same time, the strength of the molding material naturally grows with an increase in the concentration of components in the binding agent. A significant decrease in strength after annealing at 900 °C is observed in the mixture with concentrations of 333 and 54.7 g/l $Y(NO_3)_3$ and H_3PO_4, respectively, the reason for which is the high porosity of such material.

The curing mechanism of the molding mixture based on yttrium oxide powder with a binding agent based on an aqueous solution of yttrium nitrate and orthophosphoric acid is considered based on the analysis of the material structure after curing, X-ray diffraction analysis and infrared spectra of the material obtained during various stages of curing at room temperature.

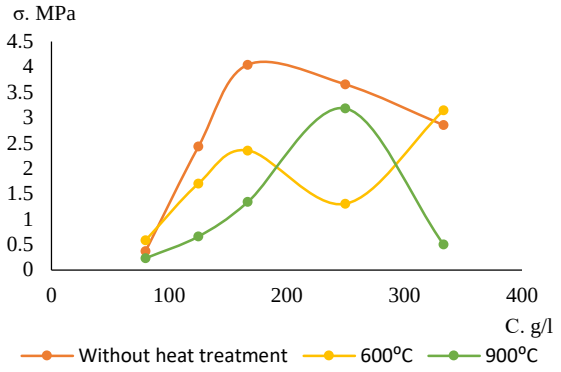


Figure 3 – Dependence of the effect of the concentration of $Y(NO_3)_3$ in the binding agent and H3PO4 in aqueous solutions on the strength limit of the molding compound

IR spectra of the sample obtained by mixing Y_2O_3 powder with a binding solution of $Y(NO_3)_3$ and H_3PO_4 167.0 g/l and 28.7 g/l were taken immediately after mixing and then after 1, 2, 3 hours and 3 days. The images were taken on an Avatar 370 CsI FT-IR spectrometer, in the spectral range of 4000-300 cm^{-1} from tablet preparations prepared by pressing 200 mg of KBr with 2 mg of sample. Experiment set-top box is Transmission E.S.P.

As follows from the data obtained, regardless of the exposure time, the spectra of such a sample (Figure 4a) contain lines characteristic of the following compounds:

yttrium oxide Y_2O_3 – 561, 464, 418, 399, 341, 310 cm^{-1} [25]; valence ν(OH)-3405 cm^{-1} and deformation δHOH-1635 cm^{-1} vibrations of water molecules [26]; yttrium orthophosphate YPO_4 - 1040, 634 cm^{-1} [25]; xenotime YPO_4 - 1076, 634 cm^{-1} [27]; group $[CO_3]^{2-}$ – 1474, 1458, 839, 825 cm^{-1} [26, 29, 30]; group $[NO_3]^{-}$ – 1763, 1384, 1346, 1040, 792 cm^{-1} [[25], [29], [30], [31]]. The band at 746 cm^{-1} can be referred to yttrium orthophosphate dihydrate YPO_4-$2H_2O$ [28], a band in this range of the spectrum is also observed in the spectra of nitrate hydrates of rare earth elements [[29], [30]]. There is a band at wave number 391 cm^{-1} in the range of Y-O valence vibrations in the spectrum of the sample; this band probably corresponds to the Me^{3+}-O bond in the carbonate [32].

Comparison of the spectra taken immediately after mixing, after 3 hours and after 3 days showed changes in the intensity of the lines (Figure 4b), indicating changes in the phase composition of the sample. The following changes are observed:

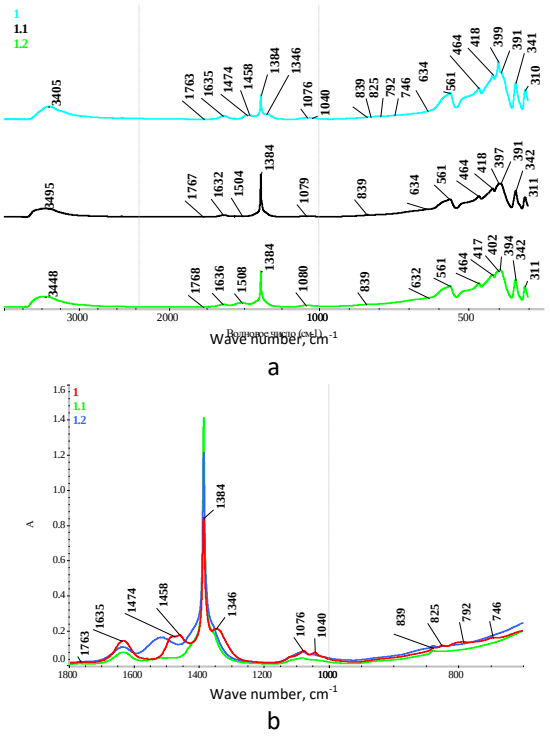


Figure 4 – Infrared spectra: (a) No. 1 suspension immediately after mixing; (b) No. 1.1 - after 3 hours; No. 1.2 - after 3 days

1. Shift of the maximum of the valence band v_3 of the $[CO_3]^{2-}$ ion to the high frequency range (1-1474, 1458 cm^{-1}; 1.1 - 1504 cm^{-1}; 1.2 - 1508 cm^{-1}), and variation of the absorption intensity. The lowest intensity of the valence vibration band v_3 of the $[CO_3]^{2-}$ ion was recorded in the spectrum of sample 1.1.

2. Varying the intensity of the valence band v_3 of the $[NO_3]^{-}$ ion.

3. Varying absorption intensities in the range of Y-O valence vibrations.

4. Displacement of the maximum of valence vibrations ν(OH):

sample 1- 3405 cm^{-1}; sample 1.1- 3495 cm^{-1}; sample 1.2- 3448 cm^{-1}.

This indicates that the processes of yttrium phosphate formation develop before ammonia drying and are associated with the reaction of yttrium nitrate with yttrium oxide and phosphoric acid.

X-ray phase analysis of such a molding compound after curing for 3 hours indicates the formation of yttrium nitrate hexahydrate (Figure 5). Its formation occurs due to the interaction of yttrium oxide and nitrate. The lines characteristic of yttrium phosphate does not appear on radiographs after ammonia drying, indicating its formation in X-ray amorphous form.

The data obtained indicate that the bond between Y_2O_3 powders is formed already at the stage of mixture curing at room temperature (Fig. 6a). Lamellar crystals of yttrium phosphate are formed after ammonia drying, intertwining with each other and binding Y_2O_3 particles (Figure 6b). This structure is maintained during further heat treatment (Figures 6c and d). It is likely that the decrease in strength of the cured molding compound after heat treatment can be explained first by the decay of ammonium nitrate, and then at 900 °C by the beginning of recrystallization of yttrium phosphate needle crystals.

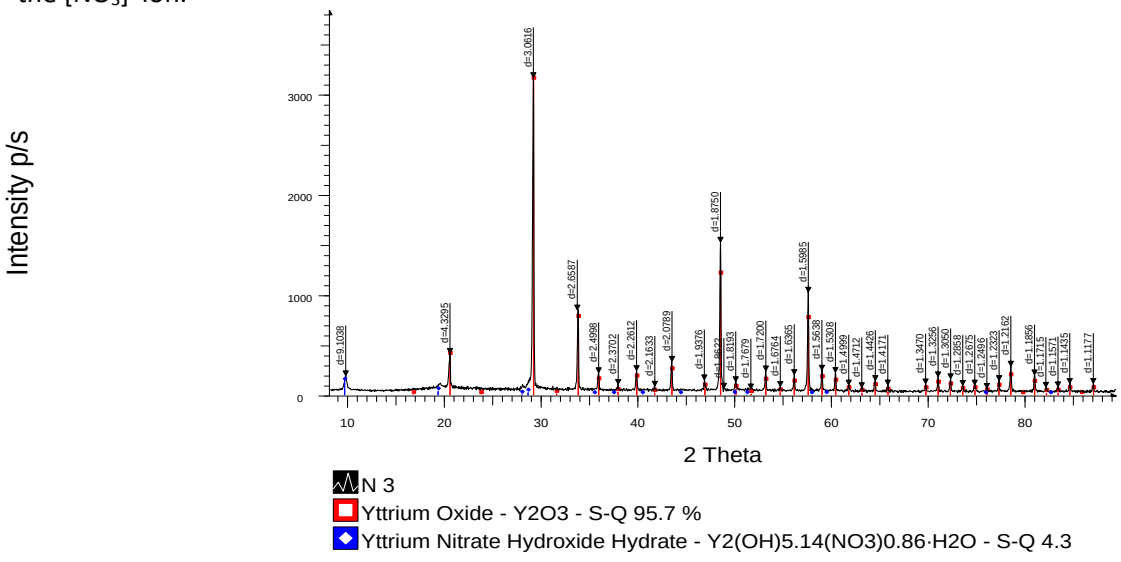


Figure 5 – X-ray diffraction pattern of the resulting mixture based on $Y(NO_3)_3 + H_3PO_4 + Y_2O_3$ without ammonia drying

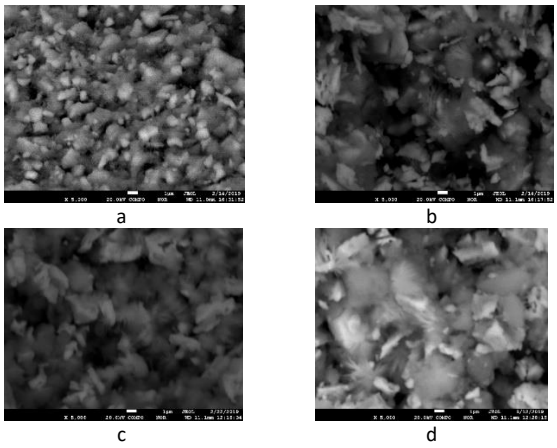


Figure 6 – Changes in the structure of molding mixture based on yttrium oxide and binder $Y(NO_3)_3$ 167,0 g/l H_3PO_4 = 28,7 g/l at different stages of treatment: (a) after curing at room temperature; (b) after ammonia drying; (c) after heat treatment at 600 °C; (d) after heat treatment at 900 °C

It has been established, based on studies of the effect of the concentration of yttrium nitrate and phosphoric acid solutions on the strength of the molding materials obtained, that the optimal concentration of yttrium nitrate and orthophosphoric acid solutions for producing Y_2O_3-based molds is 167.0 g/l and 28.7 g/l, respectively.

Production of castings into molds based on Y_2O_3 and binder YPO_4. Casting molds were made on the basis of the developed molding mixture, into which castings of titanium grade VT1-0 and titanium alloy VT6 were obtained. Casting was performed in a mold at room temperature and heated to 550 °C. The diagram of the casting unit, the casting mold, and the resulting casting are shown in Figure 7. Metallographic, electron microscopic, and microprobe examinations were performed to study the formation of an alpha layer and annealing layer on the surface of the castings.

The formation of the alpha layer occurs primarily due to the dissolution of oxygen, which titanium releases, reducing or dissolving in itself the metal oxides that make up the basis of the molding materials. The formation of an alpha layer seriously affects the mechanical properties, the structure of the surface layer of the metal and the dimensional accuracy of the castings. The thickness of such a layer depends on the chemical stability of the mold material and the contact period between the liquid titanium and the mold. The structure and thickness of the alpha layer must therefore be studied first when examining the structure of the castings.

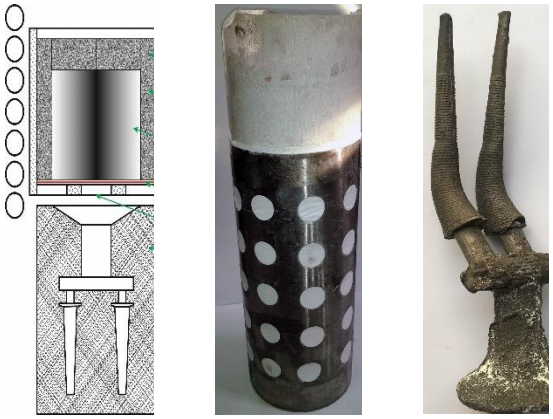


Figure 7 – Diagram of the melting unit of the UIPV-0.001 vacuum induction furnace (a), casting mold (b), casting of blanks of the femoral component of the hip endoprosthesis, obtained from titanium alloy VT6 (c): (1) titanium cylinder; (2) casting mold; (3) - tantalum foil; (4) perforated graphite ring; (5) quartz glass body; (6) lining of yttrium oxide powder

Figure 8 shows the microstructure of the burn-in layer and the near-surface layer formed when casting the alloy VT6 and titanium grade VT1-0 in a mold based on yttrium oxide with a phosphate bond at the mold temperature of 25 °C and 550 °C. The analysis of the structure shows that with an increase in the temperature of the mold, the thickness of the burn-in significantly increases (from --60 µm to 300 µm). In addition, the surface topography is distorted when casting in a heated casting mold. Microprobe analysis of the burn-in zone indicates that when the melt comes into contact with the mold material due to wetting, titanium penetrates the channels and reacts. Yttrium oxide reduction develops, after which yttrium and oxygen diffuse into the near-surface layer. Oxygen dissolves to form an alpha layer, and yttrium, after crystallization of the melt, is released as a separate phase along the grain boundaries. Titanium surface is covered by a thin oxide film in the air, so in microprobe analysis by EDS and WDS analysis methods there is a big error of oxygen measurement in the alpha layer. In this regard, the most revealing way to determine its thickness is to measure the microhardness along the cross section from the surface deep into the casting.

The microhardness measurements performed on the PMT-3 microhardness tester showed that when casting titanium alloy VT6 into cold and hot molds and titanium VT1-0 into a cold mold made of yttrium oxide, the thickness of the alpha layer does not exceed 550 μm (Fig. 9). This allows us to conclude that there is an insignificant change in the properties of the titanium casting due to the reaction interaction with the mold material. The burn-in layer that forms on the casting surface is poorly separated and can only be effectively removed by sandblasting.

The main disadvantage of casting molds from the developed molding material based on yttrium oxide is the formation of single pores ∅<0.8 mm in the alpha layer. Thermal analysis of the mold material, which underwent all stages of processing at 900 °C, was performed to identify the causes of porosity formation in the alpha layer. The studies were performed on a synchronous thermal analyzer TG-DTA / DSC STA449 F3 Jupiter® "NETZSCH". The furnace space was evacuated before heating (achievable vacuum level ~ 92%) and then purged with inert gas for 5 minutes. Heating was done to ~ 1500°C at a rate of 15°C/min. Cooling was performed at a rate of 170 °C/min. The total volume of incoming gas was kept within 90ml/min. The results obtained with the STA 449 F3 Jupiter were processed using the NETZSCH Proteus software.

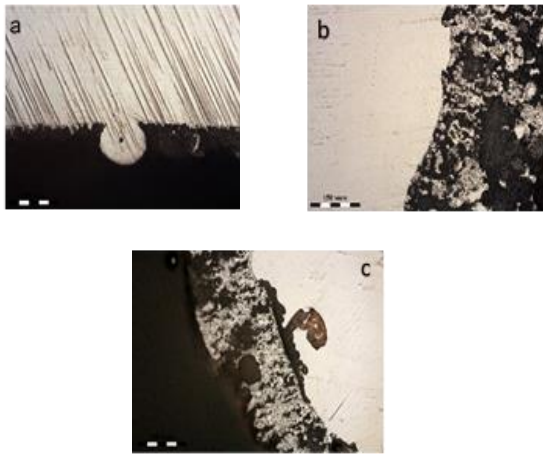


Figure 8 – Cross-sectional structure of burn-in layer and near-surface area of VT1-0 and VT6 titanium castings, formed during casting in Y_2O_3 molds with phosphate-bonding (x250): (a) VT6 mould heated to 25 °C; (b) VT6 mould heated to 550 °C; (c) VT1-0 mould heated to 25 °C

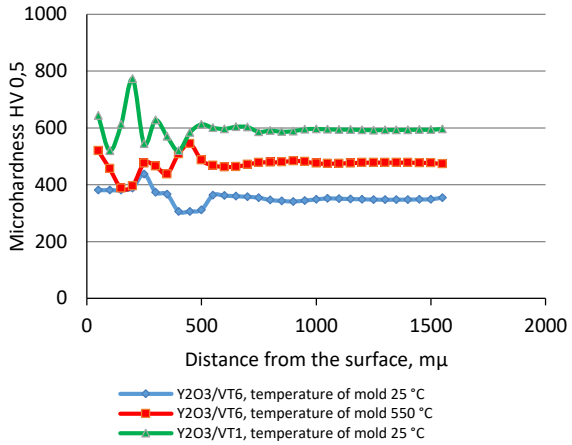


Figure 9 – Change in microhardness over the cross-section of the alpha layer of castings from VT1-0 titanium and VT6 titanium alloy, obtained by casting into molds from yttrium oxide with a phosphate binder

Figure 10 shows that when the molding compound is heated to 1500 °C, the decrease in weight is 0.25%. The main decrease in weight is caused by the dehydration process, which develops most intensively at 196.20 °C. Further weight loss occurs gradually and is probably associated with the processes of gradual decomposition of yttrium phosphate. The mold material does not undergo a phase transition when heated. Sintering processes begin at temperatures above 1380 °C. This indicates that the only reason for the formation of porosity in castings can be the reaction of the phosphate bond with the titanium melt. Presumably, the phosphorus is reduced to its elemental state and evaporates to form micro-cavities as a result of a series of reductive reactions between titanium and YPO_4 (Figure 8c). This may be due to the low solubility of phosphorus in titanium, less than 0.3% at 1495°C. Accordingly, a maximum reduction of yttrium phosphate content in the yttrium oxide-based molding mass is necessary.

In addition, it has been found that if the melt is poured after the heat-treated mold has been exposed to a normal atmosphere, the likelihood of pores in the central part of the casting increases significantly. This is due to the active absorption of moisture and carbon dioxide by yttrium oxide from the air.

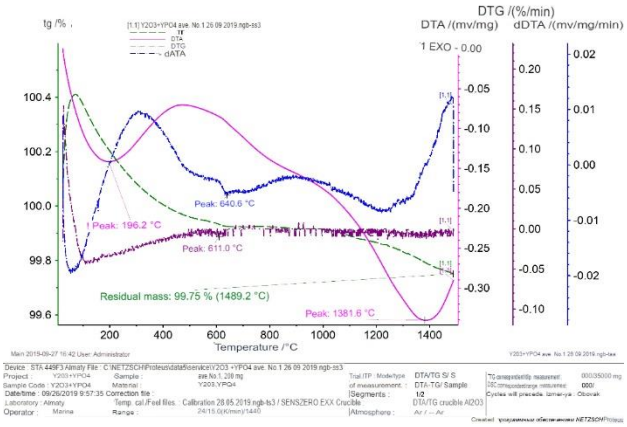


Figure 10 – Thermogram of heating the molding compound based on Y_2O_3 and YPO_4 binder

Conclusions

The use of nitric acid or yttrium nitrate solutions as binding agents for yttrium oxide powders is not promising due to the fact that the forms lose strength after thermal decomposition of yttrium nitrate hexahydrate.

Using a mixture of yttrium oxide and yttrium hydroxide as a face layer is not promising due to the fact that during drying the yttrium hydroxide gel undergoes high shrinkage, which leads to the formation of numerous cracks in the face layer. Similarly, yttrium acetate solution cannot be used as a binding agent for Y2O3 powder, due to the low strength of such a molding compound and the subsequent ammonia drying of the yttrium hydroxide gel formation leads to significant swelling of the resulting mold and its subsequent destruction;

A new composition and modes of subsequent processing of molding compound based on yttrium oxide and binding agent from yttrium nitrate solution and orthophosphoric acid, which allow to produce casting molds for casting titanium and titanium alloys with high strength level, have been developed. The mechanism of solidification of the molding compound is described by the following processes: the formation of yttrium nitrate hexahydrate in the first stage due to the interaction of yttrium oxide and nitrate, which binds the filler particles in the period from 0.25 to 3 hours after mixing the components; conversion of yttrium nitrate hexahydrate into yttrium phosphate with needle-shaped crystals in a second stage after ammonia drying. The molds of such a mixture retain their strength after heat treatment at 900°C and do not undergo polymorphic transformations when reheated. Mass loss on heating to 1500C does not exceed 0.25%.

Casting of VT1-0 and VT6 alloys into molds from the developed mixture results in the formation of an alpha layer up to 550 microns thick on the casting surface, which is associated with the reduction of yttrium oxide by titanium melt with subsequent dissolution of oxygen in the reaction zone. The microhardness increases naturally in this layer. Single pores up to 0.8 mm in size are formed in the alpha layer due to the interaction of titanium melt with yttrium phosphate. A burn-in layer with high adhesion is formed on the surface of the castings. It can be removed by sandblasting. Titanium molds must be cast directly after heat treatment or measures must be taken to protect the molds from interaction with the atmosphere due to the large surface area of yttrium oxide powders and their interaction with atmospheric carbon dioxide and moisture.

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

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Титан қорытпаларын құюға арналған иттрий оксиді негізіндегі керамикалық қалыптар

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ТҮЙІНДЕМЕ

Y_2O_3 негізіндегі құю қалыптарының физика-механикалық қасиеттеріне азот қышқылының, иттрий нитраты мен ортофосфор қышқылының және иттрий гидроксиді гелінің сулы ерітінділері негізіндегі әртүрлі байланыстырғыш заттардың әсері зерттелді. Итрий оксидінен құйма қалыптарды алу үшін ең перспективалық байланыстырғыш фосфатты байланыстырғыш екені көрсетілген. Фосфатты байланысы бар қалыптау қосылысының қатаю механизмін сипаттайтын деректер берілген. Қалыптау материалдарының қатаю және термиялық өңдеуден кейінгі беріктік сипаттамаларына байланыстырушы ерітінділер концентрациясының әсері көрсетілген. Итрий оксиді ұнтағынан жасалған құю қалыптарының ВТ1-0 және ВТ6 маркалы титан балқымасы бар фосфатты байланыстырғышпен әрекеттесуі туралы ақпарат берілген. Алынған мәліметтер әзірленген қалыптау қоспасының артықшылықтары мен кемшіліктерін сипаттауға мүмкіндік берді. Жүргізілген зерттеулердің негізінде иттрий оксиді ұнтағы негізінде иттрий фосфатының байланыстырғышы бар құю қалыптарын жасау әдісі әзірленді.

Түйін сөздер: *қалыптау қоспасы, иттрий оксиді, байланыстырғыш, құю қалыптары, титан қорытпасы*

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Керамические литейные формы на основе оксида иттрия для литья титановых сплавов

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АННОТАЦИЯ

Проведены исследования влияния различных связующих на основе водных растворов азотной кислоты, нитрата иттрия и ортофосфорной кислоты, геля гидроксида иттрия на физико-механические свойства литейных форм на основе Y_2O_3. Показано, что наиболее перспективным связующим для получения литейных форм из оксида иттрия является фосфатная связка. Приведены данные, описывающие механизм отверждения формовочной массы с фосфатной связкой. Показано влияние концентрации связующих растворов на прочностные характеристики формовочных материалов после затвердевания и термообработки. Представлена информация о взаимодействии литейных форм из порошка оксида иттрия с фосфатной связкой с титановым расплавом марок ВТ1-0 и ВТ6. Полученные данные позволили описать достоинства и недостатки разработанной формовочной смеси. На основании проведенных исследований разработан способ по изготовлению литейных форм на основе порошка оксида иттрия со связующим из фосфата иттрия.

Ключевые слова: *формовочная смесь, оксид иттрия, связующее, литейная форма, титановый сплав*

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Numerical modeling of the task of support tension near cleaning

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ABSTRACT

The problem of stresses and displacements of an oblique-layered massif near a mine working, which is located entirely in one of the rock layers, is considered when the mine is tested by the effects of cleaning works in a coal seam. This effect is taken into account by specifying a system of normal and shear forces at the boundary of the lower layered half-plane with a hole. The problem is solved by imposing the complex Kolosov – Muehehelishvili potentials and Fourier integral transforms. Based on the method of Fourier integral transforms in the theory of elasticity, a system of integral with respect to normal and tangential contact forces is obtained for the case of two different layered half-surfaces. In this work, systems of integral equations are obtained in solving the problem of the reference pressure on an obliquely buried coal seam near the mine working. In this paper, the method of integral Fourier transforms in the theory of elasticity, obtained a system of integral with respect to normal and tangential contact forces for the case of two different layered half-surfaces.

Keywords: massif, drift, reference array, complex potential, slaughter, model, coal seam, integration nodes, half- plane, Simpson's formula.

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Introduction

A new analytical description of the reference pressure on the coal seam, taking into account the variable ductility (stiffness) of the seam, which decreases (grows) with distance from the bottom, allows us to conduct research in the framework of elasticity theory without resorting to representations of the theory of plasticity.

The mechanism of the influence of the reference pressure during the overwork of the coal seam with pillars by the drop on the field drift differs significantly from the mechanism during the development of the seam along the strike; the development and distribution of stresses in the formation soil around the field drift are of a staged nature, changing in the dynamics of the treatment works.

Comprehensive studies of the stress state of field workings in the dynamics of the manifestation of reference pressure during the development of strata by pillars by fall were carried out by B. B. Atymtaev, the theoretical calculation of which was based on the finite element method [[1], [2]].

These studies indicate that so far many questions have not been fully clarified: the mechanism of interaction between treatment and preparatory workings during mining by pillars in the fall.

In the work, systems of integral equations are obtained when solving the problem of support pressure on an oblique buried coal seam near the mine. It is assumed that the inclined-layered

mountain massif the rectangular mining length $2a$ was carried out at the full capacity of the coal seam h_p (Figure 1). The top and bottom of the formation are modeled by complex half-planes I-2 and 3-4, representing heterogeneous rocks of different thicknesses of the immediate.

Experimental part

Due to the geometric symmetry of the medium relative to the axis, the problem can be divided into symmetric and antisymmetric parts (compression and shift at infinity). For a symmetric task $y > a$, the system of integral equations is as follows:

$$\frac{1}{c^2}\left[K^{\infty}+K_1(y)\right]f^B(y)+\frac{a_{11}^{\infty}}{\pi}\int_a^{\infty} f^B(t)\ln\left|y^2-t^2\right|dt+\int_a^{\infty} f^B(t)L_{11}(t,y)dt-$$
$$-a_{12}^{\infty}\int_y^{\infty} g^B(t)dt+\int_a^{\infty} g^B(t)L_{12}(t,y)dt=L_{13}(y)-$$
$$-\frac{p^0 a}{\pi}a_{11}^{\infty}\left[\frac{y}{a}\ln\frac{y-a}{y+a}-\ln\left(y^2-a^2\right)+2\right]-\frac{1}{c_2}K_1(y)p^0, \quad (1)$$
$$\frac{1}{c^2}\left[S^{\infty}+S_1(y)\right]g^B(y)+\frac{a_{21}^{\infty}}{\pi}\int_y^{\infty} f^B(t)dt+\int_a^{\infty} f^B(t)L_{12}(y,t)dt+$$
$$+\frac{a_{22}^{\infty}}{\pi}\int_a^{\infty} g^B(t)\ln\left|\frac{y-t}{y+t}\right|dt+\int_a^{\infty} g^B(t)L_{22}(t,y)dt=L_{23}(y)$$

Here $f^B(y)$ $g^B(y)$, additional normal and tangential contact stresses acting on the edges of layered half-planes. Their behavior and size in the vicinity of the mine is determined by the properties of the coal seam, its compliance [[3], [4], [5]].

$a_{ij}^{\infty}, K^{\infty}$ - constant depending on the elastic characteristics of the layers and the formation, K^{∞} can go to zero. $L_{ij}(t,y), L_{ij}(y)$ - smooth continuous functions, decreasing with increasing variable. $K_1(y), S_1(y)$ - monotonically decreasing continuous functions characterizing the deformability of the Winkler coal seam during compression and shear, respectively. p^0, τ^0 - constants characterizing the basic stress state of the rocks.

Equations of type (1), containing a variable coefficient in front of an unknown function, are assigned to Fredholm integral equations of the 3rd kind. For the reduced system, in which integration is carried out on a semi-infinite interval, moreover, with a variable lower limit, there are no studies in the literature.

Relatively $f^B(y)$ $g^B(y)$, we know that they are continuous, at large they decrease as y^{-2}, and in the vicinity the production is limited. An exception is a special case (the reservoir is absent or it is not compressible) - then the stresses tend to infinity at $y \to a$.

The authors' attempt to approximate $f^B(y)$ $g^B(y)$ by Laguerre polynomials with subsequent reduction (1) and the infinite system of linear algebraic equations (BSLAU) did not lead to success. Received BSLAU was poorly conditioned. This, obviously, is explained by the fact that $L_n(y)e^{-y}$ they are not very suitable for approximating the desired functions.

System (1), therefore, was solved numerically by the Krylov-Bogolyubov method, by piecewise approximation of the desired functions by quadratic trinomials. Unknown, accepted $f^B(t_k)$ $g^B(t_k)$.

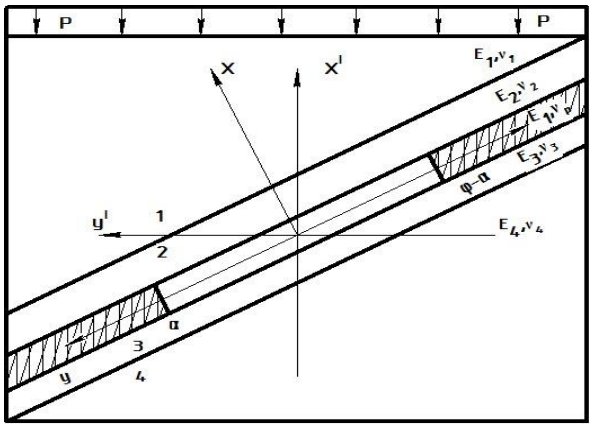


Figure 1. The name of the figure model of the array with sewage treatment

Integration nodes were assigned as follows. The value of the extreme, largest node t_{2M+1} is chosen so that it can be put with the accepted accuracy $f^B(t_{2M+1})=0,$. The interval $[t_1, t_{2M+1}](t_1 = a)$ is divided into pairs equal and increasing in arithmetic progression segments. [[5], [15]] Wherein

$$t_{2k+1} = a + u_1 K + d\frac{(K-1)K}{2},$$
$$t_{2k} = a + u_1\left(K-\frac{1}{2}\right)+\frac{d}{2}(K-1)^2, K = 1, M,$$

where u_1 is the first member of the arithmetic progression, and $d = 2\left(\frac{t_{2M+1}-a-u_1 M}{(M-1)M}\right)$ its denominator.

A variable step is necessary for anyone to ensure uniform accuracy during integration. At the beginning of integration t_k, it's close to a, the

desired functions $f^B(t_k)$ $g^B(t_k)$ change quickly and a smaller step is needed here than at a distance, where they flatten out and decrease asymptotically [[6], [7], [8]].

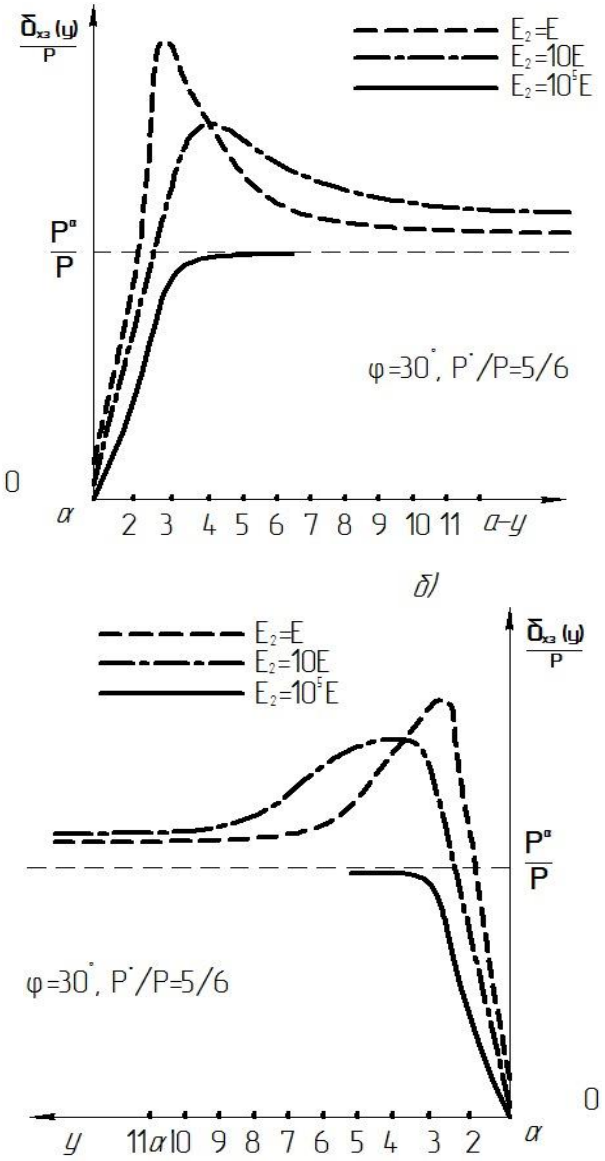


Figure 2. The name of the figure plot of reference pressure at different roof stiffness:
a) - uprising; b) - in the fall.

Replacing the integrals with sums according to the Simpson formula for unequal divisions $y_n, n=1,M$ and writing down each of the equations for the nodes, we obtain a SLAE of order 4M with respect to unknowns, $f^B(t_k)$, $g^B(t_k)$. When calculating the coefficients of the matrix of the system, all the integrals containing the logarithmic terms were calculated analytically, taking into account the fact that, $f^B(t_k)$ $g^B(t_k)$ on the interval, they are approximated by quadratic trinomials. Since the logarithmic singularity is integrable, in the expressions obtained it is easy to pass to the limit at those nodes where $y_n = t_{2M+1}$ the singularity arises. In integrals with a variable lower limit, if the lower limit fell in the middle of the pair segment y_{2m}, then the corresponding member of the sum was also calculated analytically [[9], [10],[11]].

Compiled a double precision calculation program. The system of the hundredth order $(M=25)$ was solved, while

$$t_{2M+1} = 11a,\ a=1,\ u_1 = 0{,}02$$

$$K_1(y) = \alpha_0 e^{-\alpha_1(y-a)}, S_1(y) = \delta_0 e^{-\delta_1(y-a)} \qquad (2)$$

In (2), for physical reasons, it is accepted, $\alpha_0 = \delta_0 = 100$. $\alpha_1 = \delta_1 = 5$ which corresponds to the compliance of the crushed near the formation.

The system turned out to be well-conditioned. She becomes vyrazhenny only for the mentioned special case. Even for him $t_1 = 1{,}0005$, putting the received results coincided well with the exact solution. At the nodes near the gap, where large voltages coincided, the integers coincided, and with increasing accuracy the accuracy increased - tenths coincided, then hundredths coincided [[12], [13], [14]].

It is appropriate to note here that in all cases the conditions were checked during the invoice process:

$$p^0 a = \int_a^\infty f^B(t)dt\ ,\ \tau^0 a = \int_a^\infty g^B(t)dt$$

Integration was carried out according to the Simpson formula to the node t_{2M+1} . The coincidence of such integral characteristics occurred to the nearest hundredth.

Results and discussion

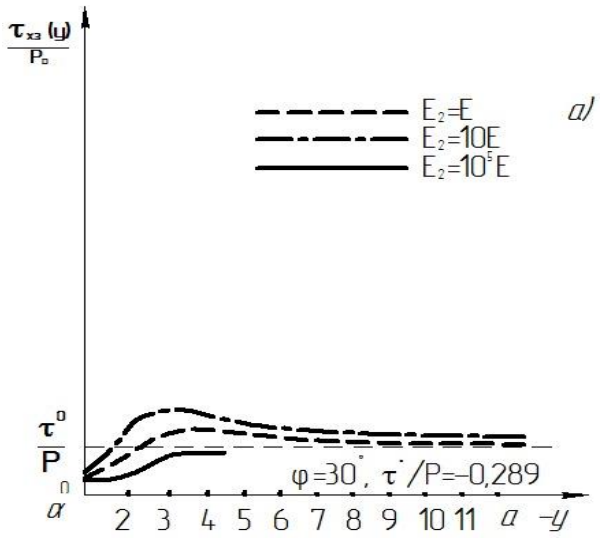
The described model of the net working out, taking into account the elastic - plastic properties of the coal seam, by introducing variable bed coefficients of the Winkler base, taking into account the angle of inclination of the layers and their heterogeneity, after numerical implementation, provided such values of the reference stresses that are completely consistent with the physical concepts

of reference pressure and qualitatively coincide with field observations.

Figures 2 and 3 give support for the total normal and tangential contact stresses obtained after the numerical implementation of symmetric and antisymmetric problems at an angle of inclination of the layers $\varphi = 30^0$.

$$\nu_j = \nu_p = 0{,}25.\ E_1 = E_p = E_4 = E,$$
$$E_3 = 10^5 E,\ E_2 = E,\ 10E,\ 10^5 E,$$
$$h_p = a = 1,\ h_1 = h_2 = 20a.$$

The proposed model of the mine working, taking into account the elastic-plastic properties of the formation, the angle of inclination of the layers and their heterogeneity, after numerical implementation, gave such values of the reference stresses that are in full agreement with the physical ones presented about the reference pressure [[15], [16], [17], [18], [19], [20]].



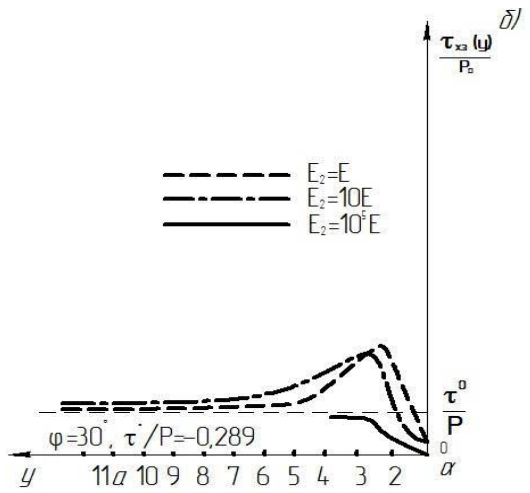


Figure 3. The name of the figure plot of the reference shear stresses of different reservoir flexibility: a) - uprising; b) - in the fall.

Conclusions

These methods are purposeful to use, it is necessary to link them with a specific system for developing coal seams and methods for preparing a minefield. Some conclusions on the choice of the location of field drifts and their maintenance from the point of view of the factor "stress state" are recommended for implementation in mines "Karagandaugol."

Thus, the developed model of drift embedded in a layered medium, in the zone of influence of the treatment space, allows one to fully study the picture of the stress-strain state of rocks around the drift up to treatment output.

Conflict of interests

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

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Штабельдегі көмірді өздігінен қыздырудың математикалық моделі

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ТҮЙІНДЕМЕ

Бұл мақалада шекаралық және бастапқы жағдайларда штабельдің қуыстарындағы оттегінің *С* көлемдік үлесі мен көмірдің өздігінен қызуының t температурасына қатысты жылу және газ алмасу процестері екінші ретті сызықты емес екі дифференциалдық теңдеулер жүйесімен сипатталатын көмірдің өздігінен қызуының математикалық моделі келтірілген. Дифференциалдық теңдеулерді құрастыру кезінде штабельдегі көмірдің өздігінен қызуы және өздігінен жанудың пайда болуы, оның ауамен жанасу бетіне жақын орналасқан және оттегінің әсер ету аймағы деп аталатын қатардың мөлшерімен салыстырғанда салыстырмалы түрде аз қабатта байқалатындығы ескеріледі. Бұл математикалық модельде құрастыру кезінде көмірдің орнықтылығын сипаттайтын *Ф* - жылу шығарудың меншікті қуаты параметрінің, көмірдің өзіндік қыздыру процесіне әсері ескерілді. Дифференциалдық теңдеулерді құрастыру кезінде температура мен өткізгіштік, диффузия коэффициенті, штабельдегі көмірдің меншікті жылу сыйымдылығы, сусымалы тығыздық, тотығудың жылу әсері, қатардың бос болуы, жылу шығару қуатының экспоненциалды өсуінің температуралық коэффициенті сияқты физикалық параметрлер қолданылды. Осы математикалық модельді іске асыру үшін өлшемсіз айнымалылар енгізілді, бұл тор әдісін қолдануға мүмкіндік береді. Алынған нәтижелерді талдау келесі нәтижелерді алуға мүмкіндік берді: уақыт өте келе температура профильдерінің өзгеруі; қатардағы оттегі концентрациясының профильдерінің уақыт өте келе өзгеруі; жылу шығарудың меншікті қуатының қатарындағы температура профиліне әсері, температураның жоғарылауымен жылу шығару қарқындылығының экспоненциялдық өсуін сипаттайтын параметрдің температура профиліне әсері. Лыковтың диффузия коэффициентіне пропорционалды критерийлері және Нуссельттің тиімді жылу өткізгіштігімен және көмірдің тиімді температуралық өткізгіштігімен байланысты критерийлері көмірдің өздігінен қызуының динамикасына ең көп әсер ететіні анықталды. Алынған нәтижелер қатардың өзіндік қызуы бір жағынан ауа оттегісінің қарқынды енуімен, ал екінші жағынан әлсіреген жылу қабылдағышқа байланысты деп айтуға мүмкіндік береді. Өзіндік қыздыру және өзіндік қыздырудың отқа ауысуы жылу соққысының күшеюі кезінде пайда болатын турбулентті диффузияның пайда болуымен байланысты, оның әсері штабельдің бетіне перпендикуляр бағытта күшейуі мүмкін.

Түйін сөздер: массив, штрек, кернеу, кенжар, модель, күрделі потенциал, көмір қабаты, интеграция түйіндері, жартылай жазықтық, Симпсон формуласы.

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Численное моделирование задачи об опорном давлении вблизи очистной выработки

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АННОТАЦИЯ

В настоящей работе рассмотрена задача о напряжениях и смещениях наклонно-слоистого массива вблизи горной выработки, целиком расположенной в одном из породных слоев, когда выработки испытывает влияния очистных работ в угольном пласте. Это влияние учитывается путем задания системы нормальных и сдвигающих усилий на границе нижней слоистой полуплоскости с отверстием. Цель исследования: определить напряженное состояние слоистой полуплоскости, ослабленной отверстием круговой формы при заданных на границе произвольных нагрузках, оценить распределение контактного напряжения на полуполосах, разведенных вдоль продольной оси и сжатых слоистыми полуплоскостями, найти напряженно состояние анизотропной плоскости вблизи свободного отверстия произвольной формы при заданных напряжениях на бесконечности и на контуре сближенного продолговатого отверстия, задача решается методом наложения комплексных потенциалов Колосова – Мусхелишвили и интегральных преобразований Фурье. На основе метода интегральных преобразований Фурье в теории упругости, получена система интегральных относительно нормальных и касательных контактных усилий для случае двух разнародных слоистых полупоскостей. В работе получены системы интегральных уравнений при решении задачи об опорном давлении на наклонно залегающий заглубленный угольный пласт вблизи очистной выработки.

Ключевые слова: массив, штрек, напряжения, забой, модель, комплексный потенциал, угольный пласт, узлы интегрирования, полуплоскость, формула Симпсона.

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