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Engineering and technology

Magnesia composite materials for layered products

Miryuk O.A.

Rudny Industrial Institute, Rudny, Kazakhstan

Corresponding author email: psm58@mail.ru

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ABSTRACT
The article presents the results of experimental studies of magnesia composite materials of layered structure obtained from molding mixtures of various densities. The aim of the work is to synthesize and study the characteristics of three–layer magnesia materials. Molding mixtures were obtained from combined binders based on caustic magnesite and technogenic silica-containing materials. Specially synthesized porous aggregates from liquid-glass raw mixtures were used as fillers. Technological techniques of horizontal and vertical molding of three-layer products have been worked out. Composite magnesia material of three-layer variatropic structure is characterized by a density of 560 kg/m^3, compressive strength of 6.1 MPa. Durability tests of layered composite materials have been carried out. Three-layer magnesia composite materials have shown satisfactory resistance in the conditions of an aqueous and aggressive salt environment. The developed magnesia material is comparable in physic-mechanical and cost parameters with an innovative block of encapsulated expanded clay. The low thermal conductivity of the developed magnesia material, equal to 0.115 W/(m·°c), will ensure a reduction in material and energy costs by 36.1% compared to the cement analogue.

Keywords: magnesia binders, porous filler, composite materials, variatropic structure, three-layer wall blocks, water resistance.

Miryuk Olga Aleksandrovna

Information about author:
Doctor of Technical Sciences, Professor, Head of the department of building construction materials, Rudny Industrial Institute, 50 let Oktyabrya str, 38, 111500, Rudny, Kazakhstan. Email: psm58@mail.ru

Introduction

Wall fencing of buildings are characterized by a variety of used materials. Single-layer walls are erected from a material that performs load-bearing and heat-shielding functions. To meet modern thermal requirements, single-layer building envelopes should have a density of no more than 800 - 900 kg / m^3, while maintaining high mechanical strength. The list of effective materials for single-layer walls is not numerous [[1], [2], [3], [4], [5]].

To ensure mechanical reliability and thermal efficiency of enclosing structures, layered systems are expedient. However, the combination of materials of different origin in the multilayer structure of the wall complicates the manufacturing process, contributes to the appearance of internal stresses and delamination of the product. The listed problems are minimized in variotropic structures, which are characterized by variable values of density and strength over the section of the molded product. Variotropic structure is suitable for walls, reduces the thickness and increases the load-bearing capacity of the structure [[6], [7], [8], [9], [10] [11], [12]]. To create products with a variotropic structure, for example, concrete mixtures of a related composition are used, which differ in density [[9], [10] [11], [12]]. In this case, a layered structure is formed, the individual elements of which smoothly change their physical and mechanical characteristics and retain a high degree of adhesion to each other. In the technology of layered products from concrete mixtures of various densities, the properties of molding masses and the intensity of concrete hardening are of great importance. Cement concrete mixtures, as a rule, are characterized by a low rate of structure formation, which requires additional costly technological measures. Therefore, fast-hardening concretes are preferred for the formation of layered products.

Trends in the priority development of technologies with a low carbon footprint focus on the development of low-energy processes and the widespread use of man-made materials.

Materials based on caustic magnesite are characterized by intense hardening and high strength. The activating ability of a mixture of oxide and magnesium chloride makes it possible to involve even latent substances in the processes of structure formation and hardening. Magnesia binders have high adhesion to materials of various origins. Thermal processes that ensure the synthesis of caustic magnesite and the hardening of materials based on it are characterized by low energy consumption [[13], [14], [15], [16], [17], [18]].

This led to the choice of magnesia composite materials as the object of this study.

The purpose of this research is to study three-layer magnesia materials based on molding sands of various compositions.

Researchh experimental part

In the experiments, caustic magnesite CMP (caustic magnesite powder) – 75 was used, it was containing 78% MgO. The specific surface area of the binder powder is 305 m^2/kg. For a plastic binder test, it is characteristic: the beginning of setting is 30 minutes, the end of setting is 1 hour 50 minutes. The binder stone reaches compressive strength at the age of 2 days 38 MPa, at the age of 28 days - 54 MPa.

To obtain a combined magnesia binder, technogenic silica-containing materials of various origins were added to caustic magnesite (Table 1).

Porous materials were used as fillers for concrete (molding) mixtures: granules of a fraction of 10–20 mm with a bulk density of 230 kg/m^3 and a porosity of an individual grain of 70–75%; crushed sand with a fraction of 1.25 - 2.5 mm with a bulk density of 300 kg / m^3, obtained by grinding substandard porous granules.

Porous fillers were obtained by low-temperature firing of granules based on the developed mixture of liquid glass and thermal energy waste [[19], [20]].

The molding sands were mixed with a solution of magnesium chloride with a density of 1230 kg/m^3.

Discussion of the results

To increase the water resistance of the magnesian binder and reduce the proportion of caustic magnesite, technogenic mineral additives were used (Table 2). A comparative analysis of the properties of combined magnesia binders showed the advantages of expanded clay dust, the introduction of which provides the greatest increase in the softening coefficient ($C_{softening}$). Expanded clay dust is formed during the firing of expanded clay gravel in rotary kilns and contains mainly metakaolinite and amorphous silica.

The increased resistance of the stone of the combined magnesia binder to the action of water is provided by weakly crystallized, sparingly soluble hydrosilicates and magnesium hydroaluminosilicates formed with the participation of expanded clay dust components. A binder based on expanded clay dust is characterized by strength comparable to that of caustic magnesite, and has the lowest stone density. When forming layered products, along with the need for adhesion of elements, it is necessary to preserve the individuality of the structure of the layers. It is unacceptable that each subsequent layer of concrete mix destroys the structure of the previous one. Technological characteristics of molding sands are largely determined by the properties of the binder component.

The study of the influence of the composition of the magnesia binder on the structural strength of the plastic mass made it possible to give preference to a composition containing 40% expanded clay dust (Figure 1). The combined binder, having increased water resistance, is characterized by comparable structural strength indicators with caustic magnesite.

Table 1 - Chemical composition of technogenic materials

Name	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O+Na_2O	SO_3	Loss on ignition
Glass fight	72.00	1.64	2.27	5.37	4.00	14.30	0.42	–
Coal mining waste	63.30	9.35	7.45	3.00	1.18	1.42	4.08	10.22
Expanded clay dust	54.00	18.48	6.70	4.00	2.25	2.39	2.18	10.00

Table 2 - Characteristics of magnesia binders

Binder Composition			**Binder stone density, kg/m^3**	**Strength, MPa, aged 2/28 days**	$C_{softening}$
Caustic magnesite, %	**Mineral supplement**				
	Type	**Compound, %**			
100	–	–	1950	42/78	0.60
50	Glass fight	50	1860	28/62	0.72
50	Coal mining waste	50	1810	33/70	0.74
50	Expanded clay dust	50	1790	37/76	0.81
40		60	1780	30/72	0.83
60		40	1810	38/75	0.78
70		30	1890	37/73	0.75

On the basis of a combined binder and porous aggregates, molding mixtures have been developed to produce coarse-pored (CP) and fine-grained (FG) concrete (Table 3). The combination and regulation of the thickness of concrete layers of different densities provides the desired mechanical and thermal characteristics of the product. The thickness of individual layers is determined by the calculation method, taking into account the dimensions of the product. For example, to ensure the required thermal resistance of the wall of a residential building, equal to 3.279 (m$^{2}\cdot{}^{o}$C)/ W, the central layer of a wall block measuring 400 x 200 x 200 mm takes 80%, the two outer layers account for 20% of the volume of the product (Figure 2).

The mobility of the molding sands, determined using the Abrams cone, corresponded to the P1 grade in terms of workability. Large-porous molding sands were characterized by a cone draft of 2–4 cm; for fine-grained molding sands, the cone draft was 1–2 cm. In the manufacture of three-layer samples, various methods of sand laying were used. Horizontal molding method: layers of mixtures differing in density were laid parallel to the bottom of the mold. In vertical molding, layers of concrete mixtures were laid perpendicular to the bottom of the mold. In order to avoid "spreading" and mixing of concrete mixtures of various compositions with the vertical method, removable partitions were installed in the molds, which were removed after laying all the layers.

In both molding methods, each subsequent layer was laid after 120 sec., including the duration of vibrating the individual layers for 50 sec.

It is noted that with horizontal molding, more precise control of the thickness of the layers is possible. The vertical method of laying requires a more intensive compaction of the layers in order to avoid the "hanging" of the mass in the mold compartment. Vertical molding ensures high quality of the working surfaces of the product.

After preliminary holding for 1.5 hr., the magnesia samples were dried according to the regime: 0.5 hr. - heating to a temperature of 50°C; 3.5 hr. - isothermal exposure; 0.5 hr. - cooling. Slight differences in the test results of the samples indicate the possibility of multivariate laying of magnesia concrete mixtures (Table 4).

The operational properties of materials of a combined structure are determined by the reliability of the adhesion of various layers. Three-layer samples were subjected to tests for resistance to changes in environmental parameters. To enhance the impact of the external environment, samples with cut ends were used, on which access to the inside of the porous filler is open. Water resistance was evaluated in terms of water absorption and water resistance (Table 4). The value of water absorption is much less than the integral porosity of materials, equal to 65%. This indicates the predominance of closed pores in the structure of the material. Water fills large voids in the central layer, penetrates into open pores on sections of samples.

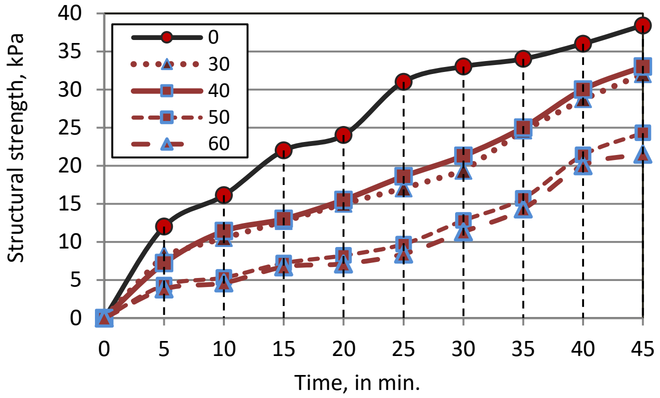


Figure 1 – Influence of expanded clay dust content on the structural strength of magnesia binder

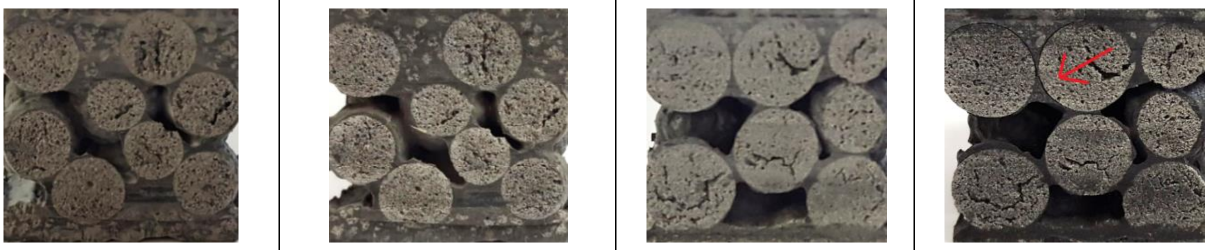
Figure 2 – Appearance of three-layer magnesia material

Table 3 – Characteristics of concretes of various compositions

Compound	The composition of the molding sand, kg/m³				Density, kg/m³	Compressive strength, MPa.
	astringent	porous aggregate		magnesium chloride solution		
		granules	crushed sand			
CP	265	210	–	127	525	5.2
FG	308	–	230	147	700	8.1

Table 4 – Characteristics of three-layer samples of various molding

Properties	Values for Forming Methods	
	horizontal	vertical
Average density, kg/m³	560	590
Compressive strength, MPa	6.1	5.7
Water absorption, %	12	11
Softening coefficient	0.78	0.77
Thermal conductivity coefficient, W/(m·°C)	0.115	1.119
Aggression resistance coefficient	1.12	1.10



Before testing	After testing	Before testing	After testing
Water resistance		Air resistance	

Figure 3 – Fragments of samples of magnesia material tested for resistance to external factors

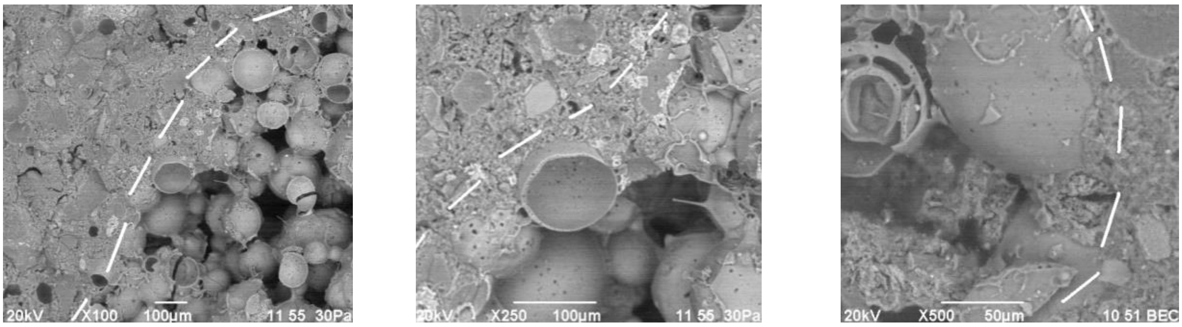


Figure 4 – Microstructure of magnesian material
(Dotted line shows the contact zones between the porous aggregate and the binder stone)

Table 5 – Comparative characteristics of three-layer wall blocks

Indicators	Material type	
	magnesian based on liquid glass granules	**cement based on encapsulated expanded clay**
Average density, kg/m^3	560	800
Thermal conductivity coefficient, W/(m·^{o}C)	0.115	0.180
Strength, MPa	6.1	6.5
Cost in KZT	727.83	728.08

The water resistance of composite materials was evaluated by the softening coefficient, taking into account the strength of the sample, which was in water for 10 days, and the strength of the original sample. No pronounced defects of the samples were found during the testing period (Figure 3).

Air resistance is characterized by the ability of a material to withstand repeated systematic moistening and drying for a long time without significant deformations and loss of mechanical strength. Test cycle: 4 hours - stay in a humid environment, 4 hours - drying in air at room temperature. The test results indicate a satisfactory resistance of composite materials (Table 4). The strength of the samples subjected to testing is 86% of the strength indicators of the control samples. In the contact zone of the samples, only small cavities around the filler grains are visible (Figure 3).

The specificity of magnesia materials predetermined the choice of the type of aggressive medium for testing. The samples were immersed in sea water containing 4% salts. The salt component of the sea water included 78% sodium chloride, 14% magnesium chloride, 6% magnesium sulfate, and 2% potassium sulfate. Within 6 months the samples were examined visually, after completion of the tests, the coefficient of resistance to aggression was determined (the ratio of the strength of the samples in an aggressive environment to the strength of the control samples). Magnesia composite material withstood exposure to sea water. The presence of magnesium chloride and sulfate in an aggressive environment favorably affected the strength of the material, for mixing which solutions are used with an average salt concentration of 25 - 27%. The results of electron microscopy confirm the reliability of the adhesion of porous granules to the matrix substance, noted during physical and mechanical tests of the samples (Figure 4).

Comparative characteristics of the developed three-layer composite material with a cement innovative block similar in structure, obtained on the basis of encapsulated expanded clay [[21], [22]], revealed comparability in terms of mechanical and cost indicators (Table 5). The economic effect is predicted due to the reduced thermal conductivity of the magnesia material.

The use of three-layer wall blocks made of magnesia composite materials will provide a reduction in material and energy costs by 36.1% and an economic effect of 16437.5 tenge/m^3 compared to the innovative block.

Conclusions

Magnesia binders make it possible to implement effective solutions in the technology of wall materials.

The high reactivity of caustic magnesite provides controlled molding properties to concrete mixtures containing a combined binder and porous aggregates.

Magnesia composite materials of a layered structure are characterized by high heat-shielding properties and resistance to operational factors.

Economic calculations indicate the effectiveness of wall products from magnesia composite materials.

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

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Қабатты бұйымдарға арналған магнезиялық композициялық материалдар

Мирюк О.А.

Рудный индустриялық институты, Рудный, Қазақстан

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ТҮЙІНДЕМЕ

Мақалада әртүрлі тығыздықтағы қалыптау қоспаларынан алынған қабатты құрылымның магнезиялық композициялық материалдарының эксперименттік зерттеулерінің нәтижелері көрсетілген. Жұмыстың мақсаты – үш қабатты магнезиялық материалдарды синтездеу және сипаттамаларын зерттеу. Қалыптау қоспалары каустикалық магнезит пен құрамында кремний бар техногендік материалдар негізінде біріктірілген тұтқыр заттардан алынды. Толтырғыштар ретінде сұйық шыны шикізат қоспаларынан арнайы синтезделген кеуекті толтырғыштар қолданылды. Үш қабатты бұйымдарды көлденең және тік қалыптаудың технологиялық әдістері жүзеге асырылды. Үш қабатты вариатропты құрылымның композициялық магнезиялық материалы 560 кг/м^3 тығыздығымен, 6,1 МПа қысу беріктігімен сипатталады. Қабатты композициялық материалдардың беріктігіне сынақтар жүргізілді. Үш қабатты магнезиялық композициялық материалдар сулы және агрессивті тұзды ортада қанағаттанарлық төзімділік көрсетті. Әзірленген магнезиялық материал физика-механикалық және құндық көрсеткіштері бойынша капсулаланған кеңейтілген саздан жасалған инновациялық блокпен салыстырылды. Әзірленген магнезиялық материалдың 0,115 Вт/(м·°С)-ге тең төмен жылу өткізгіштігі цемент аналогымен салыстырғанда материалдық және энергетикалық шығындардың 36,1% - ға төмендеуін қамтамасыз етеді.

Түйін сөздер: магнезиялық тұтқыр, кеуекті толтырғыш, композициялық материалдар, вариатропты құрылым, үш қабатты қабырға блоктары, суға төзімділік.

Мирюк Ольга Александровна

Автор туралы ақпарат:
Техника ғылымдарының докторы, профессор, Құрылыс құрылыстық материалтану кафедрасының меңгерушісі, Рудный индустриялық институты, Рудный, Қазақстан. E-mail: psm58@mail.ru

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Магнезиальные композиционные материалы для слоистых изделий

Мирюк О.А.

Рудненский индустриальный институт, Рудный, Казахстан

АННОТАЦИЯ

В статье приведены результаты экспериментальных исследований магнезиальных композиционных материалов слоистого строения, полученных из формовочных смесей различной плотности. Цель работы – синтез и исследование характеристик трехслойных магнезиальных материалов. Формовочные смеси получали из комбинированных вяжущих на основе каустического магнезита и техногенных кремнеземсодержащих материалов. В качестве заполнителей использовали специально синтезированные пористые заполнители из жидкостекольных сырьевых смесей. Отработаны технологические приемы горизонтального и вертикального формования трехслойных изделий. Композиционный магнезиальный материал трехслойного вариатропного строения характеризуется плотностью 560 кг/м^3, прочностью при сжатии 6,1 МПа. Проведены испытания долговечности слоистых композиционных материалов. Трехслойные магнезиальные композиционные материалы проявили удовлетворительную стойкость в условиях водной и агрессивной солевой среды. Разработанный магнезиальный материал сопоставим по физико-механическим и стоимостным показателям с инновационным блоком из капсулированного керамзита. Низкая теплопроводность разработанного магнезиального материала, равная 0,115 Вт/(м·^{0}С), обеспечит снижение материальных и энергетических затрат на 36,1% по сравнению с цементным аналогом.

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Ключевые слова: магнезиальные вяжущие, пористый заполнитель, композиционные материалы, вариатропная структура, трехслойные стеновые блоки, водостойкость.

Мирюк Ольга Александровна

Информация об авторе:
Доктор технических наук, профессор, заведующая кафедрой строительства и строительного материаловедения. Рудненский индустриальный институт, Рудный, Казахстан. E-mail: psm58@mail.ru

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Engineering and Technology

Influence of basalt fiber length on strength characteristics of fine-grained fiber concrete

[1]Nurbayeva M.N., [1]Lukpanov R.E., [1]Aruova L.B., [2]Gunasekaran M.

[1]L.N. Gumilyov Eurasian National University, Astana, Kazakhstan
[2]Uttaranchal University, Dehradun 248007, India

** Corresponding author email: marzhan_nurbaeva@mail.ru*

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ABSTRACT
The samples of fiber concrete with different lengths of basalt fiber have been tested. The characteristics of basalt fiber used for the manufacture of fiber concrete are given. The aim of the study is to identify the pattern of influence of fiber length on the strength characteristics of fiber concrete. The paper presents the results of determining the compressive and bending tensile strength of fine-grained fiber concrete with no fiber added (control composition) and with the addition of basalt fiber 0.2 % of the weight of cement with a fiber length of 40 mm, 20 mm, 10 mm and 5 mm. It is demonstrated that the optimal limits of basalt fiber introduction into the mixture of fine-grained concrete can be considered a length of 20 mm fibers, which leads to an increase in compressive strength up to 47.2 %, in bending tensile strength up to 2 times more in comparison with the control composition.

Keywords: Basalt fiber, reinforcement, compressive strength, bending.

	Information about authors:
Nurbayeva Marzhan Nurbaykyzy	*Ph.D. Student, Department of Technology of Industrial and Civil Construction, L.N. Gumilyov Eurasian National University, 010000, Satbayeva Street 2, Astana, Kazakhstan. Email: marzhan_nurbaeva@mail.ru*
Lukpanov Rauan Ermagambetovich	*Ph.D., Professor of the Department of Technology of Industrial and Civil Construction, L.N. Gumilyov Eurasian National University, 010000, Satbayeva Street 2, Astana, Kazakhstan. Email: rauan_82@mail.ru*
Aruova Lyazat Boranbayevna	*Dr. tech. sc., Professor of the Department of Technology of Industrial and Civil Construction, L.N. Gumilyov Eurasian National University, 010000, Satbayeva Street 2, Astana, Kazakhstan. Email: ecoeducation@mail.ru*
Gunasekaran Murali	*Professor of the Division of Research & Innovation, Uttaranchal University, Dehradun 248007, India. Email: murali_220984@yahoo.co.in*

Introduction

In the last few years, high-strength concretes with various modifying additives and fillers have been gaining popularity due to the development of high-rise buildings. The consequence of this trend is an increase in the requirements imposed on the construction materials from which the building or structure is erected. Due to the addition of various components [1], engineers achieve an increase in important indicators of the material: strength, cracking resistance, wear resistance, durability, impact resistance, service life, etc.

Fibers of natural or artificial origin are used to increase the resistance of concrete [[2], [3]]. Its effect is aimed at several characteristics of concrete: resistance to cracks, water resistance, and frost resistance. After adding the material to the concrete, it is evenly distributed throughout the mixture and increases its strength many times over, and the fiber copes with this task much better than traditional mesh reinforcement [[4], [5]].

One of the popular modern fillers used today is basalt fiber, which has high adhesion. A special place among reinforcing additives in concrete is occupied by basalt fiber, the technology of its introduction, as well as its quantitative content in concrete compositions, its influence on the formation of the structure and properties of cement mortars and concretes are of interest [6].

Basalt fiber is a special material produced from sedimentary basalt rocks with further melting and transformation into fibers [[7], [8], [9], [10]]. The diameter of the particles ranges from 20 to 500 microns, with lengths from 1 to 150 mm. Basalt fiber has a high elastic modulus (75 GPa, which is higher compared with other types of fiber, except steel (190 GPa)), a low percentage of elongation at break

(3.2%, which is lower compared with all other types of fiber), and acceptable density (2600 kg/m^3) and melting temperature (1450 °C) [2]. Basalt fiber is used in the production of dry mortars, cellular concrete blocks, chemically resistant pipes, and concrete collectors, as well as in the construction of floor screeds and foundations.

According to the authors [4], a study of the effect of highly dispersed fibrous fillers on the mechanical properties of fiber concrete using basalt micro reinforcing fiber length of 12 mm and a diameter of 10 microns, leads to increased rates of compressive and flexural strength of samples that is explained by the cohesion of basalt fibers with the cement-sand matrix [[11], [12], [13], [14]].

Basalt-fiber concrete has high flexural and tensile strength with good technological properties. It allows you to reduce the percentage of reinforcement and metal mesh in the concrete elements. It is also worth noting that concrete with the addition of basalt fiber can tolerate more elastic deformations, as basalt fiber has a high modulus of elasticity and almost no plastic deformations [15]. Basalt fiber is not subject to corrosion and has 2-2.5 times higher strength compared with metal fiber. Dispersed reinforcement of the cement matrix with basalt fiber has significant advantages: no corrosion, significantly lower specific weight, radio transparency, better bonding with the matrix, increased plasticity of the mortar and prevention of cracking [[16], [17]]. This opens up opportunities for the wide application of basalt fiber for concrete reinforcement in earthquake, hydraulic, and road construction.

The superfine fiber reacts with the cement medium as an active mineral additive, followed by the formation of needle-like crystals, increasing the strength of the concrete. However, the strongly alkaline nature of the medium affects the strength of the fiber and, ultimately, the strength characteristics of the reinforced concrete [[18], [19], [20]].

The following problems were resolved:

1. Preparation of specimens under laboratory conditions;
2. Strength in the bending;
3. Compressive strength;
4. The analysis of the Results.

Comparisons of the results of laboratory tests were carried out for five types of concrete:

Type 1: control of the composition of concrete without fiber;

Type 2: composition of concrete with basalt fiber of 40 mm length;

Type 3: concrete composition with basalt fiber with a length of 20 mm;

Type 4: Concrete composition with basalt fiber with a length of 10 mm;

Type 5: concrete composition with basalt fiber with a fiber length of 5 mm.

Purpose of the study: evaluation of the influence of the length of basalt fiber on the strength of standard concrete specimens.

Experimental technique

For the experiments as a binding used portland cement PC 400 D0 with no addition, the real density was 3100 kg/m^3, bulk density was 1100-1600 kg/m^3.

A small fraction of the sand filler used natural quartz sand with a particle size modulus of 2.23, meeting the requirements of GOST 8736-2014 "Sand for construction works.

Basalt fibers with lengths of 40 mm, 20 mm, 10 mm, and 5 mm were selected for testing the mechanical properties of fine-grained fiber concrete depending on the length of the fibers (Fig. 1).

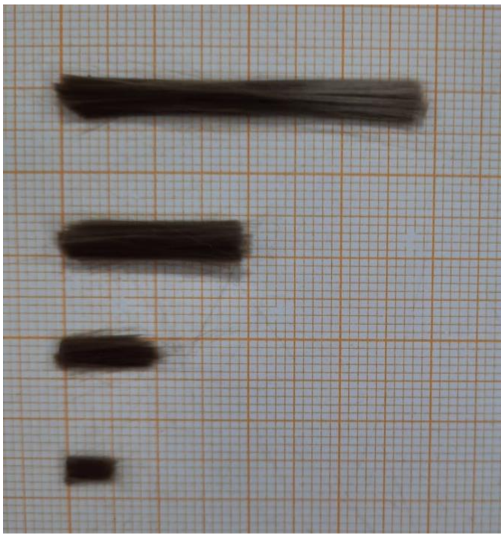

Figure 1 – Basalt fibers of various lengths

The physical and mechanical characteristics of basalt fiber are shown in Table 1.

Table 1 - Characteristics of basalt fiber

Properties	***Basalt***
Density (kg/m^3)	3100
Dia. (mkm)	18
Length (mm)	5; 10; 20; 40
Tensile strength (MPa)	3000-4840
Elongation to break, %	3.1-6.0

Water for concrete mix preparation that meets the requirements of GOST 23732-2011 «Water for concretes and mortars».

Raw material consumption of samples of cement-sand mortar is given in Table 2.

Table 2 - Cement mortar composition

Type of sample	***Cement, g***	***Quartz Sand, g***	***Bazalt Fiber, g***	***Water, g***
Type 1 Reference sample	450	1350	-	180
Type 2 Fiber length 40мм	450	1350	0.9	180.18
Type 3 Fiber length 20 мм	450	1350	0.9	180.9
Type 4 Fiber length 10мм	450	1350	0.9	182.7
Type 5 Fiber length 5мм	450	1350	0.9	184.5

The mixtures were ready by hand in a bowl for mixing in compliance with GOST 310.3-76. The previously prepared mixture of cement and sand was stirred with water for 2 minutes, after which the fibers were introduced into it for 4 minutes with continuous mixing evenly (Fig. 2).

Figure 2 – Sample preparation

The determination of the bending strength of the control and basalt cement-sand mixes was carried out on beam samples with dimensions of 40×40×160mm (Fig. 3). The test of bending strength of the concrete beams was performed following GOST 310.4-81 “Cement. Methods of Determination of Flexural and Compressive Strength”.

Figure 3 – Generated samples

To explore the fine fiber properties, samples were obtained from the mixture with different fiber lengths. The index of strength was measured as an arithmetic amount equal to 5 indexes for different curing periods (3, 7, 28 days).

Results and Discussion

Reactions on the "fiber-cement matrix" surface can also improve the properties of the composite as a consequence of increased adhesion of the matrix to the fiber, monolithic system, and improved conditions of compatibility of loading of the fibers in the composite.

Figure 4 shows a diagram of changes in the bending tensile strength of the samples as a function of curing time.

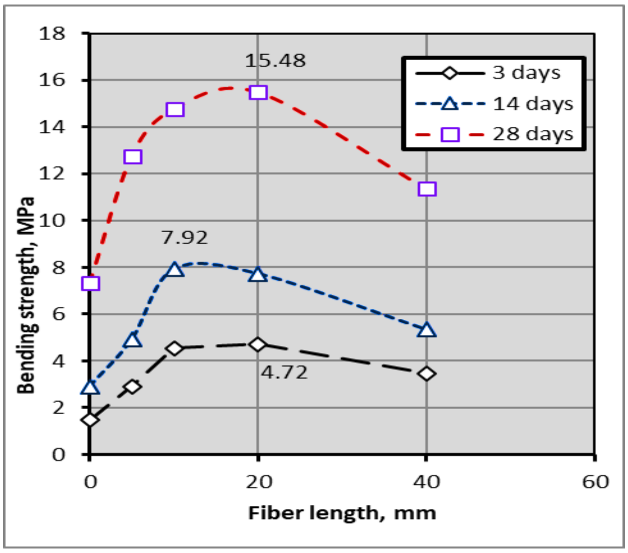

Figure 4 – Dependence of bending strength of fiber concrete on their fiber length and curing age

The analysis of the data presented in Figure 4 shows that a greater value of the strength of fiber concrete at 28 days (15.48 MPa) is achieved with the introduction of a basalt fiber length of 20 mm compared to the control samples without the addition of fiber (7.32 MPa).

At 14 days, the addition of 20 mm fiber length compared to 10 mm fiber length showed an increase in bending strength of 2.6 % (7.92 and 7.73 MPa, respectively).

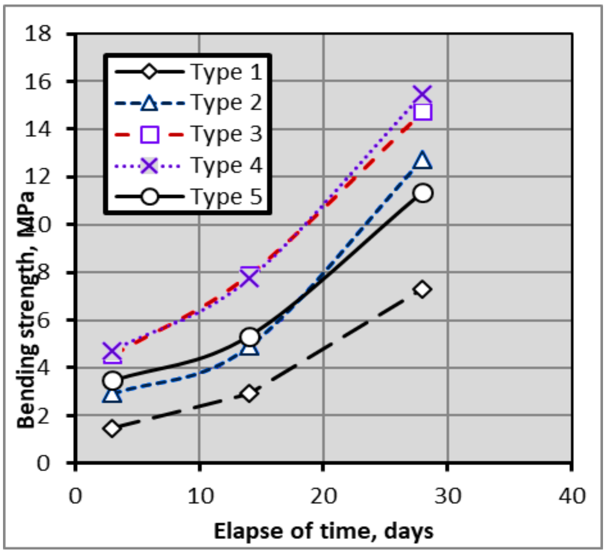

Figure 5 – Dependence of bending strength of fiber concrete on fiber length

According to the test results shown in Figure 5, the maximum average bending tensile strength of the control samples is 7.32 MPa (28 days), while the maximum average strength of samples using basalt fiber with a length of 20 mm is 15.48 MPa, that is, this figure is 2 times higher than for the control sample.

According to strength comparisons, presented in Fig. 5, for 10 mm fiber length specimens, on the 3rd and 14th day an increase in strength to 4.55 and 7.92 MPa is observed relative to specimens without fiber (type 1 - 1.48 MPa on the 3rd day and 2.91 MPa on the 14th day). On the 28th day, the tendency of increasing the strength remains. In any case, there is a positive effect of increasing the strength of samples with the addition of basalt fiber.

Analyzing the data obtained, it should be noted that the maximum effect of flexural tensile strength was achieved with the introduction of basalt fiber with a length of 20 mm, the strength of which was 15.48 MPa.

The results of determining the compressive strength of fiber concrete specimens are shown in Figure 6.

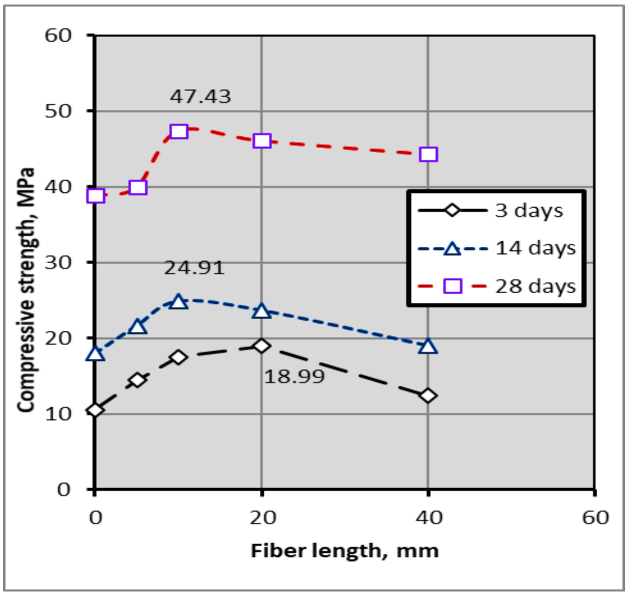

Figure 6 – Dependence of compressive strength of fiber concrete on fiber length and curing age

When comparing the index of the ultimate strength of the prepared sample, equal to 38.91 MPa, with this index for the concrete, prepared composition, which was between 40.4-47.43 MPa, we can assume that the fiber concrete is of higher quality.

As a result of the data obtained, it can be argued that the fiber concrete with basalt fiber in the first 3 days has a higher strength of 17.5-79.3%; on 14 days - 20 - 38% and 28 days - 13.9 - 21.9% in comparison with its analogs.

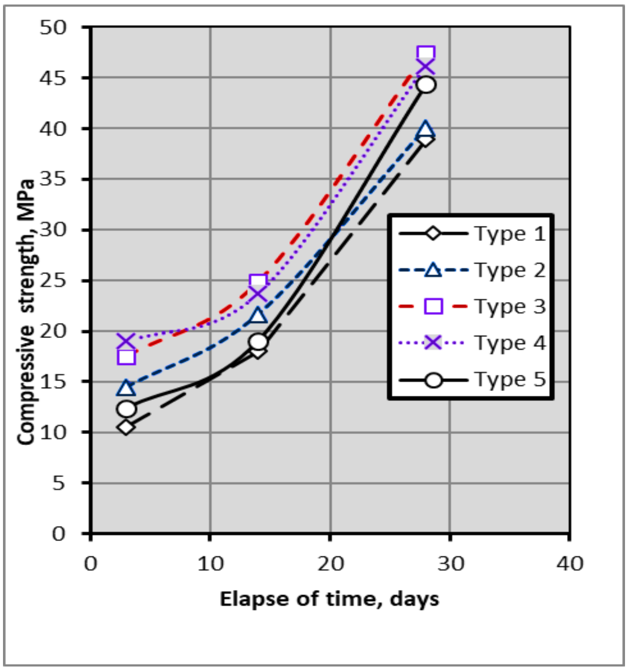

Figure 7 – Dependence of compressive strength of fiber concrete on fiber length

The reference specimens of type 1 (without the use of fiber) showed the lowest strength, a percentage less by 3.8 % compared to type 2, 21.9 % less than type 3, and 18.58 % less than type 4, 13.9 % less than type 5. The partial strength values range from 10.55 to 38.91 MPa (Fig. 7).

Type 2 specimens showed a 20.64% higher strength than Type 1 specimens, but less than Type 3 by 17.8%, Type 4 by 8.9%, and Type 5 by 9.7%. The partial strength values range from 14.48 to 40.4 MPa.

Type 3 specimens showed the highest strength, exceeding Type 1 by 42%, Type 2 by 17.8%, Type 4 by 5.32%, and Type 5 by 24.9%, Partial strength values range from 17.54 to 47.43 MPa.

Type 4 specimens showed a strength of 42.93% higher than Type 1 specimens and 2.14% higher than Type 2 specimens, but 2.77% lower than Type 4 specimens. Partial strength values ranged from 14.36 to 52.6 MPa.

Type 5 specimens showed a strength higher than Type 1 specimens by 12.2 % but lower than Type 2 specimens by 9.7 % at 28 days, Type 3 by 6.9 %, and Type 4 by 4.1 %. Particular strength values range from 12.4 to 44.35 MPa.

The reason for the increased performance is the good adhesion of basalt fiber with other concrete constituents (cement, sand).

The use of basalt fiber in the composition of the mixture helps to increase the strength of the components [[21], [22]].

Conclusions

It has been proved that the compressive strength of fine-grained fiber concrete samples depends on the length of the added fiber. At a length of 20 mm of fibers an increase in the compressive strength of concrete samples by 47.2 % is observed.

Basalt fiber reacts with the cement medium as an active mineral additive, with the subsequent formation of crystals of needle-like structure, resulting in an increase in the strength of concrete.

The bending tensile strength of the samples also depends on the length of the fibers. The highest strength is shown by the addition of 20 mm of fiber length. The increment of bending tensile strength in comparison with the control specimens is 21.9 %.

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

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Базальт талшығының ұзындығының ұсақ түйіршікті фибробетонның беріктік сипаттамаларына әсері

[1]Нұрбаева М.Н., [1]Лукпанов Р.Е., [1]Аруова Л.Б., [2]Gunasekaran M.

[1]Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Астана, Қазақстан
[2]Уттаранчал университеті, Дехрадун 248007, Үндістан

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ТҮЙІНДЕМЕ

Базальт талшығының ұзындығы әртүрлі болатын фибробетон үлгілеріне сынақтар жүргізілді. Фибробетон дайындау үшін қолданылатын базальт талшығының сипаттамалары берілген. Зерттеудің мақсаты талшық ұзындығының фибробетонның беріктік сипаттамаларына әсер ету заңдылықтарын анықтау болып табылады. Талшықтарды қоспай (бақылау құрамы) және талшық ұзындығы 40 мм, 20 мм, 10 мм және 5 мм болатын цемент массасының 0,2% базальт талшығын қосқанда ұсақ түйіршікті талшықты темірбетонды иілу кезіндегі қысу және созылу беріктігін анықтау нәтижелері ұсынылған. Ұсақ түйіршікті бетон қоспасына базальт талшығын енгізудің оңтайлы шектері талшық ұзындығы 20 мм деп санауға болатыны көрсетілген, бұл қысу беріктігінің 47,2%-ға дейін артуына әкеледі, иілу кезінде созылу беріктігі - бақылау құрамымен салыстырғанда 2 есе көп болады.

Түйін сөздер: базальт талшығы, арматуралау, қысу беріктігі, иілу беріктігі.

	Авторлар туралы ақпарат:
Нұрбаева Маржан Нұрбайқызы	*PhD докторанты, «Өнеркәсіптік және азаматтық құрылыс технологиясы» кафедрасы, Л.Н. Гумилев атындағы Еуразия ұлттық университеті, 010000, Сәтбаев көшесі 2, Астана, Қазақстан. Email: marzhan_nurbaeva@mail.ru*
Лукпанов Рауан Ермагамбетович	*PhD, «Өнеркәсіптік және азаматтық құрылыс технологиясы» кафедрасының профессоры, Л.Н. Гумилев атындағы ЕҰУ, 010000, Сәтбаев көшесі 2, Астана, Қазақстан. Email: rauan_82@mail.ru*
Аруова Лязат Боранбаевна	*Т.ғ.д., «Өнеркәсіптік және азаматтық құрылыс технологиясы» кафедрасының профессоры, Л.Н. Гумилев атындағы ЕҰУ, 010000, Сәтбаев көшесі 2, Астана, Қазақстан. Email: ecoeducation@mail.ru*
Gunasekaran Murali	*Зерттеу және инновация кафедрасының профессоры, Уттаранчал университеті, Дехрадун 248007, Үндістан. Email: murali_220984@yahoo.co.in*

Влияние длины базальтовой фибры на прочностные характеристики мелкозернистого фибробетона

[1]Нурбаева М.Н., [1]Лукпанов Р.Е., [1]Аруова Л.Б., [2]Gunasekaran M.

[1]Евразийский национальный университет им. Л.Н. Гумилева, Астана, Казахстан
[2]Уттаранчальский университет, Дехрадун 248007, Индия

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АННОТАЦИЯ

Проведены испытания образцов фибробетона с различной длиной базальтовой фибры. Даны характеристики базальтовой фибры, который используется для изготовления фибробетона. Целью исследования является выявление закономерности влияния длины фибры на прочностные характеристики фибробетона. Представлены результаты определения предела прочности при сжатии и на растяжение при изгибе мелкозернистого фибробетона без добавления фибры (контрольный состав) и с добавлением базальтовой фибры 0,2 % от массы цемента с длиной волокон 40мм, 20мм, 10 мм и 5 мм. Показано, что оптимальными пределами введения базальтовой фибры в смесь мелкозернистого бетона могут считаться длиной волокон 20 мм, что приводит к приросту прочности при сжатии до 47,2 %, на растяжение при изгибе в 2 раза больше по сравнению с контрольным составом.

Ключевые слова: базальтовая фибра, армирование, прочность при сжатии, изгиб.

	Информация об авторах:
Нурбаева Маржан Нурбайкызы	*Докторант PhD, Кафедра «Технология промышленного и гражданского строительства», ЕНУ им. Л.Н.Гумилева, 010000, улица Сатбаева 2, Астана, Казахстан. Email: marzhan_nurbaeva@mail.ru*
Лукпанов Рауан Ермагамбетович	*PhD, Профессор кафедры «Технология промышленного и гражданского строительства», ЕНУ им. Л.Н.Гумилева, 010000, улица Сатбаева 2, Астана, Казахстан. Email: rauan_82@mail.ru*
Аруова Лязат Боранбаевна	*Д.т.н., профессор кафедры «Технология промышленного и гражданского строительства», ЕНУ им. Л.Н.Гумилева, 010000, улица Сатбаева 2, Астана, Казахстан. Email: ecoeducation@mail.ru*
Gunasekaran Murali	*Профессор отдела исследований и инноваций, Университет Уттаранчал, Дехрадун 248007, Индия. Email: murali_220984@yahoo.co.in*

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Engineering and Technology

An Overview of Epoxy Resins as coating to protect metals from corrosion

[1]Makhmetova A.R., [1,2]Negim El-Sayed, [1]Ainakulova D.T., [2]Yeligbayeva G., [3]Khatib J.M.

[1]*School of Materials Science and Green Technologies, Kazakh-British Technical University, Almaty, Kazakhstan*
[2]*Department of Petroleum Engineering, Satbayev University, Almaty, Kazakhstan*
[3]*University of Wolverhampton, Wolverhampton, UK*

** Corresponding author email: al_makhmetova@kbtu.kz*

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ABSTRACT
Any structures of metal, which are used in construction work, must be qualitatively protected from the external environment, more precisely, from the development of corrosion. Under the influence of the environment as a result of corrosive processes, the metal loses its properties. The presence of corrosion reduces the service life of any equipment in production, it worsens the quality of products. To solve the problems of increasing service life and providing chemical protection of metal, which is made of equipment, constructions, and structures, use highly effective anti-corrosion coatings based on epoxy resins. These materials are chemically resistant and provide a barrier that limits the access of corrosive media to the coated surface. Epoxy resins are stable to the action of halogens, acids, and alkalis, and have high adhesion to metals. However, having a complex of positive properties, epoxy resins have significant disadvantages - high combustibility, stiffness, and relatively low physical and mechanical properties, including resistance to impact, due to the limited mobility of inter-nodal sites of the spatial network of polymer macromolecules. Therefore, epoxy is cured with various hardeners and mixed with a variety of fillers (metallic, mineral, and organic), and many other components to reduce the cost of materials and to allow the properties of the resins themselves to be improved in the desired direction. This overview article discusses the basic properties of epoxy resins and the effects of various hardeners, and modifiers on the anti-corrosive properties of epoxy coatings, as well as general applications of epoxy resins and the health risks of their use.

Keywords: anticorrosive coating; epoxy resin; hardeners; modification; composite materials; applications.

Information about authors:

Makhmetova Alina Ruslanovna	*Bachelor's Degree in Physics and Astronomy, 2nd year master student in Materials Science and Technology of New Materials. Kazakh-British Technical University, School of Materials Science and Green Technologies, st. Tole bi, 59, 050000, Almaty, Kazakhstan. Email: al_makhmetova@kbtu.kz*
Negim Attia El-Sayed	*Ph.D., Professor, Kazakh-British Technical University, School of Materials Science and Green Technologies, st. Tole bi, 59, 050000, Almaty, Kazakhstan. Email: a.negim@kbtu.kz*
Ainakulova Dana Tulegenkyzy	*Ph.D. Degree in Materials Science and Technology of New Materials, 2nd year PhD student. Kazakh-British Technical University, School of Materials Science and Green Technologies, st. Tole bi, 59, 050000, Almaty, Kazakhstan. Email: da_ainakulova@kbtu.kz*
Gulzhakhan Yeligbayeva	*Ph.D., Professor, Department of Petroleum Engineering, Satbayev University, 22a Satpaev str., 050013, Almaty, Kazakhstan Email: g.yeligbayeva@satbayev.university*
Khatib Jamal	*Ph.D., Professor, University of Wolverhampton, Wulfruna St, Wolverhampton WV1 1LY, United Kingdom. E-mail: j.m.khatib@wlv.ac.uk*

Introduction

Ensuring reliable protection of metal products against corrosion remains one of the most important tasks in the metalworking industry. Rust is considered one of the main problems of all metal structures. Its ruthless action reduces the performance characteristics of metal products, spoils the appearance, and reduces the service life by several times. The most common way to protect construction is to apply coatings on the surface of the metal, preventing its destruction under the influence of various corrosive environmental factors. The protective coatings that modern technology has at its disposal are very diverse both in their properties and in the way they are obtained. The use of protective, protective-decorative, and special coatings can solve many problems [1]. By choosing the coating material, conditions of their application, and combining metallic and non-metallic coatings, it is possible to give the surface of products a different color and texture, the necessary physical, mechanical, and chemical properties: increased hardness and wear resistance, corrosion resistance, high reflectivity, improved anti-friction properties, surface electrical conductivity, etc.

However, the optimal choice of coatings or methods of finishing is not possible without a comprehensive consideration of their properties and the peculiarities of obtaining [[2], [3]].

Nowadays, epoxy resins are widely and effectively used as a protective coating in the construction industry. Epoxy resins are a versatile class of resins that are used to produce composite materials and structures, as well as for casting, sealing, protection and bonding of various materials, and can also act as fire and corrosion-resistant coatings. Epoxy resins are widely used in industry and households because they have an excellent combination of various characteristics [4]:

– excellent resistance to many chemicals;
– moisture resistance;
– very high bonding strength;
– excellent heat resistance;
– ease of use;
– low shrinkage

The use of epoxy resins in various branches of technology as adhesives, fire- and corrosion-resistant coatings, compounds, and binders in the production of composite materials predetermines the search for new modifying additives to provide epoxy composites with reduced flammability and high deformation and strength properties that meet the requirements of most industries. Reducing the flammability, heat resistance, and combustibility of polymers, high corrosion properties, and the creation of fire-safe materials for various types of building structures, metal structures is an urgent problem that requires urgent solutions [[4], [5]].

The purpose of this review article is to determine the level of physical-mechanical and barrier properties of epoxy coatings cured with different hardeners and to select the most suitable combination of resin and hardener to create on its basis a highly effective anti-corrosion barrier-type material.

Epoxy resin: its structure, properties, and types

Epoxy resins are oligomers that contain epoxy groups and can form cross-linked polymers under the action of hardeners (polyamines, etc.).

Epoxy resins are produced in both liquid and solid states. They are thermoplastic, but under the influence of various hardeners, they turn into non-melting polymers. The use of various additives (hardeners, fillers, plasticizers, thinners, curing gas pedals) makes it possible to obtain materials with a wide variety of properties based on epoxy resins. Epoxy resins are resistant to halogens, acids, and alkalis and are characterized by high mechanical strength, water resistance, high electrical strength, and good adhesion to polar compounds, metals, porcelain, mica, etc. A significant advantage of epoxy resins is their low shrinkage during the solid-state transition [[6], [7]].

The main characteristic feature of epoxy resins is their ability, under certain conditions, to transform into polymers of a mesh structure, which makes such resins suitable for the manufacture of various plastic materials (compounds, adhesives, enamels, binders for laminated plastics, sealants, etc.). The mentioned polymer meshes are formed either because of chemical reactions of epoxy groups of resin with a polyfunctional substance or due to the polymerization of epoxy groups under the influence of catalytically active compounds. In such cases, polyfunctional substances are called hardeners (or crosslinking agents), and catalytically active substances are called catalysts of curing (or catalytically active hardeners).

The following types of epoxy resins are the most used and, as a consequence, the most important:

– epoxy resins based on bisphenol A;
– epoxy resins based on other di- and polyphenols;
– amino-epoxy resins;
– cycloaliphatic epoxy resins;
– aliphatic epoxy resins and monoglycid compounds;
– oligo urethane epoxides;
– halogen-containing epoxy resins [[7], [8]].

Effect of hardeners on the anti-corrosion properties of epoxy coatings

At present application of insulating coatings based on polymeric materials is a widespread method of surface protection of various products and structures from the effects of various environments, as well as to increase their operational life during repair and restoration work. Among polymers, epoxy resins are widely used. The use of epoxy resins as the main components of the coatings under consideration is explained by a complex of physical and mechanical characteristics, including high adhesion to most known materials, low shrinkage deformation, and the ability to cure in a wide temperature range [7]. Epoxide groups have a high chemical activity, which makes it possible to use a wide range of organic and inorganic compounds as hardeners of epoxy resins. The hardeners of epoxy resins, as a rule, are their co-monomers that allow actively influence both the processing of epoxy compositions and the properties of the resulting polymers. Increasing industrial requirements for the quality of epoxy materials, and their performance under conditions of elevated temperatures, adverse climatic effects, strong vibrations and other adverse effects require the development and industrial development of a wide range of hardeners [9].

The nature of the curing process of epoxy composites depends on several factors: reactivity, quantitative ratio, the thermal conductivity of the components to be mixed, initial temperature, etc. [[10], [11]].

Epoxy oligomers can be cured with almost any carboxylic compound, acid or Lewis's base.

Table 1 - Types of epoxy hardeners and their descriptions

Hardener types	General Description
1. Amine hardeners	The group of amine hardeners includes aliphatic, alicyclic, aryl aliphatic, aromatic, hetero-chain (dicyandiamide), and heterocyclic di- and polyamines as well as their modifications. The subgroup of aliphatic polyamines includes hardeners that cure epoxy oligomers at room temperature or under moderate heat. The most characteristic representatives of this subgroup are the condensation products of ammonia with dichloroethane, ethylene polyamines DETA (diethylenetriamine), TETA (triethylenetetramine), and the total technical product - (polyethylene polyamine), GMDA (hexamethylenediamine), DPTA (dipropylenetriamine), etc. Such compounds are very uncomfortable to handle, have a bad odor, significant vapor elasticity, and are volatile and quite toxic [[14], [15]].
2. di- and polycarboxylic acid anhydrides	Anhydride hardeners are used in the construction of electrical insulating materials as well as products with increased heat resistance. This group of hardeners includes a very wide range of anhydrides of di- and polycarboxylic acids of the aliphatic, aromatic and hydroaromatic series as well as polyanhydrides of linear aliphatic dicarboxylic acids, ester acids and other similar compounds. Adducts of maleic anhydride with various dienes (tetrahydro phthalic and endic anhydrides), products of their hydrogenation (hexahydro phthalic anhydride) and catalytic isomerization are widely used [16]. The curing ability of anhydride hardeners provides a variety of polymer materials with good thermal stability and high dielectric properties. Triazintetracarboxylic acids and 2, 4-di (alkylenoxy-6-aminoalkylene) - sim-triazines can be effective hardeners of epoxy resins. They have found applications in heat-resistant adhesives for metals.
3. oligomeric hardeners with phenolic hydroxyls, carbonyl, isocyanate, amino groups, etc.	Polyfunctional oligomers (phenol-, aminophenol-, amino aldehyde condensates, oligo ethers, oligoimides) belong to oligomeric hardeners. They are used to create materials with a specific combination of properties, such as high chemical resistance and thermal stability, the ability to maintain long-term technological properties at room temperature, to harden quickly when heated, etc. Oligomers obtained by the reaction of unsaturated nitriles with olefins with subsequent hydrogenation of the reaction products are used as hardeners of epoxy resins used to make materials with reduced ability to sorb water [17]. The water absorption of epoxy polymers produced using such hardeners is 30% lower than that of triethylenetetramine curing. It is also proposed to use diaminomaleonitrile and its derivatives as a hardener. Moist, high coke number epoxy polymers are obtained by using imidamine hardeners which are synthesized by the reaction of diamines with tetracarboxylic acids dianhydrides. This produces epoxy polymers with a softening point above 300°C. Many publications are devoted to the curing of epoxy oligomers by isocyanates and their derivatives. Polyetherurea, reaction products of urea with polyalkylene polyamine, and imidazole adducts with isocyanates are patented as hardeners. At the same time compositions providing high protective properties and dielectric properties are obtained. Such systems are used for enameling wires, as protective coatings, in the manufacture of printing plates, as anti-corrosive coatings for ship protection, etc [18].
4. catalysts and curing gas pedals for epoxy oligomers	Catalytic hardeners such as boron trifluoride complexes with amines are the most common. A characteristic feature of these hardeners is the high curing rate of epoxy resins. Depending on the activity of the curing agent and the temperature, complete curing can be achieved within a few seconds to 2-3 hours [7].

However, only a small fraction of potential hardeners is suitable for industrial use. These practically useful hardeners can be roughly divided into four types:

- amine hardeners;
- anhydrides of di- and polycarboxylic acids;
- oligomeric hardeners with phenolic hydroxyls, carboxyl, isocyanate, amino groups, etc.
- catalysts and curing gas pedals for epoxy oligomers [[12], [13]].

Each type of hardener has a characteristic eventual topology that determines the structure of the corresponding epoxy polymers Table 1.

The most important property of the assortment of hardeners is that it allows regulating within a wide range of the curing conditions and properties of polymer materials, and provides rational use of epoxy oligomers, as well as the implementation of technical services during their processing.

Epoxy based composites

One of the ways to increase the durability of buildings and constructions is the use of polymeric composite materials (PCM) in their construction, the scope of their application in construction is steadily expanding. In connection with the appearance of new chemically resistant materials, it is offered to use them for protection against harmful natural and technogenic influences.

Epoxy resins are widely used as binders in PC due to their high physical and mechanical characteristics. Epoxy resins are among the best types of binders for a large number of fiber composites, which can be explained by the following reasons [[10], [19]]:

- good adhesion to a large number of fillers, reinforcing components, and substrates;
- variety of available epoxy resins and curing agents, allowing to obtain after-curing materials with a wide combination of properties, satisfying various technology requirements;
- absence of water release or any volatile substances during chemical and small shrinkage phenomena during curing;
- chemical resistance and good electrical insulating properties [20].

Polymeric composite materials based on epoxy resins have several valuable properties: high dielectric properties, increased mechanical strength, water resistance, low shrinkage during cross-linking, and good adhesion to metals, porcelain, and glass. It allows using of them as binders in the production of polymer composites, varnishes, glues, and impregnating and pouring compounds [21].

To impart valuable technical properties to epoxy oligomers, they create a cross-linked structure, i.e., they are cured. The introduction of special hardeners ensures that under certain conditions transverse chemical bonds are formed. As a result of curing, epoxy resins are easily converted into a thermosetting state.

Choosing the type of hardener, it is possible to change the physical-mechanical and chemical properties of the resulting composites in a wide range - from rubber-like too rigid, high-strength and high-modulus composites that retain their strength indicators under prolonged exposure to temperatures up to 200°C and higher. But it is worth noting that the properties of epoxy composites are largely influenced not only by the type but also by the amount of hardener injected. The amount of hardener is adjusted depending on the epoxy number of the resin (epoxy group content), taking into account the correction factor. The value of the factor in turn depends on the number of active hydrogen atoms in the hardener which react with the epoxy group. Also, the nature of the hardener determines the density of the spatial mesh in epoxy compositions, which in turn significantly affects the value of internal stresses [22].

To improve the properties of composites (complex damping and deformation strength properties, increase of heat resistance, chemical, and atmospheric stability, adhesion, manufacturability, etc.) polymers are subjected to modification [23].

Modification of epoxy resins to improve mechanical and physical properties

Obtaining epoxy polymer composites for construction purposes with predetermined properties is usually associated with the application of physical and chemical methods of modification: the introduction of solid insoluble fillers and aggregates, surfactants, inert plasticizers, and diluents. The choice of this or that modifier or their combination makes it necessary to carry out a complex of experimental studies to determine and regulate the properties of a developed material and optimize its structure. To improve the technological, physical-mechanical, operational, and other properties of epoxy oligomers their modification is made. The modification consists of the purposeful change of the polymer's structure at different levels and related properties. There are 3 methods of modification: physical modification, chemical modification, and physical-chemical modification [24].

Physical modification is achieved by adding substances to the resin that do not enter into chemical bonding with the binder. For example, the introduction of fillers (silica sand, marshalite, asbestos) increases the hardness, heat resistance, and thermal conductivity of the composition, reduces shrinkage during curing, and thermal expansion coefficient, as well as reduces the cost of the composition.

Chemical modification is carried out by adding thinners and solvents of epoxy compositions (these include unsaturated monomer compounds such as styrene, liquid polyester acrylate TGM-3, and aliphatic epoxy resins DEG-1, MEG-1, which are self-polymerizing substances and, polymerizing under the same conditions, come into interaction with the main composition, forming a solid solution of one polymer in another). The presence of such "active diluents" makes it possible to obtain low-viscosity flowing compositions [[25], [26]].

Physical and chemical modification. Various plasticizers and modifiers (dibutyl phthalate, Thiokol, polyesters) are used. They increase the elasticity, impact strength, and frost resistance of epoxy compositions, but reduce viscosity, heat resistance, adhesion properties, moisture resistance, and electrical insulation properties [24].

The properties of epoxy resins depend on the ratio of the quantities of the reacting ingredients. Depending on the length of the molecule formed, epoxy resins can be either viscous liquids or brittle solids.

Epoxy resin compositions containing hardeners, plasticizers, solvents and other components have sufficient fluidity to fill molds, strips, gaps, gaps, pores and capillaries. Resins can be mixed with a variety of fillers (metal, mineral and organic), as well as many other components, which reduces the cost of materials and makes it possible to improve the properties of the resins themselves in the desired direction. Compositions based on epoxy resins have high adhesion to a variety of materials, have a high chemical and thermal resistance, do not cause corrosion of materials in contact with them, and are very good dielectrics [27].

Table 2 lists some of the most common Epoxy resin components and their main functions.

Table 2 - Components of Epoxy resin and their main functions

Modified components	Basic functions
1. Interaction of epoxy resins with various hardeners	The ideal diluent for viscous epoxy resin is the hardener. Initially, epoxy resin is in a semi-liquid state. But when compounds with a mobile hydrogen atom are added, they can harden to form a three-dimensional network of chemical non-melting and insoluble products. Thus, it is not the epoxy resin themselves that are thermosetting, but their mixtures with hardeners and catalysts. The high chemical activity of epoxy groups allows using a lot of classes of organic and inorganic compounds as hardeners. Diamines (hexamethylenediamine, meta phenylenediamine, polyethylene polyamine), carboxylic acids or their anhydrides (maleic, phthalic) are used as hardeners for epoxy resin. Epoxy resin mixed with hardeners form thermosetting compositions with a number of useful and valuable properties: high strength; high adhesion ability with different types of surfaces (ceramics, metal, glass, concrete, wood); high resistance to external mechanical and chemical influences; during curing they do not emit volatile products and have low shrinkage (2-2.5%); high moisture and water resistance; high dielectric properties (has low thermal conductivity); environmental friendliness (after complete curing the material is non-toxic) [[13], [15]].

Continuation of table - 2

2. Plasticizers and modifiers	Plasticizers modify the system viscosity, flexibility, and mobility of molecular structures. Many plasticizers can increase the impact toughness of the polymer without loss of strength and modulus of elasticity, and can also improve fire, light and heat resistance. Among plasticizers of interest are tricresyl phosphate (TCP) and oleic acid (OA) due to their compatibility with ER. 1. Tricresyl phosphate is an ester of tricresol or dicresol orthophosphoric acid. TCP is readily soluble in fats, oils and many organic solvents; it is insoluble in water. 2. Oleic acid is a monounsaturated fatty acid with only one unsaturated bond in its molecule; it belongs to the group of Omega-9 unsaturated fatty acids. OA is soluble in organic solvents and insoluble in water. OA is common as unsaturated fatty acids and is found in vegetable and animal fats. OA are used as components of detergents, varnishes, olives, emulsifiers and plasticizers. Plasticizers also include dibutyl phthalate, thiokol, and polyesters, which increase elasticity and impact strength, reduce viscosity, improve frost resistance of epoxy compositions, but at the same time reduce heat resistance, adhesion properties, moisture resistance, and most importantly, dielectric properties [[27], [28]]. ER is modified by introducing various chemical compounds (thermoplastics, plasticizers). We can distinguish three main groups of modifications: chemical, chemical-physical and physical, which, in turn, are divided into - chemical: changing the chemical composition of the resin, adjusting the type of hardener and adding reactive additives; - chemical-physical: alloying, adding surfactants, combining with inert plasticizers and diluents soluble in the resin, modifying solid insoluble large additives (mineral or organic); - physical: ultrasound pretreatment of resin, vibration, high-frequency currents, treatment during curing. For the plasticizer to be effective, it must be thoroughly mixed and incorporated into the polymer matrix. This is usually accomplished by heating and mixing until either the polymer dissolves into the plasticizer or the plasticizer dissolves into the polymer [29]. Epoxy derivatives of 2-hydroxybenzoic acid, 3-diethylamino-2-hydroxypropyl ether of 2-hydroxybenzoic acid, 3-diethylamino-2-hydroxypropyl ether of 2-chlorobenzoic acid and 3-diethylamino-2-hydroxypropyl ether of 2-methoxybenzoic acid are used as modifying additives for ED-20. The introduction of these modifiers into epoxy composites significantly increases the physical-mechanical and thermal characteristics of the epoxy compound to unmodified ER. The obtained epoxydian compositions can be used as coatings.
3. Fillers	Fillers are various solid particles (inorganic, organic) that can be irregular, pointed, fibrous or lamellar in shape and are used in fairly large quantities in plastics. Fillers include quartz sand, marshalite, and asbestos [30]. They increase the hardness and heat resistance of the composition, reduce shrinkage during curing, increase thermal conductivity, reduce the thermal expansion coefficient, as well as reduce the cost of the composition [31]. In [31] the effect of fillers on the resistance to aggressive environments, such as sulfuric acid (30%, d = 1.84 g/cm3) was noted. The tested ER (binder + kaolin) and (binder + lignin) retain their protective properties unchanged for 100-120 days. At the same time on unfilled samples, signs of the destruction of coatings are noted already after 60-65 days of tests. The results of the studies show that the filler gives a good effect. In this case, there is a stabilizing effect of fillers due to their compositions, since they include metal oxides, which are resistant to the action of mineral acids, and the Nelson effect is realized - the path of the passage of an aggressive liquid deep into the matrix is increased. It was found that if the concentration of the filler in the polymer system exceeds some critical value, the permeability increases sharply, and liquid transfer occurs [32].
4. Diluents and solvents	Unsaturated monomer compounds (styrene, liquid polyester acrylate TGM-3 and aliphatic epoxy resins DEG-1, MEG-1) can be referred to as thinners and solvents. They are polymerizing substances themselves and, polymerizing under the same conditions, come into interaction with the main composition, forming a solid solution of one polymer in another. In most cases, the presence of such diluents ("active diluents") in the composition of ER is caused by a certain need. For example, without them, it is impossible to obtain low viscous flowing compositions with the necessary technological properties [33]. In some cases, when making electric insulating varnishes from ER, conventional solvents (toluene, xylene, and acetone) are introduced into ER.

Modification of epoxy resins by nanoparticles

Today, a promising application of nanoparticles is the modification of polymers to improve their characteristics. Thus, a new class of materials appears - polymer nanocomposites (PNC). The simplest and most economical way to produce such materials is to mix a polymer in a liquid state with a nanoscale phase and then polymerize the resulting composite [34].

An important parameter of nanoparticles is their specific surface area, through which particles interact with the functional groups of polymers. In this case, the molecules of the polymer matrix are adsorbed onto the particles, and the adhesion forces provide a strong bond. The factors determining the efficiency of modification of polymeric materials by nanoparticles are being actively studied all over the world. Such factors as the size, shape and number of particles, their distribution in the matrix material, the surface area of "polymer-particle" interaction, as well as the improvement of system interaction through the use of surface-active agents have the greatest influence [35]. A large number of studies show that the modification of epoxy compositions with nanoparticles affects their mechanical properties. Epoxy coatings containing nanoparticles have significant barrier properties for corrosion protection and reduce the tendency for bubble formation or delamination of the coating.

In the work [36] the authors showed the influence of nanoparticles on the anticorrosive and mechanical properties of epoxy coating. In this work, the influence of nanoparticles such as SiO_2, Zn, Fe_2O_3 and halloysite clay on the surface morphology, anticorrosion behavior and Young's modulus of epoxy coatings was investigated. After analyzing the experimental data, the authors reported that the nanoparticles improved the quality of the cured epoxy coating, reduced the porosity of the coating matrix, and zigzagged the diffusion path available to harmful species, resulting in improved barrier characteristics of the epoxy coating. And the nanoparticles also improved the adhesion of the cured epoxy coating to the substrate and changed the physicochemical properties of the coating-steel interface, the specific path of which depends on the type of nanoparticles.

It was found that dispersion of Zn, SiO_2, Fe_2O_3 and halloysite clay nanoparticles in the epoxy resin matrix with a concentration of 1% of the total weight of the epoxy resin and its hardener provides a positive role of nanoparticles on the high corrosion resistance of coated steel, which was immersed in NaCl solutions with a concentration of 0.3 wt. % and 3 wt. % for 28 days.

In the work [36] the authors studied the modification of epoxy binders with silica nanoparticles and the technology of obtaining composite materials based on them with improved performance characteristics. Based on the results of the study, the authors found that it is most advantageous to introduce nanoparticles in the least viscous medium (hardener) because in such a medium the obstacles to the breakdown of agglomerates and uniform distribution of particles should be minimal. The authors of work [36] determined the optimal degrees of epoxy matrix filling with nanoparticles: from 0.20 to 0.30 wt. %. The introduction of nanoparticles in optimal proportions increases the following characteristics of the epoxy binder: tensile strength increases by 32%.

Modification of epoxy resins with sic

To impart the required properties to epoxy composites, abrasive fillers are introduced into their composition. Filling is the most widely used and highly effective way of directional regulation of the properties of epoxy polymers to improve mechanical strength and stiffness, chemical resistance and heat resistance [30].

Epoxy polymers have such a complex of properties (adhesion, mechanical, electrical, etc.) that in many cases make them indispensable as a base for adhesives, paints, compounds and reinforced plastics. But these polymers also have a number of drawbacks. One of them is increased flammability. Epoxy resin materials ignite and burn when ignited. The main volatile combustion products are CO_2 and CO, and formic acid and other substances are also found in the combustion products [11].

One of the promising directions for solving the problem of increasing the fire resistance of epoxy compositions is the use of highly dispersed silicon carbide in their composition. Silicon carbide is used in many industries due to its structure, high hardness, and inertness in many aggressive environments. It is also used as an additive that increases the fire resistance of rubbers.

Silicon carbide has increased hardness and strength at high temperatures, as well as wear resistance, chemical resistance, fire resistance and thermal shock resistance. This provides great interest in its use in many industries [37].

In the work [38] the authors studied the possibility of using highly dispersed silicon carbide in epoxy compositions to improve fire resistance. The results of the study showed that the introduction of silicon carbide in the epoxy composition allows holding the temperature of the unheated surface of the sample up to 240°C much longer. The introduction of silicon carbide in the epoxy increases the fire-retardant properties of the coatings.

Currently, to increase the activity of silicon carbide surface it is modified: by oxidation - thermal or chemical, grafting monomers, oligomers and polymers.

Application of er-based materials

Due to its properties epoxy resin has found wide application in many areas of human activity: environmental design, construction, electrical engineering, mechanical engineering, aircraft construction, and rocket and shipbuilding. In construction, ER is used for marking strips on tracks.

Resin is used to glue bridge structures, and in shipbuilding, ER is used to make ship propellers and compressor blades. Resin is the basic material to produce gas and liquid vessels. In mechanical engineering, resin corrects casting defects and is used for dies and molds. Even some tools, such as springs and springs, are made from resin. Resin-based fiberglass plastic is used to make antifriction pads. In aircraft construction, ER is used for wing cladding, fuselage, nozzle cone, and jet engine parts. It is also used to make helicopter blades, rocket engine casings, and fuel tanks [39].

Table 3 - Main applications of epoxy materials

Epoxy materials	Description
Epoxy varnishes and enamels	Epoxy varnishes and enamels have high protective properties, so they are widely used for corrosion protection of metal products and structures, concrete, and wood products, operated in different atmospheric conditions, fresh and seawater, soil, etc. The coatings are characterized by high chemical resistance, hardness, and mechanical and adhesive strength, due to which a long-term protective effect is provided. The greatest use in the production of epoxy varnishes and enamels is found in diane epoxy resins. Varnishes and enamels are produced by dissolving the film-forming agent (epoxy resin) in organic solvents (glycol ethers, aromatic hydrocarbons, ketones, alcohols). Varnishes include additives that improve pouring (urea-formaldehyde resins, silicone-organic liquids), hardeners, and hardening gas pedals (phenols, phosphoric acid). Enamels may also contain fillers, pigments, plasticizers, and thixotropic additives (bentonite, aerosol). As dyes are usually used chemically stable inorganic pigments - titanium dioxide, carbon black, chrome oxide, etc., fillers are talcum, asbestos, barite, and mica [40, 41].
Epoxy Adhesives	Epoxy adhesive is one of the most popular types of adhesives, as it can join almost all types of materials, level the surface, and fill cracks and cavities. The epoxy-based adhesive creates a strong bond and, once cured, is resistant to chemicals, grease, and oil, and has electrical insulating properties. Because of their unique characteristics, epoxy adhesives have gained well-deserved popularity in various fields. They are used in construction, engineering, aerospace, shipbuilding, and automotive industries, as well as in everyday life to repair shoes, furniture, sanitary ware, and household appliances [42]. Epoxy adhesive can reliably bond a variety of materials such as different metal alloys, plastics, ceramics, porcelain, earthenware, glass, wood, and different types of building materials, and you can bond these materials in any combination [43].
Epoxy compounds	The epoxy compound is a two-component polymer that includes epoxy resin, hardener, catalyst, thinner, filler, curing gas pedal, and plasticizer. Epoxy compounds are suitable for the production of tabletops, for the production of 3D tables, for the production of poured floors, and for the production of decorative products.
Epoxy primers	Epoxy primer is an anti-corrosive paint material. Epoxy primer protects metal surfaces from rust. This material consists of a special resin of the same name, which gives the primer its unique properties. Thus, the treated objects become resistant to corrosion and external influences. The primer improves adhesion to other substrates and prepares the surface for painting. Epoxy primer is hydrophobic. The coating acts as a quality protection for the substrate from the effects of the wet environment. It also tolerates temperature fluctuations well [44].

Continuation of table - 3

Epoxy fillers	Epoxy putty is used for surfaces of different types: concrete, ceramic, wood and even metal. Epoxy putty consists of several components: hardener, filler, and epoxy resins [45]. Epoxy putties are used for minor repairs as well as in large-scale construction for the following purposes: − Waterproofing. − Joining different materials - metal, ceramics, plastic, wood, concrete. − Alignment of various substrates, including stone, concrete, and wood. − Restoration of surfaces and masking of irregularities, and joints, elimination of various damages - potholes, cracks, and chips [30]. Epoxy fillers can be applied to a variety of substrate materials: − stone and brick; − concrete and foam concrete; glass and plexiglass; metal; plastic; ceramics [46].
Epoxy mastics	Epoxy mastic is a special material that is thick and has plastic mass. This product is made based on epoxy resins and has a mixture of dry pigment and filler. The epoxy resin is dissolved by an organic solvent with the addition of a plasticizer, which gives the material properties of increased strength and durability. Epoxy mastics are used for flooring of high strength and resistance.
Epoxy polymer concretes	Polymer concrete is an artificial stone, a modern type of concrete mortar, which uses different polymer compounds instead of the usual cement. Most often used for polymer concretes are furan, epoxy, and unsaturated polyester resins. The fillers may be basalt or granite rubble, crushed sandstone, or quartz sand. Concrete polymer is actively used in construction, production of ritual elements, furniture, pouring floors, creating tabletops, and a variety of items [47]. The main advantages of polymer concrete are: high level of water resistance, resistance to high/low temperatures, and fluctuations, and excellent resistance to aggressive chemical components - polymer concrete can be used in different conditions without the need for additional coatings, primers, impregnations, a large selection of options for appearance - polymer concrete can be different colors and textures, imitate those or other materials (malachite, granite, marble, etc.) [48].

Epoxy resin is used as a finishing coat for various surfaces in the interior, such as concrete, wood, metal, and even glass. It protects coatings from water, high temperatures, and various mechanical and chemical damage. To increase the aesthetic properties of the resin used to make objects and objects of environmental design, dyes, and glitters are added to it. In addition, non-standard solutions are often used in the addition of various fillers, including:

– cement (gives strength to the material and creates an unusual decorative effect);

– rocks and mineral stones, in crushed and natural size (the most popular are marble and garnet);

– quartz sand (used both in the manufacture of floors and countertops and when creating small decorative items);

– wood flour or bark (gives density and strength, small fractions are used in the manufacture of furniture in the manufacture of a special composite);

– aluminum powder, liquid gold (create unusual effects); natural dyes (graphite gives black color, titanium dioxide – white) [[25], [49]].

Assessment of the toxic hazard of epoxy resin

Epoxy resins have been used in manufacturing and the paint industry since the 1950s, so the risks associated with working with them are well understood. It is important to understand that epoxy is non-toxic and non-volatile, but the compounds used to cure it are hazardous to health. The type of hardener can be anything:

Amine hardeners. These hardeners have a slightly unpleasant odor, are used in the home, and are of the cold-curing type. They cure at room temperature of 23°C. An increase in odor, and therefore an increase in toxicity of the material usually occurs during the polymerization reaction, which by its nature is exothermic, that is proceeding with the release of significant heat, and from the heated epoxy mixture volatile substances are released much more actively than from the cold [14].

Acid hardeners. Carboxylic acids and their anhydrides are used - maleic, phthalic, hexahydrophthalic, and others. Acid hardeners give more reliable results but are difficult to use. This type of curing is called hot curing, and during temperature exposure (100-200°C), the epoxy improves its physical and chemical properties.

The main danger of using epoxy resin is the high allergenicity of the resin itself and the hardener. The greatest danger posed by the resin substance is severe skin lesions. The strongest skin irritations and allergic manifestations occur upon direct contact with the liquid mass with unprotected skin. Dermatitis is also accompanied by severe irritation of the respiratory tract membranes, and lesions of the mucous membranes. To avoid such effects, use gloves and a respirator with charcoal filters [50].

Safety precautions.

Protect breathing: When working with epoxy you must protect your breath with a respirator or half mask with organic vapor filters! They are also suitable for working with alcoholic inks.

The greatest amount of vapor is released when the two components are mixed and when working with the burner. The solid resin (approximately 24-48 hours after pouring) becomes harmless. A very important point is to work in a well-ventilated room. During mixing with the hardener, as well as directly during polymerization, a certain number of harmful substances are emitted.

Protect your eyes: If you work with large quantities of resin, wear special safety glasses, or do not touch your face while working. The slightest contact of the resin with your mucosa can cause severe irritation and inflammation.

Protect your skin: From the time you open the resin packs until you finish cleaning the work area, wear gloves and, preferably, sleeves or long-sleeved clothing to protect your hands from the resin [51].

Conclusions

In this article, we reviewed the types of epoxy resins and hardeners. The properties of cured epoxies depend on the type of epoxy, the hardener, and the curing process used. The strength of epoxy resins can be improved by incorporating thermoplastic components, inorganic substances, carbon fibers, clay, and carbon nanotubes. Epoxy resin is a very resistant and durable material. The resin will reliably protect the coated surface from all kinds of mechanical stresses and guarantee water resistance and act as a barrier to aggressive acid and alkaline nature. Epoxy resins have a wide range of applications, and the possibilities of its use are extremely diverse: from epoxy adhesive to transparent jewelry resin.

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

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Металдарды коррозиядан қорғау үшін жабын ретінде қолданылатын эпоксидті шайырға шолу

[1]Махметова А.Р., [1, 2]Negim El-Sayed, [1]Айнакулова Д.Т., [2]Елигбаева Г.Ж., [3]Khatib J.M.

[1]Материалтану және жасыл технологиялар мектебі, Қазақ-Британ техникалық университеті, Алматы, Қазақстан
[2]Мұнай инженерия кафедрасы, Сәтбаев университеті, Алматы, Қазақстан
[3]Вулверхэмптон Университеті, Вулверхэмптон, Ұлыбритания

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ТҮЙІНДЕМЕ

Құрылыс жұмыстарында қолданылатын кез-келген металл конструкциялар сыртқы ортаның әсерінен, дәлірек айтсақ, коррозиядан сапалы қорғалуы керек. Коррозиялық процестер нәтижесінде қоршаған ортаның әсерінен металл өзінің қасиеттерін жоғалтады. Коррозияның болуы өндірістегі кез-келген жабдықтың, металл конструкцияларының қызмет ету мерзімінің қысқаруына әкеледі, бұл өнімнің сапасын нашарлатады. Жабдықтардың және құрылымдардан жасалған металдардың қызмет ету мерзімін ұзарту және химиялық қорғауды қамтамасыз ету мәселелерін шешу үшін эпоксидті шайыр негізіндегі жоғары тиімді коррозияға қарсы жабындар қолданылады. Бұл материалдар химиялық төзімділікке ие және агрессивті ортаның жабылған бетке кіруін шектейтін тосқауыл болады. Эпоксидті шайырлар галогендердің, қышқылдардың, сілтілердің әсеріне төзімді, металдармен жоғары жабысқыштыққа ие. Алайда, осындай жақсы қасиеттерге ие бола тұра, эпоксидті шайырлардың айтарлықтай кемшіліктері де бар. Олар жоғары жанғыш, қатты және салыстырмалы түрде физикалық-механикалық қасиеттері төмен болады. Мысалы полимер макромолекулаларының кеңістіктік торының түйінаралық учаскелерінің шектеулі қозғалғыштығына байланысты соққыға төзімділігін жатқызуға болады. Сондықтан эпоксидті әртүрлі қатайтқыштармен қатайтады, сонымен қатар материалдардың құнын төмендету және шайырлардың қасиеттерін қажетті бағытта жақсартуға мүмкіндік беру үшін әртүрлі толтырғыштармен (металл, минералды және органикалық толтырғыштар) және басқа да көптеген компоненттермен араластырады. Бұл мақалада эпоксидті шайырлардың негізгі қасиеттері мен әртүрлі қатайтқыштардың, модификаторлардың эпоксидті жабындардың коррозияға қарсы қасиеттеріне әсері талқыланады. Оған қоса эпоксидті шайырларды қолданудың жалпы бағыттары мен оларды қолдану кезіндегі денсаулыққа қаупі қарастырылады.

Түйін сөздер: коррозияға қарсы жабын; эпоксидті шайыр; қатайтқыш; модификация; композициялық материалдар; қолдану.

Авторлар туралы ақпарат:

Махметова Алина Руслановна	*Физика және астрономия бакалавры, Материалтану және жаңа материалдар технологиясы бойынша магистратураның 2 курс студенті. Қазақ-Британ техникалық университеті, Материалтану және жасыл технологиялар мектебі, көш. Төле би, 59, 050000, Алматы, Қазақстан. Email: al_makhmetova@kbtu.kz*
Negim El-Sayed	*Химия ғылымдарының докторы, PhD, профессор. Қазақ-Британ техникалық университеті, Материалтану және жасыл технологиялар мектебі, көш. Төле би, 59, 050000, Алматы, Қазақстан. Email: a.negim@kbtu.kz*
Айнакулова Дана Тулегенқызы	*Материалтану және жаңа материалдар технологиясы PhD докторантурасы, 2 курс PhD докторанты. Қазақ-Британ техникалық университеті, Материалтану және жасыл технологиялар мектебі, көш. Төле би, 59, 050000, Алматы, Қазақстан. Email: da_ainakulova@kbtu.kz*
Елигбаева Гульжахан Жакпаровна	*Техника ғылымдарының докторы, PhD, Сәтбаев университетінің Мұнай инженериясы кафедрасының профессоры, Алматы, Қазақстан. E-mail: g.yeligbayeva@satbayev.university*
Khatib Jamal	*PhD, Вулверхэмптон Университетінің Профессоры, Вулверхэмптон, Ұлыбритания E-mail: j.m.khatib@wlv.ac.uk*

Обзор эпоксидной смолы как покрытие для защиты металлов от коррозии

[1]Махметова А.Р., [1,2]Negim El-Sayed, [1]Айнакулова Д.Т., [2]Елигбаева Г.Ж., [3]Khatib J.M.

[1]*Школа материаловедения и зеленых технологий, Казахстанско-Британский технический университет, Алматы, Казахстан*
[2]*Кафедра нефтяной инженерии, Университет Сатпаева, Алматы, Казахстан*
[3]*Университет Вулверхэмптона, Вулверхэмптон, Великобритания*

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АННОТАЦИЯ

Любые сооружения из металла, которые используются в строительных работах, должны быть качественно защищены от воздействия внешней среды, а точнее, от развития коррозии. Под влиянием окружающей среды в результате коррозионных процессов металл теряет свои свойства. Наличие коррозии сокращает срок службы любого оборудования на производстве, ухудшает качество выпускаемой продукции. Для решения проблем с увеличением срока службы и обеспечения химической защиты металла, из которого изготовлено оборудование, конструкции, сооружения, используют высокоэффективные антикоррозионные покрытия на основе эпоксидных смол. Эти материалы являются химически стойкими и обеспечивают барьер, ограничивающий доступ агрессивных сред к покрытой поверхности. Эпоксидные смолы устойчивы к действию галогенов, кислот и щелочей, обладают высокой адгезией к металлам. Однако, обладая комплексом положительных свойств, эпоксидные смолы имеют существенные недостатки - высокую горючесть, жесткость и относительно низкие физико-механические свойства, в том числе стойкость к ударам, обусловленные ограниченной подвижностью межузловых участков пространственной сети макромолекул полимера. Поэтому эпоксидную смолу отверждают различными отвердителями, смешивают с разнообразными наполнителями (металлическими, минеральными и органическими) и многими другими компонентами, чтобы снизить стоимость материалов и позволить улучшить свойства самих смол в желаемом направлении. В данной обзорной статье рассматриваются основные свойства эпоксидных смол и влияние различных отвердителей и модификаторов на антикоррозионные свойства эпоксидных покрытий, а также общие области применения эпоксидных смол и риски для здоровья при их использовании.

Ключевые слова: антикоррозионное покрытие; эпоксидная смола; отвердитель; модификация; композиционные материалы; применение.

	Информация об авторах:
Махметова Алина Руслановна	*Степень бакалавра по Физике и астрономии, Магистрант 2 года обучения по специальности Материаловедение и технология новых материалов. Казахстанско-Британский технический университет, Школа материаловедения и зеленых технологий, ул. Толе би, 59, 050000, Алматы, Казахстан. Email: al_makhmetova@kbtu.kz*
Negim El-Sayed	*Доктор химических наук, PhD, профессор. Казахстанско-Британский технический университет, Школа материаловедения и зеленых технологий, ул. Толе би, 59, 050000, Алматы, Казахстан. Email: a.negim@kbtu.kz*
Айнакулова Дана Тулегенкызы	*PhD материаловедения и технологии новых материалов, докторант 2 курса. Казахстанско-Британский технический университет, Школа материаловедения и зеленых технологий, ул. Толе би, 59, 050000, Алматы, Казахстан. Email: da_ainakulova@kbtu.kz*
Елигбаева Гульжахан Жакпаровна	*Доктор технических наук, PhD, профессор кафедры Нефтяной инженерии Сатпаевского университета, Алматы, Казахстан. E-mail: Gulzhakh@yandex.ru*
Khatib Jamal	*PhD, Профессор Университета Вулверхэмптона, Вулверхэмптон, Великобритания.* *E-mail: j.m.khatib@wlv.ac.uk*

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Engineering and technology

Effect of Aggregate Gradation on Asphalt Concrete Properties

[1*]Kosparmakova S.A. [1]Shashpan Zh.A., [2]Guler M.

[1] L.N. Gumilyov Eurasian National University, Astana, Kazakhstan
[2] Middle East Technical University, Ankara, Turkey

Corresponding author email: smartsam0509@gmail.com

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ABSTRACT

Economic expansion is a positive side effect of national highway construction initiatives. So, the plan is to construct these projects rapidly. This calls for premium asphalt. As a result of aggregate gradation variation, numerous asphalt mixes have been rejected and rebuilt on-site in recent decades, resulting in the waste of valuable resources and valuable time. Consequently, the goal of this study was to examine the durability of asphalt mixes where the aggregate gradation ranged from +4% above to 2% below the standard range. The aggregate gradation is inconsistent throughout HMA manufacture. The aggregate is graded at 2, 4, and 6 percent over and below the allowed range. Case in point: the gradation of the control mix design. Marshall There was a quantitative evaluation of mixed properties throughout the design phase. HMA mix performance was evaluated via high temperature and water cycles by vehicle pressure observation and Indirect Tensile Strength (ITS) testing. In hot climates, asphalt with gradations above +4% and 2% of both the higher and lower standard values showed the greatest resilience to water damage and the least rutting. In warm regions, asphalt mixture design will be constrained by the higher aggregate gradation limits.

Keywords: Asphalt Concrete, aggregate gradation, Marshall test, rutting, water resistance.

	Information about authors:
Kosparmakova Samal Akhmetaly	*Ph.D. Student, Department of Technology of Industrial and Civil Construction, L.N. Gumilyov Eurasian National University, 010000, Kazhymukhan Munaytpasov Street 13, Nur-Sultan, Kazakhstan. Email: smartsam0509@gmail.com*
Shashpan Zholaman Amangeldiyevich	*Dr. tech. sc., Professor of the Department of Technology of Industrial and Civil Construction, L.N.Gumilyov Eurasian National University, 010000, Kazhymukhan Munaytpasov Street 13, Astana, Kazakhstan.Email: zholamanalmatykz@gmail.com*
Murat Guler	*Dr. tech. sc., Professor of Middle East Technical University, Ankara, Turkey E-mail: gmurat@metu.edu.tr*

Introduction

National highways drive economic growth and social improvement. They're essential for national growth. Access to economic, social, health, and education services makes a road network essential to poverty reduction [1]. The administration has been urged to speedily complete these tasks in order to prove its effectiveness. Due to aggregate gradation variation throughout execution and production, quick project completion hurts the final output. Asphalt pavement construction involves mixing, hauling, paving, and compaction [2]. Construction procedures have several uncontrollable aspects [[3], [4]]. Variation in asphalt design and construction characteristics has consistently caused early performance issues [5]. Thus, studying the negative effects of asphalt mix design and construction variations may be beneficial [6].

Modern pavement mixtures consist of air void, asphalt binder, coarse particles, fine aggregates, and filler [[7], [8], [9]]. A multistage compound is filled with air when aggregates and fillers are bound together with an asphalt binder [10]. Well-interlocked aggregates make for good pavement performance [11]. Asphalt mixture gradation affects pavement quality and performance [12]. Asphalt grade variation causes much pavement distress [13].

Due to aggregate gradation variance, many asphalt mixtures are rejected and repaired on-site, wasting materials, time, and money [14]. This study evaluates the feasibility of adopting mixes with aggregate gradation variation (between +4% above the higher specification limit and -2% below the lower specification limit).

Much research on the influence of gradation variation on HMA characteristics, or rather the effect of gradation variance that may occur during production on HMA properties, has been conducted in the past, according to the pavement design and construction literature [[15], [16], [17], [18], [19], [20]].

How to aggregate gradation in pavement mixes affects a massive amount of capacity and rutting resilience is the subject of research [15]. Aggregates retained on sieve sizes of 1.18, 0.6, and 0.3 mm were shown to contribute more than 50% to strength attributes, whereas aggregates retained on sieve sizes of 2.36 and 4.75 mm contributed more than 50% to resistance to weight and rutting. The clogging properties of porous asphalt mixtures as a function of aggregate gradation were investigated [16]. This study found that a mixture of porosity and pavement with pore macrotexture depth before and after blockage were both substantially connected with aggregate gradation. Also, [17] investigated the aggregate qualities effect on pavement mixture stripping and creeping deformation with the result that basalt aggregate-prepared HMA specimens resist creep better than limestone aggregate-prepared HMA specimens that have not been conditioned. Mixtures made with basalt aggregate were less resistant to creep strain after conditioning compared to those made with limestone aggregate. It was found that stripping resistance is proportional to the amount of asphalt that was absorbed. Furthermore, mixtures created with aggregate that met the upper limit of dense aggregate gradation established by the American Society for Testing and Materials (ASTM) demonstrated the strongest resistance to stripping. According to research [18], Asphalt Concrete (AC) mixture rutting and fatigue resistance can be greatly improved by utilizing different gradation sizes of aggregate and with types of additives such as fibers. Another research says that [19], gradation heterogeneity has a significant impact on pavement performance.

Research [20] suggested altering the particle fraction passing the 4.75 mm sieve screen to reduce asphalt pavement rutting. Also [21] investigated how aggregate gradation variation affected asphalt mixture rutting and found that it helped pavement withstand permanent deformation. Scientists [22] examined how aggregate gradations at construction affected to pavement performances and found that rutting tolerance increased initially and then reduced as the gradation changed from fine to coarse. Researchers tested asphalt mixes with diatomite powder and lignin fiber. The compound blend of diatomite powder and lignin fiber improved asphalt mix performance more than either alone. Combinations with lower limit gradations nearly affected HMA characteristics the most. Asphalt mixtures downwardly diverted to a lower limit grade performed best.

Thus, the aggregate gradations change in HMA is the subject of this study. So far, there hasn't been much investigation into the optimal range of aggregate gradational deviations from specification limits for HMA mixture performance. So, the purpose of this research was to examine how well HMA blends performed when aggregate gradation was outside the specified range.

The major objectives of this study are to determine the range of aggregate gradation curve specifications outside of which HMA mixture performance is not negatively affected. Next, the HMA combinations made by them will be tested for their characteristics.

Vehicle monitoring with indirect tensile strength experiments would be used to evaluate the effectiveness of the control mix to the best HMA mix that is either above or below the upper or lower specification limit. Moreover, choose the best HMA blend for the skeleton, which is resistant to both high- and low-temperature rutting strain and thermal cracking.

Methods and Experiments

Materials

The 4.75 mm (No. 4) sieve was used to separate coarse and fine aggregates, with particles being retained or passed. Meanwhile, fillers were aggregate particles smaller than the No. 200 sieve (0.075 mm). All the aggregate types were consistently graded and met the allowed range for grades defined by the local technical specifications. Coarse dolomite of both the (I) and (II) grades, whose physical properties are summarized in Table 1, was also used. Asphalt concrete was made using fine siliceous sand (bulk specific gravity 2.65 g/cm3) and limestone dust (bulk specific gravity 2.85 g/cm3). The asphalt binder properties result from the traditional way of testing presented below in Table2.

Table 1 - Coarse Aggregate Properties

No.	Name of Test	Standard	Values		Specification Limits
			Type 1 (Grade I)	Type 1 (Grade II)	
1	The Bulk specific gravity (gm/cm^3)	AASHTO T-85	2.53	2.51	N/A
	The Saturated surface dry specific gravity (gm/cm^3)		2.57	2.55	
	The Apparent specific gravity (gm/cm^3)		2.71	2.69	
2	Absorption %	AASHTO T-85	2.56	2.62	≤5
3	LA Abrasion %	AASHTO T-96	20.1	22.3	≤40
4	Stripping Test %	AASHTO T-182	>95	>95	>95

Table 2 - Asphalt Binder Properties

No.	Name of Test	Standard	Values	Specification Limits
1	A penetration test (0.1 mm)	AASHTO T-49	72	70-100
2	Softening Point (^oC)	AASHTO T-53	47.6	>46
3	Flash Point (^oC)	AASHTO T-48	+230	+220
4	Kinematics viscosity (cSt)	AASHTO T-201	341	+300
5	Ductility (cm)	AASHTO T-51	+100	>95

Table 3 - Asphalt Concrete Mixes Different Gradations

Sieve Sizes	Asphalt Concrete Mixes							Limits
	G0	G1	G2	G3	G4	G5	G6	
25.0	100	100	100	100	98	96	94	100-100
19.0	100	100	100	100	98	96	94	100-100
12.5	85	100	100	100	74	72	69	75-100
9.5	73	100	100	100	59	58	55	60-85
4.75	48	66	77	88	34	33	32	35-55
2.36	29	42	49	56	20	19	18	20-35
0.600	18	26	31	35	10	9	9	10-22
0.300	11	19	22	26	6	5	5	6-16
0.150	8	14	17	19	4	3	3	4-12
0.075	5	10	11	13	2	2	2	2-8

Gradations

According to these findings, the optimal ratio of coarse aggregates for a wearing surface is 30 percent grade I, 20 percent grade II, 15 percent natural sand, 30 percent crushed sand, and 5 percent limestone dust. Table 3 displays the intended gradation of the control asphalt concrete mixture. (G0). To emphasize the several steps in the creation of asphalt, the aggregate gradation in the mixture was made to go (1) below the minimum requirements for wearing surfaces and (2) over the maximum requirements for wearing surfaces. For the first combination (G1), the percentage of variation beyond the specified upper limit was 2%; for the second and third mixes (G2 and G3), the values were 4% and 6%, respectively (G3). In contrast, G4, G5, and G6 were assigned to the three combinations that fell between 2% and 6% below the lower standard limit.

For the first step, after materials have been chosen, we'll conduct five aggregate characterization tests, including the LA abrasions, stripping values, specific gravities, water absorptions, and design gradation selections, to ensure that stones will be in direct touch with one another.

In addition, the binder will be evaluated for its ability to penetrate, soften, flash, have a high viscosity, and be ductile.

In the second step, we produced and prepared the controlling asphalt mix (G0) as well as the other five pavement mixtures (G2 to G6) in accordance with specifications [16]. The influence of aggregate gradation variation on HMA characteristics was investigated in the third stage using the Marshall Mix Design Method.

On the G0, indirect tensile strength testing and wheel load monitoring was also performed, and samples were selected from the best mixtures that have been above and below the maximum and lower standard values, respectively.

Testing by Marshall Method

Measurements of stability (in kilograms) and flow values (in millimeters) were taken for each mix using a Marshall instrument, a Marshall machine type TO-550-1 imported from the United States to evaluate the asphalt mixes' resistance to plastic flow. The term "electronic commerce" refers to the sale of electronic goods. The compacted specimens were heated after 24 hours in a water bath at 60^{o}C 30 minutes before starting of Marshall Test. The AASHTO T-245, 75-blow Marshall Compaction test criterion was applied. During the Marshall test's stability phase, samples were initially weighed in the air before being submerged in water and then reweighed, and the greater of the two loads (in kilograms) was considered the stability value. It should be noted that correction factors were imposed for sample thicknesses more than 6 cm. The flow value, on the other hand, was determined by tracking the amount of strain placed on the specimens at their maximum load.

Wheel Loading Tracking Test

The rutting depth test is conducted by a 20-4000 Wheel track testing machine which is designed to test asphalt concrete for rutting resistance in air and in water. The unit is compatible with asphalt samples obtained on a sector press or in the form of samples. Simultaneously two samples can be tested and there are several mould configurations have been developed for testing: 320x260 mm; 340x280 mm; 300x300 mm; 410x260 mm; 400x300 mm, but for tests, the diameter of the sample must be - 150 mm in 2 pieces. Overall testing procedure programs were set according to EN 12697-22. First, the samples were prepared on a 300x300 mm mold in a special sector compactor, which is designed for the preparation of compacted asphalt samples 320 x 260 mm (410 x 260 mm optional) with a height of 40-120 mm in accordance with EN12697/33, Part 5.2. Thereby the samples were prepared approximately in 10 min, with 300x300 mm and 50 mm height to save on material. After the compactor, samples were cooled at room temperature for not less than 24 hours, subsequently, tested for 20000 passage by 2 samples in parallel in 9 hours. The received results are assumed as high temperature and intensive movement rutting resistance indicators, which meet the standard.

Indirect Tensile Strength

The AASHTO T-283 test method was utilized in order to determine the tensile properties of bitumen mixtures. In order to achieve uniform stress, this method relied on a steady pace of loading the Marshall specimen using its diametric plan. In this experiment, duplicate samples of each combination were prepared for testing. They were the "control" mixture, and "best" mixtures above and below the upper and lower specification limits, respectively. The temperature of the water was kept at 60 degrees Celsius during the conditioning process, which took 24 hours. The other set of specimens was not conditioned in any way. The term "Tensile Strength Ratio" refers to the comparison that was made between the conditioned samples' averaged indirect tensile strength and the specimens' averaged indirect tensile strength that had not been conditioned (TSR).

Results

Marshall Test Results

Each blend's OAC was determined using the Marshall Test, as indicated in Table 4. After that, we assess how well the controlled combination and other mixes at different gradation lines perform. Gradational differences showed a range of

Table 4 - Variation in aggregate gradation has an effect on the investigated blends.

AC Properties	G0	G1	G2	G3	G4	G5	G6	Limits
Optimal AC %	4.7	4.5	4.2	3.7	5.2	5.5	5.7	3-6%
Stability (Kg)	1211	1197	1182	998	1316	1325	1341	900 kg (min)
Flow (mm)	3.3	4.1	3.7	5.3	2.9	1.9	1.7	2-4 mm
Stiffness (kg/mm)	384	299	334	210	481	698	842	300-500 kg/mm
Bulk specific gravity (gm/cm^3)	2.352	2.361	2.372	2.360	2.314	2.271	2.254	-
AC Air Voids %	3.54	4.35	4.22	6.0	4.44	5.92	7.66	3-5%
VMA %	16.44	15.8	15.43	15.39	18.3	19.96	20.84	-
VFA %	87.5	72.5	72.7	61.4	75.7	65.3	63.2	-

viewpoints on the subject of aggregate gradation shifts throughout the pavement production process. These various gradation lines were seen in the G0 combinations all the way up to the G6 mixtures, as shown in Fig 1. The gradation curve design employed a combination denoted by G0 (control mix). Displayed combinations in G1, G2, and G3 were +2%, +4%, and +6%, respectively, over the maximum specification limit.

G4, G5, and G6 showed the applied mixes were -2%, -4%, and -6% below the standard lower limit, respectively. The preceding G0 through G6 mixes vary at the OAC. Each blend was evaluated according to the Marshall characteristics that are shown in Table 4. They consist of characteristics such as solidity, mobility, bulk-specific gravity, air voids, mineral voids, and asphalt voids, among other characteristics. Following the completion of the data collection process, it was analyzed.

According to the findings in Table 4, the increase in the maximum specification limits for aggregates causes a reduction in the combination's overall stability. The G0 stability value for the standard sample was calculated to be 1211 kg. The stability of the mixture was generally unaffected by two successive blends (G1 and G2), although having gradation changes that were 2% and 4% higher than the maximum standard limits, respectively. These blends resulted in declines of 1.17 and 2.4%. In the succeeding mix, gradual increments of +6% beyond the maximum specification limit led to a 17.6% loss in mix stability, reaching a low of 998 kg (G3). Nonetheless, despite this, it was still over the minimal stability level of 900 kg.

The Flow value of G0 was measured at 3.30 mm, which is greater than the permitted range of values. The flow was raised by 12.1% and 24% for the succeeding two mixes (G1 and G2) despite the fact that increasing the gradational changes by the maximum specification limit of 2% and 4%, respectively, did not prevent them from meeting the criteria (2 mm Flow 4 mm). Due to the fact that the (G3 flow) was more than the suggested threshold (5.3 mm). The values of blend consistency that is lower than the criterion are shown in Table 4. The gradations variation was less than the lower standard limit by -2%, -4%, and -6%, respectively, which resulted in the stability values of 1316 kg, 1325 kg, and 1341 kg being achieved for the aforementioned three combinations. These results may be broken down as follows: (G4, G5, and G6).

The flow numbers in Table 4 illustrate that the mixtures do not meet the requirements. The flow was observed at 3.3 millimeters when G0 was evaluated. The flow rate was reduced to 2.9 mm while using the G4 blend; nevertheless, this was still an improvement over the flow rate of 0 mm that was achieved with the previous blend. This was because the minimum value of the scale had been lowered by 2% in order to account for this change. (2 mm). This amount caused a 12.1% decrease in flow when compared to the mix that was used as the baseline. (G0). Both the G5 and the G6 mixes had a flow rate that exceeded the allowable 4 millimeters.

Wheel Loading Tracking Test Results

Table 4 shows that none of the mixes met the standard for flow and stiffness, so only G0, G2, and G4 were selected for performance evaluation tests. Furthermore, G2 was the top refracted mixture up of the lower permitted limits for mixtures gradations that obey the standard requirements, while G4 was the highest diffracted mixture below it (wheel load tracking and indirect tensile test). Easily distinguishing the gradation lines in comparison to the G0 control mixture is seen in Figure 1.

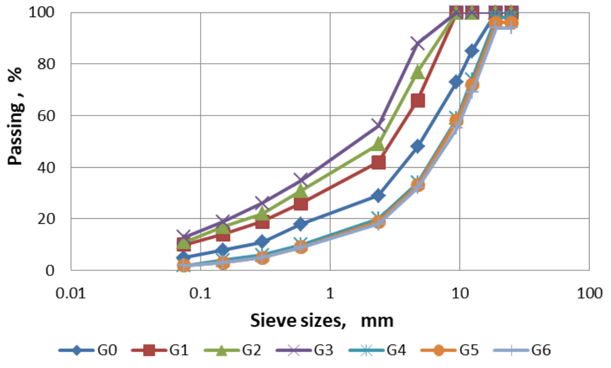

Figure 1 – Gradation lines of the mixes

Figure 2 shows the rutting depth test results for the 3 mixtures: G0 (Control), G2 (the best mixture, which is +4% over the higher specification limit), and G4 (the best mix, which is -2% below the lower specification limit). Figure 2 shows that the rutting value for the G0 mix is 3.92 mm, 4.85 mm for the G2 mix, and 4.34 mm for the G4 mix. The G2 increased its rutting depth by 18% over the G0 and 9.5% over the G4. This means that compared to mix G2, mix G4 showed a greater rutting resistance. It is related to an 11.1% improvement in stability and a 30% decrease in flow for G4 when compared to G2.

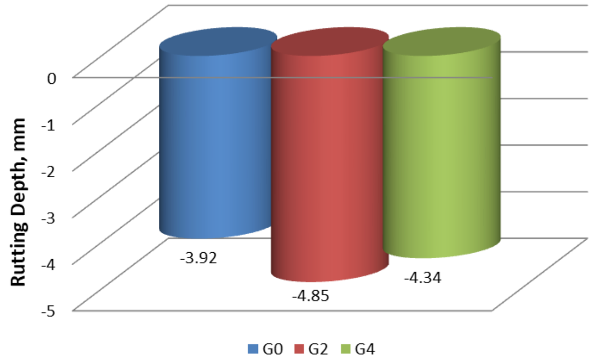

Figure 2 - Rutting Depth Results

Tensile Strength Test Results (Indirect)

TSR results for three different permutations are shown in Figure. 3. According to the same source, Mix G2 achieved a remarkable TSR of 81.62%, whereas the TSR of the G0 control Mixture was 83.87%. When compared to the G0 control mix, this indicates a decrease in TSR of 2.7%. Figure 3 also reveals that G4 had a TSR of 82.84%, which is somewhat higher than G2's 82.65%. The most important takeaway from this study is that G4 is more resistant to moisture-induced damage when compared to G2 in a combination.

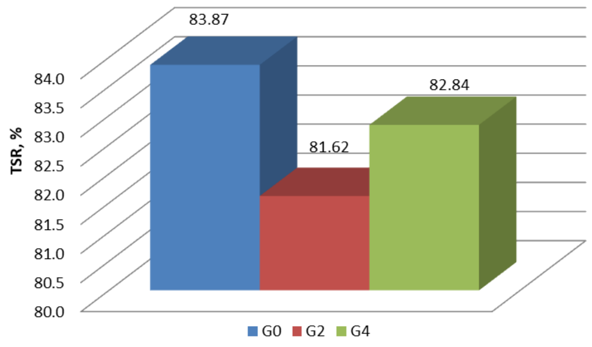

Figure 3 - TSR Outcomes

According to the results G2 and G4 mixes were more moisture resistant than the Control Asphalt Mixture. The fineness of its stone matrix increased cohesiveness between the matrix and the low asphalt component, which was harmed by the water path's high temperature. The asphalt mixes' anti-shear strength, rutting, and tensile strength rose as asphalt mastic and aggregate adhesion increased. Based on this debate, the mix at 2% below the lower gradation limit performed better against moisture-induced damage than the one at +4% above.

The results showed that compared to the Control Mixture G0, G2, and G4 had improved resistance to moisture damage. The fineness of aggregate fractions may have increased the cohesiveness between the matrix and the low asphalt component, making it more susceptible to the negative effects of the hotter water in the water route. Thus, the tensile strength of asphalt mixes improved, and the anti-shear strength and rutting of asphalt mixes were enhanced by the increased adhesive force between asphalt mastic and aggregate.

Conclusions

This research proposed a unique aggregate gradation variation of 2%, 4%, and 6% from aggregate specification limitations. After laboratory preparation and testing, wheel loading tracking, Marshall method test, and (ITS) Indirect Tensile Strength test was used to measure HMA characteristics at high-temperature performances, various asphalt blends, and their resistance to water. This is what the data seems to indicate.

G2 and G4 considerably improve asphalt mix performance. G2 mix improves water stability but not rutting resistance. G4 mixture boosts strong performance at high temperatures and resistance to water damage. G4 outperformed G2 in rutting resistance. G4 was more moisture-resistant than G2. Overall, mix G4 improves pavement service life and ride quality more than mix G2.

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

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Толтырғыш градациясының асфальтбетон қасиеттеріне әсері

[1]Коспармакова С.А., [1]Шашпан Ж.А., [2]Guler M.

[1] Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Астана, Қазақстан
[2] Таяу-Шығыс Техникалық университеті, Анкара, Түркия

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ТҮЙІНДЕМЕ

Ұлттық жол құрылысы жобалары экономикалық өсуді ынталандыратын ұлттық табысқа әсер етеді. Осылайша, шешім қабылдаушылар бұл жобаларды тез құруы үшін жоғары сапалы асфальт қажеттігін ескерді. Соңғы он жылдықтардағы басты мәселе – көптеген асфальт-бетон қоспалары қайта өңделіп, шикізаттың, шығындардың және уақыттың жоғалуына әкелетін толтырғыш градациясының айырмашылығына байланысты деген шешімге тірелді. Бұл зерттеуде агрегаттың градациясы талаптың жоғарғы шегінен +4% - дан спецификацияның төменгі шегі -2% - ға дейін өзгеретін асфальт қоспаларының жарамдылығы қарастырылады. Ыстық асфальт қоспасын (ЫАҚ) өндіруде толтырғыштың градациясы спецификациядан асып түседі. Толтырғыштардың градациясы белгіленген шектерден 2%, 4% және 6% жоғары және төмен алынатын болады. Бақылау жағдайы: бақылау қоспасының гранулометриялық құрамы. Marshall Mix жобасы бойынша жасалып қоспаның қасиеттері өлшенеді. Жоғары температура мен су циклдері кезінде ЫАҚ-ның өнімділігін бағалау үшін доңғалақ жүктемесін бақылау және жанама созылу беріктігін сынау (ITS) қолданылды. Спецификацияның жоғарғы және төменгі шегінің +4%-дан -2%-ға дейінгі градациясы бар қоспалар стандартты асфальт қоспаларымен салыстырғанда, ең аз дөңгелек ізінің тереңдігіне және ыстық жерлерде судың әсерінен бұзылуына барынша төзімділікке ие болды.Толтырғыш градациясының жоғарылауы ыстық климатта асфальтбетон қоспаларын жобалау кезінде нұсқаулық болады.

Түйін сөздер: асфальтобетон, тас градациясы, маршалл тест, дөңгелек ізі, ылғалға төзімділік.

	Авторлар туралы ақпарат:
Коспармакова Самал Ахметалыевна	*PhD докторанты, «Өнеркәсіптік және азаматтық құрылыс технологиясы» кафедрасы, Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Астана, Қазақстан. Email: smartsam0509@gmail.com*
Шашпан Жоламан Амангелдиевич	*Т.ғ.д, «Өнеркәсіптік және азаматтық құрылыс технологиясы» кафедрасының профессорі, Л.Н. Гумилев атындағы ЕҰУ, Астана, Қазақстан. Email: zholamanalmatykz@gmail.com*
Murat Guler	*Т.ғ.д., профессор Таяу-Шығыс Техникалық университеті, Анкара, Түркия* *E-mail: gmurat@metu.edu.tr*

Влияние градации заполнителя на свойства асфальтобетона

[1]Коспармакова С.А., [1]Шашпан Ж.А., [2]Guler M.

[1] Евразийский национальный университет им. Л.Н. Гумилева, Астана, Казахстан
[2] Ближневосточный Технический университет, Анкара, Турция

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АННОТАЦИЯ

Проекты строительства национальных дорог влияют на национальный доход, что стимулирует экономический рост. Таким образом, лица, принимающие решения, намерены строить эти проекты быстро. Для этого требуется высококачественный асфальт. Основной проблемой последних десятилетий является то, что многие асфальтобетонные смеси отбраковываются и переделываются на месте из-за разницы в градации заполнителя, что приводит к потере сырья, затрат и времени. Таким образом, в данном исследовании рассматривается приемлемость асфальтовых смесей с изменением градации заполнителя от +4% выше верхнего предела спецификации до -2% ниже нижнего предела спецификации. При производстве горячей асфальтовой смеси (ГАС) градация заполнителя выходит за рамки спецификации. Градации заполнителей на 2%, 4% и 6% выше и ниже установленных пределов. Контрольный случай: гранулометрический состав контрольной смеси. Измеренные качества смеси по проекту Marshall Mix. Для оценки характеристик смеси HMA при высоких температурах и водных циклах использовались мониторинг нагрузки на колеса и испытания на непрямую прочность при растяжении (ITS). Смеси с градацией от +4% до -2% от верхнего и нижнего пределов спецификации имели наименьшую глубину колейности и максимальную устойчивость к разрушению водой в горячих местах по сравнению со стандартными асфальтобетонными смесями. Повышенные ограничения по градации заполнителя будут служить руководством при проектировании асфальтобетонных смесей в жарком климате.

Ключевые слова: асфальтобетон, градация заполнителя, испытание Маршалла, колейность, водонепроницаемость.

Информация об авторах:

Коспармакова Самал Ахметалыевна — *Докторант PhD, Кафедра «Технология промышленного и гражданского строительства», ЕНУ им. Л.Н.Гумилева, Астана, Казахстан. Email: smartsam0509@gmail.com*

Шашпан Жоламан Амангелдиевич — *Д.т.н, профессор кафедры «Технология промышленного и граждакнского строительства», ЕНУ им. Л.Н.Гумилева, Астана, Казахстан. Email: zholamanalmatykz@gmail.com*

Murat Guler — *Д.т.н, профессор Ближневосточного технического университета, Анкара, Турция. E-mail: gmurat@metu.edu.tr*

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Engineering and Technology

Stability study of emulsions based on modified xanthan gum

[1*]Kusherova P.T., [1]Yerzhanov Y.B., [1]Tleugalieva Z.A., [2]Khaldun M. Al Azzam,
[3]Aidarova S. B., [4]Mohammad Azmi Bustam

[1]School of Chemical Engineering, Kazakh-British Technical University, Almaty, Kazakhstan
[2]Pharmacological and Diagnostic Research Centre (PDRC), Faculty of Pharmacy, Al-Ahliyya Amman University, Amman 19328, Jordan
[3]School of Materials Science and Green Technologies, Kazakh-British Technical University, Almaty, Kazakhstan
[4]CO2 Research Centre (CO2RES), Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia

** Corresponding author email: partykush@mail.ru*

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ABSTRACT
Modified xanthan gum is often used in a variety of industries such as pharmaceuticals, the food industry, and the oil industry. The use of modified xanthan gum in emulsions can solve two problems, stabilize and thicken. This work is dedicated to the study of oil-in-water emulsion stability. The continuous phase of the emulsion consists of aqueous solutions of modified xanthan gum (XG-g-MMA), alkyl polyglycoside (APG), and silicon dioxide nanoparticles (SiO_2), and kerosene was used as a dispersed phase. Modified XG was prepared by grafting with methyl methacrylate to improve its properties. To determine the stability, the stratification time was monitored, and rheological properties and droplet sizes of emulsions were determined. The results showed that the emulsions based on XG-g-MMA and APG have better properties than the emulsions based on XG and sodium lauryl ethoxy-sulphate (SLES). Emulsions with 0.3% XG-g-MMA, 5% APG and 0.2% SiO2 demonstrated stability for up to 2 years, whereas emulsions with 0.3% XG stay stable for up to 1 year.

Keywords: emulsion stability, modified xanthan gum, grafted polymer.

	Information about authors:
Kusherova Parassat Tulegenovna	*Ph.D. student at the School of Chemical Engineering, Kazakh-British Technical University, Almaty, Kazakhstan. Email: partykush@mail.ru*
Yerzhanov Yerbolat Bakytzhanovich	*Bachelor's student at Kazakh-British Technical University, Almaty, Kazakhstan. Email: yeroha777@gmail.com*
Tleugalieva Zhanetta Ashatovna	*Bachelor's student at the School of Chemical Engineering, Kazakh-British Technical University, Almaty, Kazakhstan. E-mail: tleugalievazhanetta@gmail.com*
Khaldun M. Al Azzam	*Pharmacological and Diagnostic Research Centre (PDRC), Faculty of Pharmacy, Al-Ahliyya Amman University, Amman 19328, Jordan. E-mail: azzamkha@yahoo.com*
Aidarova Saule Bailyarovna	*Professor, Doctor of chemical sciences. School of Materials Science and Green Technologies, Kazakh-British Technical University, Almaty, Kazakhstan.*
Mohammad Azmi Bustam	*CO2 Research Centre (CO2RES), Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak, Malaysia. E-mail: azmibustam@utp.edu.my*

Introduction

Many building materials, paints, lubricants, etc. are being emulsions. In the cosmetic industry, all creams and lotions are W/O, O/W and W/O/W emulsions, which makes it possible to select creams depending on skin type. There are new medical preparations based on emulsions with functional, useful components [[1], [2]].

However, emulsions are thermodynamically unstable systems, undergo coalescence, gravitational separation, flocculation, form water and oil phases, so a stabilizers are required for their long-term stability. Basically, synthetic surfactants are used to stabilize emulsions, but synthetic surfactants are considered aggressive and limit the scope of use of emulsions. In this regard, biological surfactants are proposed which are safe and biodegredable. An example of biosurfactant is alkyl polyglycoside (APG). APG is a nonionic biosurfactant, which is a derivative of glucose and fatty acids [3]. The raw materials for obtaining these surfactants are starch, glucose and fatty alcohols. These products are derived from corn and other grains, therefore considered renewable. The final product of the reaction using acid catalysts is a mixture of compounds containing a hydrophilic sucrose part and a hydrophobic alkyl part [[4], [5]]. APG is used as a foaming agent in detergents, replaces surfactants such as lauryl sulfate, lauryl ethoxysulfate, and has a milder effect on the skin [6]. Biopolymers are often used as stabilizers which are less toxic and biodegradable [[7], [8], [9]]. One of the biopolymers, xanthan gum, is an extracellular polysaccharide of the bacterium Xanthomonas Campestris [10]. Xanthan is widely used in medicine, cooking, construction and other areas, but there are many works proving the great effectiveness of Modified xanthan [[11], [12], [13], [14], [15], [16], [17], [18],]19]]. After modification xanthan gum demonstrates better properties as viscosity, solubility and stability [[20], [21], [22], [23]].

In this work modified xanthan was used to improve the stability of the emulsion. The ratios of the ingredients are shown in Table 1.

Experimental part

Materials

Biopolymer Xanthan gum (XG) as a powder (Sigma-Aldrich Chemical Co., USA), alkylpolyglucoside (APG) as a 50% solution (Spec Chem Industry Inc., China), sodium lauryl ethoxysulfate (SLES) – 70% solution (OMED, China), silicon dioxide nanoparticles (40 nm) as a 40% solution (Sigma-Aldrich Chemical Co., USA) and kerosene (Kloriant, Kazakhstan) were used. Modified xanthan gum was produced in a laboratory.

Emulsion preparation

Aqueous sol solution surfactant, polymer, and silicon dioxide were mixed and distilled water was added till the required volume. The solution was placed on a magnetic stirrer and kerosene was added while stirring. After adding kerosene, the solution was stirred for 15 minutes at a speed of 700 rpm. Prepared emulsion immediately was poured into a measuring cylinder and observed for phase separation over time. Thus, emulsions were prepared with different ratios of components to determine the best concentration of each of the components.

Measurements

The stability of the emulsions was determined by visual observation, the time of the kerosene phase appearance (the formation of a layer of kerosene on the surface of the emulsion) was noted over time. To determine the effect of salinity on stability, sodium chloride solution was added to the emulsion. The content of sodium chloride in the emulsions was 5, 15, and 30 g/L.

The samples that showed the highest stability were analyzed on a Bohlin rheometer, Rheolab QC to study the rheological properties. Rheological tests (viscosity and shear stress versus shear rate) were carried out at 30, 60, and 80°C.

The sizes of the dispersed phase droplets were measured on a scanning electron microscope Auriga Crossbeam 540 Carl Zeiss. To obtain images before analysis, the samples were applied to a film and dried at room temperature. In this way, photographs of capsules of volatilized kerosene were obtained.

Table 1 - Content of emulsions

Sample №	XG, %	XG-g-MMA, %	SiO_2, %	APG, %	SDS, %	Distilled water, ml	Kerosene, ml	Salinity, g/l
1	0.1		**2**	5		7	3	
2	0.1		**1**	5		7	3	
3	**0.1**		**0.2**	5		7	3	
4	0.1		**0.1**	5		7	3	
5	0.1		**0**	5		7	3	
6	0.2		**2**	5		7	3	
7	0.2		**1**	5		7	3	
8	**0.2**		**0.2**	5		7	3	
9	0.2		**0.1**	5		7	3	
10	0.2		**0**	5		7	3	
11	**0.3**		0.2	5		7	3	
12	0.2		0.2	**2**		7	3	
13	0.2		0.2	**3**		7	3	
14	0.2		0.2		**3**	7	3	
15	0.2		0.2		**5**	7	3	
16		**0.2**	0.2	5		7	3	
17		**0.3**	0.2	5		**7**	**3**	
18		0.3	0.2	5		**9**	**1**	
19		0.3	0.2	5		**6**	**4**	
20		0.3	0.2	5		7	3	**5**
21		0.3	0.2	5		7	3	**15**
22		0.3	0.2	5		7	3	**30**

Results and discussions

Emulsion stability

Observations have shown that the stability of the emulsion depends on the amount of each component. Emulsions prepared with 5% APG were more stable than with SLES (the same ratio). Also, emulsions with 0.3% XG-g-MMA stayed stable for more than 2 years, while emulsions with XG with the same amount stayed stable for about 1 year. However, with an increase in the polymer content, the emulsion became a gel-like state. The nanoparticles showed stabilizing effect at a concentration of 0.2%.

Also, the statement proved that with an increase in the ratio of the oil phase, the stability of an emulsion increases, so with the increase of the kerosene volume increased the stability of the emulsion. Salinity stability testing showed that emulsions with XG-g-MMA stay stable at salinities up to 30 g/l, while XG emulsions break down already at 5 g/l salinity. The visual observations are shown in Table 2.

Table 2 - Results of emulsion stability by visual control

Sample №	Stability
1	Not stable
2	Not stable
3	Not stable
4	Not stable
5	Not stable
6	Not stable
7	Not stable
8	Stable for 1 month
9	Not stable
10	Not stable
11	Stable for over 1 year
12	Not stable
13	Not stable
14	Not stable
15	Not stable
16	Not stable
17	Stable for over 2 years
18	Not stable
19	Stable for over 2 year
20	Stable for over 1 year
21	Stable for over 1 year
22	Stable for over 1 year

Rheology properties

To determine the rheological properties, the most stable emulsions with the composition XG(0.3)-APG(5)-SiO2(0.2) and XG-g-MMA(0.3)-APG(5)-SiO_2(0.2) were chosen. The results of viscosity and shear stress measuring showed that at 30°C with a change of shear rate from 1 to 100 s^{-1}, the shear stress of the XG-g-MMA(0.3)-APG(5)-SiO_2(0.2) emulsion reaches 16 Pa, XG(0.3)-APG(5)-SiO_2(0.2) reaches 9 Pa. And the viscosities of XG-g-MMA(0.3)-APG(5)-SiO_2(0.2) and XG(0.3)-APG(5)-SiO_2(0.2) decrease to 0.16 Pa·s and 0.09 Pa·s respectively.

The rheology performance decreases with the rise of temperature, which can be seen in Diagrams 1, 2, and 3. At 60°C the shear stress of the XG-g-MMA(0.3)-APG(5)-SiO_2(0.2) emulsion reaches 12.5 Pa, XG(0.3)-APG(5)-SiO_2(0.2) reaches 7 Pa. The viscosity of both emulsions changes slightly, showing 0.13 Pa s and 0.07 Pa·s. At 80 ºC the maximum values drop to 9.5 Pa for XG-g-MMA(0.3)-APG(5)-SiO_2(0.2) and to 4.7 Pa for XG(0.3)-APG(5)-SiO_2(0.2).

Thus, it can be noted that emulsions with XG-g-MMA(0.3)-APG(5)-SiO_2(0.2) showed better results compared to XG(0.3)-APG(5)-SiO_2(0.2).

Emulsions prepared using modified xanthan have demonstrated resistance to salinity. With the addition of salt up to 30 g/l the rheological parameters of the XG-g-MMA(0.3)-APG(5)-SiO_2(0.2) emulsions did not differ much (Diagram 4), showing 14-16 Pa.

Drop sizes

SEM images showed that the kerosene capsules emulsified with XG had diameters ranging from 2 to 45 µm, with an average diameter of ~20 µm (Figure 1). Kerosene capsules emulsified with XG-g-MMA had diameters ranging from 2 to 20 µm, with an average diameter of ~10 µm (Figure 2). Thus, it can be understood that the stability of the emulsion with XG-g-MMA is due to the uniform formation of smaller capsules compared to the emulsion with XG.

Traces of nanoparticles can be seen on the walls of the capsules which also have a stabilizing effect, forming a layer at the oil-water interface (Figure 3).

Diagram 1 - Rheological properties at 30ºC

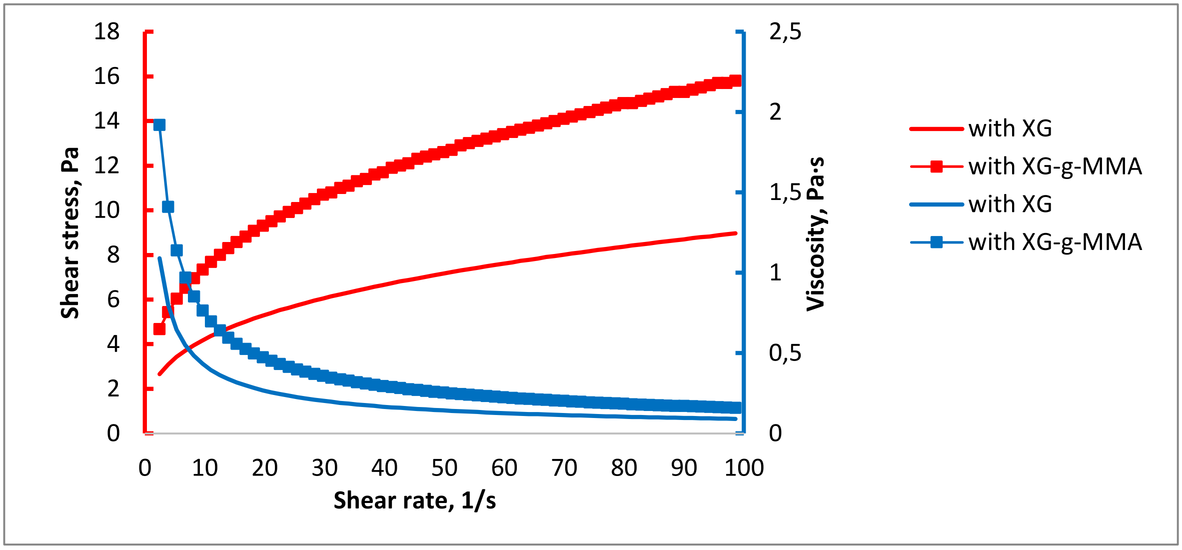


Diagram 2 - Rheological properties at 60ºC

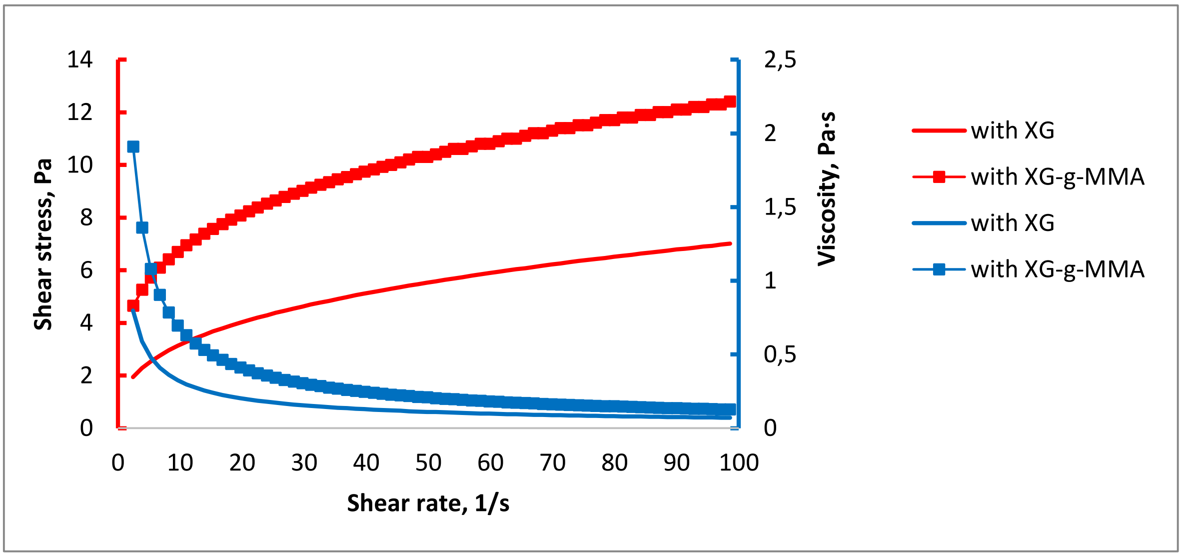


Diagram 3 - Rheological properties at 80ºC

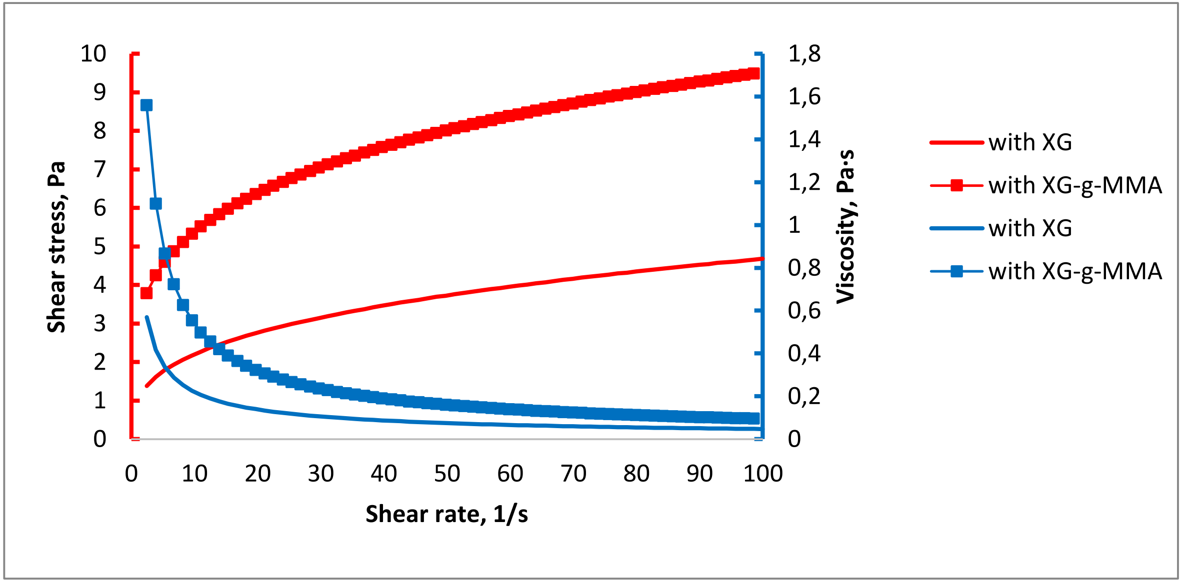
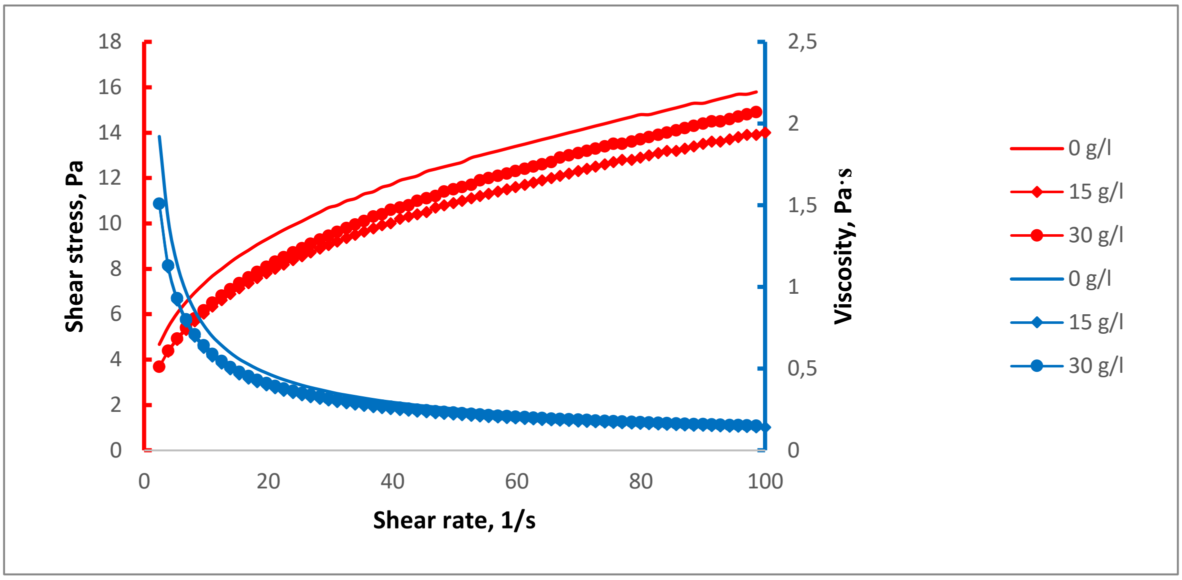


Diagram 4 - The dependence of rheology of emulsions on salinity at 30ºC



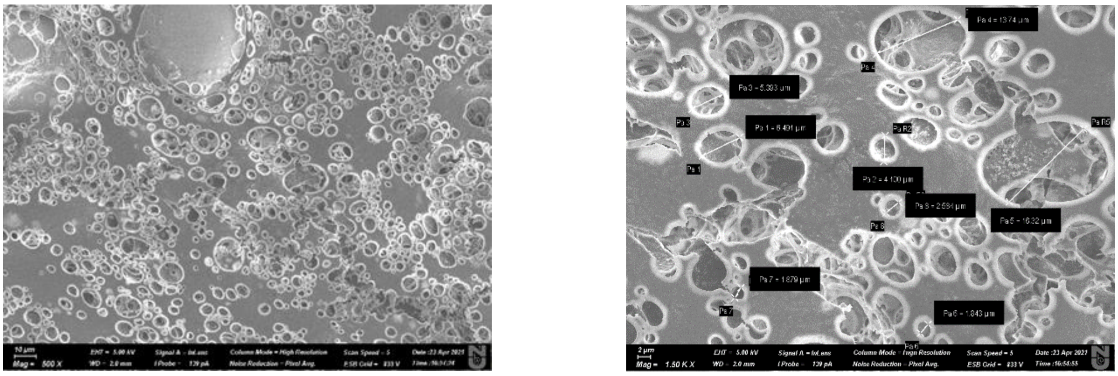


Figure 1 - Capsules of kerosene in emulsion XG(0.3)-APG(5)-SiO_2(0.2)

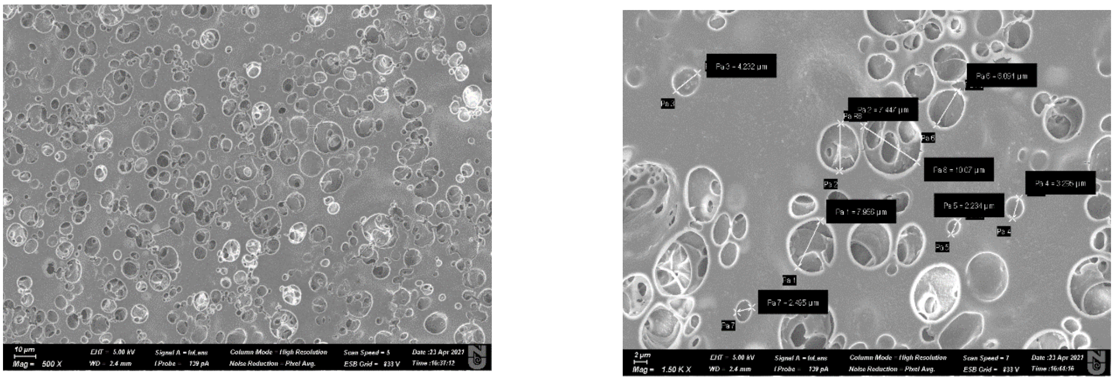


Figure 2 - Capsules of kerosene in emulsion XG-g-MMA(0.3)-APG(5)-SiO_2(0.2)

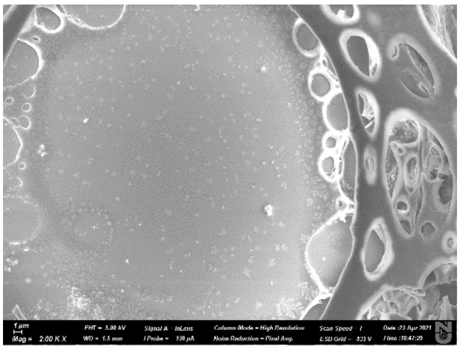


Figure 3 - Nanoparticles of SiO_2 at oil/water interface

Conclusions

The results of the stability study showed that the emulsion prepared with the addition of modified xanthan gum (XG-g-MMA(0.3)-APG(5)-SiO_2(0.2)) remains stable for more than 2 years, while the emulsion with the addition of unmodified xanthan gum (XG(0.3)-APG(5)-SiO_2(0.2)) remains stable for more than 1 year. When the alkylpolyglycoside is replaced with sodium ethoxysulfate, the stability drops markedly.

According to the results of the study of rheological properties, it was found that the emulsion with the addition of XG-g-MMA has a shear stress value of 16 Pa at 30ºC, 12.5 Pa at 60ºC and 9.5 Pa at 80ºC, while the emulsion with the addition of XG reaches 1.8 times less value - 9 Pa at 30ºC, 7 Pa at 60ºC and 4.7 Pa at 80ºC. Also, the emulsion with the addition of modified xanthan gum shows resistance to salinity up to 30 g/l, while the emulsion with the addition of xanthan gum breaks down at a salinity of 5 g/l.

Thus, the use of an emulsion with modified xanthan gum XG-g-MMA(0.3)-APG(5)-SiO_2(0.2) can become one of the effective methods used in enhanced oil recovery or other industries.

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

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Модификацияланған ксантан шайыры негізіндегі эмульсиялардың тұрақтылығын зерттеу

[1*]Кушерова П.Т., [1]Ержанов Е.Б., [1]Тлеугалиева Ж.А., [2]Khaldun M. Al Azzam,
[3]Айдарова С.Б., [4]Mohammad Azmi Bustam

[1]Химиялық инженерия мектебі, Қазақ-Британ техникалық университеті, Алматы, Қазақстан
[2]Фармакологиялық және диагностикалық зерттеу орталығы (PDRC), Аль-Ахлия Амман университеті, Амман, 19328, Иордания
[3]Материалтану және жасыл технологиялар мектебі, Қазақ-Британ техникалық университеті, Алматы, Қазақстан
[4]CO2 зерттеу орталығы (CO2RES), PETRONAS технологиялық университеті, 32610 Bandar Seri Iskandar, Перак, Малайзия

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ТҮЙІНДЕМЕ

Модификацияланған ксантан шайыры фармацевтика, тамақ және мұнай өнеркәсібі сияқты әртүрлі салаларда жиі қолданылады. Модификацияланған ксантан шайырын эмульсияларда қолдану, тұрақтандыру және қоюландыру сияқты екі мәселені шешуі мүмкін. Бұл жұмыс мұнайдың судағы эмульсиясының тұрақтылығын зерттеуге арналған. Эмульсияның үздіксіз фазасы модификацияланған ксантан шайырының (XG-g-MMA), алкилполигликозидтің (APG) және кремний диоксиді нанобөлшектерінің (SiO_2) сулы ерітінділерінен тұрады, ал дисперсті фаза ретінде керосин қолданылған. Модификацияланған XG, оның қасиеттерін жақсарту үшін метилметакрилатты егу арқылы алынды. Тұрақтылықты анықтау үшін қатпарлану уақыты бақыланды, эмульсия тамшыларының реологиялық қасиеттері мен өлшемдері анықталды. Нәтижелер XG-g-MMA және APG негізіндегі эмульсиялардың XG және натрий лаурил этоксисульфаты (SLES) негізіндегі эмульсияларға қарағанда жақсы қасиеттерге ие болатынын көрсетті. Құрамындағы 0,3% XG-g-MMA, 5% APG және 0,2% SiO2 бар эмульсия 2 жылға дейін тұрақты болатынын көрсетті, ал құрамындағы 0,3% XG бар эмульсиялар тек 1 жылға дейін тұрақты болып қалды.

Түйін сөздер: эмульсия тұрақтылығы, модификацияланған ксантан сағызы, егілген полимер.

	Авторлар туралы ақпарат:
Кушерова Парасат Тулегеновна	*Докторант, Химиялық инженерия мектебі, Қазақ-Британ техникалық университеті, Алматы, Қазақстан. Email: partykush@mail.ru*
Ержанов Ерболат Бакытжанович	*Студент-бакалавр, Химиялық инженерия мектебі, Қазақ-Британ техникалық университеті, Алматы, Қазақстан. Email: yeroha777@gmail.com*
Тлеугалиева Жанетта Асхатовна	*Студент-бакалавр, Химиялық инженерия мектебі, Қазақ-Британ техникалық университеті, Алматы, Қазақстан. E-mail: tleugalievazhanetta@gmail.com*

Халдун М. Аль Аззам	*Фармакологиялық және диагностикалық зерттеу орталығы (PDRC), Аль-Ахлия Амман университеті, Амман, 19328, Иордания. E-mail: azzamkha@yahoo.com*
Айдарова Сауле Байляровна	*Докторант, Материалтану және жасыл технологиялар мектебі, Қазақ-Британ техникалық университеті, Алматы, Қазақстан*
Мохамад Азми Бустам	*CO2 зерттеу орталығы (CO2RES), Universiti Technology PETRONAS, 32610 Bandar Seri Iskandar, Перак, Малайзия. E-mail: azmibustam@utp.edu.my*

Исследование стабильности эмульсий на основе модифицированной ксантановой камеди

[1*]Кушерова П.Т., [1]Ержанов Е.Б., [1]Тлеугалиева Ж.А., [2]Khaldun M. Al Azzam,
[3]Айдарова С.Б., [4]Mohammad Azmi Bustam

[1]Инженерно-химический факультет Казахстанско-Британского технического университета, Алматы, Казахстан
[2]Центр фармакологических и диагностических исследований (PDRC), фармацевтический факультет,
Амманский университет Аль-Ахлия, Амман 19328, Иордания
[3]Школа материаловедения и зеленых технологий Казахстанско-Британского технического университета,
Алматы, Казахстан
[4]Исследовательский центр 4CO2 (CO2RES), Технологический университет PETRONAS,
32610 Бандар-Сери-Искандар, Перак, Малайзия

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АННОТАЦИЯ

Модифицированная ксантановая камедь часто используется в различных отраслях промышленности, таких как фармацевтика, пищевая промышленность и нефтяная промышленность. Использование модифицированной ксантановой камеди в эмульсиях может решить две проблемы: стабилизировать и загустить. Данная работа посвящена исследованию стабильности эмульсии нефти-в-воде. Непрерывная фаза эмульсии состоит из водных растворов модифицированной ксантановой камеди (XG-g-MMA), алкилполигликозида (APG) и наночастиц диоксида кремния (SiO_2), а в качестве дисперсной фазы использован керосин. Модифицированная XG была получена путем прививки метилметакрилата для улучшения его свойств. Для определения стабильности контролировали время расслоения, определяли реологические свойства и размеры капель эмульсий. Результаты показали, что эмульсии на основе XG-g-MMA и APG обладают лучшими свойствами, чем эмульсии на основе XG и лаурилэтоксисульфата натрия (SLES). Эмульсия с 0,3 % XG-g-MMA, 5 % APG и 0,2 % SiO2 показала стабильность до 2 лет, тогда как эмульсии с 0,3 % XG остаются стабильными до 1 года.

Ключевые слова: стабильность эмульсии, модифицированная ксантановая камедь, привитый полимер.

Information about authors:

Кушерова Парасат Тулегеновна	*Докторант, Школа Химической инженерии, Казахстанско-Британский технический университет, Алматы, Казахстан. Email: partykush@mail.ru*
Ержанов Ерболат Бакытжанович	*Студент-бакалавр, Школа Химической инженерии, Казахстанско-Британский технический университет, Алматы, Казахстан. Email: yeroha777@gmail.com*
Тлеугалиева Жанетта Асхатовна	*Студент-бакалавр, Школа Химической инженерии, Казахстанско-Британский технический университет, Алматы, Казахстан. E-mail: tleugalievazhanetta@gmail.com*
Халдун М. Аль Аззам	*Центр фармакологических и диагностических исследований (PDRC), фармацевтический факультет Амманского университета Аль-Ахлия, Амман 19328, Иордания E-mail: azzamkha@yahoo.com*
Айдарова Сауле Байляровна	*Докторант, Школа Химической инженерии, Казахстанско-Британский технический университет, Алматы, Казахстан.*
Мохамад Азми Бустам	*Исследовательский центр CO2 (CO2RES), Технологический университет PETRONAS, 32610 Бандар-Сери-Искандар, Перак, Малайзия. E-mail: azmibustam@utp.edu.my*

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Metallurgy

Improving the quality of converting products by the joint smelting of high-sulfur copper concentrate with copper-lead matte

Argyn A.A., *Zoldasbay E.E., Dosmukhamedov N.K.

Satbayev University, Almaty, Kazakhstan

** Corresponding author email: zhte@mail.ru*

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ABSTRACT

The paper presents the results of studies on the processing of copper-lead mattes with high-sulfur copper concentrate in a converter. The effect of high-sulfur copper concentrate on the quality of converting products is shown. Based on the obtained results, a comparative analysis of the technological indicators of the 1st period of converting copper-lead mattes according to the existing technology and in the joint processing of copper-lead mattes with copper concentrate was carried out. It has been established that when the high-sulfur copper concentrate is used as a sulfidizing agent, excess sulfur released as a result of the dissociation of higher sulfides is completely absorbed by the slag melt. It is shown that elemental sulfur, interacting with oxides of non-ferrous metals and impurities, has a significant effect on the equilibrium distribution of metals between the converting products and their extraction into targeted products. The influence of sulfur on the destruction of magnetite in the process of converting was also established. New data on the distribution of non-ferrous and associated metal impurities (As, Sb, etc.) were obtained during the conversion of copper-lead mattes with high-sulfur copper concentrate. High values were established for the extraction of non-ferrous metals and impurities into targeted products: copper into matte - up to 98%, lead, zinc, arsenic, and antimony into dust - 87%, 91%, 84%, and 38%, respectively. The possibility of a significant improvement in technical and economic indicators, the quality of converting products, and environmental protection during the joint smelting of high-sulfur copper concentrate with a copper-lead matte are shown. The developed technology for converting copper-lead mattes, with high-sulfur copper concentrate, is easily integrated into the plant structure of Kazzinc LLP without any special material costs.

Keywords: copper-lead matte, sulfide copper concentrate, converting, converter slag, white matte, sulfiding, distribution.

	Information about authors:
Argyn Aidar Abdilmalikuly	*Ph.D., Satbayev University, 050013, Almaty, 22 Satbayev St., Kazakhstan. E-mail: aidarargyn@gmail.com*
Zoldasbay Erzhan Esenbaiuly	*Ph.D., Satbayev University, 050013, Almaty, 22 Satbayev St., Kazakhstan. E-mail: zhte@mail.ru*
Dosmukhamedov Nurlan Kalievich	*Candidate of Technical Sciences, Professor, Satbayev University, 050013, Almaty, 22 Satbayev St., Kazakhstan. E-mail: nurdos@bk.ru*

Introduction

In the scientific literature ,there is a sufficient number of works devoted to the improvement of the converting process, including the solution to the issue of converter slag processing [[1], [2]]. The results of extensive studies on the processing of copper concentrates in converters [[3], [4], [5], [6], [7], [8], [9], [10], [11]] have opened up wide opportunities for using the converter as a smelting unit for solid materials. This especially refers to the first period of converting copper matte, which ultimately leads to a significant reduction in total costs and an increase in the complexity of the use of raw materials. However, their introduction into production remains without due attention. Most plants continue to use well-established standard methods for processing them according to existing schemes.

The existing positive practical experience of direct processing of copper concentrates in converters shows that there are some ways that can be found to improve the quality of the resulting smelting products in the course of the converting technology itself. Moreover, such an approach, in our opinion, seems to be one of the most promising areas for improving the processing of copper-containing raw materials, both from a technological and economic point of view and from an environmental point of view. This is due to the fact that the involvement in the processing of primary raw materials with a complex chemical and mineralogical composition, the technological indicators of existing processes, and the quality of the obtained products of melts undergo significant changes in the direction of deterioration. Regarding the converting process, there is a strong complication of the compositions of converter slags, and a decrease in the quality of the converting products, which indicates the need to find rational methods for converting.

The direct transfer of the experience of foreign plants, both in terms of the design of aggregates and process modes, in relation to sulphide concentrates of Kazakhstan is complicated, due to their polymetallic nature, low copper content, and higher contents of impurities - Pb, As, Sb. Nevertheless, the search and development of technologies for the complex processing of difficult-to-recycle polymetallic copper-zinc, copper-lead-zinc concentrates in converters could be a significant reserve for metallurgical enterprises in terms of additional extraction of Cu, Au, Ag, and related - Zn, Pb, etc. metals into targeted commercial products.

It should be noted that in the known technologies of direct processing of copper concentrates in converters, the main goal was to use the converter exclusively as a smelting unit and obtain an additional amount of copper by smelting the concentrate. Despite the positive results achieved, the developed technologies also had a number of serious drawbacks in terms of loading a finely dispersed concentrate into the converter. In particular, the loading of the concentrate into the converter required careful special preparation (drying, grinding, using a complex loading installation). When loading the concentrate into the converter, it was not possible to ensure a low quantity of dust losses [12]. The method of loading finely dispersed materials into the converter, developed by the authors of [13], seems to be highly effective, which ensures the loading of the material into the converter with a minimum (no more than 0.5% of the weight of the loaded material) of its dust removal as a loss. The solution to the issue of loading finely dispersed material into the converter, which is important for practice, allowed the authors to simplify the technology of direct processing of concentrates in converters and improve the technological parameters of the converting process.

Due to the minimum dust losses, the injection unit developed in [13] was used to load high-sulfur copper concentrate into the converter.

It seems promising to simultaneously use high-sulfur copper concentrate not only as an additional source of copper production but also as a sulfidizing agent, which improves the quality of the resulting converting products. Detailed studies of industrial tests for the processing of copper and copper-zinc high-sulfur concentrates with copper mattes showed the fundamental possibility of improving not only the technological indicators of converting but also a significant increase in the quality of the obtained products [14].

The application of the developed technologies has particular relevance for the conditions of converting copper-lead mattes of Kazzinc LLP, where mattes are characterized by an increased content of harmful metal impurities: up to 25% lead, up to 4% arsenic, and up to 1.0% antimony. As a result of converting such mattes, poor-quality blister copper (96-98% Cu) is obtained. At the same time, recycled converter slags contain up to 35% lead, ~3% copper, and up to 1.5% total arsenic and antimony. Despite these shortcomings and low technological indicators of the process, due to the lack of an alternative method for processing copper-lead mattes, converting remains the main stage in the production of blister copper in the general technological flowsheet of lead production.

The purpose of this work is to study the behavior of non-ferrous and associated metals during the joint processing of high-sulfur copper concentrate with copper-lead matte in converters and to evaluate the effect of the concentrate on improving the quality of converter slag.

Experimental methodology

The solution of the set tasks was carried out on the basis of mathematical models [[15], [16], [17], [18], [19]], which describe with sufficient accuracy the calculation of the equilibrium yield of smelting products and the composition of chemically reacting systems. The methodology for determining the optimal technological parameters for converting copper-lead mattes is based on the analysis of the obtained results and plant practice data. An industrial array was accepted for analysis, including the number of material flows and the composition of the obtained products - mattes, slags, dust, and blister copper, the results of the forms of metals in the converting products, and the thermodynamic analysis of the behavior of non-ferrous and related metals.

The primary analysis of plant practice data was reduced to clarifying the factors influencing the distribution of metals between converting products.

The second stage included the determination of the optimal technological regimes and process parameters (matte composition, blast consumption, quartz consumption, blowing time) that affect the technological parameters of the process.

Technological indicators of converting were established using a specially developed program, which is based on an iterative algorithm for modeling the converting process. The developed program describes with sufficiently high accuracy the existing process of converting copper-lead mattes and makes it possible to predict the optimal parameters and technological modes of the process for the condition of joint melting of matte with high-sulfur copper concentrate.

The total array of data subjected to mathematical processing amounted to 65 observations. The results of metallurgical calculations of the process of converting copper-lead mattes, obtained for the given input parameters of plant practice, showed a good agreement in terms of the quantity and composition of the obtained products, and the distribution of metals between the converting products. This testifies to the high reliability of the research results obtained in the work, as well as the developed program, which establishes, on its basis, the physicochemical processes that occur during the converting of copper-lead mattes with high-sulfur concentrate, and outlines ways to improve the technological parameters of the process.

Results and discussion

As a sulfidizing agent, a high-sulfur copper concentrate of the Zyryanovsky deposit was used, composition %: 24.51 Cu; 2.5 Pb; 3.4 Zn; 28.6 Fe; 0.1 As; 0.2 Sb; 35 S; 3.6 SiO_2. 30% of the weight of the resulting converter slag was taken as the optimal concentrate consumption [20]. The concentrate was loaded 10 min before the converter slag was discharged.

In the process of research, two modes of the process of converting copper-lead mattes were studied: the first is converting according to the existing technology and the second is the converting of copper-lead mattes with high-sulfur copper concentrate.

To evaluate the behavior of Cu, Pb, Zn, As, and Sb during the converting process, the following plant data were analyzed: the temperatures of converter slags at each unloading from the converter, one-time measurements of the melt temperature during each loading of a new portion of the matte and its blowing.

A comparative analysis of technological indicators of 2 converting modes is given in Table 1.

Table 1 - Results of technological indicators of converting copper-lead mattes: 1 – the mode according to the existing technology; 2 - converting copper-lead mattes with high sulfur copper concentrate

1st mode - existing technology

# of discharge	Products	Chemical compositions of products, %								Air, m^3	Flux (SiO_2 85%), t	Blowing time, min
		Cu	Pb	Zn	As	Sb	Fe	S	SiO_2			
Initial products	Initial matte	35.50	26.00	1.42	2.81	0.71	15.15	15.09	-	-	-	-
	Converter slag	3.83	33.5	4.54	2.8	0.95	12.7	-	15.7			
Discharge #1	Matte	49.59	22.94	0.61	3.34	0.97	6.71	13.40	-	6946.66	1.58	60
	Slag	4.07	26.74	2.34	1.04	0.13	26.74		28.36			
	Dust	0.83	56.35	4.22	6.13	0.03	0.98	6.36	1.20			
Discharge #2	Matte	54.37	22.09	0.16	3.61	1.03	3.99	12.74	-	3327.21	0.76	30
	Slag	3.91	23.17	2.72	0.77	0.16	27.10	-	23.70			
	Dust	0.63	48.99	8.58	4.30	0.47	1.52	2.50	1.90			
Discharge #3	Matte	55.71	21.04	0.18	3.70	1.04	3.43	13.11		1390.69	0.45	12
	Slag	4.34	24.59	1.51	0.78	0.16	22.88		25.11			
	Dust	0.41	53.79	3.31	1.76	0.53	0.96	2.23	1.37			
Discharge #4	White matte	56.82	20.46	0.22	3.62	1.05	2.95	13.59		718.41	0.25	10
	Slag	11.94	18.42	1.27	0.77	0.10	23.40		23.64			
	Dust	1.07	25.24	0.02	4.37	0.67	1.52	2.26	0.82			

2nd mode - new technology: converting copper-lead mattes with high-sulfur copper concentrate

# of discharge	Products	Chemical compositions of products, %								Air, m^3	Flux (SiO_2 85%), t	Blowing time, min
		Cu	Pb	Zn	As	Sb	Fe	S	SiO_2			
Initial products	Initial matte	35.50	26.00	1.42	2.81	0.71	15.15	15.09	-	-	-	-
	Converter slag	3.83	33.5	4.54	2.8	0.95	12.7	-	15.7			
	Copper concentrate	24.51	2.5	3.4	0.1	0.2	28.6	35	3.6			
Discharge #1	Matte	52.43	19.23	0.50	2.31	0.78	7.49	14.00		5262.62	1.03	50
	Slag	1.09	1.26	0.21	0.07	0.10	48.13		26.88			
	Dust	0.59	63.02	9.03	5.76	0.70	1.30	5.85	0.46			
Discharge #2	Matte	58.78	15.37	0.30	1.53	0.76	5.28	15.05		2234.16	0.44	25
	Slag	0.58	1.08	0.33	0.06	0.07	47.37		28.07			
	Dust	0.62	55.82	9.69	8.12	0.73	2.90	8.82	1.14			
Discharge #3	Matte	64.86	8.28	0.28	0.74	0.70	5.10	17.33		818.56	0.16	17
	Slag	1.47	0.67	0.35	0.05	0.06	47.16		26.06			
	Dust	1.22	64.71	7.31	6.94	0.87	2.84	8.82	1.01			
Discharge #4	White matte	70.57	4.01	0.22	0.56	0.65	3.54	18.16		879.69	0.17	19
	Slag	0.39	0.15	0.23	0.03	0.04	48.06		27.32			
	Dust	0.79	58.82	10.80	2.80	1.03	3.86	11.31	1.81			

It has been established that under the conditions of the existing practice of converting, there is a large overconsumption of quartz (more than 1.5 times), from its optimal consumption (Table 1). An excess of quartz requires additional heat consumption for its melting and further transfer to slag, which is covered by an increase in blast consumption. This significantly reduces the quality (compositions) of the resulting products (Table 1), which leads to a negative redistribution of non-ferrous and related metals among the conversion products.

An important change in technological parameters is observed in the conditions of converting copper-lead mattes with high-sulfur copper concentrate.

When loading sulfide copper concentrate into the converter, it is necessary to take into account the additional amount of iron introduced with the concentrate in order to make a calculated correction to the flow rate of the loaded quartz flux. On the basis of statistical and information processing and multivariate analysis of the results of studies on the depletion of converter slags with concentrate and industrial data on the composition of the conversion products (matte, slag), an equation was constructed that allows determining the required flux consumption (Gf). Equation depends on the composition of the matte, slag, and consumption of the concentrate loaded into the converter. As a result of mathematical processing, the following equation was obtained:

$$G_f = -2{,}411 - 0{,}2719[Cu] + 0{,}481[Fe] + 0{,}1661[G_c] + 0{,}7453(SiO2) + 0{,}0869(Fe),\ r = 0{,}87 \qquad (1)$$

where:
[Cu], [Fe] – the content of copper, iron in the original matte, % (wt.);
(SiO2), (Fe) – the content of silica, iron in the converter slag, % (wt.);
$[G_c]$ – concentrate consumption, % of matte weight.

From the analysis of equation (1) it follows that the flux consumption is largely correlated with the iron content in the matte and the SiO2 content in the converter slag. Concentrate consumption has a less significant effect on flux consumption.

The total consumption of quartz flux according to the existing technology is 3.04 tons per ton of matte and is 1.6 times higher than its consumption (1.87 tons per ton of matte). When converting mattes with high-sulfur copper concentrate, the total consumption of quartz flux increases slightly from its optimal level - 1.97 tons per ton of matte.

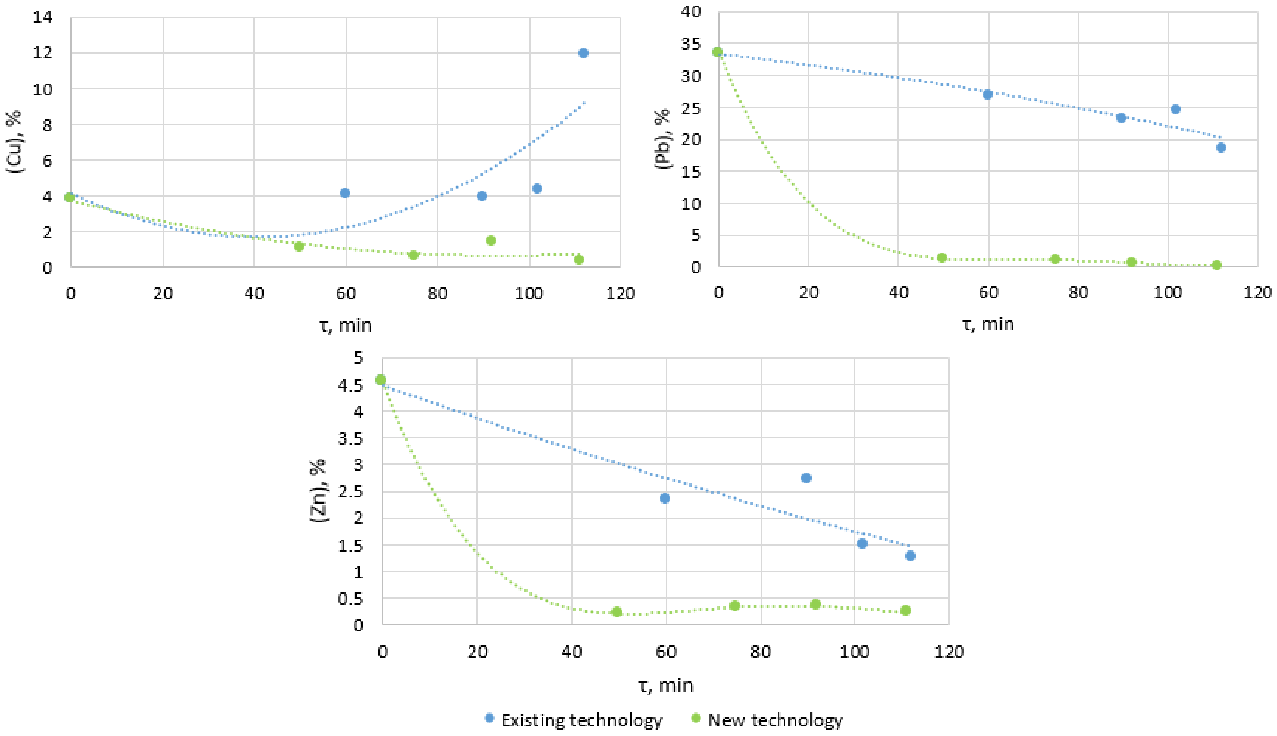


Figure 1 - Dynamics of changes in the content of Cu, Pb, and Zn in the converter slag on the duration of the process

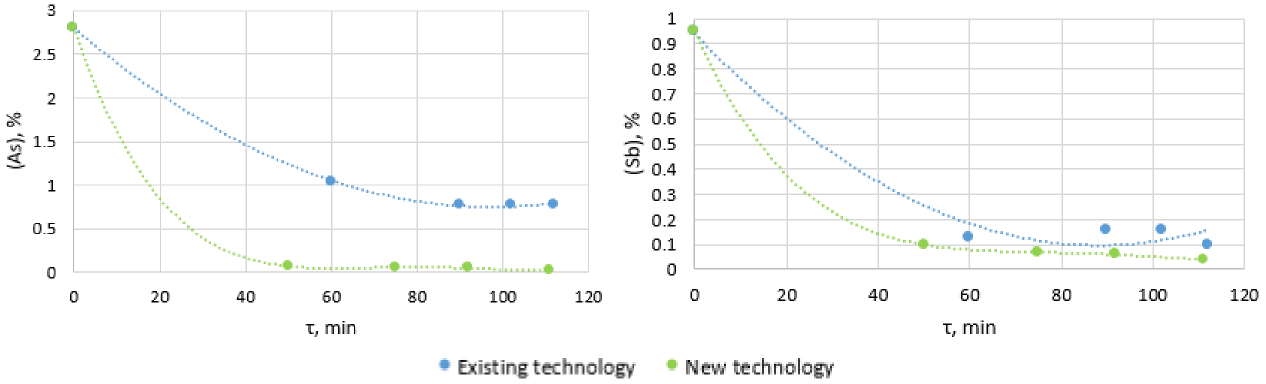


Figure 2 - Dynamics of changes in the content of As and Sb in the converter slag on the duration of the process

The results of a comparative analysis of the dynamics of changes in the content of Cu, Pb, Zn, As, and Sb in converter slags depending on the duration of the process according to the existing technology and during direct smelting of high-sulfur copper concentrate with a matte are shown in Figs. 1 and 2.

For the existing technology, with the exception of copper, the content of impurity metals - Pb, Zn, As, and Sb, in the 1st converting period, depending on the duration of the process, decreases. The increase in copper content seems quite natural. The accumulation of sulfide mass in the converter with an increase in the duration of the 1st period provides for an increase in the copper content in it; therefore, according to the general dependence ***(Cu) – f [Cu]*** established for oxidative processes [21], the copper content in matte will grow.

The observed decrease in the content of Pb, Zn, As and Sb in the converter slag is consistent with the theory of the converting process. In this case, the completeness of their sublimation into dust depends on the consumption of quartz. Figures 1, 2, and Table 1 show that the contents of Cu, Pb, Zn, As, and Sb in converter slags remain quite high. This has a significant impact on the overall throughput of the process and the quality of the blister copper.

During converting copper-lead mattes with high-sulfur copper concentrate, a sharp decrease in metal impurities in converter slags is observed depending on the blowing time: Pb - 6.5 times, Zn - 6 times, As - 7.5 times. For antimony, although a decrease in

Table 2 - Comparative analysis of the compositions of the products of converting copper-lead mattes of the 1st period

Products	**Chemical composition, wt. %**							
	Cu	**Pb**	**Zn**	**Fe**	**As**	**Sb**	**S**	**SiO_2**
White matte	56.39 70.55	20.98 4.03	0.20 0.22	3.54 2.91	3.59 0.56	1.04 0.65	13.55 18.16	-
Converter slag	7.94 1.19	22.25 0.72	2.07 0.23	24.71 47.85	2.40 0.27	0.61 0.2	-	22.28 26.8
Converter dust	1.13 0.81	55.73 58.89	0.85 8.7	2.62 0.36	5.25 5.33	0.80 1.34	5.92 9.98	1.11 0.32

The numerator is existing technology. **The denominator** is a new technology.

slags is observed (~ 2 times), it is not significant, which is associated with the complex form of its presence in slags. The copper content in converter slags decreases by about 3 times, which is explained by a sharp decrease in the magnetite content in slags. As shown by the results of mineralogical studies of converter slag samples, the magnetite content in them is reduced from 18% according to the existing technology to ~3%.

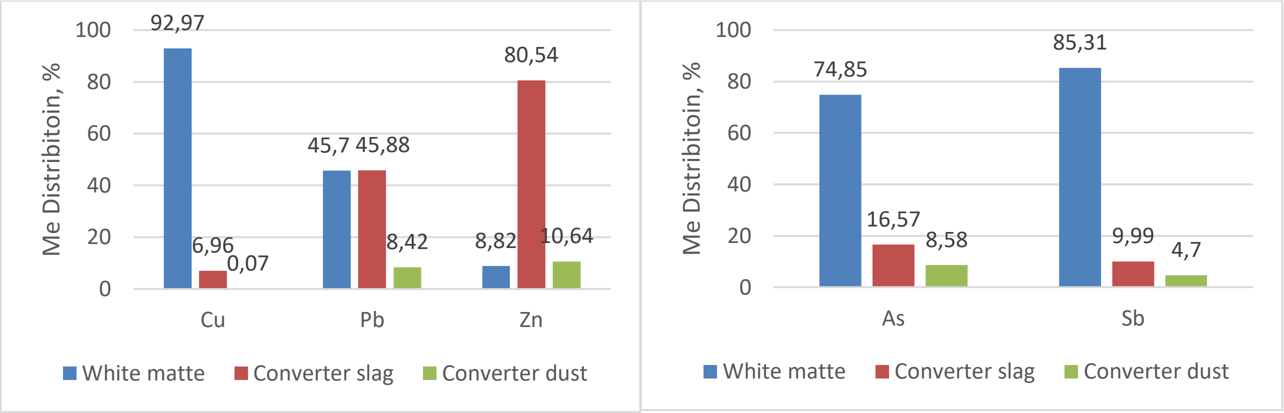
The obtained results fully confirm the conclusions made on the basis of thermodynamic calculations [20] that under the conditions of matte converting, together with copper concentrate, a sufficiently deep "washing" of the slag melt with drops of copper concentrate sulfides occurs with further coalescing of finely dispersed matte droplets and their precipitation into the bottom phase. The active behavior of the sublimation of impurities - Pb, Zn, As, and Sb into dust is ensured due to the high rates of the interaction of their oxides with the dissociation products of higher sulfides and complete sulfidation of the converter slag due to elemental sulfur and iron sulfide introduced with the concentrate.

The results shown in Figures 1 and 2 show that direct processing of the concentrate in converters significantly increases the quality of the obtained converter slag. At the same time, the possibility of reducing the total duration of the 1st conversion period, in comparison with the existing technology, by about 20 minutes is visible.

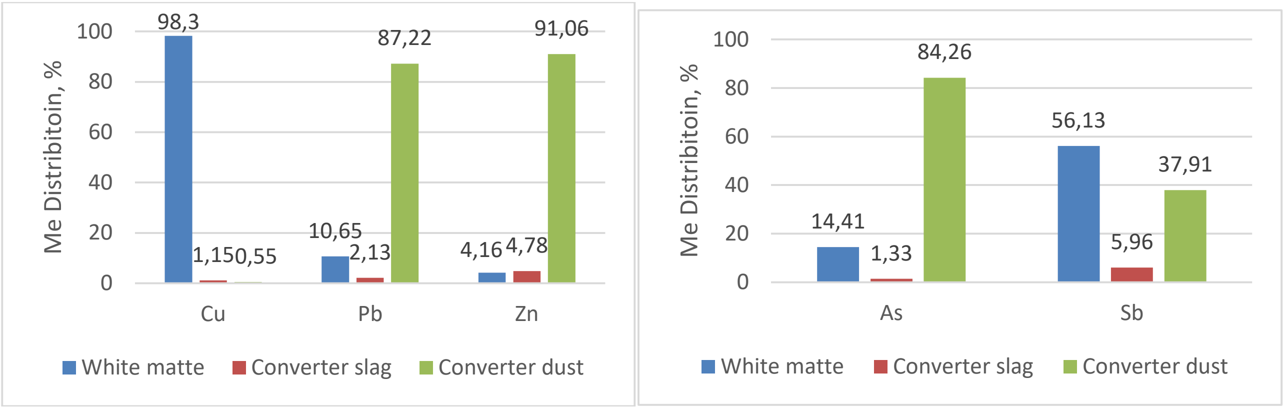
A comparative analysis of the results on the composition of products obtained under the conditions of the 1st period of converting copper-lead mattes according to the existing technology and during the joint processing of high-sulfur copper concentrate together with the matte is shown in Table 2.

It is easy to see a significant improvement in the quality of the resulting converter slag. The copper content in them is reduced by more than 6 times. A sharp decrease in lead from 22% to 0.72% was achieved, which indicates its high sublimation into dust. The content of zinc and arsenic in the slag is reduced by 10 times, and the content of antimony in them is 3 times less.

As evidenced by the data of a comparative analysis of the distribution of metals between the products of the 1st conversion period (Fig. 3), when the copper concentrate is added, high rates of distribution of metals into the targeted products are achieved. It can be argued that direct processing of high-sulfur copper concentrate with matte in a converter under conditions of vigorous bubbling of the melt achieves complete assimilation of sulfur by the melt and a significant increase in the quality of the products obtained compared to the existing technology.



A)



B)

Figure 3 - Distribution of non-ferrous metals and impurities between converting products: according to the existing technology (A); new technology (B).

Conclusions

Based on the study of the behavior of non-ferrous and related metals (Pb, Zn, As, Sb), the principal possibility of improving the quality of converting products during direct processing of high-sulfur copper concentrate with copper-lead matte in converters are shown.

A comparative assessment of the technological parameters of the existing technology for converting copper-lead mattes and the new technology for converting copper-lead mattes with high-sulfur copper concentrate was carried out. It has been established that during the direct processing of copper concentrate in the converter, a high recovery of copper into blister copper (up to 98.3%) is achieved by reducing its losses with converter slag.

The use of concentrate as a sulfiding agent provides high values for the distribution of impurity metals - Pb, Zn, As, and Sb into dust: 87.22; 91.06; 84.26, and 37.91%, respectively. This leads to their removal from the "smelting-converting" process chain and significantly improves the quality of the obtained products.

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

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Жоғары күкіртті мыс концентратын мыс-қорғасын штейнімен бірге балқыту арқылы конвертерлеу өнімдерінің сапасын арттыру

Арғын А.Ә., Жолдасбай Е.Е., Досмұхамедов Н.Қ.

Сәтбаев университеті, Алматы, Қазақстан

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ТҮЙІНДЕМЕ

Жұмыста конвертерде жоғары күкіртті мыс концентратымен бірге мыс-қорғасын штейндерін қайта өңдеу бойынша зерттеулердің нәтижелері келтірілген. Жоғары күкіртті мыс концентратының конвертер өнімдерінің сапасына әсері көрсетілген. Алынған нәтижелер негізінде мыс-қорғасын штейндерін қолданыстағы технология бойынша және мыс-қорғасын штейндерін мыс концентратымен бірлге өңдеу кезінде конвертерлеудің 1-ші кезеңінің технологиялық көрсеткіштеріне салыстырмалы талдау жүргізілді. Жоғары күкіртті мыс концентратын сульфидизатор ретінде пайдаланған кезде жоғары сульфидтердің диссоциациялануы нәтижесінде бөлінетін артық күкірт шлак балқымасына толық сіңетіні анықталды. Түсті металл оксидтерімен және қоспалармен әрекеттесетін күкірт металдардың конвертер өнімдері арасында тепе-тең бөлініп таралуына және олардың мақсатты өнімдерге бөлініп алуына айтарлықтай әсер ететіні көрсетілген. Сондай-ақ, күкірттің конвертерлеу процесінде магнетиттің бүлінуіне әсері анықталды. Мыс-қорғасын штейндерін жоғары күкіртті мыс концентратымен бірге конвертерлеу кезінде түсті және ілеспе қоспа-металдардың (As, Sb және т.б.) бөлініп таралуы бойынша жаңа деректер алынды. Түсті металдар мен қоспалардың мақсатты өнімдерге бөліп алу бойынша жоғары мәндер анықталды: мыстың штейнге өтуі –98% – ға дейін, қорғасын, мырыш, мышьяк және сурьманың шаңға өтуі тиісінше 87%, 91%, 84% және 38% болады. Мыс-қорғасын штейнімен бірге жоғары күкіртті мыс концентратын бірге балқыту кезінде техникалық-экономикалық көрсеткіштерді, конвертерлеу өнімдерінің сапасын және қоршаған ортаны қорғауды айтарлықтай жақсарту мүмкіндігі көрсетілген. Мыс-қорғасын штейндерін жоғары күкіртті мыс концентратымен бірге конвертрлеу технологиясы "Қазцинк" ЖШС зауыттық құрылымына материалдық шығындарсыз оңай интеграцияланады.

Түйін сөздер: мыс-қорғасын штейні, сульфидті мыс концентраты, конвертерлеу, конвертерлі шлак, ақ матт, сульфидтеу, бөлініп таралу.

Авторлар туралы ақпарат:

Арғын Айдар Әбділмәлікұлы	*PhD, Satbayev University, 050013, Алматы, Сатпаев көш. 22, Казақстан. E-mail: aidarargyn@gmail.com*
Жолдасбай Ержан Есенбайұлы	*PhD, Satbayev University, 050013, Алматы, Сатпаев көш. 22, Казақстан. E-mail: zhte@mail.ru*
Досмухамедов Нурлан Калиевич	*Т.ғ.к., профессор, Satbayev University, 050013, Алматы, Сатпаев көш. 22, Казақстан. E-mail: nurdos@bk.ru*

Повышение качества продуктов конвертирования путем совместной плавки высокосернистого медного концентрата с медно-свинцовым штейном

Аргын А.А., Жолдасбай Е.Е., Досмухамедов Н.К.

Satbayev University, Алматы, Казахстан

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АННОТАЦИЯ

В работе приведены результаты исследований по переработке медно-свинцовых штейнов совместно с высокосернистым медным концентратом в конвертере. Показано влияние высокосернистого медного концентрата на качество продуктов конвертирования. На основании полученных результатов проведен сравнительный анализ технологических показателей 1-го периода конвертирования медно-свинцовых штейнов по существующей технологии и при совместной переработке медно-свинцовых штейнов с медным концентратом. Установлено, что при использовании высокосернистого медного концентрата в качестве сульфидизатора, выделяемая в результате диссоциации высших сульфидов избыточная сера полностью усваивается шлаковым расплавом. Показано, что элементарная сера, вступая во взаимодействие с оксидами цветных металлов и примесей, оказывает существенное влияние на равновесное распределение металлов между продуктами конвертирования и их извлечению в целевые продукты. Установлена также влияние серы на разрушение магнетита в процессе конвертирования. Получены новые данные по распределению цветных и сопутствующих металлов-примесей (As, Sb и др.) при конвертировании медно-свинцовых штейнов совместно с высокосернистым медным концентратом. Установлены высокие значения по извлечению цветных металлов и примесей в целевые продукты: меди в штейн – до 98%, свинца, цинка, мышьяка и сурьмы в пыль – 87%, 91%, 84% и 38 %, соответственно. Показана возможность существенного улучшения технико-экономических показателей, качества продуктов конвертирования и охраны окружающей среды при совместной плавке высокосернистого медного концентрата совместно с медно-свинцовым штейном. Разработанная технология конвертирования медно-свинцовых штейнов совместно с высокосернистым медным концентратом легко интегрируется в заводскую структуру ТОО «Казцинк» без особых материальных затрат.

Ключевые слова: медно-свинцовый штейн, сульфидный медный концентрат, конвертирование, конвертерный шлак, белый матт, сульфидирование, распределение.

Информация об авторах:

Аргын Айдар Абдилмаликулы	*PhD, Satbayev University, 050013, Алматы, ул. Сатпаева 22, Казахстан. E-mail: aidarargyn@gmail.com*
Жолдасбай Ержан Есенбайулы	*PhD, Satbayev University, 050013, Алматы, ул. Сатпаева 22, Казахстан. E-mail: zhte@mail.ru*
Досмухамедов Нурлан Калиевич	*К.т.н., Профессор. Satbayev University, 050013, Алматы, ул. Сатпаева 22, Казахстан. E-mail: nurdos@bk.ru*

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Metallurgy

Study of the isothermal kinetics of reduction of sinter from mill scale

[1]Zhunusov A.K., [1]Bykov P.O., [1*]Kenzhebekova A.Ye., [1]Zhunussova A.K., [2]Rahmat Azis Nabawi

[1]Department of "Metallurgy", Torayghirov University, Pavlodar, Kazakhstan
[2]Department of Mechanical Engineering, Faculty of Engineeing, Universitas Negeri Padang, Indonesia

**Corresponding author email: kenzhebekova_psu@mail.ru*

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ABSTRACT

Studies of the isothermal kinetics of the reduction of sinter from mill scale were carried out at Zh. Abisheva Chemical and Metallurgical Institute (Karaganda). The influence of temperature and heating time on the degree of reduction of iron and other elements was studied in the Tamman furnace by the thermogravimetric method. The amount of reducing agent was taken in the experiments based on the stoichiometrically necessary amount of carbon for the complete reduction of iron oxides by more than 60%, as well as for the carburization of the resulting metal to 2.0% C. To obtain the kinetic characteristics of the reduction of the studied materials, depending on the temperature and duration of the process, processing of the received data array according to the models developed especially for these cases. The results of experimental data processing according to the Gistling-Brownstein model are presented. As a general assessment, this model with a sufficiently high correlation (R not less than 0.9) describes the studied process, which confirms its diffusion character. Analyzing the calculated data of the activation energy, one can assume the diffusion nature of the inhibition of the reduction reaction of all the materials under study. The value of the activation energy of the process shows that the agglomerate with dolomite (fluxed agglomerate) has the highest reducibility. During the frontal reduction of oxides of iron and other elements with carbon, a slag shell is formed around the grains of materials, which consists mainly of acidic oxides of barren rock, non-metallic inclusions of lightweight scrap and reducing agent ash and has a high viscosity. Its thickness depends on the composition of the material, temperature, time and degree of reduction.

Keywords: Mill scale, mill scale, reducibility, kinetics, diffusion barrier, activation energy.

	Information about authors:
Zhunusov Ablay Kairtassovich	*Candidate of Technical Sciences. Professor, Department of "Metallurgy". Torayghirov University, Pavlodar, Kazakhstan. Email: zhunusov_ab@mail.ru*
Bykov Petr Olegovich	*Candidate of Technical Sciences, Professor,* Department of "Metallurgy"*, Torayghirov University, Pavlodar, Kazakhstan. Email: bykov_petr@mail.ru*
Kenzhebekova Anar Yerbolatovna	*Student PhD, Department of "Metallurgy", Torayghirov University, Pavlodar, Kazakhstan. Email: kenzhebekova_psu@mail.ru*
Zhunussova Aygul Kairgeldinovna	*Student PhD, Department of "Metallurgy", Torayghirov University, Pavlodar, Kazakhstan. Email: zhunusova.aig@mail.ru*
Rahmat Azis Nabawi	*Head of Manufacturing Laboratory, Department of Mechanical Engineering, Faculty of Engineering, Universitas Negeri Padang, Indonesia. Email: raazna@ft.unp.ac.id*

Introduction

Rolling scale is an oxidized product that is formed in the process of metal reduction in rolling mills in large quantities. From the total steel production, scale formation is 2% [1]. According to [2], about 13 million tons of mill scale are formed annually around the world. In world practice, much attention is paid to the recycling and use of industrial waste in the metallurgical process [[3], [4], [5], [6]]. Rolling scale and other wastes generated at metallurgical plants are involved in production with their use as additional iron-containing material [[7], [8], [9], [10]] in the form of briquettes and sinter [[11], [12], [13]].

Technical and economic indicators of the technology of smelting iron and ferroalloys [14] depend on the recovery rate of the leading element (Fe, Si, Mn, Cr and other elements) and the nature of the slag formation process. These factors are affected by the process temperature, the chemical composition of the materials used and their softening point, the electrical resistivity of the charge, the reducibility of the materials, and the

Table 1 – Chemical composition of materials

Material	Chemical composition, %								
	Fe_{gen}	FeO	Al_2O_3	CaO	MgO	SiO_2	S	C	P
Agglomerate	38.0	24.9	15.8	4.96	4.86	11.3	0.05	-	0.005
Agglomerate with dolomite	55.0	12.1	1.46	7.06	6.80	5.10	0.07	-	0.001

types of reducing agents used. In [15], the kinetic reduction briquettes obtained from mill scale is carried out with hydrogen. As a result, it is shown that the recovery process is controlled by the process diffusion, and the activation energy ranges from 61.5 to 72.25 kJ/mol. In other studies [16], the kinetics and mechanism of reduction of agglomerates are studied using traditional types of reducing agents.

In this research, the authors obtained agglomerates from mill scale mixed with various metallurgical wastes, and studied the isothermal kinetics of agglomerate reduction. The obtained experimental data will help to better understand the mechanisms of carbothermal reduction of the sinter and the improvement of metallurgical processes.

Experimental part

When conducting research, lightweight steel scrap was used as a charge in a mixture with agglomerated ordinary iron ore and sinter with dolomite additives (up to 10% dolomite in sinter), produced in large-scale laboratory conditions of the Zh. Abisheva Chemical and Metallurgical Institute (Karaganda).

The studies were carried out on a charge, the ore part of which is represented by a mixture of lumpy iron ore (70%) and fine iron ore or agglomerates from mill scale (30%). PRC metallurgical coke (11.2% Ac, 4.20% Vg, 3.01% W) was used as a reducing agent. The composition of raw materials and coke ash is shown in Table 1.

The effect of temperature and heating time on the degree of reduction of iron and other elements was studied in the Tamman furnace by the thermogravimetric method. The method is fairly accurate and simple, does not require complex devices, and is acceptable for processes occurring at high temperatures. It is based on the assumption that during the reduction of charge oxides with carbon, only carbon monoxide is released in any period of time. This is only an assumption, because the charge material (ore) always contains moisture and carbon dioxide, which, at high temperatures, are added to the released gas. In the chosen method, these precipitates are also taken into account by the weighing device, and we get a general picture of the apparent activation energy. To eliminate the influence of the particle size distribution of materials and the reducing agent on the results of the study of reducibility, all charge materials were pre-crushed to a fraction of 0–1 mm.

The amount of reducing agent in the experiments was taken based on the stoichiometrically necessary amount of carbon for the complete reduction of iron oxides by more than 60%, as well as for the carburization of the resulting metal to 2.0% C. For each experiment, samples were taken consisting of 75 g of the ore mixture and the corresponding amount coke. The weighed mixture was placed in a graphite crucible and placed in a furnace heated to a given temperature, suspended from an analytical balance with a molybdenum wire. The melting unit in the installation was a Tamman furnace with a graphite heater. The experiments were carried out in isothermal mode at temperatures of 1100; 1200; 1300; 1400; 1500 ºC for 1 hour. The temperature was measured with a VR-5/20 thermocouple. The input power was regulated smoothly, so that the temperature could be maintained in the desired range. The temperature deviation from the set value did not exceed ±5 degrees. The crucible was cooled in air. The degree of recovery was judged by the weight loss of the sample. From the practice of studying the reducibility of iron ore materials, it is known [17] that the degree of reduction is determined by the ratio of the mass of oxygen taken away during the reduction to the mass of the initial oxygen bound in the material sample with the reduced iron. The degree of recovery was determined by the formula:

$$\alpha = \frac{O_2^B}{O_2^{\text{И}}}, \qquad (1)$$

where $O_2^{\text{И}}$ and O_2^B - the mass of oxygen in the original and reduced (exposed to the reducing agent for a certain period of time) samples of iron ore material.

For calculation α according to the experimental data, we used the following formula:

$$\alpha = \frac{O_2^B}{O_2^И} = \frac{\Delta m \cdot 16/28}{O_2^И}, \qquad (2)$$

where Δm - weight loss, gr.

Due to the fact that iron-bound oxygen is not determined by direct chemical analysis, the value $O_2^И$ It is usually calculated using calculation formulas in which, instead of oxygen, there are quantities that are more convenient for direct experimental determination, for example, those obtained by chemical analysis of the content of iron oxides and other elements. Assuming that in the original ore material under study and in the coke ash, oxygen is bound to iron in ratios determined by the stoichiometry of pure oxides, it is possible to calculate the mass of oxygen in the iron ore material and coke.

Research results and discussions

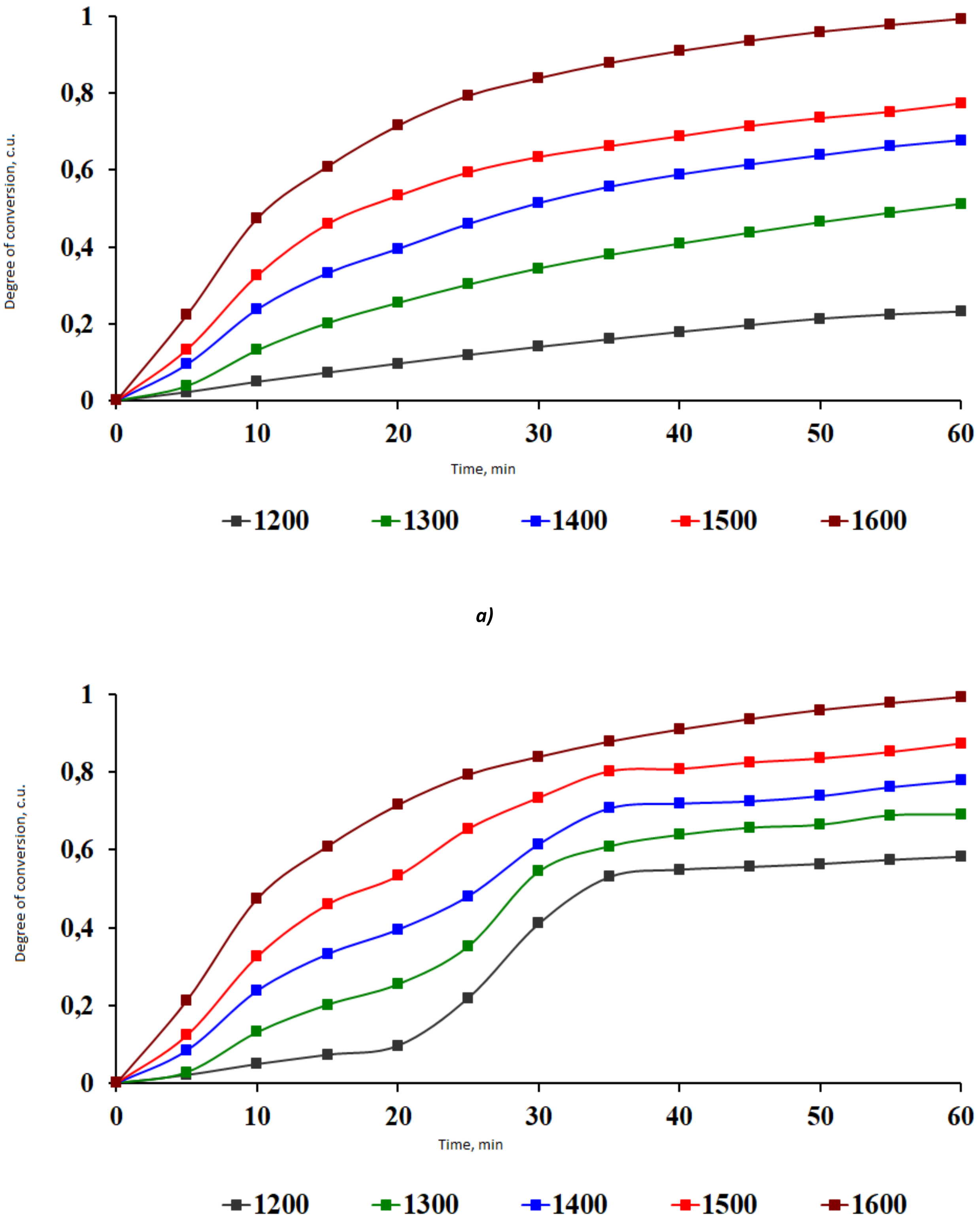
Table 2 gives the entire material of the experiment on the study of the reducibility of various materials under study by coke carbon.

To obtain the kinetic characteristics of the reduction of the studied materials, depending on the temperature and duration of the process, the obtained data array was processed according to specially developed models for these cases.

Figure 1 shows the kinetic curves for the reduction of various mixtures of light-weight scrap charge with conventional sinter and fluxed sinter under various temperature conditions.

Table 2 – The degree of recovery of materials

t, °C	Degree of conversion (α) at time (τ, min)					
	5	10	15	20	25	30
Lightweight scrap + sinter						
1100	0.022	0.049	0.073	0.097	0.119	0.140
1200	0.038	0.131	0.202	0.254	0.302	0.344
1300	0.094	0.238	0.332	0.395	0.460	0.514
1400	0.133	0.326	0.460	0.533	0.594	0.634
1500	0.223	0.474	0.609	0.715	0.793	0.839
Lightweight scrap and fluxed sinter						
1100	0.021	0.049	0.073	0.097	0.219	0.410
1200	0.028	0.131	0.202	0.254	0.352	0.544
1300	0.084	0.238	0.332	0.395	0.481	0.614
1400	0.123	0.326	0.460	0.533	0.654	0.734
1500	0.213	0.474	0.609	0.715	0.793	0.839
t, °C	Degree of conversion (α) at time (τ, min)					
	35	40	45	50	55	60
Lightweight scrap + sinter						
1100	0.160	0.179	0.197	0.214	0.224	0.232
1200	0.379	0.409	0.437	0.464	0.489	0.512
1300	0.556	0.589	0.615	0.638	0.661	0.678
1400	0.662	0.688	0.714	0.735	0.752	0.773
1500	0.878	0.909	0.936	0.960	0.977	0.993
Lightweight scrap and fluxed sinter						
1100	0.530	0.549	0.556	0.564	0.574	0.582
1200	0.609	0.639	0.657	0.664	0.689	0.691
1300	0.706	0.719	0.725	0.738	0.761	0.778
1400	0.802	0.808	0.824	0.835	0.852	0.873
1500	0.878	0.909	0.936	0.960	0.977	0.993



a)

b)

а – light scrap + agglomerate; *б* – light weight scrap and fluxed sinter

Figure 1 – Kinetic recovery curves of various iron ore materials at 1200-1600 ºC

For inside the diffusion region, Jander, based on the parabolic distribution of the growth law of the product layer, proposed the equation:

$$\left(1-\sqrt[3]{1-\alpha}\right)^2 = k\tau, \quad (3)$$

where α - conversion rate;

k – process rate constant;

τ - time elapsed since the start of the experiment.

A more correct equation for describing the constant of the solid-state process in a spherical grain was obtained by Gistling and Brownstein:

$$1-(2/3\cdot\alpha)-(1-\alpha)^{2/3} = k\tau, \quad (4)$$

It should be noted that the Jander equation (3) and Gistling-Brownstein equation (4) are based on the general assumption that the rate of the diffusion process is inversely proportional to the thickness of the reaction product layer. The difference between these equations, which model a solid-phase process, is based only on different geometric assumptions: Jander considers diffusion leading to the formation of a reaction product at a flat interface; Ginstling and Brownstein solve the problem of diffusion in a spherical grain. According to the Gistling-Brownstein equation, most often used in studies of the kinetics of reduction of various materials [[18], [19], [20]], the mathematical model of the dependence of the degree of transformation of manganese ore on time is expressed as a straight line equation:

$$\alpha = a + bx, \quad (5)$$

where (b) – slope, represents the rate constant of the process.

Table 3 shows the results of processing experimental data using the Gistling-Brownstein model. As a general assessment, it can be indicated that this model with a sufficiently high correlation (R not less than 0.9) describes the studied process, which once again confirms its diffusion character, since this equation is developed for such processes.

Analyzing the data in Table 3, we can conclude that at the same temperature, various manganese ore materials are arranged in the following order in order to increase the rate constant of their interaction with coke carbon: manganese ore → unfluxed sinter → sinter with dolomite. Thus, at 1100 °C, the reduction rate constant of sinter with dolomite is 3.0 times higher than that of light-weight scrap mixed with conventional sinter. A similar effect can be achieved by increasing the process temperature.

Using the data in Table 3, one can find the temperature dependence of the rate constant for various types of materials under study. To do this, we set the following formula for the dependence of the rate constant on temperature, called in physical chemistry the Arrhenius equation

$$k = A\cdot exp\left(-\frac{E_{act}}{RT}\right), \quad (6)$$

where A - constant;

E_{act} - process activation energy;

R - universal gas constant (8.3144 J/mol·K);

T- temperature, К.

Table 3 – Results of experimental data processing according to the Gistling-Brownstein model

Material	t, °C	$y = a + bx$		R	$k\cdot10^{-3}$
		a	b		
Lightweight scrap with agglomerate	1100	-3.995	0.779	0.962	14.343
	1200	-3.559	0.756	0.989	21.533
	1300	-3.008	0.716	0.988	35.379
	1400	-2.257	0.589	0.978	61.649
	1500	-2.081	0.670	0.983	83.594
Lightweight scrap with fluxed agglomerate	1100	-2.720	0.653	0.976	43.004
	1200	-2.224	0.587	0.974	63.542
	1300	-1.795	0.535	0.982	88.951
	1400	-1.493	0.522	0.987	117.226
	1500	-1.420	0.590	0.996	142.725

Table 4 – Kinetic characteristics of recovery

Material	Equation	R	A	E_{act}, kJ/mol
Lightweight scrap (LVS) and sinter	lnk= –12722.0/T + 3.814	0.998	70.43	105.775
Lightweight scrap and fluxed sinter	lnk= –8408.37/T + 1.0171	0.997	8.34	69.9105

Taking the logarithm of this expression gives the dependence

$$\ln k = ln\,A - \frac{E_{act}}{R} \cdot \frac{1}{T}, \qquad (7)$$

which can be represented as an equation of a straight line

$$\alpha = a + bx \qquad (8)$$

Table 2 Data Processing in Coordinates $\ln k - 1/T$ makes it possible to find the coefficient b in equation (4.9), numerically equal to $-E_{act}/R$, and coefficient a, equal $ln\,A$. With a known R (8,3144) one can find the activation energy of the process and the value of the pre-exponential coefficient A. The results of the calculations are placed in Table 4, which lists the required equations, correlation coefficients (R) and values of the apparent activation energy (E_{act}).

Analyzing the calculated activation energy data in Table 4, we can assume the diffusion nature of the inhibition of the reduction reaction of all the materials under study. Judging by the values of the activation energy of the process, the sinter with dolomite has the highest reducibility.

During the frontal reduction of oxides of iron and other elements with carbon, a slag shell is formed around the grains of materials, which consists mainly of acidic oxides of barren rock, non-metallic inclusions of lightweight scrap and reducing agent ash and has a high viscosity. Its thickness depends on the composition of the material, temperature, time and degree of reduction [19]. This shell is a slag barrier for the development of recovery along the depth of the grains of the materials used. Calcium and magnesium oxides, contained in an increased amount in dolomite, dissolve in the process of reduction in acidic and viscous slag-forming oxides - products that appear during the reduction of the leading elements of the agglomerate, and as a result, the formation of more basic and, accordingly, liquid slags. Such slags easily destroy the slag diffusion barrier and expose the surface of the sinter core for a new contact between iron oxides and carbon.

Thus, the magnesium contained in the agglomerate removes the frontally occurring reactions of ore reduction, a diffusion barrier and contributes to a more complete and intensive reduction of oxides of iron and other elements.

Conclusions

The reduction kinetics of manganese agglomerates has been experimentally studied in comparison with other manganese ore materials currently used in the practice of silicomanganese production in the temperature range of 1100-1500°C. Experimental data are processed according to the Khrushchev kinetic model, which establishes a relationship between the degree of transformation of a substance and the process time at a constant temperature.

According to the increase in the rate constant of their interaction with coke carbon, the studied materials are arranged in the following order: light-weight scrap → non-fluxed sinter → fluxed sinter.

The kinetic characteristics of the reduction of agglomerated mill scale with carbon have been determined. The activation energies of the reduction processes of the studied materials are calculated, analyzing which it is possible to draw a conclusion about the diffusion nature of the inhibition of the reduction reaction of all the studied materials. The development of the reduction process is limited by the slag shell, which consists mainly of acidic oxides of the waste rock of the ore and reducing agent ash, which have a high viscosity.

In dolomite-fluxed agglomerate, the negative effect of the slag barrier is reduced due to the increased content of basic calcium and magnesium oxides in its composition, which dissolve in viscous slag-forming oxides during the reduction process, resulting in the formation of low-melting and liquid-moving slags on the contact surface. Such slags easily destroy the slag diffusion barrier and expose the surface of the core of minerals for a new contact between the oxides of iron, silicon and other elements with carbon, contributing to their more complete and intensive recovery.

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

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Илемделген отқабыршақтан агломераттың тотықсыздануының изотермиялық кинетикасын зерттеу

[1]Жүнісов А.Қ., [1]Быков П.О., [1]Кенжебекова А.Е., [1]Жүнісова А.Қ., [2]Rahmat Azis Nabawi

[1]Торайғыров университеті, Павлодар, Қазақстан
[2]Паданг мемлекеттік университеті, Индонезия

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ТҮЙІНДЕМЕ

Илемделген отқабыршақтан агломератты қалпына келтірудің изотермиялық кинетикасын зерттеу Ж. Әбішев атындағы Химия-металлургиялық институтта жүргізілді. (Қарағанды қ.). Темірдің және басқа элементтердің тотықсыздану дәрежесіне температура мен қыздыру уақытының әсері Тамман пешінде термогравиметриялық әдіспен зерттелді. Тәжірибелерде тотықсыздандырғыштың мөлшері темір оксидтерін 60%-дан астам толық тотықсыздандыру үшін, сондай-ақ алынған металды 2,0% С-ға дейін көміртектендіру үшін көміртегінің стехиометриялық қажетті мөлшерін негізге ала отырып алынды. Температура мен процестің ұзақтығына байланысты зерттелетін материалдардың тотықсыздануының кинетикалық сипаттамаларын алу үшін алынған деректер ауқымы осы жағдайлар үшін арнайы әзірленген модельдер бойынша өңделді. Гистлинг-Браунштейн моделі бойынша мәліметтерді тәжірибелік өңдеу нәтижелері келтірілген. Жалпы бағалау ретінде жеткілікті жоғары корреляцияланғандыққа ие (R 0,9 кем емес) бұл модель оның диффузиялық сипатын растайтын зерттелетін процесті сипаттайды. Белсендіру энергиясының есептелген мәліметтерін талдай отырып, барлық зерттелетін материалдардың тотықсыздану реакциясының тежелуінің диффузиялық сипатын болжауға болады. Процестің белсендіру энергиясының мәні агломераттың доломитпен (флюстелген агломерат) тотықсыздану қабілетінің жоғары екенін көрсетеді. Темірдің және басқа элементтердің оксидтерінің көміртегімен фронтальды тотықсыздануы кезінде материалдар түйіршіктерінің айналасында қож қабығы түзіледі, ол негізінен бос тау жыныстарының қышқылдық оксидтерінен, салмағы жеңіл сынықтардан, тотықсыздандырғыш күлдің металл емес қосындыларынан тұрады және жоғары тұтқырлыққа ие болады. Оның қалыңдығы материалдың құрамына, температураға, уақытқа және қалпына келу дәрежесіне байланысты.

Түйін сөздер: Илемделген отқабыршақ, отқабыршақ, қалпына келу, кинетика, диффузиялық кедергі, белсендіру энергиясы.

	Авторлар туралы ақпарат:
Жүнісов Абылай Қайыртасұлы	*Техника ғылымдарының кандидаты, профессор, «Металлургия» кафедрасы, Торайғыров университеті, Павлодар, Қазақстан. Email: zhunusov_ab@mail.ru*
Быков Пётр Олегович	*Техника ғылымдарының кандидаты, профессор, «Металлургия» кафедрасы, Торайғыров университеті, Павлодар, Қазақстан. Email: bykov_petr@mail.ru*
Кенжебекова Анар Ерболатқызы	*Докторант, Металлургия кафедрасы, Торайғыров университеті, Павлодар, Қазақстан. Email: kenzhebekova_psu@mail.ru*
Жүнісова Айгүл Қайыргелдықызы	*Докторант, Металлургия кафедрасы, Торайғыров университеті, Павлодар, Қазақстан. Email: zhunusova.aig@mail.ru*
Rahmat Azis Nabawi	*Паданг мемлекеттік университетінің инженерлік факультеті, машина жасау кафедрасы, өндіріс зертханасының меңгерушісі, Индонезия. Email: raazna@ft.unp.ac.id*

Исследование изотермической кинетики восстановления агломерата из прокатной окалины

[1]Жунусов А.К., [1]Быков П.О., [1]Кенжебекова А.Е., [1]Жунусова А.К. [2]Rahmat Azis Nabawi

[1]Торайгыров Университет, Павлодар, Казахстан
[2]Падангский государственный университет, Индонезия

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АННОТАЦИЯ

Исследования изотермической кинетики восстановления агломерата из прокатной окалины проводили в Химико-металлургическом институте им.Ж. Абишева (г. Караганды). Влияние температуры и времени нагрева на степень восстановления железа и других элементов исследовали в печи Таммана термогравиметрическим методом. Количество восстановителя в опытах принимали исходя из стехиометрически необходимого количества углерода для полного восстановления оксидов железа на более чем 60 %, а также на науглероживание полученного металла до 2,0 % С. Для получения кинетических характеристик восстановления исследуемых материалов в зависимости от температуры и продолжительности процесса проведена обработка полученного массива данных по специально для этих случаев разработанным моделям. Приведены результаты обработки экспериментальных данных по модели Гистлинга - Броунштейна. В качестве общей оценки данная модель с достаточно высокой коррелированностью (R не менее 0,9) описывает изученный процесс, что подтверждает его диффузионный характер. Анализируя расчетные данные энергии активации можно предположить диффузионный характер торможения реакции восстановления всех исследуемых материалов. Величина энергии активации процесса показывает, что наиболее высокой восстановимостью обладает агломерат с доломитом (офлюсованный агломерат). При фронтальном восстановлении оксидов железа и других элементов углеродом вокруг зерен материалов образуется шлаковая оболочка, состоящая преимущественно из кислых оксидов пустой породы, неметаллических включений легковесного лома и золы восстановителя и обладающая высокой вязкостью. Толщина ее зависит от состава материала, температуры, времени и степени восстановления.

Ключевые слова: Прокатная окалина, окалина, восстановимость, кинетика, диффузионный барьер, энергия активации.

Информация об авторах:

Жунусов Аблай Каиртасович	*Кандидат технических наук, профессор, Кафедра «Металлургия», Torayghirov University, Павлодар, Казахстан. Email: zhunusov_ab@mail.ru*
Быков Петр Олегович	*Кандидат технических наук, профессор, Кафедра «Металлургия», Torayghirov University, Павлодар, Казахстан. Email: bykov_petr@mail.ru*
Кенжебекова Анар Ерболатовна	*Докторант, Кафедра «Металлургия», Torayghirov University, Павлодар, Казахстан. Email: kenzhebekova_psu@mail.ru*
Жунусова Айгуль Каиргельдиновна	*Докторант, Кафедра «Металлургия», Torayghirov University, Павлодар, Казахстан. Email: zhunusova.aig@mail.ru*
Rahmat Azis Nabawi	*Заведующий производственной лабораторией кафедры машиностроения инженерного факультета Падангского государственного университета, Индонезия. Email: raazna@ft.unp.ac.id*

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Earth sciences

Monitoring of the stress-strain state during preparatory workings

[1*]**Khalikova E.R.**, [1]**Diomin V.F.**, [1]**Mussin R.A.**, [2]**Krakovsky A.P.**, [1]**Khanafin U.Zh.**

[1] *Non-profit joint-stock company "Abylkas Saginov Karaganda Technical University", Karaganda, Kazakhstan*
[2] *N.S. Polyakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine Institute of Geotechnical Array, Dnipro, Ukraine*

** Corresponding author email: Salyahova_e@mail.ru*

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ABSTRACT

Maintaining and increasing the volume of underground coal mining is possible only if there is a highly efficient technology for conducting and maintaining preparatory workings. The purpose of the research was to assess the parameters of stability control of the contours of the mine workings, anchored with anchorage, to create a technology for intensive and safe excavation of mine workings based on the identified patterns of behavior of adjacent rock massifs. The idea of the approach is to use a man-made stress-strain state to develop an effective technology for fixing a contour rock mass. The mechanism of deformation, displacement, and collapse of rocks in a structurally disturbed inhomogeneous mountain range is investigated to assess the state of the rock mass around the mine workings. The technology of fastening contiguous soil rocks has been developed taking into account the state of the mountain massif around the workings and the parameters of the operation of the anchor supports in mines for fixing rods in workings in order to ensure the safety of mining operations in the mines of the Karaganda coal basin have been determined.

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

Information about authors:

Khalikova Elvira Ravilovna	*Ph.D., Senior lecturer of the Department of "Development of Mineral Deposits" of Non-profit joint-stock company "Abylkas Saginov Karaganda Technical University", 100027, Kazakhstan, Karaganda, Ave. Nursultan Nazarbayev, 56. E-mail: Salyahova_e@mail.ru*
Diomin Vladimir Fedorovich	*Doctor of Technical Sciences, Professor of the Department of "Development of Mineral Deposits" of Non-profit joint-stock company "Abylkas Saginov Karaganda Technical University", 100027, Kazakhstan, Karaganda, Ave. Nursultan Nazarbayev, 56. E-mail: vladfdemin@mail.ru*
Mussin Ravil Altafovich	*Ph.D., Senior lecturer of the Department of "Development of Mineral Deposits" of Non-profit joint-stock company "Abylkas Saginov Karaganda Technical University", 100027, Kazakhstan, Karaganda, Ave. Nursultan Nazarbayev, 56. E-mail: R.A.Mussin@mail.ru*
Krakovsky Alexander Petrovich	*Doctor of Technical Sciences, Professor, Deputy Director of the N.S. Polyakov Institute of Geotechnical Mechanics of the National Academy of Sciences of Ukraine, Institute of Geotechnics of the Massif, 49005, Dnipro, Ukraine, ul. Simferopol, 2a. E-mail: igtm@ukr.net*
Khanafin Ulan Zhomartovich	*Master's student of the GDM-22-2 group of the Department of "Development of Mineral Deposits" of Non-profit joint-stock company "Abylkas Saginov Karaganda Technical University", 100027, Kazakhstan, Karaganda, Ave. Nursultan Nazarbayev, 56. E-mail: Ulan_khanafin@mail.ru*

Introduction

Stable growth in the volume of underground coal mining is possible only when using effective and safe technology to conduct and maintain production workings.

Currently, more than 65% of all mine workings in the Karaganda coal basin are anchored, which allows to expand the technological possibilities of underground coal mining [[1, [2]].

An anchoring system of the carbon rock mass limits deformation and allows horizontal stress to hold the roof in place without destroying it. If the height of the stratified rock is lower than the anchoring level, the condition of the excavation will be satisfied, ensuring that the rock stress remains unchanged. If the height of the stratified rock in the roof is higher than the first level of the excavation anchoring, the increase in stress before the face, will cause the collapse of the roof. Longer second level anchors will be required to maintain the excavation. In practice the non-pillar development systems used in direct ventilation schemes, it is reasonable to use workings.

World experience of advanced coal-mining countries (USA, Australia, China, etc.) shows that effective and reliable fastening of capital and preparatory mine workings can be provided by using steel-polymer anchors with a load-bearing strength of at least 100 - 130 kN [3]. Monitoring the use of anchorage in coal mines shows that it is used in accordance with existing regulations as the main and auxiliary in combination with metal frame compressible support. The existing methods for determining the parameters of anchoring are based on the fixing of excavations by creating an anchor bridge or "hanger" of relatively weak layers to the strong zone of hard grounds [[4], [5]].

Improvement of anchoring technology and expansion of the area of anchoring support are a priority in the mining industry, which allows for an increase in the stability of mine workings at a high rate and reduces the cost of their support [6].

To increase the efficiency of rock mass support around the excavation for its strengthening, a purposeful geotechnological impact on the stressed and deformed zones with active manifestations of pressure around mine workings on the basis of the results of production monitoring and modeling of the "wall rock mass - contour support" system is necessary [[7], [8]].

Therefore, one of the important scientific and applied research in the coal mining industry is the application of strengthening technology using anchoring in soft wall rock around the rock artificial cavities supported behind the face on the border with the mined-out space, taking into account the technogenic state of the adjacent rocks of the rock massif.

The use of various types of supports with unsatisfactory load-bearing capacity and constructive suppleness with relatively low rock strength is the main reason for the unsatisfactory condition of underground mine workings [[9], [10]].

Conducting mine workings with active support systems is one of the most common and progressive types of mine support. The use of this type of support can significantly improve conditions for safe work performance. The main advantage of active fastening is that the fastener begins to function as soon as it is installed. This prevents the collapse of the rock mass, reduces the zone of non-elastic deformations around the excavation, and thus increases the stability of the excavation with a minimum amount of supporting material [[11], [12]].

Increasing the level of underground coal mining is possible only if there is a rational technology and reliable support of preparatory workings, providing an increase in the volume of tunneling work. Therefore, the development of advanced technology of mine workings based on the definition of the stress-strain state (SSS) of the massif and its influence on the parameters of support and subsequent maintenance, is an important scientific and technical task of mining production [[13], [14]].

Study methods: a comprehensive research methodology was used, including the generalization, assessment, and analysis of specialized information contained in the production practice, literature sources; statistical processing of numerical information; experimental mine studies [[15], [16]].

Experimental part

To solve various problems associated with finding the most effective method of supporting preparatory mine workings, in practice a large number of methods of actual measurement are used. According to their physical essence, these studies are reduced to measuring the density of rocks, observation of deformations, and displacements of excavation contours [[17], [18]].

To determine the characteristics of deformation and development of displacement of contour rock mass near the preparatory workings, we conducted field observations of displacements of rocks roof, soil, and sides of preparatory workings (for example, conveyor entry 231k19-s - Table 1) of Abaiskaya mine of the Karaganda coal basin. To assess the complexity, disturbance, and methods of impact on the rock massif, Figure 1 shows the types of complex conditions, the characteristics of the rock massif, the nature of the manifestation of complexity, and the nature of the manifestation of deformations.

Analysis of mining-geological and mining-technical conditions of the conveyor entry 231k$_{19}$-c of Abaiskaya mine showed that among the factors that have adverse effects noted: the possibility of encountering unpredictable small-amplitude disturbances, opening and departure from the formation, encountering a geological fault with H=0,9 m, a geological fault of "up-throw" type with the amplitude of H=17 m.

Table 1 - Technical characteristics of belt entry 231k$_{19}$-c

Name of workings	Length, m	Width, m	Height, m	Cross-section, m^2	Support type	Set lagging type
Belt entry 231к$_{19}$-с	1120	4.5	3.0	13.5	Anchor	mesh /ZMP

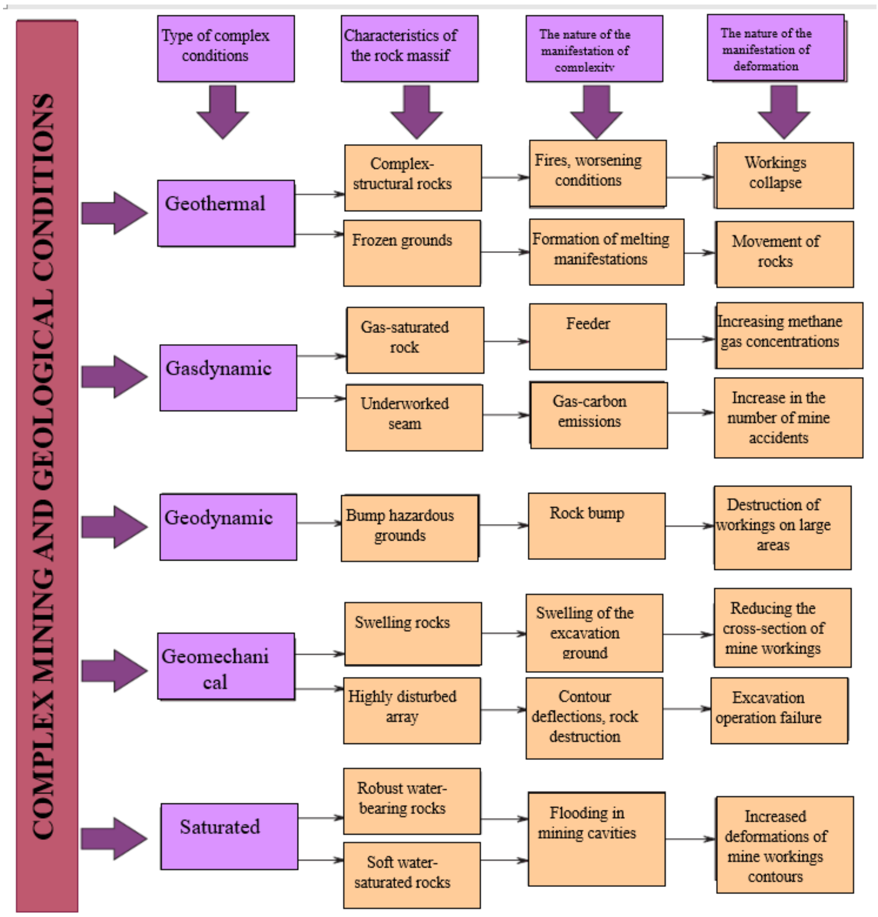


Figure 1 – Assessment of deformation manifestations considering mining and geological conditions of development

In the zones of interception rocks are fractured, kaolized, stable, prone to collapse, and falling out [[19], [20]]. Figure 2 shows the section of the excavation during its implementation.

Discussion of results

Field studies of the condition of the belt entry 231k$_{19}$-c for 3 months showed that, in general, the deformation processes proceed evenly throughout the contour of the excavation. In some places, the most intense displacements of the sides and roof of the workings are observed. Also, ground swelling in the excavation was detected. Figure 3 shows the dynamics of displacement of the left (a) and right (b) sides of the excavation.

According to field observations, in the first month after the installation of the measuring device displacement and deformation of the left side of the excavation was 6 mm. In the second month, the deformation of the left side was 7 mm. The third month of field observations of the mine working condition showed that the displacements were 5 mm. The total deformation and displacement of the left side of the excavation over 3 months was 17 mm.

Full-scale observations of the condition of the sides of the workings showed that the displacement and deformation in the first month amounted to 6 mm, in the second month the deformation was - 5 mm. In the third month the displacement was 7 mm. The total deformation and displacement of the sides of the excavation for 3 months was 18 mm. In general, the values obtained are within the range of permissible displacements of the mine workings. The displacements of the excavation sides are the result of elastic deformations of the massif. The total deformation and displacement of the excavation roof was 10 mm - figure 4.

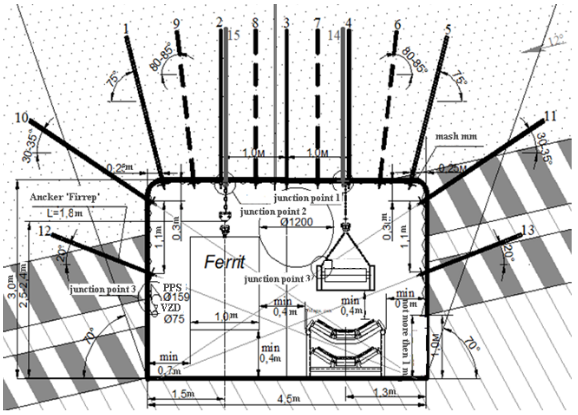
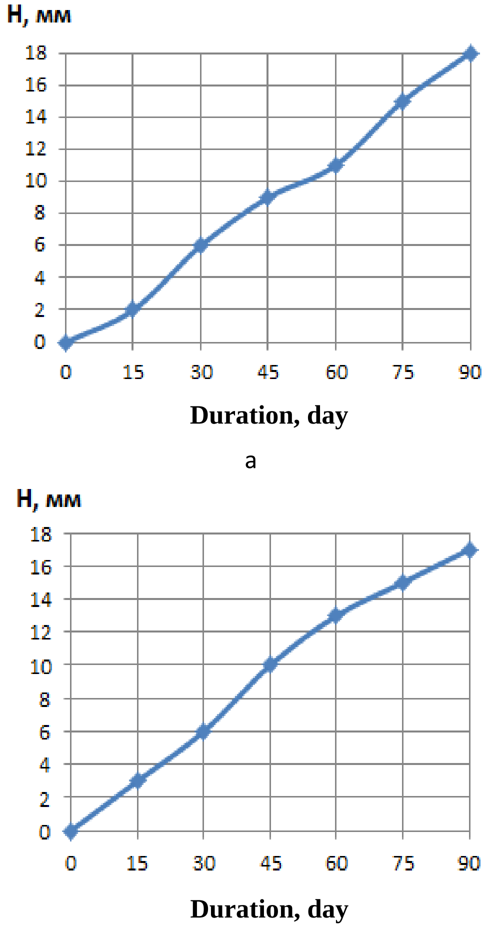


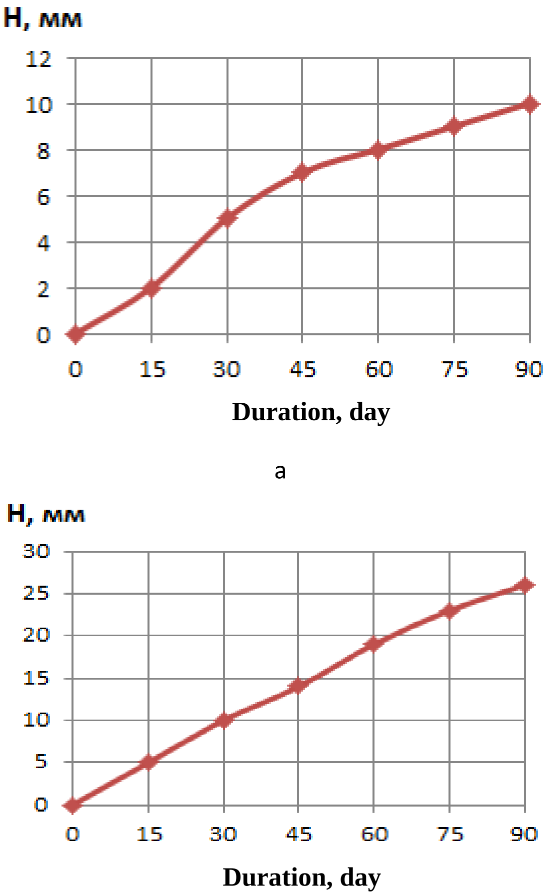
Figure 2 – Excavation cross-section during its conduct of the belt entry 231k$_{19}$-s



a

b

Figure 3 – Dynamics of development of displacements of the right (a) and left (b) sides of the belt entry 231k$_{19}$-c



a

b

Figure 4 – Dynamics of displacement of roof rocks (a) and ground (b) of belt entry 231k$_{19}$-c

On average, the total values of ground swelling were 26 mm. The most intense ground swelling was recorded on the right side of the excavation and reached 40 mm - figure 5.

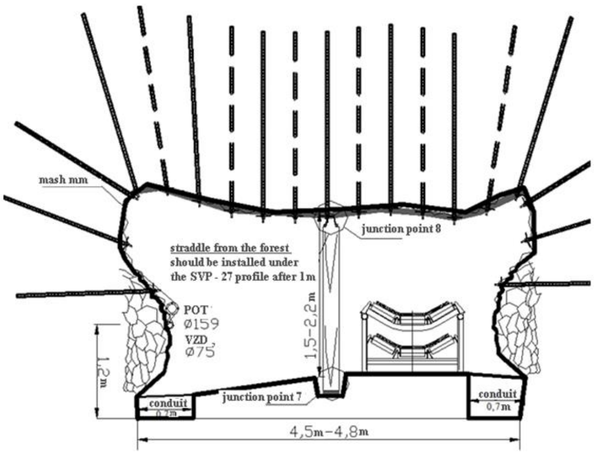


Figure 5 – Operational cross-section of belt entry 231k$_{19}$-c and during field production observations

Figure 5 clearly shows that the negative condition of the mine is influenced by the unloaded rock mass, which was formed as a result of previous mining operations at face $231k_{18}$-c.

Figure 6 shows the deformation of the contours of the belt entry $231k_{19}$-c during field observation of the condition of the contours of the excavation.

Figure 6 – Deformations of contours of belt entry $231k_{19}$-s of Abaiskaya mine, Karaganda coal basin

Functional dependences of the deformations of excavation contours in time were established (regression coefficient 0.99):

- swelling of the ground: $y_{см}^{к}=0{,}095\ ln(x)+0{,}2$;

- roof displacements: $y_{см}^{к}=0{,}045\ ln(x)+0{,}1$;

- side displacements: $y_{см}^{к}=0{,}035\ ln(x)+0{,}1$.

Conclusions

Studies of the state of mine workings (by the example of the belt entry $231k_{19}$-s) of Abaiskaya mine allowed to determine the degree of influence of mining-geological and mining-technical factors on the displacement in the near-contour rocks using different methods of mine workings support. The identified patterns in the deformations of mine workings contours can be used to select and calculate the most optimal method of supporting preparatory mine workings in various mining and geological conditions. Functional dependences of the deformations of excavation contours in time were established (regression coefficient 0.99): swelling of the ground: $yп=0{,}095\ ln(x)+0{,}2$; roof: $yк=0{,}045\ ln(x)+0{,}1$ and sides displacements: $yб=0{,}035\ ln(x)+0{,}1$, that can be used to determine the parameters of support of mine workings.

Assessment of geomechanical processes taking place in the rock massif with the establishment of optimal parameters of support, taking into account the current economic indicators for the conduct of preparatory excavations, taking into account the technogenic state of the massive rocks.

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

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Дайындық қазбаларын жүргізу кезіндегі кернеулі-деформацияланған жай-күйдің мониторингі

[1]Халикова Э.Р., [1] Демин В.Ф., [1]Мусин Р.А., [2]Круковский А.П., [1]Ханафин У.Ж.

[1] «Әбілқас Сағынов атындағы Қарағанды техникалық университеті» коммерциялық емес акционерлік қоғамы, Қарағанды, Қазақстан

[2] Украина Ұлттық ғылым академиясы, Н.С. Поляков атындағы Тау массивінің геотехникасы институты, Днепр, Украина

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ТҮЙІНДЕМЕ

Көмір өндірудің жерасты көлемін қалыпты ұстап тұру және ұлғайту дайындық қазбаларын жүргізу мен қолдаудың жоғары тиімді технологиясы болған жағдайда ғана мүмкін болады. Зерттеудің мақсаты іргелес тау жыныстары массивтерінің анықталған әрекет ету заңдылықтары негізінде қазба тау-кен қазбаларын қарқынды және қауіпсіз жүргізу технологиясын құру үшін якорь бекіткішімен бекітілген тау-кен қазбалары контурларының тұрақтылығын басқару параметрлерін бағалау болды. Тәсілдің идеясы контурлық тау жотасын бекітудің тиімді технологиясын әзірлеу үшін техногендік кернеулі-деформацияланған күйді пайдалану болып табылады. Тау-кен қазбаларының айналасындағы тау жыныстарының жай-күйін бағалау үшін құрылымдық бұзылған гетерогенді тау жыныстарындағы жыныстардың деформациясы, жылжуы және құлау механизмі зерттелді. Қарағанды көмір бассейнінің шахталарында тау-кен жұмыстарын жүргізу қауіпсіздігін қамтамасыз ету мақсатында қазбаларда штангаларды бекіту үшін шахталарда якорь бекіткіштерін пайдалану параметрлері айқындалды.

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

Авторлар туралы ақпарат:

Халикова Эльвира Равиловна	*Ph.D., "Әбілқас Сағынов атындағы Қарағанды техникалық университеті" КЕАҚ "Пайдалы қазбалар кен орындарын игеру" кафедрасының аға оқытушысы, 100027, Қазақстан, Қарағанды, пр . Нұрсұлтан Назарбаев, 56. E-mail: Salyahova_e@mail.ru*
Демин Владимир Федорович	*Техника ғылымдарының докторы, "Әбілқас Сағынов атындағы Қарағанды техникалық университеті" КЕАҚ "Пайдалы қазбалар кен орындарын игеру" кафедрасының профессоры, 100027, Қазақстан, Қарағанды, пр. Нұрсұлтан Назарбаев, 56. E-mail: vladfdemin@mail.ru*
Мусин Равиль Альтавович	*Ph.D., "Әбілқас Сағынов атындағы Қарағанды техникалық университеті" КЕАҚ "Пайдалы қазбалар кен орындарын игеру" кафедрасының аға оқытушысы, 100027, Қазақстан, Қарағанды, пр . Нұрсұлтан Назарбаев, 56. E-mail: R.A.Mussin@mail.ru*
Круковский Александр Петрович	*Техника ғылымдарының докторы, профессор, институт директорының орынбасары, Украина Ұлттық ғылым академиясы, Н.С. Поляков атындағы Тау массивінің геотехникасы институты, 49005, Днепр, Украина, көш. Симферопольская, 2а. E-mail: igtm@ukr.net*
Ханафин Улан Жомартович	*"Әбілқас Сағынов атындағы Қарағанды техникалық университеті" КЕАҚ "Пайдалы қазбалар кен орындарын игеру" кафедрасының ГДМ-22-2 тобының магистранты, 100027, Қазақстан, Қарағанды, Нұрсұлтан Назарбаев даңғылы, 56. E-mail: Ulan_khanafin@mail.ru*

Мониторинг напряженно-деформированного состояния при проведении подготовительных выработок

[1]Халикова Э.Р., [1]Демин В.Ф., [1]Мусин Р.А., [2]Круковский А. П., [1]Ханафин У.Ж.

[1] НАО «Карагандинский технический университет имени Абылкаса Сагинова», Караганда, Казахстан
[2] НАН Украины, Институт геотехники горного массива им. Н.С. Полякова, Днепр, Украина

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АННОТАЦИЯ

Поддержание и увеличение объема подземной добычи угля возможно лишь при наличии высокоэффективной технологии проведения и поддержания подготовительных выработок. Целью исследований явилась оценка параметров управления устойчивостью контуров горных выработок, закрепленных анкерной крепью, для создания технологии интенсивного и безопасного проведения выемочных горных выработок на основе выявленных закономерностей поведения примыкающих к ним массивов горных пород. Идея подхода заключается в использовании техногенного напряженно-деформированного состояния для разработки эффективной технологии крепления приконтурного горного массива. Исследован механизм деформирования, сдвижения и обрушения пород в структурно нарушенном неоднородном горном массиве для оценки состояния породного массива вокруг горных выработок. Разработана технология крепления приконтурных пород почвы с учетом состояния горного массива вокруг выработки и определены параметры эксплуатации анкерной крепи на шахтах для закрепления штанг в выработках в целях обеспечения безопасности ведения горных работ на шахтах Карагандинского угольного бассейна.

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

Халикова Эльвира Равиловна	***Информация об авторах:*** *Ph.D., старший преподаватель кафедры «Разработка месторождений полезных ископаемых» НАО «Карагандинский технический университет имени Абылкаса Сагинова», 100027, Казахстан, Караганда, пр. Нурсултана Назарбаева, 56. E-mail: Salyahova_e@mail.ru*
Демин Владимир Федорович	*Доктор технических наук, профессор кафедры «Разработка месторождений полезных ископаемых» НАО «Карагандинский технический университет имени Абылкаса Сагинова», 100027, Казахстан, Караганда, пр. Нурсултана Назарбаева, 56. E-mail: vladfdemin@mail.ru*
Мусин Равиль Альтавович	*Ph.D., старший преподаватель кафедры «Разработка месторождений полезных ископаемых» НАО «Карагандинский технический университет имени Абылкаса Сагинова», 100027, Казахстан, Караганда, пр. Нурсултана Назарбаева, 56. E-mail: R.A.Mussin@mail.ru*
Круковский Александр Петрович	*Доктор технических наук, профессор, заместитель директора Института геотехники горного массива им. Н.С. Полякова, НАН Украины, 49005, Днепр, Украина, ул. Симферопольская, 2а. E-mail: igtm@ukr.net*
Ханафин Улан Жомартович	*Магистрант группы ГДМ-22-2 кафедры «Разработка месторождений полезных ископаемых» НАО «Карагандинский технический университет имени Абылкаса Сагинова», 100027, Казахстан, Караганда, пр. Нурсултана Назарбаева, 56. E-mail: Ulan_khanafin@mail.ru*

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Earth sciences

Gold and rare earth elements in enrichment products from the technogenic wastes of the Caspian Mining-Metallurgical Plant (Aktau, Kazakhstan)

***Bekenova G.K., Peregudov V.V., Levin V.L., Kanatbaev Y.T., Muratkhanov D.B.**

Satbayev University, K.I. Satbayev Institute of Geological Sciences, Almaty, Kazakhstan

** Corresponding author email: bekenova@mail.ru*

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ABSTRACT

The paper presents the outcome of a comprehensive study at macro- to nanoscale levels of enrichment products from technogenic wastes. The products were obtained thanks to the experience of gravity enrichment during the treatment and preparation of the gold and REE sample material with preliminary mechanical and thermal activation. Thermal activation was applied for the first time. Native gold was identified in the form of single, micron-sized grains and, according to technological testing of enrichment products, there is a predominance of "invisible" dispersed gold. The gold content in the initial material was 2.93 g/t, which upon thermal activation of the sample increased to 6.37 g/t. According to the spectral analysis and electron probe microanalysis, the products of all enrichment stages are characterized by an increased content of yttrium and REEs. The REEs occurrence forms were determined. REEs are mainly found in micro- and nano-sized fluorine and fluorine-free phosphates (in apatite, by substitution of calcium), in REE-phosphates (in xenotime), and less often, possibly, in complex sulfo-phosphates and phosphate silicates. In thermal products consisting of inhomogeneous aggregates of nanosized phases, according to X-ray phase analysis, considering the elemental composition, REEs are included in the composition of phosphates: florensite and phases $Ce(P_5O_{14})$, $Ca_8MgSm(PO_4)_7$

Keywords: gold, REEs, micro- and nano-sized grains, technogenic wastes, Caspian Mining-Metallurgical Plant, Kazakhstan.

	Information about authors
Bekenova Galiya Kabeshovna	*Doctor of Sciences (Geology-Mineralogy), Satbayev University, Head of Mineralogy Laboratory in K.I. Satbayev Institute of Geological Sciences, Kabanbai batyr str., 69, 050010, Almaty, Kazakhstan. Email: bekenova@mail.ru*
Peregudov Valerii Vasilevich	*Geologist, scientific researcher, Satbayev University, Mineralogy Laboratory in K.I. Satbayev Institute of Geological Sciences, Kabanbai batyr str., 69, 050010, Almaty, Kazakhstan. Email: pereval1946@mail.ru*
Levin Vladimir Leonidovich	*Candidate of Sciences (Geology-Mineralogy), leading scientific researcher, Satbayev University, Mineralogy Laboratory in K.I. Satbayev Institute of Geological Sciences, Kabanbai batyr str., 69, 050010, Almaty, Kazakhstan. Email: levin_v@inbox.ru*
Kanatbayev Yerlan Temirbekuly	*Scientific Researcher Satbayev University, Laboratory of Physical and Chemical Research Methods in K.I. Satbayev Institute of Geological Sciences, Kabanbai batyr str., 69, 050010, Almaty, Kazakhstan. Email: 7087788@mail.ru*
Muratkhanov Daulet Bolatovich	*Doctoral student, scientific researcher, Satbayev University, Rare and rare-earth metals Laboratory in K.I. Satbayev Institute of Geological Sciences, Kabanbai batyr str., 69, 050010, Almaty, Kazakhstan. Email: daulet.muratkhanov@satbayev.university*

Introduction

Accumulated for decades and occupying vast lands, technogenic wastes of large enrichment combines, factories, and plants, are rightly considered as technogenic deposits of valuable elements, and their study results may well comprise a separate section of metallogeny.

In the Mangistau oblast, the uranium-phosphorite deposits of Melovoe, Tomak, and others provided raw materials for the Caspian Mining and Metallurgical Plant (CMMP) [[1], [2], [3]]. According to open sources literature [[4], [5], [6], [7], [8], [9]], the CMMP ore process was as follows:

1. the clays were washed and classified, separating the washed phosphatized fish bones into large classes;

2. the washed bone detritus was sent to the plant's hydrometallurgical reprocessing for extraction of uranium and phosphorus, and the REEs were sent for storage in a sludge reservoir.

This way, two types of technogenic deposits were accumulated in Aktau:

- ore wash tailings: black, organically enriched clays, the most abundant;
- rare earth industrial sludge, limited by the sludge reservoir volume.

According to E.A. Pirmatov et al. [7], the content of rare-earth oxides in Aktau mineral technogenic formations comprises 3.67%, including 0.24% of the most valuable heavy group.

The research objective: a study of phase and mineral composition of enrichment products from technogenic wastes, that is phosphogypsum, formed as a result of reprocessing of uranium-phosphorus concentrates of fish bone detritus of Neogene-Paleogene marine clays. Of interest are gold and rare-earth phases (minerals) of micro- and nano-size.

Sample preparation and research methods

Material preparation and enrichment to obtain representative samples (enrichment products) for mineralogical, chemical, and other types of analyses were implemented according to the developed technological procedure for the enrichment of gold and rare earth element (REE) samples [[10], [11]]. The technology included additional operations for deep disintegration of sample material in a self-crushing mill and thermal activation (RK Patent No. 7613 [10]) of bulk analytical samples allowing approaching closely to the enrichment and quantitative determination of micro- and nano-components of ores.

Products of all reprocessing stages were analyzed in the Mineralogy Laboratory in K.I. Satbayev Institute of Geological Sciences (Almaty). To study the mineral and elemental composition, the samples were separated in heavy liquids into light and heavy fractions, followed by the separation of the heavy fraction into magnetic, electromagnetic, and non-magnetic. Grains of minerals, selected under a binocular, were studied by drop-microchemical, luminescent analyses, and electron probe microanalysis.

The following research methods were employed to identify micro- and nano-mineral components of enrichment products from technogenic wastes: optical microscopy (LEICA DM2500P), X-ray phase (DRON-3 with PDF2 Release 2022), spectral (semi-quantitative) analyses, atomic absorption (Thermo ICE 3500 spectrometer) analyses, electron probe (JCXA 733 with INCA ENERGY energy dispersive spectrometer). The chemical analyses were implemented in an accredited laboratory (NKZ.T03.1460 as of February 28, 2019) by EcoLux-As LLP (Stepnogorsk).

Research results

The initial material was white with a yellowish tint homogenous sludge formed from the sulphuric acid processing of uranium-phosphate ores at the hydrometallurgical plant.

Thanks to our own technique of initial material pre-processing of mechanical and thermal activation (RK Patent No. 7613 [10]), it became possible to concentrate ore load in small weight mineralogical batches (finishing concentrates) and to obtain the technological parameters on gravitation enrichment of gold (Table 1, Table 2) and REE (Table 3). Table 1 shows the results of the gravity concentration of stockpiled tailings (sludge) after mechanical activation in a self-crushing mill. As the material is fine-grained and clumpy, manual disintegration was ineffective. The yield of non-disintegrated "lumps" was ~15 %, mechanical ~1.5 %. Therefore, enrichment was carried out after the mechanical activation of the initial material in the self-crushing mill.

Native gold in the form of single, micron-sized grains was detected in the gravity concentration products. In Figure 1, the gold particle is in phosphate-(Fe). The elemental composition according to electron probe microanalysis (%) is Cu 12.85, Ag 4.51, and Au 82.65.

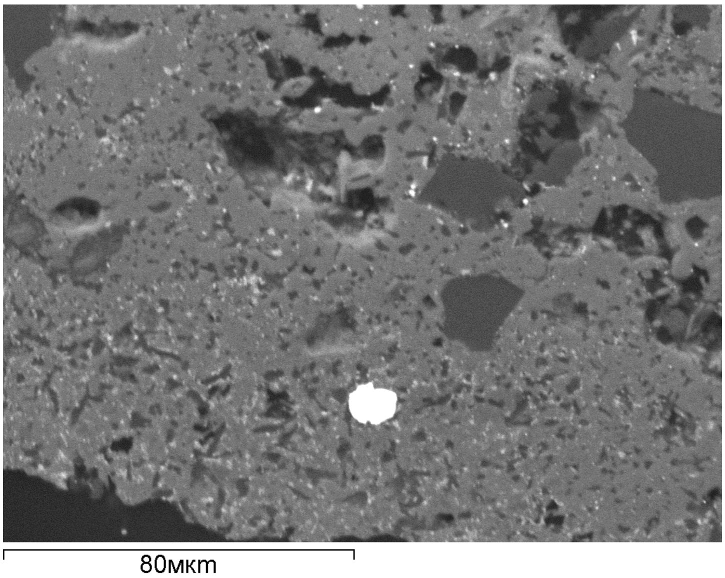
To study dispersed gold, samples were taken from the final tailings after their mechanical and thermal treatments (at 750-800°C) in a thermal activator [10]. It is assumed that heating causes the enlargement of dispersed gold nanoparticles up to micron size [[10], [11]] with their subsequent extraction into grave-concentrate (Table 2).

"Invisible" dispersed gold predominates in the technogenic wastes according to a study of enrichment products. The gold content in the initial material was 2.93 g/t, which after thermal activation of the sample increased to 6.37 g/t.

Table 1 - Results of gravity concentration of stockpiled tailings (sludge) after mechanical activation in the self-crushing mill

Enrichment products	**Output**		**Gold content, g/t***	**Gold recovery, %**
	kg	**%**		
Vibratory screw separator concentrate re-processing concentrate (VCRC)	0.025	0.17	4.79	0.27
Vibratory screw separator concentrate re-processing tailings (VCRT)	0.092	0.62	2.36	0.50
Centrifugal apparatus concentrate (CAC)	0.031	0.21	6.74	0.47
The final tails	14.652	99.0	2.92	98.60
Source material: stockpiled sludge (sludge)	14.80	100	2.93	100

Note: *Protocol No.0003 of the Eco-Lux-As LLP dated 06.01.2022



The matrix material is phosphate-(Fe) (gray) in association with REE-bearing phosphate-Silicate-Fe nanoparticles (white dots), quartz (dark gray)

Figure 1 – Micron inclusion of gold (white). *BEI*

Table 2 - Results of gravity concentration of final tailings after their mechanical and thermal treatments with thermal activator coal

Enrichment products	**Output**		**Gold content, g/t***	**Gold recovery, %**
	kg	**%**		
Thermal activator coal	130	34.12	2.25	12.09
Centrifugal apparatus concentrate (CAC)	30	7.88	5.06	6.38
Tails	221	58.0	8.97	81.63
Initial (Ini.) material (enrichment products + thermal activator coal)	381	100	6.37	100

Note: *Protocol No.0013 of Eco-Lux-As LLP dated 20.01.2022

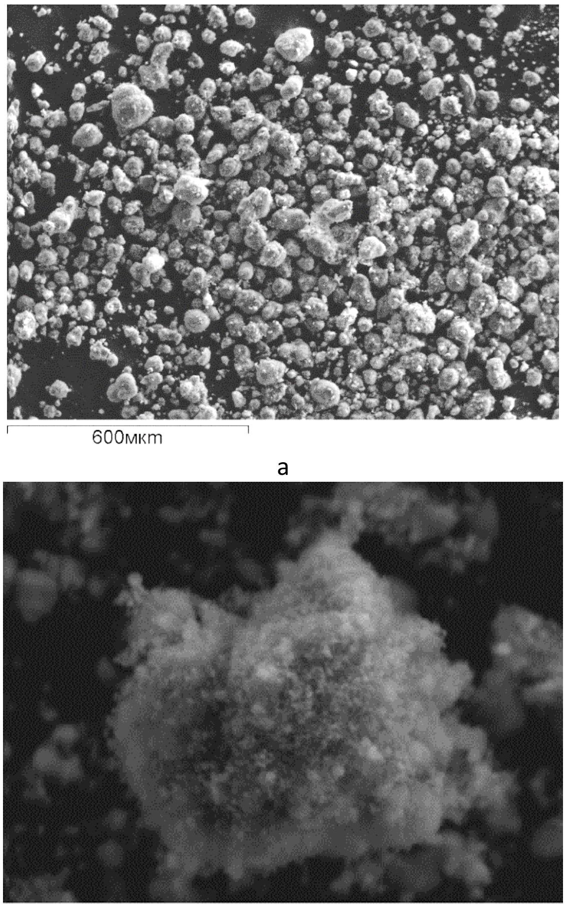
Table 3 – Bulk chemical composition (normalized to 100%) (wt.) of heavy fraction sample from enrichment products (average for 3 analyses)

Analysis components	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
O	43.50	38.00	41.57	39.44	40.06	40.73	38.74	45.06	39.64
F	0.00	0.00	9.18	9.39	9.06	9.65	8.78	0.00	0.00
Na	1.07	1.12	0.48	0.61	0.80	0.80	0.57	2.14	0.94
Mg	1.59	1.67	3.43	3.72	1.7	3.75	4.12	1.84	1.66
Al	3.22	3.39	3.95	3.89	2.35	4.16	4.20	5.07	3.57
Si	9.22	8.47	1.21	0.51	4.58	1.59	0.85	12.40	11.52
P	10.75	10.31	19.49	21.97	10.28	18.69	22.17	7.88	8.92
S	0.37	0.41	0.59	0.32	2.50	0.84	0.53	0.82	0.66
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.27	0.15
K	0.61	0.69	0.19	0.04	0.29	0.18	0.10	1.47	0.81
Ca	5.09	2.36	5.53	3.83	14.29	6.20	3.56	6.16	5.30
Ti	0.00	0.36	0.00	0.00	0.00	0.00	0.00	0.29	0.47
Cr	0.85	4.49	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	21.2	24.29	11.62	12.26	11.27	11.70	12.84	15.88	25.32
Ni	0.83	2.53	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	2.01	0.39	0.00	0.00	0.00
La	0.27	0.67	0.55	0.73	0.15	0.41	0.66	0.34	0.38
Ce	0.68	0.94	1.01	1.45	0.67	0.92	1.26	0.37	0.64
Pr	0.17	0.00	0.27	0.41	0.00	0.00	0.28	0.00	0.00
Nd	0.32	0.00	0.56	0.68	0.00	0.00	0.75	0.00	0.00
Sm	0.23	0.00	0.26	0.26	0.00	0.00	0.31	0.00	0.00
Eu	0.21	0.00	0.00	0.20	0.00	0.00	0.12	0.00	0.00
Gd	0.12	0.00	0.2	0.29	0.00	0.00	0.26	0.00	0.00
∑	100	100	100	100	100	100	100	100	100

Note: 1 - REE-1 Fc (finishing concentrate) of technogenic mineral formations (TMF) concentrate sample, 2 - REE-2 Fc of TMF concentrate sample, 3 – REE VCRT sample, 4 –REE tailing sample, 5 – REE CAC sample, 6 – REE VCRC sample, 7 – REE VCRT sample, 8 – REE-1 Ini. Fc of VCRC sample, 9 – REE-1 Ini. Fc of VCRC sample

During the study of the material composition of samples for REE, the refined products were divided into light, magnetic, electromagnetic, and non-magnetic fractions. The light fraction was found to contain gypsum, quartz, feldspar, hydromica, chlorite, phosphates, and rarely carbonates. The magnetic fraction contained mainly dark brown iron ochre in the form of crusts and rarely magnetite in the form of rounded formations. The electromagnetic fraction contained the main mass in the form of phosphates, less often hematite, ilmenite, iron hydroxides, limonite on pyrite, amphibole, epidote-zoisite, light pink garnet, dark green pyroxene, and extremely rare single occurrences of tourmaline, titanite, mica (biotite). The non-magnetic fraction of samples has mainly white, light gray spherical, and columnar aggregates of phosphates and sulfates, transparent apatite; less often zircon, pyrite, rutile, white barite, and carbonates.

According to the spectral analysis, products of all stages of enrichment are characterized by high content (g/t) of yttrium up to 500, light and heavy REEs: lanthanum up to 500, cerium up to 1500, praseodymium up to 10 000, neodymium up to 3 000, samarium up to 1 500, gadolinium up to 1 500, terbium up to 1 000, dysprosium up to 1 000, erbium up to 300, ytterbium up to 1 000. According to electron-probe microanalysis, the bulk elemental composition of products mainly contains light REEs, with high values (%) for cerium up to 1.49; lanthanum up to 0.88; praseodymium up to 0.86; neodymium up to 1.03 (Table 3). The grains of heavy fraction samples selected and preliminary studied on pucks (semi-quantitative analysis) in SEI mode are mainly lumpy loose rounded macroaggregates (Figure 2 a) made of nano-sized grains (Figure 2 b).



a

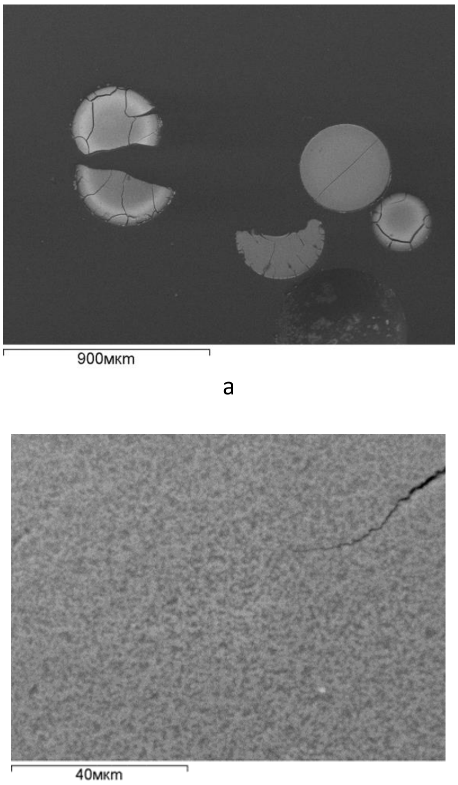
b

Figure 2 – Micro-aggregates from heavy fraction sample. *SEI.* General view of rounded lumpy micro-aggregates – a, shape and size of a rounded micro-aggregate consisting of nano-sized grains of Fe phosphates and REE-bearing apatites – b.

To determine elemental composition and forms of REEs occurrence in *BEI* mode (compo), grains of samples, i.e. concentrates of different reprocessing stages from the non-magnetic fraction were placed on polished sections. In the detailed figure, the grains turned out to be inhomogeneous aggregates consisting of many nano-sized phases. In finishing concentrate (sample REE-2 Fc of TMF concentrates) light and heavy REEs were revealed in heterogeneous xenotime phase (Table 4, analysis 1); light REEs and yttrium are part of fluorine-free apatite (Table 4, analyses 2-5).

In analysis 2-5, the remaining iron, aluminum, magnesium, and chromium, according to X-ray phase analysis (Table 3), can enter lipscombite $Fe_{2.95}(PO_4)_2(OH)_2$, iron and aluminum phosphate $Al_{0.67}Fe_{0.33}(PO_4)$, magnetite $Mg_{0.04}Fe_{2.96}O_4$, Mg-bearing hercynite $Fe_{0.77}Mg_{0.29}Al_{1.91}O_4$, Mg-bearing chromite $(Fe_{0.65}Mg_{0.35})Cr_2O_4$. In Figure 1, a microparticle of gold in phosphate-(Fe) (analysis 6) is in association with nano-sized grains of REE-bearing phosphate Silicate-Fe and quartz.

In addition to rounded loose macroaggregates, there are homogeneous and zonal globular micro formations in the VRRC sample, cracked under conditions of high vacuum and temperature effect of the electron beam. In slices, the globular formations are homogeneous or zonal (Figure 3 a). In zonal ones, the outer rim consists of a heavy REE-bearing phase of sulfo-phosphate Ca and F, while the composition of the inner part is the same only with lower REEs content. In the detailed figure of the central part of globular formations, their heterogeneity is clearly visible. Like loose micro-aggregates, these formations are composed of nano-sized phases (Figure 3 b).



a

b

Figure 3 - Spherical formations of VRRC sample. *BEI*. The zoning of globular formations - a, heterogeneous structure of the inner part of the globular formation - b.

Table 4 - Chemical composition (wt.%) of heterogeneous grains in the finishing concentrate sample

Analysis	**1**	**2**	**3**	**4**	**5**	**6**
Components	**Finishing concentrate sample (sample REE-2 Fc of TMF concentrates)**					
F	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O	0.00	0.00	0.00	0.00	0.00	1.70
MgO	0.00	2.24	3.77	2.26	2.27	0.73
Al_2O_3	0.00	6.15	8.22	5.85	5.47	1.43
SiO_2	0.00	0.00	0.00	0.00	0.00	0.00
P_2O_5	38.39	51.45	50.25	46.36	44.95	40.83
SO_3	0.00	0.00	0.00	0.00	0.00	0.00
CaO	2.73	4.55	3.14	5.09	4.46	3.21
TiO_2	0.00	0.56	0.00	0.33	0.65	0.25
Cr_2O_3	0.00	0.00	0.85	0.58	0.60	1.89
FeO	1.95	25.66	21.59	21.90	20.97	47.15
NiO	0.00	0.00	0.00	0.00	0.00	0.82
Y_2O_3	23.31	2.72	1.85	3.39	2.19	0.00
La_2O_3	3.46	1.65	1.39	1.19	1.85	0.00
Ce_2O_3	6.33	2.28	2.45	1.70	2.23	0.00
Pr_2O_3	1.07	0.05	0.46	0.19	0.03	0.00
Nd_2O_3	3.77	0.94	1.61	1.07	1.29	0.00
Sm_2O_3	1.45	0.14	0.27	0.35	0.73	0.00
Eu_2O_3	0.67	0.21	0.30	0.16	0.50	0.00
Gd_2O_3	2.92	0.35	0.64	0.13	0.60	0.00
Tb_2O_3	0.62	0.00	0.00	0.00	0.00	0.00
Dy_2O_3	3.11	0.00	0.00	0.00	0.00	0.00
Ho_2O_3	0.46	0.00	0.00	0.00	0.00	0.00
Er_2O_3	2.13	0.00	0.00	0.00	0.00	0.00
Σ	92.37	93.51	93.08	83.78	84.42	98.01

The enriched products studied by X-ray phase analysis are represented by poorly crystallised phases, which (considering the results of electron probe microanalysis) may presumably be of the following composition (Table 3): whitlockite $Ca_{18}Mg_2H_2(PO_4)_{14}$, iron hydroxide phosphate $Fe_4(PO_4)_3(OH)_3$, iron and aluminium phosphate $Al_{0.67}Fe_{0.33}(PO_4)$, lipscombite $Fe_{2.95}(PO_4)_2(OH)_2$, pyroaurite $(Mg_6Fe_2(OH)_{16}(CO_3)(H_2O)_{4.5})_{0.25}$, phosphocyclite-(Fe) $Fe_2(P_4O_{12})$, rhodolicoite $Fe(PO_4)$, hydroxyapatite $Ca_5(PO_4)_{2.928}O_{1.3}H_{1.44}$, F-bearing hydroxyapatite $Ca_5(PO_4)_3((OH)_{0.8}F_{0.2})$, aluminium phosphohydroxide $Al_4(PO_3H)_6$, $Al(H_2P_3O_{10})(H_2O)_2$, $Al_2(P_2O_{11})FH_7$, iron phosphate $Fe_2(P_4O_{12})$, where REEs are apparently present in fluorine and fluorine-free phosphates (in apatite, by substitution of calcium, and in xenotime, monazite).

Initial samples, tailings and concentrates after thermal treatment in thermal activator [10] were again divided into light, magnetic, electromagnetic and non-magnetic fractions and studied by a complex of methods. Minerals of the light fraction are represented by quartz, feldspar, mica, graphite and fragments of grayish-black phosphorus-bearing minerals. The magnetic fraction contains brown and dark-brown iron ochres (technogenic) in the form of crusts; the electromagnetic fraction consists of iron hydroxides, hematite, less frequently epidote-zoisite, light pink garnet, dark green pyroxene, ilmenite, titanite, and ash-grey lumpy phosphorus-bearing aggregates; non-magnetic fraction, mainly light grey, ash-grey phosphate, rarely apatite and columnar white phosphate, zircon, pyrite.

According to semi-quantitative spectral analysis, content of all thermal products (thermal tails, thermal concentrate, thermal initial) increased (g/t) as follows: yttrium up to 5000; REE: lanthanum up to 1500, cerium up to 5000, praseodymium <10,000, neodymium <10,000, samarium up to 1000, gadolinium up to 2000, dysprosium up to 1500, erbium up to 500, lutetium up to 300.

According to electron probe microanalysis, the bulk elemental composition of three thermo samples contain significant amounts of light REEs compared to heavy ones (%): cerium up to 1.76; lanthanum up to 1.10; neodymium up to 0.98; samarium up to 0.42; gadolinium up to 0.62; europium up to 0.62. For exact determination of REEs occurence, polished sections with selected grains of non-magnetic fraction of thermal products were prepared. The secondary electron images (SEI) show thermal samples as aggregates of rounded, sometimes hollow, microparticles (Figure 4).

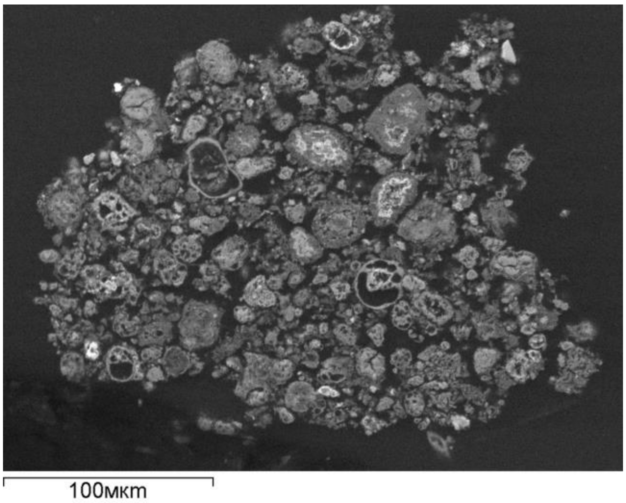


Figure 4 - Porous aggregates of thermo-products (thermo-tails) consisting of round particles. *SEI*

The rounded aggregates are heterogeneous, often zonal (Figure 5) and consist of nano-sized phases. The heavy phases are phosphates of REEs and Fe. The dense phases of the rims do not contain REEs and are close in composition to iron phosphates. There are frequent phases closer to the florensite composition, with significant contents of light REEs. In zonal rounded aggregates (Figure 5), the central part consists of nano-sized REE-bearing heavy phases: REE and iron phosphates, the outer shell is lighter due to the lower content of REE phosphate.

In thermal products, according to X-ray phase analysis, REEs are included in phosphates: florensite and phases $Ce(P_5O_{14})$, $Ca_8MgSm(PO_4)_7$. In Figure 6, heavy rounded inhomogeneous microinclusions of REE phosphate (florensite) and iron phosphate are located in a porous matrix of lazulite composition $MgAl_2[PO_4]_2(OH)_2$.

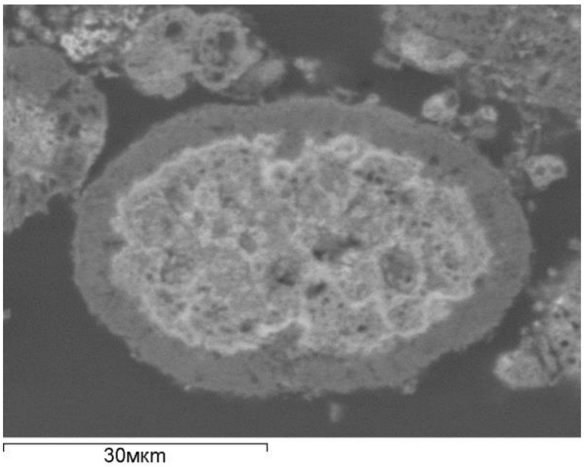


Figure 5 - Rounded formations of a thermal sample. BEI. The central part of rounded heavy formations (white) with a high content of REE, the shell with a lower content of REE is a lighter phase (gray)

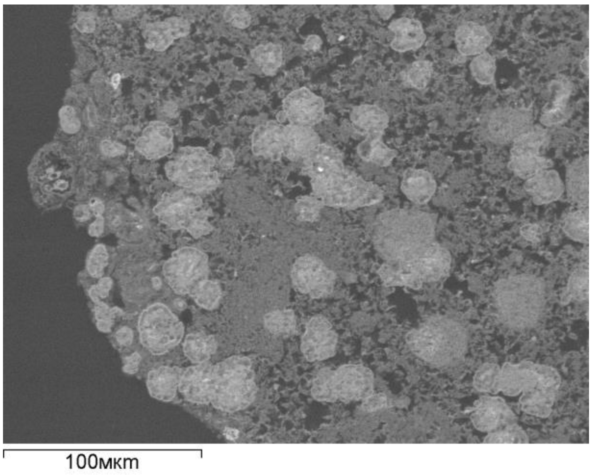


Figure 6 - Rounded inhomogeneous grains of REE-bearing inclusions (florensite) in a porous matrix of lazulite composition. Pores (black). *BEI*

The diffraction patterns of the three thermal products, as well as the bulk elemental composition, almost do not differ from each other (Table 5). According to X-ray phase analysis, the main phases in the heavy fraction of thermal products, considering the bulk elemental composition presumably can be: iron phosphates $Fe_2Fe(P_2O_7)_2$, rodolicoite $Fe(PO_4)$, phosphocyclite-(Fe) $Fe_2(P_4O_{12})$; REE-bearing phosphates $Ce(P_5O_{14})$, florensite-(Ce) $Al_3(Ce_{0.54}La_{0.27}Nd_{0.11}Sm_{0.04}Ca_{0.04})(PO_4)_2(OH)_6$ and $Ca_8MgSm(PO_4)_7$, and iron oxides.

Table 5 – X-ray powder diffraction pattern for thermal products

Thermal tails		Thermal concentrate		Thermal inital		Phase
I	*d*изм., Å	*I*	*d*изм., Å	*I*	*d*изм., Å	
-	-	-	-	17.8	4.32	$Fe_2Fe(P_2O_7)_2$, Rodolicoite $Fe(PO_4)$, phosphocyclite -(Fe) $Fe_2(P_4O_{12})$, $Ca_8MgSm(PO_4)$
53.2	4.14	45.9	4.14	53.9	4.13	Al(PO4), $Ca_8MgSm(PO_4)$, $Al(PO_4)$, $Ca_{19.1}Mg_{1.56}Fe_{0.44}(PO_4)_{14}$
-	-	15.1	3.69	-	-	$Al(PO_4)$
17.0	3.46	28.6	3.45	15.3	3.45	$Fe_2Fe(P_2O_7)_2$, Rodolicoite $Fe(PO_4)$, florencite -(Ce) $Al_3(Ce,La,Nd,Sm,Ca)(PO_4)_2(OH)_6$, $Ca_8MgSm(PO_4)$,
-	-	28.4	3.35	-	-	$Fe_2Fe(P_2O_7)_2$, florencite-(Ce) $Al_3(Ce,La,Nd,Sm,Ca)(PO_4)_2(OH)_6$, $Ca_8MgSm(PO_4)$
100.0	3.03	100.0	3.03	100.0	3.03	$Fe_2Fe(P_2O_7)_2$, phosphocyclite-(Fe) $Fe_2(P_4O_{12})$, calcite $Ca(CO_3)$, $Ca_8MgSm(PO_4)$, $Ca_{19.1}Mg_{1.56}Fe_{0.44}(PO_4)_{14}$
36.5	2.93	40.7	2.93	39.1	2.93	$Fe_2Fe(P_2O_7)_2$, florencite-(Ce) $Al_3(Ce,La,Nd,Sm,Ca)(PO_4)_2(OH)_6$
34. 8	2.86	40.6	2.86	28.2	2.85	$Fe_2Fe(P_2O_7)_2$, $Ca_8MgSm(PO_4)$,
-	-	10.3	2.70	-	-	$Fe_2Fe(P_2O_7)_2$, florencite-(Ce) $Al_3(Ce,La,Nd,Sm,Ca)(PO_4)_2(OH)_6$, phosphocyclite-(Fe) $Fe_2(P_4O_{12})$, $Ca_8MgSm(PO_4)$, hematite $Fe_{1.987}O_3$
16.8	2.54	20.3	2.55	18.8	2.55	$Fe_2Fe(P_2O_7)_2$, Al(PO4), $Ca_8MgSm(PO_4)$, hematite $Fe_{1.987}O_3$, $Al(PO_4)$, $Ca_{19.1}Mg_{1.56}Fe_{0.44}(PO_4)_{14}$
-	-	10.5	2.13	-	-	florencite-(Ce) $Al_3(Ce,La,Nd,Sm,Ca)(PO_4)_2(OH)_6$, phosphocyclite-(Fe) $Fe_2(P_4O_{12})$

Research Discussions

The enrichment products from technogenic wastes are difficult objects for research, because are represented by heterogeneous micro-sized aggregates with nano-sized grains of various minerals and phases (Figure 2 b, 4). X-ray analysis in the case of nano-sized grains is uninformative, since such samples are X-ray amorphous. In an electron probe, even under a focused beam on nano-sized inhomogeneity, the bulk elemental composition of several nano-sized dispersed phases is obtained. The composition varies not only from grain to grain, but also from site to site in one grain. The identification of phases is hindered by a diverse set of elements, and the construction of correlations is hindered by their different number. So, it may turn out in practice that complex REE-bearing sulfo-phosphates and phosphate silicates are mixtures of nano-sized grains of sulfate (gypsum) with apatite and apatite with silicate, respectively, therefore, it is necessary to return to the study of technogenic wastes every time to clarify the technology of their enrichment.

The authors of this study revealed fine gold and increased REE content in technogenic deposits of uranium-phosphate processing of CMMP deposits for the first time. According to earlier studies, gold and other noble metals are present in phosphate deposits in different regions of the world (Alaska, North Africa, East European platform, oth.) [[12], [13], [14], [15], [16]]. A tendency was established for selective concentration of gold in phosphorites, the genesis of which is associated with organic matter of bottom sediments, extracting these elements from sea or silt water [15]. Chinese colleagues noted the presence of platinum, silver and, less frequently, gold in phosphorites [12], with platinum being extracted for many years from phosphorite enrichment tailings. In this regard, of scientific interest is the obtainment of a formation of phosphorus-rare-earth with nanoscale gold from the coastal-marine and shelf zones of ancient Cretaceous-Paleogene deposits of Kazakhstan, as a new very promising source of gold and rare earths.

In the Mangistau region, the known uranium-phosphorite deposits Melovoye, Tomak, Taibor, and Tasmuryn, where technogenic deposits we have already studied, are the objects of the Mangistau scandium-rare-earth-phosphorus-uranium Oligocene mineral complex of the Caspian uranium-ore province. They are found in sedimentary deposits, organogenic clays saturated with fragments of bone and plant detritus, and sulphides. In addition to uranium, they contain rare earth, phosphorous, rhenium, and other elements. As the researchers note, all of them are unique, syndiageneous, complex scandium-rare-earth-phosphorus-uranium, sorbobiogenic, associated with dark grey clay horizons, saturated with bone, mainly fish, detritus [[17], [18], [19], [20], [21]].

In view of the above, other areas in Kazakhstan, where similar marine phosphorite-bearing deposits of Cretaceous-Paleogene age are also developed, are of interest.

There are phosphorite deposits in the Aktobe Urals region and in the Mangyshlak Island, which belong to the Cretaceous Mangystau-Aktobe phosphorus terrigenous mineragenic complex (Shilisai, Alga, etc.) [[18], [19]]. The Cretaceous phosphorite-bearing sediments include sandy, calcareous clays, glauconitic-quartz sandstones, carbonaceous clays, siltstones, marls, chalks, partially cemented nodular-sandy phosphorites, quartz-glaukonitic sands, polymictic crossbedded sands impregnated with iron oxides with small iron peas, boulder-like sandy-limey concretions.

Phosphorite-bearing objects of Eocene age are common in East Aral, and are associated with the glauconite-terrigenous formation. The rocks contain isolated fragments of ostracod shells and sponge spicules. In thin sections, scraps of minute diatoms replaced by brown carbonaceous matter and phosphate are observed in the phosphate cement matter. In the Syr Darya region, Central Kyzylkum [19], the phosphorite-bearing sediments are represented by terrigenous carbonate formation. The granular phosphorites and phosphorite-bearing rocks are mainly composed of phosphatized organogenic material (phosphate biomorphoses, bones) and chemogenic formations, oolites.

The phosphorus-rich brown-iron objects of the Ayat iron-ore basin are of interest [22]. At the Ayat deposit, depressions of the Paleozoic basement contain Lower Cretaceous lake-marsh-type sediments: clays, sands, and sandstones with commercial deposits of bauxite and refractory clays, and above are Cretaceous and Tertiary marine deposits represented by basal conglomerates, siderite sandstones, quartz and quartz-glauconite sands, clays and loams with phosphorites and marine fauna.

During geological surveys in the eastern side of the Turgai Trough, geologists found [19] significant areas of Upper Cretaceous and Paleogene phosphoritic nodules close to the surface.

In Northern Kazakhstan, glauconite and phosphorite occurrences of the Cretaceous age are widespread in the Selety district [[19], [23], [24], [25]] (phosphorite and glauconite deposit of Selety, glauconite of Izobilnenskoye).

In the Upper Jurassic-Lower Cretaceous age soil-infiltration deposit of Semizbai the maximum uranium content is noted in clay horizons with a significant admixture of carbonized plant detritus [17].

Conclusions

The enrichment products from technogenic wastes of the Caspian Mining and Metallurgical Plant are difficult objects for research because are represented by heterogeneous micro-sized aggregates with nano-sized grains of various minerals and phases. With nanosized inhomogeneity, the result of electron probe microanalysis will be the bulk elemental composition of several nano-sized dispersed phases, which complicates their identification.

A technological sampling of enrichment products shows that "invisible" dispersed gold predominates in technogenic wastes. Native gold is revealed as single, micron-sized grains. The gold content in the initial material is 2.93 g/t, which increases to 6.37 g/t after sample thermal activation.

According to the data of electron probe microanalysis, REEs are mainly found in nano-sized fluorine and fluorine-free phosphates (in apatite, by substitution of calcium), and in REE phosphates (in xenotime and monazite). In thermal products, REEs are included in phosphates: florensite and phases $Ce(P_5O_{14})$, $Ca_8MgSm(PO_4)_7$.

Total sampling is proposed for gold of the Cretaceous-Paleogene phosphorus-bearing coastal-marine quartz-glauconite and overlapping black Paleogene clays in Selety-Teniz area of Akmola region, Aktobe and Kostanay regions; of infiltration uranium deposits (Semizbai and others), etc. Besides REE, attention should be paid to scandium and rhenium. Sample processing should be carried out with mechanical and subsequent thermal activation of sample material according to the flow chart developed by the authors of this study.

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

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Каспий тау-кен металлургиялық комбинатының техногендік шөгінділерінен өңделген өнімдердегі алтын және сирек жер элементтері (Ақтау, Қазақстан)

***Бекенова Г.К., Перегудов В.В., Левин В.Л., Канатбаев Е.Т., Муратханов Д.Б.**

Сәтбаев университеті, Қ. И. Сәтбаев атындағы геологиялық ғылымдар институты, Алматы, Қазақстан

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ТҮЙІНДЕМЕ

Техногендік шөгінділердің макро- нано-өлшемді деңгейіне дейін өңделген өнімдерін кешенді зерттеу нәтижелері берілген. Өнімдер алдын ала механикалық және термиялық активтендіру арқылы алтын мен СЖЭ үшін зерттелетін үлгі материалды өңдеу және дайындау кезінде гравитациялық байыту әдістерінің әзірлемелерін пайдалану арқылы алынды. Нәтижесінде дара, микрон өлшемді түйіршіктер түріндегі таза алтын және байыту өнімдерін технологиялық сынауға сәйкес, «көзге көрінбейтін» майда дисперсиялық алтынның басымдығы анықталды. Алтынның мөлшері бастапқы материалда 2,93 г/т болса, ал үлгі термиялық белсендірілгеннен кейін 6,37 г/т дейін артады. Спектрлік талдау және электронды зондтық микроанализ нәтижелері бойынша байытудың барлық кезеңдерінің өнімдері иттрий мен СЖЭ мөлшерлері жоғарылайды. СЖЭ пайда болу формалары анықталған. СЖЭ негізінен микро және нано өлшемді фтор және фторсыз фосфаттарда (апатитте, кальцийді алмастыру арқылы), СЖЭ-фосфаттардың өзінде (ксенотимде) және сирек, мүмкін, күрделі сульфофосфаттар мен фосфатты силикаттарда кездеседі. Рентгендік дифракциялық талдауға сәйкес элементтік құрамын ескере отырып наноөлшемді фазалардың біртекті емес агрегаттарынан тұратын термиялық өнімдерде, СЖЭ фосфаттарға кіреді: олар флоренсит және $Ce(P_5O_{14})$, $Ca_8MgSm(PO_4)_7$ фазалары.

Түйін сөздер: алтын, СЖЭ, микро- және наноөлшемді түйірлер, техногендыік шөгінділер, Каспий кен-металлургиялық комбинаты, Қазақстан

	Авторлар туралы ақпарат:
Бекенова Галия Кабешовна	*Геол-мин. ғыл, докторы, профессор, Сәтбаев университеті, минералогия зертханасының жетекшісі, Қ.И. Сәтбаев атындағы Геологиялық ғылымдар институты, Қабанбай батыр к., 69, 050010, Алматы, Қазақстан. Email: bekenova@mail.ru*
Перегудов Валерий Васильевич	*Геолог, ғылыми қызметкер, Сәтбаев университеті, минералогия зертханасы, Қ.И. Сәтбаев атындағы Геологиялық ғылымдар институты, Қабанбай батыр к., 69, 050010, Алматы, Қазақстан. Email: pereval1946@mail.ru*
Левин Владимир Леонидович	*Геол-мин. ғыл, кандидаты, жетекші ғылыми қызметкер, Сәтбаев университеті, минералогия зертханасы, Қ.И. Сәтбаев атындағы Геологиялық ғылымдар институты, Қабанбай батыр к., 69, 050010, Алматы, Қазақстан. Email: levin_v@inbox.ru*
Канатбаев Ерлан Темирбекулы	*Ғылыми қызметкер, Сәтбаев университеті, физикалық-химиялық зерттеу әдістері зертханасы, Қ.И. Сәтбаев атындағы Геологиялық ғылымдар институты, Қабанбай батыр к., 69, 050010, Алматы, Қазақстан. Email: 7087788@mail.ru*
Муратханов Даулет Болатович	*Докторант, ғылыми қызметкер, Сәтбаев университеті, сирек және сирек жер металдар зертханасы, Қ.И. Сәтбаев атындағы Геологиялық ғылымдар институты, Қабанбай Батыр к., 69, 050010, Алматы, Қазақстан. Email: daulet.muratkhanov@satbayev.university*

Золото и редкоземельные элементы в продуктах переработки из техногенных отложений Прикаспийского Горно-Металлургического Комбината (г. Актау, Казахстан)

***Бекенова Г.К., Перегудов В.В., Левин В.Л., Канатбаев Е.Т., Муратханов Д.Б.**

Сатпаев университет, Институт Геологических Наук имени К. И. Сатпаева, Алматы, Казахстан

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АННОТАЦИЯ

Изложены результаты комплексного изучения от макро- до наноразмерного уровня продуктов переработки из техногенных отложений. Продукты получены благодаря использованию наработок по гравитационным методам обогащения в обработке и подготовке исследуемого материала проб на золото и РЗЭ с предварительной их механической и термической активацией. Выявлено: самородное золото в виде единичных, микронной размерности, зерен и, по данным технологического опробования продуктов обогащения, преобладание «невидимого» тонкодисперсного. Содержание золота в исходном материале составляет 2,93 г/т, которое после термоактивации пробы увеличивается до 6,37 г/т. По результатам спектрального анализа и электроннозондового микроанализа для продуктов всех стадий обогащения характерно повышенное содержание иттрия и РЗЭ. Определены формы вхождения РЗЭ. РЗЭ, в основном, находятся в микро- и наноразмерных фтористых и бесфтористых фосфатах (в апатите, путем замещения кальция), в собственно РЗЭ-фосфатах (в ксенотиме) и реже, возможно, сложных сульфофосфатах и фосфатсиликатах. В термопродуктах, состоящих из неоднородных агрегатов наноразмерных фаз, по данным рентгенофазового анализа с учетом элементного состава, РЗЭ входят в состав фосфатов: флоренсита и фаз $Ce(P_5O_{14})$, $Ca_8MgSm(PO_4)_7$.

Ключевые слова: золото, РЗЭ, микро- и наноразмерные частицы, техногенные отложения, Прикаспийский горно-металлургический комбинат, Казахстан.

Информация об авторах:

Бекенова Галия Кабешовна	*Доктор геол.-минер. наук, Сатпаев Университет, Заведующий лабораторией Минералогии, Институт Геологических наук им К.И. Сатпаева, ул. Кабанбай Батыра, 69, 050010, Алматы, Қазақстан. Email: bekenova@mail.ru*
Перегудов Валерий Васильевич	*Геолог-поисковик, научный сотрудник, Сатпаев Университет, лаборатория Минералогии, Институт Геологических наук им К.И. Сатпаева, ул. Кабанбай Батыра, 69, 050010, Алматы, Қазақстан. Email: pereval1946@mail.ru*
Левин Владимир Леонидович	*Кандидат геол.-минер. наук, Сатпаев Университет, лаборатория Минералогии, Институт Геологических наук им К.И. Сатпаева, ул. Кабанбай Батыра, 69, 050010, Алматы, Қазақстан. Email: levin_v@inbox.ru*
Канатбаев Ерлан Темирбекулы	*Научный сотрудник, Сатпаев Университет, лаборатория физических и химических методов исследований, Институт Геологических наук им К.И. Сатпаева, ул. Кабанбай Батыра, 69, 050010, Алматы, Қазақстан. Email: 7087788@mail.ru*
Муратханов Даулет Болатович	*Докторант, научный сотрудник, Сатпаев Университет, лаборатория Редких и редкоземельных металлов, Институт Геологических наук им К.И. Сатпаева, ул. Кабанбай Батыра, 69, 050010, Алматы, Қазақстан. Email: daulet.muratkhanov@satbayev.university*

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Earth sciences

Significant impact on the growth of Solanum lycopersicum in Microbially augmented organic waste

[1]Munir Z.M., [2]Abbasi M.H., [3]Khawar M.B., [1*]Sheikh N.

[1]Institute of Zoology, University of the Punjab, Q-A Campus, Lahore, 54590, Pakistan
[2]Department of Zoology, University of Okara, Okara, Pakistan
[3]Department of Zoology, University of Narowal, Narowal, Pakistan

**Corresponding author email: nadeem.zool@pu.edu.pk*

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ABSTRACT

The objectives of this study were to convert organic and tea waste to organic soil cond conditioners and achieve a 68% reduction in landfilling and illegal dumping of organic waste. The tea was mixed at an incremental ratio of 10% with the organic waste, and the groups were designated as T0-T100 groups, indicating 0% of tea waste and 100% of organic waste in T0 group and 100% of tea waste, and 0% of organic waste in T100 group. The impact of this soil conditioner was later studied on the growth of the *Solanum lycopersicum* (tomato) plant for twenty-one weeks along with the augmentation of waste sludge from the yeast manufacturing unit. Microbial examination, and other physicochemical parameters like pH, temperature, organic carbon, C/N ratio, moisture, cation exchange capacity (CEC), and humidity of the compost were studied. A visual color change indicated the compost maturity for further application. The quality of the soil was analyzed in both pre-compost and post-compost applications. The electrical conductivity of the soil was 3.0 mho with 8.3 pH, 0.84 % organic matter, phosphorous 1.0 mg/kg, and potassium 225 mg/kg with a saturation level of 40%. There was an inverse relation between organic waste and organic matter with the highest percentage of organic matter in the T0 group. Maximum nitrogen content (9.07%), the highest levels of phosphorous (0.7%), and potassium (2.3%) were recorded in the aerobic T0 group. The highest amount of organic carbon (78.23%), maximum CEC (109.09 meq/100g) was found in the aerobic T100 group. The best vegetative post-application growth of tomato plants, flowering, and fruiting was observed in the T60 group. Taken together with our findings, it can be concluded that the organic compost boosted the soil fertility by up to 70% which positively affected the growth of tomato plants.

Keywords: Organic waste, Plant growth, *Solanum lycopersicum*, Environment.

Munir Z.M.	*M. Phil., Institute of Zoology, University of the Punjab, Q-A Campus, Lahore, 54590, Pakistan. Email: zillayisp@gmail.com*
Abbasi M.H.	*Dr., Department of Zoology, University of Okara, Okara, Pakistan. Email: Dr.muddasir@uo.edu.pk*
Khawar M.B.	*Dr. Department of Zoology, University of Narowal, Narowal, Pakistan. Email: babarkhawar@yahoo.com*
Sheikh N.	*Dr., Institute of Zoology, University of the Punjab, Q-A Campus, Lahore, 54590, Pakistan. Email: Nadeem.zool@pu.edu.pk*

Introduction

Organic waste generated in urban settings severely impacts soil health due to its contamination, and application of inorganic fertilizer that leads to poor air quality as well. Recycling waste is a useful way to improve the air and soil quality, by increasing soil fertility through natural ways and cutting down the application of inorganic fertilizers. An average of 72,000 tons of waste is produced and dumped in the ecosystem annually [1] with around a quarter of which gets recycled. Poor recycling of waste is a result of inappropriate recycling regulations in Pakistan [[2], [3]].

Sustainable soil reclamation tends to reduce biological hazards to the farmers in an agricultural community however, the farmers are yet reluctant to apply any soil conditioner to their agricultural land [[1], [4]]. The huge quantities of dumped organic waste can contaminate the soil due to mismanagement or the absence of any regulatory provisions. However, there exist scientific ways to handle the problem, and organic waste can be converted into compost and its application can be suitable and sustainable for environmental solutions. Composting reduces the need for inorganic fertilizers and enhances the growth of beneficial bacteria in the soil that increases fertility. The use of organic waste instead of inorganic fertilizers is more effective both environmentally and economically [5].

Globally, tea is harvested over an area of 2,461 thousand hectares with 3.60 million tons of tea produced in 2007 [5]. According to Food and Agriculture Organization of the United Nations (FAO) reports, the consumption of black tea is expected to reach 2,50,755 tons by 2027 in comparison to 1,72,911 tons in 2007 [6]. Tea waste can be a new climate change agent if it is not properly managed and treated. Aerobic digestion and *in situ* microbes can compost the tea waste in the presence of organic waste at different proportions [7]. For bioremediation of the soils, bioactive molecules and microorganisms share a great nutritional resource [8] that can be considered as an alternate fertilizer that can replace inorganic fertilizers.

Therefore, the aim of this work was to study the impact of microbially decomposed tea and organic waste mix under aerobic and anaerobic conditions, and the potential effects of this compost on the growth of *Solanum lycopersicum* (tomato) plant.

Materials and Methods

Research Design

At the beginning of the research, the design was to collect the raw material from 4 different densely populated areas of Lahore generating a variety of organic waste for composting followed by experiments to study the cherry tomatoes growing in the soil with and without compost. After collection, the samples were sorted to prepare windrows for composting and physicochemical and microbial studies. The four zones were identified as Taj Bagh Housing Society, Wapda Town, Allama Iqbal Town, and Islam Pura.

Investigational Setting

The entire investigation setting was installed at an integrated waste management site, with coordinates 31°24’16.9” N & 74°21’29.5” E and latitude and longitude with sea level elevation of 217 m and equipped with facilities, i.e., good quality water, soil quality and space for experiment setup.

Collection of Raw Materials (Tea and organic waste)

The organic waste containing fruits and vegetable waste was collected besides used tea waste, which was later mixed in different ratios from 0-100%. About a ton of organic waste (rotten fruits & vegetables along with peels) was collected from the designated zones and was transferred to a composting plant in Lahore. At the composting site, the waste was divided into ten weight-based sections and subdivided into two streams, i.e., aerobic, and anaerobic streams. Around 100 kg/day of used tea waste was collected for ten days from the commercial places of Lahore, that included roadside dhabas, restaurants, and hotels in designated zones, and was transported to a composting facility, rinsed with clean water, weighed after removing excess water and portioned. Excessive moisture content was reduced through sun drying without any further physical processing for two consecutive days.

Selection of plant (Tomato)

Solanum lycopersicum (Cherry tomato) seeds were purchased from the market and the plant growth was studied under the impact of compost application in triplicates. The plant selection was based on the area cultivated globally [9].

Chemical Composition of Domestic Organic Waste

Organic waste was examined for C and N, with their ratios estimated, micronutrients like potassium and phosphorus, and organic matter. The chemical composition of tea waste was investigated to determine its C: N ratios, organic matter, and the cation exchange capacity (CEC) value. The acidic nature of tea waste causes its interaction with the organic elements of the organic waste and helps in the conversion of the organic waste to carbon-rich compost.

Water Quality

Good quality bottled water was used during the entire experimentation and the quality and physical characteristics of the water used to water the plants were checked. The values of temperature, pH, chloride, dissolved oxygen (DO), turbidity, nitrate, and phosphate were recorded. Standard operating protocols were followed and laboratory precautions were observed [10] while testing the water quality.

Experimental Setup and Installation

Organic waste including tea waste was shredded and added to the compost plant periodically for 21 weeks after collection from households and tea shops and was further converted into compost through aerobic digestion for further 45 days. Ten windrows (200 Kg compostable material in each windrow) of different combination ratios of tea waste and organic waste (0:100 to 100:0) were prepared for the aerobic composting purpose. Whereas ten composting bins (250 liters) were used for the anaerobic digestion of organic waste. The ratios were calculated using wet tea waste and organic waste along with the augmentation of microbial-rich sludge (90 % liquid and 10 % solids) as a starting point. Temperature, pH, and moisture content were measured daily using calibrated instruments. For the baseline data, samples were obtained and sent to the laboratory. After three days, manual turning was done for periodic aeration of the setup. Effective microorganisms including yeast and prolactin from yeast manufacturing industry wastewater treatment plant sludge were added to the windrows to ensure maximum performance. Sludge was rich in molasses and peptone along with rich microbial growth. The microbial community added ensured speedy organic waste degradation once at the start of the experiment. Compost piles were kept moist (30%) to support microbial growth for degradation of organic content.

Conversion of Organic and Tea Waste into Compost

Windrow and bin composting were used for aerobic and anaerobic composting, respectively. Each sample was carried in a similar environment for ten days, resulting in an equivalent quantity of 100 kg sample for both organic waste and tea waste being mixed in various ratios. Each windrow measured 0.5 m in height, 1.5 m in breadth, and 3 m in length and was separated by about 0.61 m.

The schematic layout of the windrow is provided in Figure 1.

Alluvium soil consisted of river-transported deposits brown in color, homogenous in size, soft to solid silty clay with dissolved salts was used as topsoil. The soil was selected for plantation after examining its pH, permeability, nutritional value, and microbial fauna.

Soil aeration was ensured by manually turning the interior mass of compost to the surface after every 3 days for optimum aeration. Anaerobic decomposition was processed in bins.

Monitoring and Evaluation of Plant Growth Parameters

The compost was applied for 21 weeks to the tomato plant in the experimental groups (T0- T100). Physical, chemical, and biological observations were recorded on weekly basis.

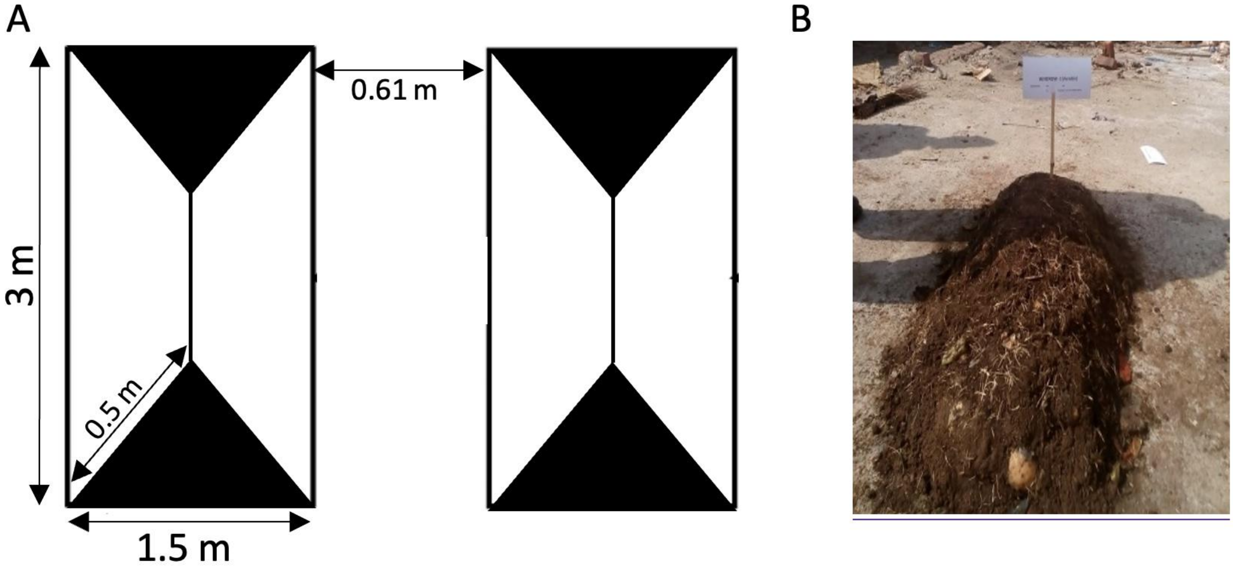

Figure 1 - Windrow (aerobic decomposition) Layout as designed at the experimental site. Each windrow measured 0.5 m high, 1.5 m wide, 3 meters long, and 0.61m apart from each other (A). Each windrow can house 100kg of the tea and waste (percentage-based mix; original picture of windrow; B).

Every week, plant growth indicators like height, flowers, and fruits per pot, were recorded. The physical appearance of the plants, such as the overall condition of the leaf, color, and size was also observed and recorded.

Compost Analysis

Moisture Content

The compost samples were analyzed for moisture by using ASTM D2216-10 standard method. A sample of 0.5 kg compost was weighed and then air dried for twenty-four hours by placing it in a drying oven at 105°C. The weight of the sample was monitored after a regular interval of six hours until no further weight reduction was observed. Hereafter, the final weight along with moisture content was measured through the application of the following formula:

$$Moisture\ Content = \left(\frac{Ww - Dw}{Ww}\right) \times 100$$

Where Dw = Dry weight, and Ww = Wet weight

Temperature

Increased temperature support compost maturation as well as fungal and seed culture growth. A temperature rise predicts the initiation of fungal as well as microbial growth. The thermometer helps to observe the temperature and was inserted in each bag. The temperature rise was monitored in each bag and lately, ambient air temperature was noted for comparison.

Nitrogen

Concentrated acid was used followed by the mixing of homogeneous sample solution, boiling led to decompose N present in organic samples. The excess base (ammonium hydroxide) was added to the acid digestion mixture to convert NH_4^+ to NH_3, followed by boiling and condensation of the ammonia NH_3 gas in a receiving solution. Finally, to quantify the amount of ammonia in the receiving solution titration was conducted and the amount of N in a sample was calculated from the quantified amount of NH_3^+ in the receiving solution.

Odor

Active microbial activity spreads a peculiar odor in compost seeds. Foul order indicates the presence of Nitrogen and its conversion to ammonia. This marks a clear sign of losing nutrients from the soil thus degrading compost seed quality. Excessive release of Ammonia reduces microbial activity in compost seed thus directly affecting the product formed. While reduced order maintains nutrients in the soil thus enhancing compost quality. Excessive release of ammonia gas hinders the microbial activity thus resulting in compost seed degraded quality. Decreased ammonia odor indicates the availability of Nitrogen in the compost seed thus relating to high-quality compost seed.

Color

The change in color of the compost was observed and recorded every week.

pH

The effectiveness of a biological system is determined through the pH factor. pH meter (0-14 scale) was used to determine the pH of the compost thus indicating healthy microbial growth in the compost seed.

Carbon to Nitrogen (C/N) ratios

Another strong parameter that defines the effectiveness of the compost system is the carbon-to-nitrogen ratio. The presence of green leaves, grass trimmings, and clippings of plant structure was high in the Nitrogen versus carbon ratio. In an ideal compost system, the carbon ratio to nitrogen ranges from 20:1 to 30:1. To adjust the ratio, activated sludge was added as a supplement.

Statistical Analysis:

Each experimental setup had three replicates. The data is presented as Mean ± S.E.M. and is analyzed using Pearson correlation and the association was found statistically significant at the level of $P<0.05$.

Research Results

Microbial Augmentation

Tea waste and the organic waste mix were treated aerobically and anaerobically, by applying microbe-rich sludge (90% water, 10 % solid) obtained from the yeast manufacturing unit. The sludge treatment was meant to enhance the decomposition of organic waste under both conditions due to the presence of gram-positive and gram-negative bacteria.

Physical observation of the organic waste has shown a complete color change from light brown to brown to dark brown which indicates the conversion of the organic waste to compost. This color change was an indicator of compost maturation (Figure 2).

Figure 2 - Color change of the compost indicating compost maturation. The color ranges from Light Brown (A) to Brown (B), to Dark Brown (C) which is referred to as mature compost.

Chemical Composition of Organic Waste

The organic waste was found to be rich in different components with varied percentages as listed in Table 1.

Table 1 - Composition of Organic Waste represented in percentage fraction of the weight.

Parameter	Weight (%)	Parameter	Weight (%)
Total volatile solids	45.8	Fat	4.7
Moisture content	76.5	Hemicellulose	8.6
Total organic Carbon	55.6	Lignin	7.9
C/N ratio	18.7	Protein	5.9
Total solids	13.2	Kjeldahl Nitrogen [34]	1.2
Ash	9.4		

Physical Variables of Compost

Average Temperature (°C), pH, and average humidity (%) was recorded further in the first 9 weeks of the experimental period, and found that the average temperature of compost had a decreasing trend, ranging from 11.10 °C in the (8th and 9th week) to maximum of 27.80 °C measured in the 1st week with a mean temperature of 16.29 °C whereas the pH and average humidity had an increasing trend. The lowest pH was 6.12 in the 6th week and the highest pH was in the 9th week of the experiment with an average of 7.08. The minimum humidity recorded was 49% in the 4th week and the maximum humidity was 80.50% in the 6th week of the experiment, with an average humidity of 63.17%.

Physical changes in Compost

Changes in the physical appearance and odor of the compost were recorded during the study period from light to dark brown to black by the 9th week. Similarly, the odor of the compost transitioned from a rotten egg smell to odorless by 7th week making it more environmentally and socially applicable in the fields.

Irrigation Water Quality

The results demonstrated that the bottled water used to irrigate the plants has pH 7.21, turbidity 0.16 NTU, total dissolved solids (TDS) of 1290 mgL-1, sodium, 342.7, potassium 5.4 and fluoride 0.86 mg L-1. All the quality parameters were in range in comparison to standard values of PEQs except TDS and chloride, which were higher than the permissible limits of 1000 mg L-1. and 250 mg L-1, respectively.

Soil Quality

The analysis of soil quality has shown that it has an electrical conductivity is 3.0 mho, pH of 8.3, and organic matter of 0.84%. The quantity of available phosphorous was recorded as 1.0 mg/kg, potassium 225 mg/kg with a saturation level of 40%.

Comparison of Aerobic and Anaerobic Compost

Aerobically and anaerobically prepared compost were analyzed for their contents like organic matter, organic carbon, nitrogen, CEC, phosphorous, and potassium and results were statistically compared with each other (Table 2).

Organic Matter (OM)

An inverse relation was observed between organic waste and organic matter. The highest percentage of OM was recorded in the aerobic T0 group of compost (90.09%) and the lowest (42.86%)

in the T100 group, i.e., 42.86% that shows as the quantity of organic waste increases the percentage of organic matter decreases. For anaerobic conditions, minimum organic matter was found in the T0 group and maximum in the T50 group (85.9%) (Table 2).

Organic Carbon

The highest amount of organic carbon (78.23%) was found in the aerobic T100 group and the lowest (17.32%) in the T0 group. Under anaerobic conditions, the organic carbon was 66.45% in the T100 group whereas it was 16 % in the T0 group (Table 2).

Nitrogen

The maximum nitrogen content (9.07%) was recorded in the aerobic T0 group and the lowest (0.07%) in the T100 group. Under anaerobic conditions, the percentage of nitrogen content increased from T0 to T40 with the highest value of 4.42%, whereas in subsequent samples the percentage of nitrogen content started decreasing to 0.07% in the T100 group (Table 2).

Cation Exchange Capacity (CEC)

The maximum CEC (109.09 meq/100g) was observed in the aerobic T100 group and the lowest CEC in the T0 group. Under anaerobic conditions, CEC was maximum in the T100 group (103.21 meq/100g) (Table 2).

Phosphorous

The highest levels (0.7%) of P were measured in aerobic T0 compost and the lowest (0.02%) in the T100 group. Under anaerobic conditions, the maximum phosphorous percentage (0.70%) was found in the T60 group and the lowest (0.02%) in the T100 group (Table 2).

Potassium

The highest level (2.3%) of potassium was observed in the aerobic T0 group and the lowest (0.05%) in the T100 group. Under anaerobic conditions, the highest levels of potassium were 1.9% in the T0 group, whereas the lowest level of 0.04% was recorded in the T100 group (Table 2).

Correlation of Aerobic Variables

The Pearson correlation and p-values indicated a significant correlation among the different parameters studied. A statistically highly significant and positive correlation was found in OC and OW ($p=0.000$), CEC and OW ($p=0.001$) whereas the correlation of PC and OM ($p=0.000$), N and OM ($p=0.000$), P and OM ($p=0.000$) and K and OM ($p=0.003$) was statistically significant and positive. A significant negative correlation was observed between OM and OW, N and OW, P and OW, and K and OW whereas, the correlation of CEC and N and K and CEC was not significant (Table 23).

Correlation of Anaerobic Variables

The Pearson correlation and p-value for different variables have shown significant correlation, and some variables were negatively correlated. Positive and highly significant correlation ($p<0.01$) was found between variables, OC and OW, CEC and OW, K and N, K and P. A significant correlation ($p<0.05$) was found between K and OC, N and OC, P, and CEC. N and OW, P and OW, K and OW, K and CEC have shown a significant negative correlation (Table 4).

Growth Parameters of Tomato Plant

Three replicates for each treatment and control group were used to study the growth parameters and pattern. Overall, the plants showed a significant increase in growth, height, biomass, flowers, and number of fruits with an increase in the compost application to a limit, which was significantly better in comparison with the control plants. The visual observation indicated that the plants in experimental replicates were lusher green, with greater biomass and leaf area as compared to the control and T100 groups. The plants showed stunted growth and reduced flowers, and fruit numbers per pot containing 100% compost. The experimental setup has no supplement of chemical fertilizer.

Height of Plants

The changes in plant heights were observed after the application of 10 grams of compost in the 8th week. An abrupt increase in height was observed in the pot with 60% organic waste reaching 49.4 inches, followed by all other percentages of organic waste except control and 100% organic waste in which the plant reached a height of 32 and 29.75 inches, respectively (Table 5; Figure 3).

Number of Flowers

The flowering started in the 14th week after the plantation. The first flowering was observed with 3 and 4 flowers per plant in the presence of 60% and 50% organic waste, respectively, with the maximum number of 8 flowers by the 21st week. The control group had an average of one flower and plants grown in 100% organic waste had no flower, whereas by the 21st week, the control group had an average of 2 flowers, and plants grown in 100% organic waste had no flower.

Number of Fruits

Fruiting of plants started in the 18th week after plantation with the first fruit appearing in plants in T60 and T70 groups. The control and 100% organic waste had no fruit by this time. The maximum flowering was observed on plants in T60 and T70 groups by the 21st week whereas, the plants in the control and T100 groups did not get any fruit by the 21st week of planting.

Table 2 - Comparison of aerobic and anaerobic methods of composting and its effects on different parameters of the compost

Sample #	Groups	Tea: Organic Waste (%)	Organic matter (OM)%		Organic carbon (OC)%		Nitrogen (N)%		CEC meq/100 gm		Phosphorous		Potassium	
			Aerobic (A)	Anaerobic (AA)	A	AA	A	AA	A	AA	A	AA	A	AA
	Limits		<45%		<20%		<1%		<60%		<0.02%		<0.8 %	
0	T0	0:100	90.09	29.09	17.32	16	9.07	3.1	55.15	50.08	0.7	0.68	2.3	1.9
1	T10	10:90	84.65	32.98	21.67	33.08	8.61	3.67	61.92	53.75	0.66	0.61	2.11	1.8
2	T20	20:80	78.07	39.09	23.5	48.23	7.93	3.99	66.08	59.63	0.61	0.58	2.01	1.7
3	T30	30:70	71.05	44.23	26.33	46.09	7.28	4.1	73.00	68.12	0.58	0.41	1.19	1.5
4	T40	40:60	68.28	53.85	31.04	40.6	6.56	4.42	87.00	78.9	0.5	0.45	1.1	1.3
5	T50	50:50	88.71	85.9	51.4	49.8	3.1	0.69	49.40	80.02	0.65	0.56	0.9	0.6
6	T60	60:40	53.85	68.19	38.23	39.55	4.42	3.32	96.50	100.5	0.36	0.70	1.3	1.1
7	T70	70:30	51.03	66.08	47.65	49.12	2.97	2.14	100.05	98.00	0.13	0.36	1.00	0.07
8	T80	80:20	47.21	62.53	63.28	57.98	1.25	1.98	102.09	101	0.09	0.11	0.08	0.06
9	T90	90:10	44.56	46.25	71.09	61.09	0.09	1.36	106.11	102.01	0.05	0.06	0.07	0.05
10	T100	100:0	42.86	42.86	78.23	66.45	0.07	0.07	109.09	103.21	0.02	0.02	0.05	0.04

Table 3 - Correlation of Aerobic Variables

	OW (%)		**OM %**		**OC %**		**N%**		**CEC (meq/100 g)**		**P**	
OM%	-0.897	0.000‡										
OC%	0.957	0.000‡	-0.773	0.005†								
N%	-0.976	0.000‡	0.803	0.003†	-0.985	0.000‡						
CEC	0.831	0.001‡	-0.988	0.000‡	0.312	0.014	-0.74	0.009				
P	-0.933	0.000‡	0.964	0.000‡	-0.869	0.001‡	0.883	0.000‡	-0.942	0.000‡		
K	-0.943	0.000‡	0.804	0.003‡	-0.964	0.0000‡	0.941	0.000‡	0.753	0.007	0.847	0.001‡

Table 4 - Correlation of Anaerobic Variables

	OW (%)		**OM %**		**OC %**		**N%**		**CEC (meq/100 g)**		**P**	
OM%	0.439	0.177										
OC%	0.859	0.001‡	0.339	0.308								
N%	-0.727	0.011†	-0.372	0.26	-0.617	0.043†						
CEC	0.962	0.000‡	0.561	0.072	0.748	0.008‡	-0.602	0.050†				
P	-0.821	0.002‡	-0.014	0.967	-0.830	0.002‡	0.605	0.048†	-0.675	0.023†		
K	-0.949	0.000‡	-0.52	0.101	-0.811	0.002‡	0.798	0.003‡	-0.902	0.000‡	0.804	0.003‡

Highly Significant=‡ (<0.001), Significant=† (<0.005)

Table 5 - Growth of plants record from week 2 onwards after sowing the seeds. The plant growth started increase after the application of the compost in week 8

Week	Control	T0	T10	T20	T30	T40	T50	T60	T70	T80	T90	T100
2	0.73±0.01	0.78±0.01	0.88±0.01	0.88±0.01	0.69±0.01	0.89±0.01	0.69±0.01	0.74±0.02	0.88±0.01	0.84±0.03	0.79±0.01	0.75±0.03
3	3.6±0.04	2.98±0.01	2.43±0.73	3.27±0.06	3.4±0.03	3.06±0.18	3.62±0.37	4.01±0.01	3.99±0.01	3.36±0.31	3.6±0.28	3.92±0.02
4	5.27±0.12	5.4±0.06	5.37±0.09	5.47±0.09	5.4±0.06	5.7±0.06	5.6±0.06	5.8±0.15	5.73±0.09	5.33±0.88	5.57±0.09	5.8±0.06
5	6.5±0.06	6.4±0.06	6.7±0.06	6.5±0.06	6.6±0.06	6.4±0.06	6.9±0.06	6.7±0.15	6.5±0.12	6.4±0.17	6.7±0.12	6.6±0.06
6	7.05±0.03	7.11±0.07	7.08±0.03	7.12±0.02	7.15±0.02	7.13±0.04	7.07±0.05	7.09±0.02	7.08±0.04	7.1±0.05	7.15±0.02	7.12±0.05
7	8.62±0.04	8.69±0.02	8.72±0.04	8.79±0.04	8.41±0.22	8.37±0.2	8.27±0.08	8.65±0.01	8.76±0.06	8.55±0.2	8.17±0.01	8.19±0.01
8	10.62±0.01	10.63±0.03	10.63±0.12	10.59±0.32	10.77±0.12	10.68±0.06	10.4±0.22	10.36±0.22	10.71±0.17	10.71±0.06	10.4±0.22	10.33±0.2
9	13.41±0.32	13.71±0.09	14.11±0.22	14.34±0.28	14.38±0.36	14.12±0.35	13.16±0.4	13.23±0.67	13.67±0.56	14.09±0.37	13.66±0.13	13.2±0.43
10	14.15±0.51	14.5±0.38	14.99±0.58	15.53±0.64	15.58±0.79	16.36±0.19	16.11±0.4	14.72±1.19	13.89±1.08	15.05±1	15.18±0.11	14.47±1.06
11	13.7±0.01	16.53±0.03	18.57±0.18	16.67±0.09	16.53±0.09	16.4±0.06	16.33±0.09	16.36±0.09	16.33±0.09	16.6±0.21	16.27±0.12	14.3±0.06
12	16.79±1.38	16.86±1.42	18.39±0.22	18.6±0.25	18.46±0.22	18.42±0.14	18.48±0.26	17.37±1.09	15.84±1.26	15.58±1.56	16.68±1.33	17.14±0.94
13	18.57±1.39	19.68±0.18	19.52±0.19	21.04±1.43	23.1±1.9	23.03±2	23.08±0.82	22.51±1.76	20.34±2.01	18.07±1.72	18.48±1.35	18.78±0.92
14	20.23±1.53	21.4±0.42	22.02±0.04	22.84±1.02	25.49±2.21	24.07±2.8	21.96±1.45	23.5±3.05	21.15±0.69	20.07±1.56	19.39±1.11	21.69±0.57
15	20.98±0.32	22.04±0.48	22.01±0.49	23.09±0.91	23.6±2.56	22±9.46	25.76±10.19	24.1±3.31	23.42±11.26	22±0.86	21.76±0.36	24.8±0.55
16	21.98±0.89	23.5±0.06	23.76±0.06	23.99±0.05	23.5±0.24	24.18±1.25	27.98±2.86	26.6±4.17	24±0.13	23.5±0.02	23.5±0.89	26.5±1.8
17	23.89±0.97	25.79±0.05	25.36±0.32	24.78±0.05	27.99±0.12	26.39±1.16	31.72±3.02	34.16±3.61	26.38±0.57	26.82±1.59	29.49±0.51	27.89±1.85
18	24.68±1.64	28.29±0.34	28.7±0.27	27.88±0.27	28.26±0.93	30.9±0.78	34.53±2.07	37.75±0.93	34.57±1.32	31.74±0.2	30.59±0.74	28.19±0.51
19	27.25±0.82	29.33±0.44	30.29±0.08	30.94±0.5	32.25±0.31	34.09±1.21	38.56±2.04	40.64±1.99	35.67±1	33.4±0.27	32.03±0.82	30.35±0.07
20	28.25±0.86	31.06±0.59	33.23±0.72	38.71±4.06	38.94±3.61	34.44±2.2	39.36±3.76	46.13±4.53	37.78±3.94	40.95±2.17	40.6±2.51	33.16±2.54
21	30.68±0.91	32.82±0.32	33.56±0.11	34.51±0.73	36.55±0.57	38.57±0.88	43.34±3.01	49.58±0.21	46.58±3.42	38.17±1.58	34.3±0.7	35.88±2.03

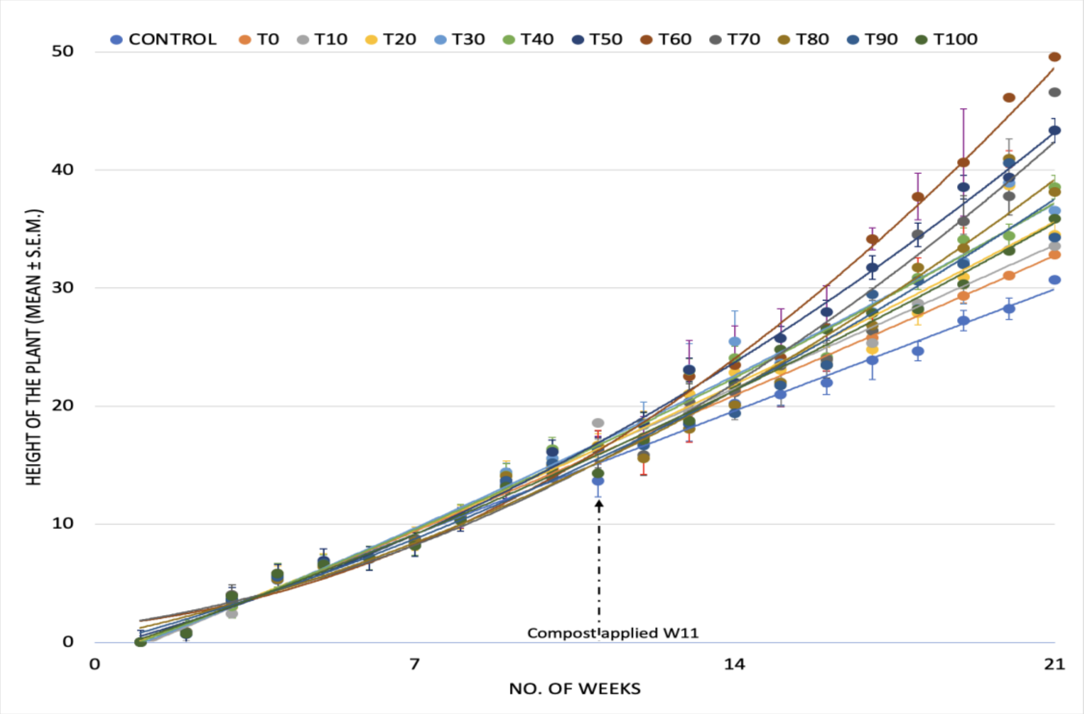

Figure 3 - Growth potential of microbially augmented organic waste-based compost applied to the plant at different combinations of tea and organic waste. The compost with a 60:40 ratio of tea: organic waste reflects the maximum growth of the plant Solanum lycopersicum.

Research Discussions

One of the main challenges of the society is the development of sustainable solutions for waste management. These solutions should help to preserve these resources present in food waste to achieve economic, social, and environmental benefits. The development of sustainable solutions for food waste management represents one of the main challenges for society [11]. The organic waste in Lahore has significant quality of organic matter which differs from the developed countries where there is a systematic way of sorting and segregation is present [[12], [13]]. Composting not only reduces the environmental burden of landfill sites but also helps to keep the groundwater clean from contaminations by decreasing the use of inorganic fertilizers resulting in economic benefits as well [14]. Being a self-sustainable biological process, composting has been used as a sustainable waste management solution and is utilized as a soil conditioner [[15], [13]].

The organic waste collected from sample sites was found to be rich in moisture content, organic carbon, and C/N ratio that adds nutrients, essential micro-organisms, and water-soluble compounds to the soil [[16], [17], [18]]. An earlier study has reported an increase in soil nitrogen through composting increasing the rate of nutrient cycling [19].

Waste tea along with vegetable and fruits waste has increased the concentration of nutrients essentially required for the growth and development of plants as compared to the regular soil which are Chloride, Sulphate, Total Phosphorus, Available Phosphorus, Organic matter, Calcium and Magnesium [20]. An overall increase in the percentage of organic carbon, Phosphorus, Potassium, and Nitrogen was recorded through aerobic and anaerobic composting that help to enhance the soil quality with subsequent positive effects on plant growth [21]. These findings are in agreement with previous studies and a significant correlation has been reported among the application of compost on agricultural fields and increased soil nitrogen, microbial, phosphate, carbon content and other micro-nutrients [[22], [17]]. This increased soil nitrogen indicates the compost’s potential to as an organic fertilizer in agricultural farms.

Recalcitrant organic pollutants are biodegraded by the various microbial communities found in composting materials. This degrading procedure could take the form of unidirectional extracellular oxidation, co-metabolism, or full mineralization/metabolism [[3], [23]]. Several studies have identified species that can mineralize these contaminants. For instance, *Acinetobacter lwoffii*, *Bacillus subtilis* and *Raoultella ornithinolytica* can degrade crude oil. Moreover, high temperatures during the composting (thermophilic phase) also enhance degradation by making the contaminants less viscous and more bioavailable [24].

Our results report a significant effect of compost application on soil microbial activity and nutrients on plant growth and tomato yield which is in accordance with the previously reported studies [[15], [18]]. However, some studies have also related that compost tea has neutral or non-significant effects on plants and crop yield [[25], [26], [13]].

The application of compost on soil increases the chlorophyll level in lettuce leaves and *Brassica oleracea L.* Contrary to these findings, another study reported that nitrogen content in leaves did not differ between compost or foliar sprays on strawberries [25] and there were no effects of compost application observed on blueberry fruit [26]. A higher yield of tomatoes has been reported with the use of organic fertilizer and compost in comparison with the use of no fertilizers [[3], [27]]. Several factors influence aerobic and anaerobic composting such as aeration (for aerobic composting), temperature i.e., for aerobic two temperature ranges, are required i.e., low temperature (mesophilic; 20-45°C) and high temperature (thermophilic; 50-70°C) phase and for anaerobic composting 35°C, moisture content (for aerobic composting 40-65%), pH for aerobic 7.5 and anaerobic 6.8-7.2, C: N for aerobic 40:1 and for the anaerobic initial substrate is required [[28], [29], [30], [31], [32], [33]].

Conclusion

Taken together our findings, it can be concluded that organic and tea waste can be used effectively for the preparation of compost to reduce the organic waste burden on the environment. This compost as an organic fertilizer can be an alternative to synthetic fertilizer, which can increase soil fertility, and improve plant health and immunity against diseases. The future recommendations include but are not limited to, the installation of composting plants at the municipality level to minimize organic waste and the implementation of the windrow composting method at landfill sites. Besides environmental benefits, it will have a huge economic impact by cutting down the cost of synthetic fertilizer consumption. Additionally, composting of organic municipal waste can be achieved at the domestic (household) level which needs an awareness campaign to educate the community that will lead to reducing household waste. Above all, a system of on-site organic waste segregation procedures needs to be implemented.

Authors' contributions. The authors confirm their contribution to the paper as follows: study conception and design: ZMM, NS; experimental work and data collection: ZMM; analysis and interpretation of results: ZMM, MHA, NS; draft manuscript preparation: ZMM, MHA, MBK, approval of the manuscript MHA and NS. All authors reviewed the results and approved the final version of the manuscript.

Conflicts of Interest. The authors declare no conflict of interest.

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Микробтармен байытылған органикалық қалдықтардың Solanum lycopersicum (қызанақтың) өсуіне әсері

[1]Munir Z.M., [2]Abbasi M.H., [3]Khawar M.B., [1]Sheikh N.

[1]Зоология институты, Пенджаб университеті, Q-A кампусы, Лахор, 54590, Пәкістан
[2]Окара университетінің зоология бөлімі, Окара, Пәкістан
[3]Наровал университетінің зоология бөлімі, Наровал, Пәкістан

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ТҮЙІНДЕМЕ

Бұл зерттеудің мақсаты органикалық қалдықтарды көму мен органикалық қалдықтарды заңсыз тастауды 68% азайтуға қол жеткізу үшін органикалық қалдықтарды және шай қалдықтарын органикалық топырақ кондиционеріне айналдыру болды. Шай органикалық қалдықтармен 10% қосымша қатынаста араластырылды және топтар Т0-Т100 деп белгіленді, бұл Т0-да 0% шай және 100% органикалық қалдықтарды және 100% шай қалдықтарын және Т100-де 0% органикалық қалдықтарды көрсетеді. Бұл топырақ кондиционерінің әсері кейінірек ашытқы өндіру қондырғысының қалдық шламын көбейтумен бірге жиырма бір апта бойы Solanum lycopersicum (қызанақ) өсімдігінің өсуі зерттелді. Микробтық зерттеу және компосттың pH, температура, органикалық көміртегі, C/N қатынасы, ылғалдылық, CEC және ылғалдылық сияқты басқа да физика-химиялық параметрлері зерттелді. Компосттың түсінің өзгеруінен, оны әрі қарай қолдануы анықталды. Топырақтың сапасы компостқа дейінгі және кейінгі қосымшаларда талданды. Топырақтың электр өткізгіштігі 3,0 мхо, pH 8,3, органикалық заттар 0,84 %, фосфор 1,0 мг/кг, калий 225 мг/кг, қанығу деңгейі 40% болды. Т0 тобында органикалық қалдықтар мен органикалық заттардың ең жоғары пайызы бар органикалық заттар арасында кері байланыс болды. Азоттың ең жоғары мөлшері (9,07%), фосфордың (0,7%) және калийдің (2,3%) ең жоғары деңгейі аэробты Т0 тобында тіркелді. Органикалық көміртектің ең жоғары мөлшері (78,23%), максималды CEC (109,09 мэкв/100г) аэробты Т100 тобында табылды. Т60 тобында қызанақ өсімдіктерінің қолданудан кейінгі ең жақсы вегетативті өсуі, гүлденуі және жеміс беруі байқалды. Біздің жұмыстарымыздың нәтижесінде органикалық компост топырақ құнарлығын 70% дейін арттыратыны анықталды, бұл қызанақ өсімдіктерінің өсуіне оң әсер етті.

Түйін сөздер: органикалық қалдықтар, өсімдіктердің өсуі, solanum lycopersicum (қызанақ), қоршаған орта.

Авторлар туралы ақпарат:

Munir Z.M. *Философия магистрі, Зоология институты, Пенджаб университеті, q-a Кампусы, Лахор, 54590, E-mail: zillayisp@gmail.com*

Abbasi M.H. *Доктор, Окара университетінің зоология бөлімі, Окара, Пәкістан. E-mail: Dr.muddasir@uo.edu.pk*

Khawar M.B. *Наровал университетінің зоология кафедрасының докторы, Наровал, Пәкістан. E-mail: babarkhawar@yahoo.com*

Sheikh N. *Доктор, Зоология институты, Пенджаб университеті, Q-A кампусы, Лахор, 54590, Пәкістан. E-mail: Nadeem.zool@pu.edu.pk*

Влияние органических отходов, обогащенных микроорганизмами на рост Solanum lycopersicum (помидора)

[1]Munir Z.M., [2]Abbasi M.H., [3]Khawar M.B., [1]Sheikh N.

[1]Институт зоологии Пенджабского университета, кампус Q-A, Лахор, 54590, Пакистан
[2]Кафедра зоологии, Окарский университет, Окара, Пакистан
[3]Кафедра зоологии, Университет Наровала, Наровал, Пакистан

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АННОТАЦИЯ

Целью этого исследования было преобразовать органические отходы и отходы чая в органический кондиционер для почвы, чтобы добиться сокращения на 68% количества захоронений и незаконных сбросов органических отходов. Чай смешивали с органическими отходами в пропорции 10%, а группы обозначали Т0-Т100, что указывает на 0% отходов чая и 100% органических отходов в Т0 и 100% отходов чая и 0% органических отходов на Т100. Позже было изучено влияние этого почвенного кондиционера на рост растения Solanum lycopersicum (помидор) в течение двадцати одной недели наряду с увеличением количества шлама с завода по производству дрожжей. Были изучены микробиологические исследования и другие физико-химические параметры, такие как pH, температура, органический углерод, соотношение C/N, влажность, CEC и влажность компоста. Визуальное изменение цвета указывало на зрелость компоста для дальнейшего применения. Качество почвы было проанализировано как до, так и после внесения компоста. Электропроводность почвы составила 3,0 МОм при pH 8,3, органическом веществе 0,84 %, фосфоре 1,0 мг/кг, калии 225 мг/кг при уровне насыщения 40 %. Между органическими отходами и органическим веществом наблюдалась обратная зависимость с наибольшим процентным содержанием органического вещества в группе Т0. Максимальное содержание азота (9,07%), самые высокие уровни фосфора (0,7%) и калия (2,3%) были зарегистрированы в аэробной группе Т0. Наибольшее количество органического углерода (78,23%), максимальная ЕКО (109,09 мэкв/100 г) было обнаружено в аэробной группе Т100. Лучший вегетативный рост растений томата после обработки, цветение и плодоношение наблюдались в группе Т60. В совокупности с нашими выводами можно сделать вывод, что органический компост повысил плодородие почвы до 70%, что положительно повлияло на рост растений томата.

Ключевые слова: органические отходы, рост растений, Solanum lycopersicum (помидор), окружающая среда.

Информация об авторах:

Munir Z.M.	*Магистр философии, Институт зоологии Пенджабского университета, Кампус Q-A, Лахор, 54590, Пакистан. E-mail: zillayisp@gmail.com*
Abbasi M.H.	*Доктор, кафедра зоологии, Окарский университет, Окара, Пакистан. E-mail: Dr.muddasir@uo.edu.pk*
Khawar M.B.	*Доктор, кафедра зоологии Университета Наровала, Наровал, Пакистан. E-mail: babarkhawar@yahoo.com*
Sheikh N.	*Доктор, Институт зоологии Пенджабского университета, кампус Q-A, Лахор, 54590, Пакистан. E-mail: Nadeem.zool@pu.edu.pk*

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Earth sciences

On the matter of composition and technological properties of uranium ores of the Semizbai deposit (North Kazakhstan)

***Baibatsha A.B., Bashilova E.S.**

Satbayev University, Almaty, Kazakhstan

**Corresponding author email: a.baibatsha@satbayev.university*

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ABSTRACT

Currently, uranium production occupies a decisive place in the world energy industry. In Kazakhstan, to meet the demand for uranium, hydrogenous deposits with technologically and economically favorable natural indicators are being developed, including the large Semizbai deposit. The deposit by genesis belongs to the hydrothermal-hydrogenous polygenic type in terrigenous sandy-clayey deposits. As a result of geological studies, the stratification of the ore-bearing deposits of the Semizbai suite was established: the lower and upper ore-bearing sub suites, the geometrization of the deposit was performed, and the morphology, number, and size of ore bodies were identified. Most of the balance reserves of the Semizbai deposit are concentrated in large and medium ore bodies. Analytical work and description of thin sections and polished sections under a microscope determined the material composition, textures, and structures of uranium ores, the main ore minerals, and their distribution in ores. When carrying out field and laboratory work, geological indicators of the deposit were obtained to select the technology for extracting ores. To select and justify the field development technology, special technological studies were carried out in the experimental area. Based on the geological indicators of uranium ores for the Semizbay deposit, well-in-situ leaching was chosen as the most rational for hydrogenous deposits. The characteristic of associated useful components of uranium ores is given, and the increased content of selenium, germanium, and scandium in them is established. The obtained research results can serve as a basis for improving the technology used for mining uranium ores and extracting associated components from them.

Keywords: hydrogenous uranium deposit, uranium-bearing terrigenous rocks, uranium minerals, types of ores, associated useful components, borehole underground leaching.

	Information about authors:
Baibatsha Adilkhan Bekdildauly	*Doctor of Geological and Mineralogical Sciences, Professor, Head of the Innovative Geological and Mineralogical Laboratory of Satbayev University, 050013, 22 Satbaev Str., Almaty, Kazakhstan. Email: a.baibatsha@satbayev.university*
Bashilova Elena Sergeevna	*Ph.D. student, Satbayev University, 050013, 22 Satbaev Str., Almaty, Kazakhstan. Email: elenab84@mail.ru*

Introduction

Kazakhstan in the world takes first place in uranium mining and the leading place in its natural resources, which is noted in official publications [[1], [2], [3]]. Among the developed deposits is Semizbai. Industrial mineralization and dispersion halos of uranium mineralization of the Semizbai deposit are established within the paleo valley of the same name at a distance of up to 36 km. With a paleo valley width of 2-7 km, taking into account the territory of its nearest framing, the deposit area is 370 km^2. According to the depression morphology, and differences in the degree of exploration and ore content, the deposit district is divided into six sections: North-Western, Western, Central, Eastern, Jamantuz, and Northern (Figure 1).

The accumulated factual material allows us to establish the main features and features of the location, morphology, and internal structure of all types of ore formations of the Semizbai deposit, located within the Semizbai depression [[4], [5], [6], [7]]. The geological and mineralogical features of deposits and their economic minerals are the main ones in choosing a rational mining technology and extracting associated valuable components from them. Such indicators are the basis for choosing a technology for the development of both technogenic [[8], [9]] and natural ores [[10], [11], [12], [13], [14], [15], [16], [17], [18], [19], [20], [21]].

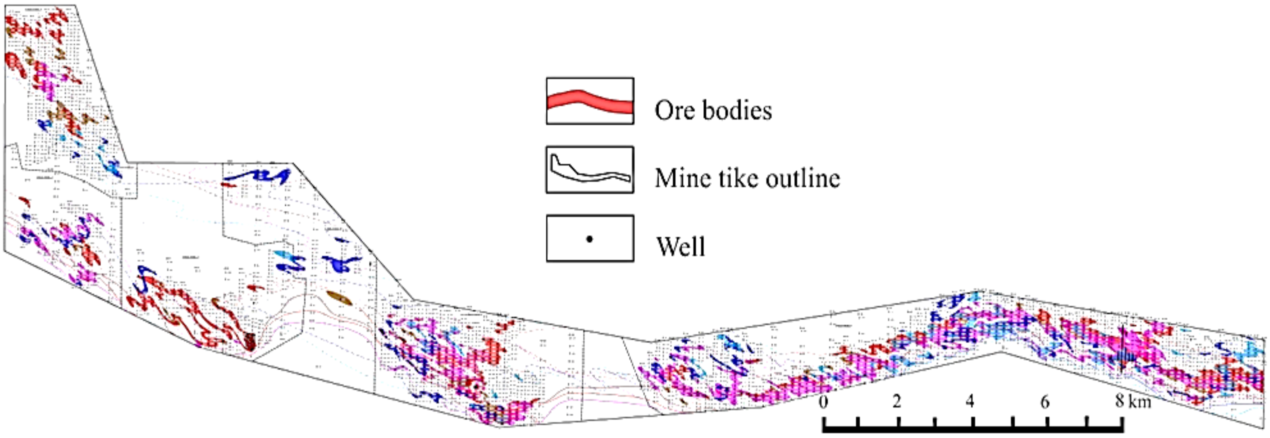


Figure 1 - Overview map of the ore content of the Semizbay deposit

Industrial uranium mineralization of the Semizbai deposit is represented by stratiform ore bodies, which are established in the lower part of the section of the Semizbai suite – from its basal layers to the silt-sand horizon inclusive. Within the identified productive stratum, ore formations are concentrated in permeable sediments at two levels – in the Lower Semizbai ore-bearing horizon, which combines conglomerate-gravelite and sandstone packs, and the Upper Semizbai ore-bearing horizon (USH), coinciding with the silt-sandstone stratigraphic horizon (Figure 2). The impermeable deposits of the clayey horizon separating them and the overlying formations of the regional aquiclude do not contain mineralization.

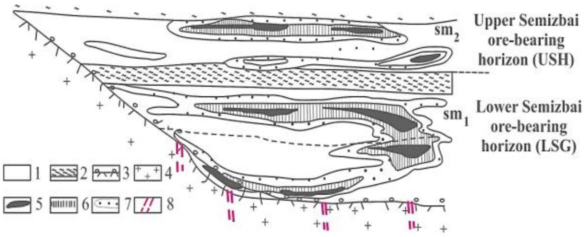


Figure 2 - Ore formations of different levels of the Southern ore-bearing zone: 1 - permeable horizons, 2 - water-resistant horizons, 3 - basal layers and permeable weathering crust; 4 - rocks of the Paleozoic basement; 5 - balance ore deposits; 6 - off-balance mineralization (not outlined in sections); 7 - anomalous zones with gamma activity of more than 30 μR/h

The balance ore deposits of the deposit are surrounded by poor ores, which in turn are replaced by extensive uranium dispersion halos, forming gamma-anomalous zones. The outer contour of the ore deposits is an isoline of 30 μR/h, which corresponds approximately to a uranium content of 0.001-0.002 %. The areas of the deposit with lower gamma activity are classified as completely barren formations, which have a normal background of 8-10 μR/h. The productive stratum includes all industrial mineralization of the deposit, occurs at depths of 26-180 m from the surface and has a variable thickness, which naturally increases from west to east along the long axis of the depression from 30 to 100 m.

Experimental part

The experiments were carried out according to the methodology, including fieldwork, testing, and preparation of selected samples, as microscopic and analytical studies. Mineralogical documentation of the core of more than 70 exploration wells was carried out, 2000 thin sections and polished sections were studied using radiography, chemical, spectral and schlich analyzes of ore samples were performed. For the diagnosis of individual minerals, X-ray diffraction, thermal and other types of analyzes were used. Sample preparation, preparation of thin sections and polished sections, and their microscopic description were carried out in the "Innovative Geological and Mineralogical Laboratory" of Satbayev University. Field geological studies and geometrization of the ore-bearing strata of the Semizbaiskoe deposit established 263 ore deposits, contoured with a cut-off uranium content of 0.03 %. 205 of them are in operation and include industrial reserves, and the remaining 58 are classified as off-balance sheets. The configuration of deposits in a generalized form is displayed on master plans and all geological and graphic documents (Figure 3).

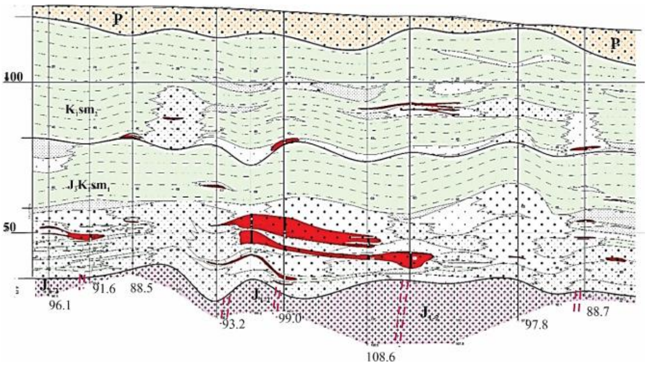


Figure 3 - Geological section

The parameters of mineralization and its statistical characteristics under various conditions, as well as determining the conditions for the localization of ore objects in the Central section of the deposit, were established according to exploratory drilling: first, a "cross" was drilled (PR 104-50 m with a total length of 740 and with a step of 6.25 m and a main line 230 with a length of 450 m with a step of 12.5 m), and then - an experimental operational exploration part with a network of wells 6.25x12.5 m in an area of 100x200 m (263 wells in total).

The study of the parameters, morphology, and conditions of ore occurrences showed that all deposits are represented by strongly flattened, discontinuous in area and thickness, stratiform bodies with a complex distribution of uranium mineralization. They are of the same type in structure but differ significantly in size and configuration. Thus, with an average thickness of all 205 industrial ore bodies of the deposit equal to 2.1 m, for some of them it ranges from 0.2 to 7.3 m, and the area, with an average value of 9000 m^2, varies from 4 to 930 thousand m^2.

The analysis of ore deposits of various morphological groups gives grounds to systematize them and identify several classes in terms of size and types according to the configuration in the plan (Table 1).

As can be seen from Table 1, four classes of ore deposits are distinguished by size at the Semizbai deposit:

– very large (area more than 250 thousand m^2), which include deposit No. 1-2-003 for the deposit with an area of about 1 million m^2, including 12.5 % of metal reserves, and deposit No. 1-2-001, which - 430 thousand m^2 and 9.2 %;

– large (100-250 thousand m^2);

– middle (40-99 thousand m^2);

– small (less than 40 thousand m^2).

Table 1 - Distribution of ore bodies by their size and morphological types

Morphological types of ore bodies	Classes of ore bodies by size				
	very large	*large*	*middle*	*small*	*total*
Ribbon-like	1	2	3	7	13
Elongated lenticular	3	6	9	57	75
Lenticular (isometric)	1	1	8	87	97
indeterminate form	-	2	16	2	20
Total	5	11	36	153	205

An analysis of the distribution of ore reserves by bodies shows that about 90 % of the balance reserves of the deposit are concentrated in large and medium ore bodies, including 70 % in 16 large and 5 very large bodies, the average area of which is 500 thousand m^2, containing 47 % of uranium ores of the Semizbai deposit. The bodies with the maximum size are also characterized by greater thickness, higher metal content, and productivity. At the same time, 153 small bodies (75 % of their total amount) contain only 11 % of uranium reserves.

Ore bodies not only differ significantly in size but also have a variety of shapes in plan, being elongated objects to varying degrees. Their length varies from 100 m to 5.2 km, and their width varies from 20 to 800 m with fluctuations in the ratio of length to width from 1 to 12. In this regard, three morphological types of ore bodies are distinguished: ribbon-like – narrow, winding, strongly elongated along strike, with an elongation factor (K_{elong}) of more than 5; elongated lenticular (K_{elong} 2-5) and lenticular (or isometric) - K_{elong} less than 2. For 20 ore deposits explored by single wells along a sparse network, the shape has not been reliably established. Research data show that over 50 % of the metal reserves are contained in elongated lenticular deposits (37 % of their total amount), and in all other types of deposits, the reserves are distributed approximately equally.

The average uranium content for individual ore bodies after averaging hurricane values varies from 0.041 to 0.240 %. Significantly greater limits of fluctuations are noted inside the ore bodies – for through complete intersections from 0.04 to 0.5 % and for some rare (before averaging) up to 2 %. In individual core samples, the metal content was found to be from 3-5 to 8 %. In individual core samples, the metal content was found to be from

3-5 to 8 %. In individual C*org* samples, the metal content was found to be from 3-5 to 8 %. The highest quality is characterized by ores in areas enriched in C*org* and sulfides, which, however, are randomly distributed within the deposits and do not form large independent accumulations.

The deposit as a whole is represented by ordinary ores, but the main reserves of metal (74 % are contained in the class of ores above 0.1 %, the uranium content which is 1.5 times higher than the average. It is also important to note that 65 % of the metal reserves are located in highly productive, central parts of ore deposits, which account for only 25 % of their area.

Research discussion of the results

A systematic geological, mineralogical, and technological study of the ores of the Semizbai deposit began from the moment of its discovery and continues at the present time.

Mineral composition of ores. Uranium mineralization at the Semizbai deposit has been established in all lithological varieties of rocks of the ore-bearing strata. Insignificant concentrations of uranium have also been found in the basement granites of the Semizbai depression. The composition of clasts of ore-bearing rocks is arkosic, polymictic, and less often quartz. Fragments of coalified organics are noted in significant amounts in separate interlayers. The most common accessory minerals are magnetite, titanomagnetite, ilmenite, spinel, leucoxene, zircon, sphene, apatite, tourmaline, garnet, epidote, and anatase.

The cement of the rocks is mostly sandy-argillaceous, silty-argillaceous, and clayey. Separate interlayers have a clay-carbonate and carbonate composition of cement. Cement is formed largely by authigenic minerals - kaolinite, montmorillonite, hydromicas, carbonates, sulfides, iron oxides and hydroxides, and uranium minerals.

Uranium in ores is found in the mineral and adsorbed form. The latter is widely distributed, but in rich ores, the bulk of uranium is associated with mineral forms. The sorbed uranium in ores is associated with carbonized plant fragments, clay minerals of cement, and iron hydroxides. Uranium minerals are represented by coffinite, pitchblende (uraninite), uranium black, and rare secondary minerals. In addition, uranium-bearing ilmenite, titanomagnetite, and leucoxene are present in small amounts. In isolated cases, detrital brannerite is noted.

In some areas of ore bodies, increased radioactivity is due to radium-bearing barite and iron hydroxides.

The distribution of uranium minerals in the ores is uneven – in poor ores they are noted only in the form of small and rare segregations, in areas of rich mineralization they form dense dissemination and small nodules, sometimes completely replacing clayey cement and partially developing along the fragments. In most cases, pitchblende and coffinite are in close association with pyrite and marcasite.

Below is a description of uranium, uranium-containing, and accompanying minerals in the ores of the Semizbai deposit based on polished sections made by cementing a loose core.

Coffinite is one of the most common ore minerals. It occurs in almost all types of ores but is most characteristic of carbonatized varieties. It is in close association with sulfides. Coffinite forms irregularly shaped segregations, collomorphic crusts, and nested clusters ranging in size from thousandths of an mm to 1 cm (Figure 4).

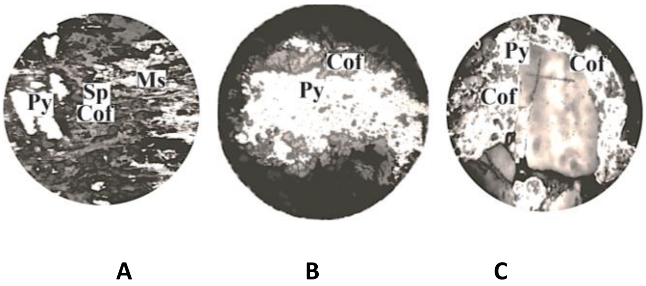
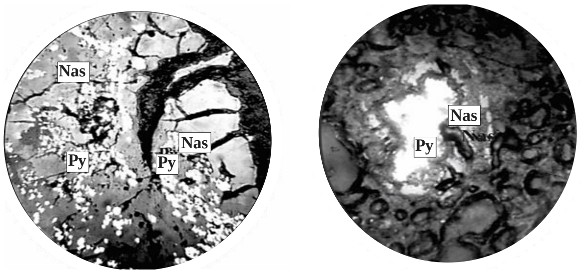


Figure 4 - Mineral composition of ores in polished section: A - pyrite (Py), marcasite (Ms), sphalerite (Sp) and coffinite (Cof) in medium-grained sandstone cement; B - coffinite (Cof) around pyrite nodules (Py); C - coffinite (Cof), developing after collomorphic pyrite (Py)

In ores, coffinite is represented by three generations. Coffinite I has a black color, it was isolated after microglobular pyrite, is pseudomorphically replaced by pitchblende I, and is identified from the preserved primary crystal forms. Coffinite II is black with brown reflections, reflectivity R = 8.2 %, microhardness H = 265 kg/mm^2, formed before marcasite after the main mass of pyrite. Coffinite III crystallized after marcasite. It has greenish-brown and light brown internal reflections, low reflectivity R = 4 %, and microhardness H = 205 kg/mm^2. Coffinite is confirmed by X-ray diffraction analysis.

Nasturan (uraninite) is much rarer than coffinite. It occurs together with it, as well as in the form of independent secretions and accumulations 0.003-2.0 mm in size. It forms outer zones in coffinite rims and accumulations around iron sulfides (Figure 5). It is also noted as a thin dissemination in the cement and less often as microveinlets in terrigenous fragments. In addition, relatively large (up to 5 mm) accumulations of pyrite-nasturan composition are found in spotted carbonate ores. There are two generations of Nasturan. The first, the earliest, is developed after coffinite I and has a low reflectivity R = 8–10%. Crystal lattice parameters a = 5.39 Å. Nasturan II is characterized by a higher reflectivity R = 15 %. Crystal lattice parameters a = 5.39 Å. Sometimes it contains small inclusions of galena.



A **B**

Figure 5 - Mineral composition of ores in polished section: A - *Nasturan* (Nas) with dissemination of fine-crystalline pyrite (Py); B - Nasturan (Nas) and uranium black (Nas) around accumulations of pyrite (Py) in siltstone

Uranium black forms loose accumulations in association with melnikovite and sooty organic matter and thin films on the surface of terrigenous fragments and segregations of pitchblende and coffinite; they are also present in a finely dispersed state in clayey cement.

Brannerite is rare in rich ores in the form of small (up to 0.5 mm) detrital grains.

Secondary uranium minerals are represented by *zippeite, uranophane*; they are found in small amounts in ores with organic matter and in carbonate rocks. They are found in areas of carbonate destruction in the form of thin yellow precipitates on the surface of minerals, powdery accumulations near pitchblende and coffinite.

Uranium-bearing minerals are represented by ilmenite, leucoxene, titanomagnetite, and anatase. They are usually found in rich ores in the form of single small (fractions of mm) grains and small clusters. The distribution of uranium in them is uniform.

Organic matter is widely distributed. Its content in terms of C*org* varies from tenths to 5 %. It is represented by carbonized plant residues (leaves, roots, stems, bark, trunks), coal detritus, accumulations of sooty carbonaceous matter. The content of uranium in carbonized plant residues varies widely, reaching 1 %. Uranium-enriched coals differ from barren coals by a higher degree of oxidation and a smaller amount of aromatic compounds. Noteworthy is the noticeable concentration of germanium, reaching 0.2 % in some samples.

Iron hydroxides are widely developed in ores. Their formation is associated both with the processes of sediment formation and with subsequent epigenetic transformations (hydrohematization, reservoir oxidation, gley reduction). They are represented by goethite, hydrogoethite, hydrohematite, which impregnate fragments of rocks and minerals and clayey cement, form clots, accumulations, films, point selections. In ore intervals, a significant amount of uranium and especially radium is sorbed on iron hydroxides.

Sulfides are represented by pyrite, marcasite, and melnikovite. Bravoite, sphalerite, chalcopyrite, galena are very rare.

Structural features of ores. In ordinary ores, uniformly dispersed, spotty, and mixed structures are most common; in rich ores, in addition, disseminated, clotted, and cementitious structures are common. Ores of other structures occur occasionally. Mixed structures are a combination of two or three different structures. The cement structures is characteristic of rich ores localized in medium- and coarse-grained sandstones, whose clayey cement is completely replaced by coffinite, pitchblende, and iron disulfides, which are closely intergrown with them.

Textures of ores. Based on the nature of segregations and the relationship of uranium minerals with other neoformations and terrigenous minerals, the following main textures of ores are established. The texture of peripheral rims is widespread in carbonate ores, as well as in rocks with clayey cement enriched in iron sulfides. Coffinite and Nasturan develop around accumulations of iron sulfides in the form of continuous and discontinuous rims. The concentric-zonal texture is due to the presence of zonal-collomorphic segregations of pyrite, in which individual zones are composed of coffinite. The corrosion texture is revealed in intergrowths of uranium minerals with iron sulfides, in which distinct corrosion contacts of pyrite or marcasite with coffinite and pitchblende developing over them are established. The relic texture is formed as a result of the replacement of pyrite and marcasite by uranium minerals, in which iron sulfides remain only in the form of relics. The mineral composition of ores and their textural and structural features are the basis for choosing the technology of deposit development and effective reagents.

Characteristics of associated useful components. Associated useful components such as selenium, germanium and scandium were found in the uranium ores of the deposit. The possibility of industrial use of these components still remains problematic due to low contents and requires technological solutions. The mineral forms of their occurrence and distribution in ores have not yet been sufficiently studied. Selenium is probably found as an isomorphic impurity in iron sulfides. Germanium is closely related to organic matter. However, when uranium is leached from the ores of the deposit, only scandium passes from the mentioned elements into solutions and accumulates, which in the future may be of industrial interest.

Neutron-activation, X-ray spectral, and chemical analyzes have established elevated contents of selenium (5-30 g/t), germanium (1-15 g/t), and scandium (2-7 g/t) in ores. In individual combined core samples in ore intervals, the content of germanium reaches 320 and scandium – 76 g/t. Elevated contents of germanium are noted in samples enriched with C*org*; the relationship between elevated contents of scandium and any constituent components of ores has not been established. The presence of selenium in uranium ores was established in 12 out of 1303 analyzed sectional samples. In one sample (4/1328), the selenium content reached 0.04 %. Any mineral forms of finding these elements have not been established. Presumably, selenium occurs as an isomorphic impurity in iron sulfides. Germanium is associated with C*org* (correlation coefficient is 0.7) and is distributed not only in ores, but also in host rocks.

The estimate of the expected reserves of associated components is determined in the ore mass, which in the process of in-situ leaching will possibly be treated with leaching reagents. Since the study of the distribution of selenium, germanium and scandium did not reveal a relationship between them and uranium, the average content of associated elements in the ore mass was taken to be the same as in the ore.

Table 2 shows the estimated amount of associated useful components (AUC) per tonne of balance reserves of uranium.

Table 2 - AUC/U ratio in uranium ores of the Semizbai deposit.

Components	AUC/U ratio, kg/t
Selenium	52
Germanium	12
Scandium	9

For the first time, the characteristics of the ores of the Semizbai deposit are given according to the results of preliminary exploration (V. Pigulsky et al., 1975), in which their division into natural types and technological grades took into account both the possibility of a traditional mining method and the use of Underground leaching (UL). This was based on three principles – permeability (K*l* separation level 0.5 m/day), carbonate content (2 % CO_2), and coal content (3 % C*org*), in connection with which the corresponding natural types of ores were distinguished.

At present, natural types of ores are separated only by their lithological composition, since they do not differ significantly in other features, in particular, in mineral composition. The following four types of ores have been established: 1) in clays and siltstones; 2) in clayey sands and sandstones; 3) in gravelstones and conglomerates with sandy-argillaceous cement; 4) in sandstones and conglomerates with carbonate cement. Due to the small distribution of ore in rocks enriched with carbonized organic matter, it is not distinguished as an independent natural type. The distribution of ore types in the deposit is given in Table 3.

Table 3 - Relative distribution of natural types of ores of the Semizbai deposit

Types of ores according to the lithological composition of rocks	Ratio, %	
	balance reserves	off-balance reserves
1. Clays and siltstones	14.5	23.1
2. Clay sands and sandstones	48.2	48.8
3. Coarse-clastic rocks with sandy-argillaceous cement	23.2	23.9
4. Clastic rocks with carbonate cement	14.1	4.2

As can be seen from Table 2, off-balance ores, to a greater extent than balance ores, develop over clay rocks. The clastic part of the ore (pebbles, gravel, and pieces of monolithic carbonate rocks that do not soak in water) in the ores of the Upper ore-bearing horizon (UOH) is 5-8%, Lower ore-bearing horizon (LOH) – 25-30 %; in general, about 20 % for the deposit.

Ore-bearing clays and siltstones occur predominantly in the form of thin layers among mineralized sandstones or in thicker layers limiting them from the side of the roof and soil. Uranium is associated mainly with dark gray and gray varieties of clays enriched in organic matter and iron sulfides. The C*org* content ranges from 0.2 to 8-5 % (occasionally up to 19.8 %); the number of sulfides, according to chemical analysis 1-5, in some cases 10 %. The content of uranium is mainly 0.04-0.07 %, occasionally up to 0.2 %. Its distribution is mainly finely dispersed, mainly in the adsorbed form. Nasturan, coffinite, and uranium black are fixed only in enriched areas.

Ore-bearing sandstones of various grain sizes are the most common type of ores. These are mainly gray and greenish-gray varieties with a high content of C*org* (0.25-7.0 %) and iron sulfides (0.5-5 %). Uranium mineralization is represented by nasturan, coffinite, and black uranium, which form dissemination and clots in areas enriched in sulfides. A significant part of uranium is in the adsorbed form in clay cement and carbonized organic matter. The uranium content fluctuates over a wide range, reaching 5-8 % in fragments of carbonized wood and near sulfide accumulations.

Ore-bearing gravel stones and conglomerates of gray, greenish-gray, and spotted color are characterized by poor sorting of the material. They also contain iron sulfides and fragments of carbonized wood. Uranium mineralization has an uneven patchy distribution. Uranium is in the adsorbed form in clay minerals and fragments of organic matter, but a significant part of it is contained in accumulations of pitchblende, coffinite, and black uranium in association with iron sulfides.

Ores in clayey rocks stand out sharply from the described types in terms of the content and distribution of uranium. They are characterized by a uniform distribution of metal and a lower average content (1.5-2 times lower than the average over the horizon). All other types do not differ significantly from each other in terms of uranium concentration and are characterized by a patchy distribution of mineralization. The enriched areas (clumps) in them are associated with the concentration of uranium minerals near pyrite accumulations and in fragments of the coalified mass.

The selected natural types of ores do not form independent ore bodies or large areas within them, they occur in complex thin interbedding with each other.

The results of chemical analyzes and data on the mineral composition of technological samples suggest that the ores of the deposit as a whole are aluminosilicate with a low content of carbonates.

The closest relationship of uranium is observed with sulfur and C*org*, which is explained, on the one hand, by the presence of a close paragenetic association of uranium minerals with iron sulfides and, on the other hand, by the sorption of uranium by carbonized plant residues and a close relationship between sulfur and C*org*. Uranium also has a weak but significant correlation with germanium and CO_2. The first is natural since both germanium and uranium have a direct correlation with C*org*. The second is manifested in the LOH and is apparently due to the regeneration and some concentration of uranium in the process of carbonatization of detrital rocks.

Deposit development technology. The Semizbai uranium deposit is being developed by the most rational for this type of deposit by underground well leaching (UWL). The use of UWL is based on three indicators of ore-bearing rocks: permeability (K*f* ≥0.5 m/day), carbonate content (2 % CO_2) and coal content (3% Corg). At present, natural types of ores are separated only by their lithological composition, since they do not differ significantly in other features, in particular, in mineral composition. As mentioned above, four types of ores have been identified at the deposit. Due to the small distribution, ores in rocks enriched with carbonized organic matter are not distinguished as an independent natural type. The obtained research results are the initial basis for improving the technology in uranium ore production and effective reagents to increase the extraction of metals.

Conclusions

The results of the studies performed provided additional material for concluding that the ores of the Semizbai deposit were original of hydrothermal genesis, which as the Mesozoic-Cenozoic depression developed, were transformed and redeposited by hydrogenic processes in the artesian and expelled basins.

The obtained results of the laboratory and field geological study of the natural features of the uranium ores of the Semizbai deposit can serve as a basis for improving the technology of uranium mining and creating an initial base for extracting associated rare elements. Ores according to geological and technological indicators are divided as follows:

– in terms of uranium content in general for the deposit to ordinary monometallic ones. Selenium, germanium, and scandium are present in certain amounts;

– in terms of the form of uranium – to nasturan-coffinite with a significant proportion of metal in the adsorbed form on clay minerals and organic matter;

– according to the composition of the ore mass - to aluminosilicate rocks with a small number of carbonates (4-5%);

– in terms of the size of mineral aggregates and textural and structural features - to scattered-clot. The sizes of pitchblende-coffinite-sulfide aggregates are up to several mm, and a significant part of uranium is in the form of fine dissemination and in the sorbed form;

– the basis of ores is represented by sands and weakly cemented sandstones, gravel stones, conglomerates, siltstones, and clays soaking in water; the clastic part of the rocks is on average 20 %.

Currently, in addition to uranium, rare and rare-earth elements accompanying them are in demand. Assessing the associated useful components (AUC) and choosing a technology for extracting them from uranium ore solutions will increase the value and make it possible to develop even off-balance ores of uranium deposits.

Conflict of interest. The authors have no conflict of interest.

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Семізбай кенорнындағы уран кенінің заттық құрамы және технологиялық қасиеттері туралы (Солтүстік Қазақстан)

***Байбатша Ә.Б., Башилова Е.С.**

Сәтбаев университеті, Алматы, Қазақстан

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ТҮЙІНДЕМЕ

Қазіргі уақытта уран өндіру әлемдік энергетикада елеулі орын алады. Қазақстанда уранға деген сұранысты қанағаттандыру үшін технологиялық және экономикалық жағынан қолайлы табиғи көрсеткіштерге ие гидрогендік кенорындар бар, солардың ішінде ірі Семізбай кенорны игерілуде. Кенорын генезисі бойынша терригендік құм-саз шөгінділердегі гидротермалық-гидрогендік, яғни полигендік типке жатады. Геологиялық зерттеулер нәтижесінде семізбай дестесінің рудалы түзілімдері стратификацияланған: төменгі және жоғарғы рудалы дестешелер бөлінген, кенорынды геометризациялау жүргізілген, рудалы жатындардың морфологиясы, саны және өлшемдері анықталған. Кенорын баланстық қорының басым бөлігі ірі және орташа кен денелерде шоғырланған. Аналитикалық жұмыстар, шлифтер мен аншлифтерді микроскоппен сипаттау арқылы уран рудаларының заттық құрамын, бітімі мен құрылымын, негізгі кен минералдарын және олардың кендерде таралуы анықталған. Далалық және зертханалық жұмыстарды жүргізу кезінде кен өндіру технологиясын таңдауға негіз болатын кенорынның геологиялық көрсеткіштері алынды. Кен өндіру технологиясын таңдау және негіздеу үшін тәжірибелік бөлікшеде арнайы технологиялық зерттеулер жүргізілді. Семізбай кенорны үшін уран кендерінің геологиялық көрсеткіштеріне сүйене отырып, гидрогендік кенорындар үшін ең ұтымдысы ретінде жерасты ұңғымаларында шаймалау технологиясы таңдалған. Уран кендерінің ілеспе пайдалы компоненттерінің сипаттамасы берілген, олардағы селен, германий және скандий мөлшерінің жоғары екендігі анықталған. Алынған зерттеу нәтижелері уран кендерін өндіру және олардан ілеспе пайдалы компоненттерді айырып алу үшін қолданылатын технологияны жетілдіруге негіз бола алады.

Түйін сөздер: уранның гидрогендік кенорны, уранды терригендік таужыныстары, уран кенінің минералдары, кен типтері, ілеспе пайдалы компоненттер, жерасты ұңғымаларда шаймалау.

	Авторлар туралы ақпарат:
Байбатша Әділхан Бекділдаұлы	*Геология-минералогия ғылымдарының докторы, профессор, Сәтбаев университеті Инновациялық геология-минералогия лабораториясының мегерушісі, 050013, Сәтбаев көшесі, 22, Алматы, Қазақстан. Email: baibatsha48@mail.ru*
Башилова Елена Сергеевна	*Сәтбаев университетінің PhD докторанты, 050013, Сәтбаев көшесі, 22, Алматы, Қазақстан. Email: elenab84@mail.ru*

О вещественном составе и технологических свойствах урановых руд Семизбайского месторождения (Северный Казахстан)

***Байбатша А.Б., Башилова Е.С.**

Satbayev University, Алматы, Казахстан

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АННОТАЦИЯ

В настоящее время производство урана занимает определяющее место в мировой энергетике. В Казахстане для удовлетворения потребности в уране разрабатываются гидрогенные месторождения с технологически и эконически выгодными природными показателями, в числе которых и крупное Семизбайское месторождение. Месторождение по генезису относится с гидротермально-гидрогенному полигенному типу в терригенных песчано-глинистых отложениях. В результате геологических исследований установлена стратификация рудоносных отложений семизбайской свиты: нижний и верхний рудоносные горизонты, выполнена геометризация месторождения, выделена морфология, количество и размеры рудных залежей. Большинство балансовых запасов месторождения сосредоточены в крупных и средних рудных залежах. Аналитическими работами, описанием шлифов и аншлифов под микроскопом определен вещественный состав, изучены текстуры и структуры урановых руд, основные рудные минералы и их распределение в рудах. При проведении полевых и лабораторных работ получены геологические показатели месторождения для выбора технологии добычи руд. Для выбора и обоснования технологию разработки месторождения проведены специальные технологические исследования в экспериментальном участке. Исходя их геологических показателей урановых руд для Семизбайского месторождения выбрано подземное скважинное выщелачивание как самое рациональное для гидрогенных месторождений. Дана характеристика попутным полезным компонентам урановых руд, установлено повышенное содержание в них селена, германия и скандия. Полученные результаты исследований могут служить основой для совершенствования применяемой технологии добычи урановых руд и извлечения из них попутных полезных компонентов.

Ключевые слова: гидрогенное урановое месторождение, ураноносные терригенные породы, минералы урановых руд, типы руд, попутные полезные компоненты, подземное скважинное выщелачивание.

	Информация об авторах:
Байбатша Адильхан Бекдильдаулы	*Доктор геолого-минералогических наук, профессор, заведующий Инновационной геолого-минералогической лабораторией Satbayev University, 050013, ул. Сатпаева, 22, Алматы, Казахстан. Email: baibatsha48@mail.ru*
Башилова Елена Сергеевна	*PhD докторант Satbayev University, 050013, ул. Сатпаева, 22, Алматы, Казахстан. Email: elenab84@mail.ru*

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EARTH SCIENCES

Техникалық редакторлар:
Г.К. Қасымова, Н.М.Айтжанова, Т.И. Қожахметов

Компьютердегі макет:
Г.К. Қасымова

Дизайнер:
Г.К. Қасымова, Н.М.Айтжанова

Металлургия және кен байыту институты; Сәтбаев Университеті
050010, Қазақстан Республикасы, Алматы қаласы, Шевченко к-сі, 29/133

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Технические редакторы:
Г.К. Касымова, Н.М. Айтжанова, Т.И. Кожахметов

Верстка на компьютере:
Г.К. Касымова

Дизайнер:
Г.К. Касымова, Н.М.Айтжанова

Институт металлургии и обогащения; Сатпаев Университет
050010, г. Алматы, Республика Казахстан. ул. Шевченко, 29/133

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G.K. Kassymova, N.M. Aitzhanova

Institute of Metallurgy and Ore Benficiation; Satbayev University,
050010, Almaty city, the Republic of Kazakhstan. Shevchenko str., 29/133

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