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Fax. +7 (727) 298-45-03, Tel. +7 (727) 298-45-02, +7 (727) 298-45-19
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Aluminum-lithium alloys: types, properties, application, and production technologies. Overview

*Ablakatov I.K., Baiserikov B.M., Ismailov M.B., Nurgozhin M.R.

National Center for Space Research and Technology JSC, Almaty, Kazakhstan

**Corresponding author email: termostators@gmail.com*

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ABSTRACT

The article provides a brief overview of the aluminum industry development in Kazakhstan and the possibility of obtaining high-strength structural aluminum-lithium alloys. The country's enterprises produce aluminum of technical purity and aluminum alloys of low and medium strength of 6060, 6063, 6463, 6082, AK5M2, ADS-12, AD-31, AD-35, which are available materials for the construction industry. In Kazakhstan, there is progressive development of mechanical engineering which requires stronger alloys of 300-400 MPa, and for special engineering (defense, aerospace, and other advanced industries) - strengths above 415 MPa. High-strength structural aluminum alloys are based on Al-Cu-Mg, Al-Zn-Mg-Cu, Al-Li systems. Among these systems, relatively new Al-Li alloys are of great interest, having a great potential for further improvement of characteristics. The Al-Li system alloys with record-high specific strengths, corrosion-resistant, and good welded joints are widely used in the aerospace industry, where they are used for the production of power elements and housings. The article provides an overview of the known aluminum-lithium alloys, as well as the main technological stages of their production.

Keywords: alloy, aluminum, lithium, magnesium, zirconium, strength, technology.

Information about the authors

Ablakatov Ilyas Kabylashimuly	*Junior Researcher, National Center for Space Research and Technology JSC, Almaty, Kazakhstan. ORCID ID: 0000-0003-4912-9289. Email: termostators@gmail.com*
Bayserikov Berdiyar Meyirzhanuly	*Junior Researcher, National Center for Space Research and Technology JSC, Almaty, Kazakhstan. ORCID ID: 0000-0003-0804-3147. Email: baiserik.b.91@mail.ru*
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Introduction

Currently, the main aluminum alloys produced in the world are alloys of the Al-Si, Al-Mn, Al-Mg, Al-Mg-Si, Al-Cu-Mg, Al-Li systems with a specific strength of 64-223 m^2/s^2. According to strength characteristics, aluminum alloys are divided into three classes: alloys of low, medium, and high specific strength (Table 1).

The high-strength alloys include alloys of the Al-Cu-Mg, Al-Zn-Mg-Cu, and Al-Li systems as can be seen from the table. The alloys of these systems have high strength compared to other alloys, however, the alloys of the Al-Cu-Mg and Al-Zn-Mg-Cu systems are not amenable to arc welding, and have a high density due to the copper and zinc included in the composition. The characteristics of high-strength alloys of the Al-Cu-Mg and Al-Zn-Mg-Cu systems do not meet the requirements of weight reduction and good weldability of the structure. These properties are a priority when creating airplanes and spacecraft. The alloys of the Al-Cu-Mg and Al-Zn-Mg-Cu systems are very susceptible to corrosion and require anodizing of the surfaces.

Among all aluminum alloys, the alloys of the Al-Li system have not only high strength characteristics but are also easily amenable to any type of welding, have high corrosion resistance, which makes them a promising new class among high-strength aluminum alloys [[1], [2], [3]]. The huge interest in aluminum-lithium alloys is caused by the fact that each percentage of lithium included in the alloy reduces the density by 3%, increases the modulus of elasticity by 6%, increases the resistance of the alloy to crack propagation [4].

Table 1 - Mechanical properties of aluminum alloys [[1], [2], [3]]

Characteristics of alloys	System	Grades	Specific strength, m^2/s^2	Arc welding	Corrosion resistance
Low strength alloys	Al-Si	AK12 AK9 AK7	64 98 83	Good	Good
	Al-Mn	AMc	80	Good	Good
Medium strength alloys	Al-Mg-Si	AD31 AD33 AD35	92 118 122	Average	Average
	Al-Mg	AMg5 AMg6	112 151	Good	Good
	Al-Zn-Mg	1915 1925	134 123	Average	Low
High-strength alloys	Al-Cu-Mg	D1 D16	147 160	Low	Low
	Al-Zn-Mg-Cu	B95	182-200	Low	Low
	Al-Li	1420 1460 2090 8090	180 215 223 171	Good	Good

But the main advantage of Al-Li alloys is that they are easy to weld, allowing the use of such types as laser, friction welding with stirring, and argon arc welding with the use of additive materials [[5], [6]]. The use of these technologies in the creation of welded structures of aerospace vehicles and other vehicles made of Al-Li alloys gives a huge weight advantage compared to riveted structures made of traditional aluminum alloys, which saves fuel consumption by reducing the weight of the product by 15-25% [7].

Aluminum-lithium alloys: history, types, and applications. Development of aluminum-lithium alloys began in 1950 and alloys of various purposes have been created to date: alloys of the Al-Li-Mg system for welded and riveted structures; high-strength alloys of the Al-Li-Cu system to replace the B95 type alloy; high crack resistance alloys of the Al-Li-Mg-Cu system to replace the alloy type D16; heat-resistant and high-strength alloys of the Al-Li-Cu-Mp-Cd system; welded high-strength alloys of the Al-Li-Cu-Sc system for operation at low temperatures. The aluminum-lithium alloys are divided into three generations. Al-Li alloys of the first generation are mainly researched and developed in USA and USSR in the period 1950-1960; Al-Li alloys of the second generation were obtained in the USA, Europe, and Russia in the period of 1970-1980; Al-Li alloys of the third generation are studied mainly in the USA. Their development began in the early 90s and continues to the present. The chemical composition and mechanical properties of the known aluminum-lithium alloys are given in Table 2 [[8], [9], [10], [11]].

The first aluminum-lithium alloy 2020 was developed in 1957 by Alcoa (USA). Alloy 2020 had high strength and high creep resistance at 150-200 ˚C and was used to manufacture the wings of the Ra-5C Vigilante BMC aircraft. In 1960, alloy 2020 was discontinued due to production problems related to its high brittleness and poor ductility [12].

The first Soviet aluminum-lithium alloy VAD23 with lithium content was developed in 1960. Alloy VAD23 has a 5% low density and a 5% high modulus of elasticity compared to alloy D16. VAD23 has high heat resistance at temperatures up to 225°C due to the content of manganese and cadmium. However, the low strength and plastic characteristics of welded joints, and the tendency to crack did not make it possible to use the alloyVAD23 in practice [[12], [13], [14], [15], [16]].

In 1965, on the basis of the Al-Li-Mg system, the first original, patented, lightest (2.4 g/m^3), weldable, corrosion-resistant alloy 1420 was developed. Alloy 1420 had high corrosion resistance, good weldability, high modulus of elasticity, sufficient strength, and low density. Alloy 1420 is 12% lighter and the modulus of elasticity is 8% higher compared to alloy D16. There are no existing analogs of alloy 1420 outside Russia [15].

In 1971, alloy 1420 was used in the riveted fuselage structure of the Yak-36 aircraft, reducing the bulk to 24%. Due to the weldability of all types of welding, alloy 1420 was used in 1980 to create the world's first welded MiG-29 aircraft (Figure 1). As a result, welded sealed tanks and the cockpit were made of alloy 1420 [17].

Alloys 1421, and 1423 with a high yield strength (up to 25%) were obtained on the basis of 1420 due to the addition of scandium. Alloy 1421 is widely used in the rocket housings of Makeev State Rocket Center JSC, which made it possible to reduce the mass by up to 15%. Alloy 1423 containing magnesium and scandium was developed in 1985-1986 and was used for the manufacture of sheet parts of complex shapes [15].

In order to replace alloys of the D16 type based on the Al-Li-Mg-Cu system, alloys 1430, 1441, and 1440 with low density (by 8%), high modulus of elasticity (by 10%) and crack resistance have been developed. Alloys 1430 and 1441 differ from alloy 1440 in high ductility (1.5-2 times) [[15], [18]].

Based on the Al-Cu-Li system, alloys 1450 and 1451 have been developed, which have high strength at elevated temperatures and high corrosion resistance. When replacing the B95 alloy with alloys 1450 and 1451, the weight of the structures is reduced by 8-10%; with an increase in stiffness by 10%. As a result of additional alloying with zirconium and scandium alloys of the Al-Cu-Li system, a weldable alloy 1460 was developed for welded cryogenic fuel tanks for space and aviation purposes [15].

Table 2 - Chemical composition of aluminum-lithium alloys

Alloy grade	**Content of elements in the mass.%**										
	Li	***Cu***	***Mn***	***Mg***	***Sc***	***Ag***	***Cr***	***Zr***	***Ti***	***Zn***	***Manufacturer***
1st generation. Specific strength 169-180 m^2/s^2											
2020	1.2	4.5	0.5								Alcoa 1958
1420	2.2		to 0.25	6.2				0.1			VIAM 1965
1421	2.2		0.2	6.1	0.35			0.1			VIAM 1965
1423	2.0		0.2	4.4	0.12			0.1			VIAM 1965
1424	1.8		0.25	5.1	0.08			0.1	0.2		VIAM 1965
5091	1.4			4.2							Alcoa 1958
2nd generation. Specific strength 176-223 m^2/s^2											
1440	2.3	1.9	0.08	1.1				0.2	0.1		VIAM 1980e
1430	1.7	1.6		2.7				0.11			VIAM 1980e
1441	2.0	1.9	0.4	1.1				0.16	0.07		VIAM 1980e
1450	2.0	3.2	0.08	0.1				0.2	0.15		VIAM 1980e
1460	2.3	3.3	0.1	0.1				0.12	0.15		VIAM 1980e
1461	1.8	3.5	0.5	0.6	0.8		0.05	0.12	0.05		VIAM 1980e
1464	1.8	3.2	0.4	0.7	0.09			0.11			VIAM 1980e
1469	1.7	4.5	0.5	0.5	0.28	1.5		0.2			VIAM 1980e
2090	2.6	3.0	0.0	0.3			0.05	0.1	0.1		Alcoa 1984
2091	2.3	2.5	0.1	1.9			0.1	0.1	0.1		Pechiney 1985
2094	1.4	5.2	0.2	0.8		0.6		0.12	0.1		EAA, 1984
8090	2.4	1.2		0.8				0.11			EAA, 1984
3rd generation. Specific strength 181-242 m^2/s^2											
2195	1.0	4.0		0.4		0.4		0.11			LM/Reynolds 1992
2196	1.75	2.9	0.3	0.5		0.4		0.11		0.3	LM/Reynolds 2000
2297	1.4	2.8	0.3	0.25				0.11		0.5	LM/Reynolds 1997
2397	1.4	2.8	0.3	0.2				0.11		0.1	Alcoa 1993
B-1469	1.2	3.2		0.3	0.1	0.4		0.09			VIAM 2000e
B-1461	1.8	2.8		0.5	0.1			0.08		0.6	VIAM 2000e
2098	1.05	3.5	0.35	0.53		0.4		0.11		0.3	
2198	1.0	3.2	0.5	0.5		0.4		0.11		0.3	Reynolds/McCook 2005
2099	1.8	2.7	0.3	0.3				0.09		0.7	Alcoa 2003
2199	1.6	2.6	0.3	0.2				0.09		0.6	Alcoa 2005
2050	1.0	3.6	0.3	0.4		0.4		0.11		0.2	Pechiney 2004
2296	1.6	2.4	0.2	0.6		0.4		0.11		0.2	Alcan, 2010
2060	0.7	3.9	0.3	0.8		0.2		0.11		0.4	Alcoa 2011
2055	1.1	3.7	0.3	0.4		0.4		0.11		0.5	Alcoa 2012
2065	1.2	4.2	0.4	0.5		0.3		0.11		0.2	Constellium 2012
2076	1.5	2.3	0.3	0.5		0.2		0.11		0.3	Constellium 2012

Based on the developed alloy 1420, Alcoa, Alcan, Pechiney intensive work on aluminum-lithium alloys were carried out. As a result of these works, foreign alloys 2060, 2090, 2091, 8090, Navalite and others were developed [[19], [20], [21]].

Aluminum-lithium alloys are used in the manufacture of wings and horizontal stabilizer of the American military aircraft A-5 "Vigilante", in the lower wing skin of the Airbus A380, the internal structure of the Airbus A350 wing, Bombardier CSeries fuselage (where alloys make up 24% of the fuselage) [22], in the cargo floor of the Boeing 777X [23] and in the blades the fan of the Pratt & Whitney PurePower turbofan aircraft engine [24]. Welded hulls of the well-known Proton and Angara launch vehicles (Russia) are made of aluminum-lithium alloys.

In space technology, tanks for fuel and oxidizer of the first and second stages of the Falcon 9 launch vehicle are made of aluminum-lithium alloys using friction welding with mixing (Figure 2) [25]. The Falcon 9 is a two-stage liquid-fuel rocket with a diameter of 3.66 m. The tanks of both stages are made of sheets and plates of Al-Li 2198.

Figure 1 - MiG-29 FTR

The thrust panels of the Space Shuttle launch vehicle tank were also made of Al-Li alloys 2090, 2195, which made it possible to reduce the weight of the product by 3000 kg than when using alloy 2219 (Figure 3) [11].

Figure 2 - Falcon 9 fuel tank made of aluminum-lithium alloy 2198

The use of Al-Li alloys for future cryogenic tanks was studied by the European Space Association (ESA) [[26], [27]]. Al–Li alloys are used in the Centaur upper stage in the Atlas V rocket (Figure 4) [28] and the Orion spacecraft (Figure 5) [[29], [30]]. Orion has a crew module and a maintenance module. Both modules use aluminum-lithium alloys 2195 for the main bearing spars and alloy 2050 for other components, including frames, ribs and window sections.

Figure 3 - External fuel tanks and thrust panels of the Space Shuttle tank made of aluminum-lithium alloys 2090 and 2195

Figure 4 - Centaur upper stage in the Atlas V rocket

The key technology for manufacturing Al-Li alloy components and structures for spacecraft, especially tanks and tank domes, is friction mixing welding. Friction welding with mixing was used to connect the components of the Orion crew module Al-Li, including the final 11.3 m long weld connecting the forward cone assembly and the crew tunnel with the aft assembly [[31], [32]]. Friction welding with mixing has also been used to manufacture spin domes of fuel tanks made of Al-Li alloy 2195 [33] and it is planned to use this technology to connect parts of the main tank made of alloy 2219 for the Ariane 5 launcher [34].

Figure 5 - Al-Li alloys used in the American Orion spacecraft

Aluminum-lithium alloys are also beginning to be used in shipbuilding and the automotive industry.

Technology for the production of aluminum-lithium alloys. Aluminum-lithium alloys used in aerospace, defense technology and other high-tech industries have high mechanical properties ($\sigma_{in} \geq$ 415 MPa) and are subject to international export control agreements for dual-use goods and technologies [[35], [36], [37], [38]]. The countries producing such materials do not publish the technologies used, and the finished materials are sold to third countries only under intergovernmental agreements, similar to arms sales. In open sources, only the grades of the alloy, its chemical composition, mechanical properties, and in some cases possible prices are given. International export control agreements do not restrict the rights of third countries to develop and manufacture dual-use materials.

Despite the fact that there are no direct descriptions of the production technology of dual-use aluminum-lithium alloys in the literature, their main principal stages can be described in a general way, based on standard operations for the production of traditional aluminum alloys [39].

The simplest and most commonly used aluminum-lithium alloy is alloy 1420 (Table 2). Alloy 1420 belongs to the Al-M–Li system. A feature of this alloy is its very strong oxidizability during melting and casting, due to the presence of lithium. It is believed that the introduction of lithium and refractory zirconium into the melt requires the development of special technological techniques. The technological stages of obtaining aluminum-lithium alloy 1420, most likely consist of the following stages:

1. *Preparation of the charge.* At the beginning of the operation, the components of the charge are calculated by % weight. Alloying components are used in the form of pure metal or aluminum ligature Al-Li, Al-Zr, and Al-Mg. The technology of introducing alloying components is not described in the literature, they need to be determined experimentally [[40], [41], [42]].

2. *Melting.* The charge is melted in an induction vacuum furnace in an argon or helium medium at a temperature of about 660-700°C for 10-120 minutes. It is allowed to increase the temperature to 780 ± 15°C for uniform distribution of refractory zirconium over the melt volume. Heating over 800°C is not desirable due to the strong oxidizability of lithium and loss of magnesium. There are no data on melting pressure. However, it can be assumed that the residual pre-vacuum pressure will be sufficient [[43], [44], [45]].

3. *Degassing.* The melt is kept in a vacuum chamber at a residual pressure of 266-1333 Pa (2-10 mmHg) and at a temperature of 750-800°C for 5-20 minutes. Using such treatment of the melt with a chlorine-containing flux, the hydrogen content decreases to 0.10 cm ^{3}/100 g [45].

4. *Casting.* The finished melt is poured and cooled in steel or graphite molds in an argon or helium medium [45].

5. *The chemical composition* of the cast sample should be within the following limits: Mg – 5-6%, Li – 1.9-2.3%, Zr – 0.09-0.15%, Si – 0.1-0.3%, res. Al.

6. *Homogenization annealing* of the sample varies at the following intervals: 450± 10 °C for 1.5-6 hours. The vacuum in the chamber should not be lower than 0.1MPa (1 atm) [[46], [47]].

7. *Sample tempering* varies at the following intervals: 450°C-490°C for 20 - 120 minutes and cooled in air or water [[46], [47], [48], [49], [50], [51]].

8. *Sample aging* is carried out under the following conditions [[47], [48], [49], [50]]:

- 120-180°C- 5-16 h
- 120 ° C-12 h, + 180 °C – 12 h

9. *Sample deformation* varies at the following intervals: deformation of 15-30% at a rate of 1s^{-1} for 0.5-1 hour at 20-550°C and a pressure of 6 MPa [[46], [51], [52]].

10. *Sample recrystallization is* carried out at 510°C for 30 minutes [51].

11. *Determination of sample properties.*

The above-proposed stages of 1420 alloy production can be implemented at Kazakhstan plants to produce aluminum alloys and products.

Aluminum industry in Kazakhstan. Kazakhstan has a good raw material base for the production of aluminum and its alloys. The only alumina producer in the country is the Pavlodar Aluminum Plant, which uses alumina as a raw material for the production of primary metallic aluminum. Pavlodar Aluminum Plant is part of the association of Aluminum of Kazakhstan JSC. The plant was put into operation in 1964 and until today its production capacity has reached 1.5 million tons of alumina per year.

The main consumers of commercial alumina of Aluminum of Kazakhstan JSC are enterprises of the Russian Federation, Tajikistan, China and the Kazakh enterprise Kazakhstan Electrolysis Plant JSC.

The Kazakhstan Electrolysis Plant was founded in 2007 in the southeast of Pavlodar and is also the only producer of primary aluminum in the country. To date, the Kazakhstan Electrolysis Plant produces technical purity aluminum (Al>99.0%) and high purity aluminum (Al>99.95%). The capacity of the enterprise is 250 thousand tons of aluminum per year.

According to the Ministry of Industry and Infrastructure Development of the Republic of Kazakhstan, the country is working on the implementation of a project for the construction of a new electrolysis plant in the city of Pavlodar, which is scheduled to be launched in 2025. After its launch, the processing of alumina in Kazakhstan will be increased to one million tons per year, followed by the production of primary aluminum up to 500 thousand tons per year. The finished products are planned to be delivered to the countries of the European Union and Asia, as well as to the domestic market of the country.

At the moment, the Kazakhstan Electrolysis Plant sends about 90% of finished products to foreign markets and supplies the remaining 10% to Kazakhstani enterprises such as Aluminum of Kazakhstan, Giessenhaus, Alprof, Casting, Tsvetlit, Gold Aluminum. These enterprises, using primary aluminum, produce the following types of aluminum alloys and products from them:

1. The German-Russian enterprise Giessenhaus LLP, which is located in the Pavlodar region, produces 36-40 thousand tons of alloyed high-strength aluminum alloy per year. The alloyed aluminum produced consists of aluminum, silicon, magnesium, titanium, and manganese (the specific production technology of the German parent company LVG GmbH is closed). The finished alloyed aluminum alloy is sent to Vector-Pavlodar LLP, where cast car wheels are produced.
2. Aluminum of Kazakhstan LLP (Hoffmann Aluminum) produces aluminum alloys of 6060, 6063, 6463, 6082 grades (Almaty). The company produces 16,200 tons of aluminum alloys per year. The plant has a full production cycle: from loading the charge into the furnace to the production of finished products of any complexity. The plant's capacities are not fully loaded.
3. Casting LLP (Almaty) produces casting and deformable aluminum alloys of AK5M2 and ADS-12 grades. Enterprise capacity Casting LLP makes 12 thousand tons of aluminum alloys per year.
4. Alprof LLP (Almaty) produces various types of semi-finished products and products made of aluminum alloys of AD 31, AD 35, 6060, 6063 grades.
5. Gold Aluminum (Shymkent) manufactures various profiles from structural aluminum alloy 6063. The plant produces 750 tons of aluminum profiles per year.
6. Tsvetlit LLP (Shymkent) produces aluminum wire rods and aluminum alloys. The productive capacity of the enterprise is 24 thousand tons of wire rods and 12 tons of alloys.

The aluminum alloys produced at these enterprises have low and medium strength characteristics and are intended for the production of aluminum reinforcement for construction. The products of these plants are intended for internal use; these alloys are not in demand in other countries and do not have export potential.

Kazakhstan exports the following types of aluminum products, namely heat-resistant, a corrosion-resistant high-strength aluminum alloy of Giessenhaus LLP; primary aluminum of technical and high purity of the enterprise of Kazakhstan Electrolysis Plant JSC, and alumina of Aluminum Kazakhstan JSC. The products of these enterprises are in demand not only in the CIS countries, but in Germany, Austria, and Poland.

Table 3 shows the comparative prices of alumina, aluminum, and alloys of construction fittings produced in Kazakhstan, as well as alloy 1420.

Table 3 - Prices of alumina, aluminum and alloys

Material	Price, KZT/kg
Alumina	143-156
Aluminum	450-615
Alloys for construction fittings	626-1000
Alloy 1420	1827

As can be seen, alloy 1420 is 2-3 times more expensive than alloys of the type silumin, duralumin, avial, and others produced in Kazakhstan. Aluminum-lithium alloys, including alloy 1420, are in high demand on the international market. The development of the 1420 alloy production technology and its implementation at the factories of Kazakhstan is an urgent and cost-effective task since this material is of high processing and high technology.

The composition of alloy 1420 includes zirconium, magnesium, and lithium. These alloying elements are currently freely available on the international market in the form of pure metal or ligature. In the future, it would be possible to use zirconium and lithium of their own production. On this issue, the situation is as follows:

1. The Obukhov Mining and Processing Plant (North Kazakhstan region) produces zirconium concentrate. Expoengineering LLP processes titanium-zirconium ore at the Shokash deposit in the Aktobe region.

2. Primary magnesium in ingots is produced by Ust-Kamenogorsk Titanium and Magnesium Plant JSC (Ust-Kamenogorsk) At the moment, 100% of finished products are exported to countries such as the USA, Russia, China, and others.

3. According to the representative of "NC KAZAKH INVEST" - Aitkulov B., it is planned to build mining and processing plants near lithium deposits in the East Kazakhstan region, Aktobe, Kostanay, and West Kazakhstan regions. The cost of the project in the East Kazakhstan region is estimated at USD102 mln., and the production capacity will reach 4 thousand tons of lithium carbonate per year. According to geological research, lithium reserves in Kazakhstan amount to about 80 thousand tons. Kazakhstan has every opportunity to implement a full cycle of lithium production in the coming years and, consequently, alloys with its use.

Conclusions

There is an increasing demand in the world for high-strength aluminum-based alloys with strength characteristics ≥ 415 MPa for promising engineering tasks. The development of technologies for the production of the high-strength alloy to develop exports of domestic finished products to other countries is relevant. This would allow Kazakhstan to take a worthy place among manufacturers and suppliers of competitive aluminum-lithium alloys.

Conflict of interest

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

Gratitude

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Алюминий-литий қорытпалары: түрлері, қасиеттері, қолданылуы және өндіру технологиясы. Шолу

Аблакатов И.К., Байсериков Б.М., Исмаилов М.Б., Нургожин М.Р.

АО «Национальный центр космических исследовании и технологии», Алматы, Казахстан

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ТҮЙІНДЕМЕ

Мақалада Қазақстанның алюминий өнеркәсібінің даму жағдайына және беріктігі жоғары конструкциялық алюминий-литий қорытпаларын алу мүмкіндігіне қысқаша шолу келтіріледі. Еліміздің кәсіпорындарында техникалық таза алюминий мен құрылыс индустриясы үшін жалпыға қолжетімді материалдар болып табылатын беріктігі төмен және орташа болатын 6060, 6063, 6463, 6082, АК5М2, АДС-12, АД-31, АД-35 маркалы алюминий қорытпаларын өндіреді. Қазақстанда машина жасаудың үдемелі дамуы жүріп жатыр, ол үшін беріктігі 300-400 МПа, ал арнайы машина жасау (қорғаныс, аэроғарыш және басқа да озық салалар) үшін беріктігі 415 МПа - дан жоғары неғұрлым берік қорытпалар қажет болады. Жоғары беріктігі бар алюминий қорытпалары Al-Cu-Mg, Al-Zn-Mg-Cu, Al-Li жүйелеріне негізделген. Осы жүйелердің ішінде салыстырмалы түрде жаңа Al-Li қорытпалары үлкен қызығушылық тудырады, олардың сипаттамаларын одан әрі жақсартуға үлкен әлеуеті бар. Al-Li жүйесінің қорытпалары рекордтық жоғары беріктігі, коррозияға төзімділігі, дәнекерленген қосылыстардың жақсы көрсеткіштері бойынша аэроғарыш саласында кеңінен қолданылады, онда олар қуат элементтері мен корпустардың өндірісінде қолданылады. Жұмыста белгілі алюминий-литий қорытпаларының сипаттамаларына, сондай-ақ оларды өндірудің негізгі технологиялық кезеңдеріне шолу жасалады.

Түйін сөздер: қорытпа, алюминий, литий, магний, цирконий, беріктік, технология.

	Авторлар туралы ақпарат:
Аблакатов Іляс Қабылашымұлы	*Кіші ғылыми қызметкер," Ұлттық ғарыштық зерттеулер мен технологиялар орталығы "АҚ, Алматы, Қазақстан. ORCID ID: 0000-0003-4912-9289. Email: termostators@gmail.com*
Байсеріков Бердияр Мейiржанұлы	*Кіші ғылыми қызметкер," Ұлттық ғарыштық зерттеулер мен технологиялар орталығы " АҚ, Алматы, Қазақстан. ORCID ID: 0000-0003-0804-3147. Email: baiserik.b.91@mail.ru*
Исмаилов Марат Базаралыұлы	*Техника ғылымдарының докторы, профессор, ғарыштық материалтану және аспап жасау департаментінің директоры, "Ұлттық ғарыштық зерттеу және технологиялар орталығы" АҚ, Алматы, Қазақстан. ORCID ID: 0000-0002-1111-4658. Email: m.ismailov@gmail.com*
Нұрғожин Марат Рахмалиұлы	*Техника ғылымдарының докторы, профессор, ҚР Халықаралық Ақпараттандыру және инженерлік академиясының академигі. "Ұлттық ғарыштық зерттеулер мен технологиялар орталығы" АҚ Басқарма төрағасы, Алматы, Қазақстан. Email: m.nurguzhin@spaceres.kz*

Алюминиево-литиевые сплавы: виды, свойства, применение и технологии получения. Обзор

Аблакатов И.К., Байсериков Б.М., Исмаилов М.Б., Нургожин М.Р.

АО «Национальный центр космических исследовании и технологии», Алматы, Казахстан

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АННОТАЦИЯ

В статье приводится краткий обзор по состоянию развития алюминиевой промышленности Казахстана и возможности получения высокопрочных конструкционных алюминиево-литиевых сплавов. В предприятиях страны производят алюминий технической чистоты и алюминиевые сплавы низкой и средней прочности 6060, 6063, 6463, 6082, АК5М2, АДС-12, АД-31, АД-35, которые являются общедоступными материалами для строительной индустрии. В Казахстане идет поступательное развитие машиностроения, для которого требуются более прочные сплавы с прочностями 300-400 МПа, а для специального машиностроения (оборонная, аэрокосмическая и другие передовые отрасли) - с прочностями выше 415 МПа. Высокопрочные конструкционные алюминиевые сплавы основаны на системах Al-Cu-Mg, Al-Zn-Mg-Cu, Al-Li. Среди этих систем большой интерес представляют относительно новые сплавы Al-Li, имеющие, по-видимому, большой потенциал дальнейшего улучшения характеристик. Сплавы системы Al-Li с рекордно высокими удельными прочностями, стойкими к коррозии, хорошими показателями сварных соединений находят широкое применение в аэрокосмической промышленности, где используются для производства силовых элементов и корпусов. В работе дается обзор характеристик известных алюминиево-литиевых сплавов, а также основные технологические этапы их производства.

Ключевые слова: сплав, алюминий, литий, магний, цирконий, прочность, технология.

	Информация об авторах:
Аблакатов Ильяс Кабылашимулы	*Младший научный сотрудник, АО «Национальный центр космических исследовании и технологии», Алматы, Казахстан. ORCID ID: 0000-0003-4912-9289. Email: termostators@gmail.com*
Байсериков Бердияр Мейиржанулы	*Младший научный сотрудник, АО «Национальный центр космических исследовании и технологии», Алматы, Казахстан. ORCID ID: 0000-0003-0804-3147. Email: baiserik.b.91@mail.ru*
Исмаилов Марат Базаралиевич	*Доктор технических наук, профессор, директор департамента космического материаловедения и приборостроения, АО «Национальный центр космических исследовании и технологии», Алматы, Казахстан. ORCID ID: 0000-0002-1111-4658. Email: m.ismailov@gmail.com*
Нургожин Марат Рахмалиевич	*Доктор технических наук, профессор, академик Международной академии информатизации и Инженерной академии РК. Председатель правления АО «Национальный центр космических исследовании и технологии», Алматы, Казахстан. Email: m.nurguzhin@spaceres.kz*

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Porous composite material based on liquid glass

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 a composite material obtained on the basis of liquid glass and mineral fillers of technogenic origin. The structure of the composite material is formed by porous granules bonded with a liquid-glass matrix. The porous filler is synthesized from a mixture of liquid glass and combined filler (cullet, flake overburden, coal mining waste, and ash microsphere). Regulation of composition and content of the filler in the raw mixture ensures porous granules production with a bulk density of 270 – 330 kg/m^3. Analysis of mathematical models reflecting the dependence of the density and strength of the composite material on the composition of the moulding mixture allowed us to establish a reasonable ratio between the liquid glass and the filler, the matrix, and the porous filler. Optimal proportions of the composite material are characterized by a density of 450 – 600 kg/m^{3}and compressive strength of at least 5.5 MPa. Strong adhesion of the liquid-glass matrix to the surface of the porous filler ensures the resistance of the composite material to diverse effects. The structure of the materials was studied by electron microscopy. The development of composite material is aimed at improving the energy efficiency of construction.

Keywords: composite material, liquid glass, technogenic filler, porous granules, lightweight concrete.

Information about authors:

Miryuk Olga Aleksandrovna

Doctor of Technical Sciences, Professor. Head of the department of building construction materials, Rudny Industrial Institute, Rudny, Kazakhstan. Email: psm58@mail.ru, https://orcid.org /0000-0001-6892-2763.

Introduction

The energy efficiency of construction is largely ensured by the use of composite materials with a porous structure. The advantages of cellular concretes are extensive raw material base, a variety of products and their cost-effectiveness. However, the porous structure of cellular concrete is unstable, which often leads to a decrease in the strength and heat-shielding performance of products. This limits cellular concretes' application [[1], [2], [3], [4]].

Lightweight concretes based on porous fillers are promising composite materials for energy-efficient construction [[5], [6], [7], [8], [9]]. Porous filler is a dominant component, which makes up to 80% of concrete's mass. Structural characteristics of porous filler affect the structure of composite materials, and determine thermal and physicomechanical properties of lightweight concretes. The development of effective porous concrete technology is associated with the modification of raw materials, and improvement of moulding sand composition.

The structure of composite materials consists of a matrix and a discrete component distributed in the matrix. The block of hardened binder serves as a matrix in light concretes, the discrete component is represented by grains of porous filler. Thermal and physicomechanical properties of lightweight concrete depend on the characteristics of porous filler and a matrix. The matrix connects the filler particles into a monolith and provides uniform distribution of stresses throughout the volume of the material. Types of cement are mainly used as a matrix of lightweight concretes.

Liquid glass is an aqueous solution of alkaline (often sodium) silicates. Liquid glass is characterized by chemical activity and has a high adhesive ability. The rheological properties of liquid glass are regulated by additives and thermal effects. The formation of a highly porous structure of liquid glass is carried out by swelling, which is accompanied by the formation of cells of various sizes. The introduction of powdered filler into liquid glass can change the nature of swelling. Filled liquid glass compositions serve as a binder for moulding sand to produce porous filler.

Analysis of the last year's achievements indicates the creation of effective porous products based on liquid glass. The technology of granular foam-glass-ceramic materials from industrial waste is being actively developed. Thermal power engineering waste, waste from ores mining and processing, and metallurgical slags are used to obtain porous fillers [[10], [11], [12], [13], [14], [15], [16], [17], [18], [19], [20]]. A number of developments are devoted to highly porous granular materials based on the thermal swelling of liquid glass [[14], [15], [18], [19]]. Polarization of liquid glass composites is carried out mainly by swelling. The choice of fillers, aimed at optimizing compositions' technological state is of importance for the development of effective liquid glass materials. Information about lightweight concretes obtained on the basis of liquid glass is scarce.

The aim of the research is to study composite materials with porous filler; their main component is sodium liquid glass.

Experimental part

The object of the study is composite materials based on liquid glass, of which both components of lightweight concrete were synthesized.

Sodium liquid glass ($Na_2O·mSiO_2 + mH_2O$) – an aqueous solution of sodium silicate with a density of 1430 kg/m^3 was used in the experiments. Liquid glass provides binding of components powdered and promotes the thermal expansion of the raw mass.

Materials of various origins were introduced into the liquid glass as filler.

A finely ground cullet of quartz glass (cullet) is fragments of sheet and container glass. The basis of technogenic glass is amorphous silica. Chemical composition of cullet, wt. % as follows: SiO_2 –74; Al_2O_3 – 4; Fe_2O_3 – 2; CaO – 6; MgO – 1; R_2O –13.

Flask sedimentary rock is the overburden during mining. The flask rock is predominantly composed of amorphous opal and includes cristobalite, tridymite, and admixtures of clay minerals. Chemical composition, wt. % as follows: SiO_2 – 81; Al_2O_3 – 5; Fe_2O_3 – 2; CaO – 2; MgO – 1; R_2O –1. oth. – 7.

Overburdened rocks of the coal basin are coal mining waste. The mineral composition is represented by quartz, kaolinite, pyrite, and siderite; there are feldspars, montmorillonite, anhydrite, and calcite. Chemical composition of overburden rocks, wt %: SiO_2 – 65; Al_2O_3 – 10; Fe_2O_3 –7; CaO – 3; MgO –1; S –3; C – 6; oth. - 5.

Ash microsphere is a loose material consisting of hollow spherical particles with a diameter of 100 – 350 microns. It is formed as a light fraction of ash from the combustion of solid fuels. The bulk density is 400 kg/m^3. Chemical composition, %: SiO_2 – 83; Al_2O_3 – 5; Fe_2O_3 – 2; CaO – 10.

Moulding compounds were prepared from liquid glass binder and porous filler was developed. The porous filler was synthesized by thermal treatment of the granular material. Granules were moulded on a laboratory drum pelletizer from a mixture of liquid glass and mineral filler.

Discussion of results

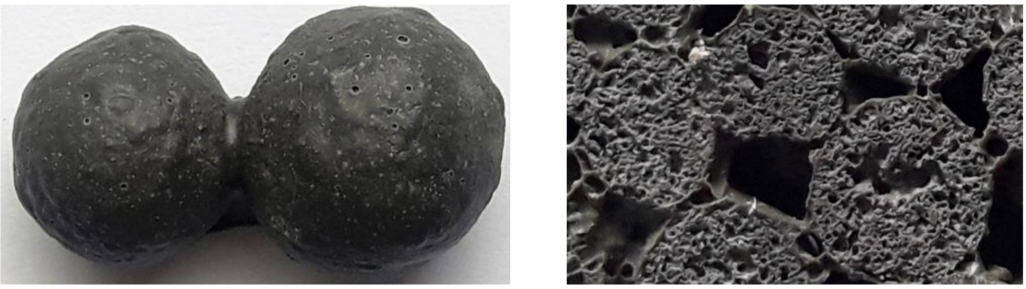
The combination of fillers of different proportions makes it possible to control the viscous and plastic properties of liquid glass and determines the nature of the thermal swelling of the granules. Regulation of the content and composition of the mineral filler affects the temperature of swelling and properties of granular material (Table 1).

Porous granules with a diameter of 6 – 10 mm are characterized by a porosity of 75 – 80%. The porosity of granules fired at 750^{0}C is represented by swelling cells. In granules fired at 350^{0}C, the porous structure is formed by microsphere cavities and swelling cells in the liquid glass component. The efficiency of liquid glass granules is determined by improved thermal performance.

Calculations show that in order to provide thermal resistance of 3.3 (m^{2}·^{0}C)/W, the heat-insulating layer of liquid glass granules (thermal conductivity coefficient is 0.06 W/(m·^{0}C)) should be 20 cm; and the expanded clay layer (thermal conductivity coefficient is 0.09 W/(m ·^{0}C)) is 36 cm.

Table 1 – Characteristics of the raw mixture and porous granules based on it

Composition of filler in the raw mix, %				Swelling temperature, ^{o}C	Bulk density, kg/m^3	Structure of the granules
cullet	flask rock	coal mining waste	ash microsphere			
50	20	30	–	750	270	
–	–	60	40	350	330	



Picture 1 – Granules grouting by the matrix and porous matrix

Porous liquid glass filler forms the basis of lightweight concretes' structure. A liquid glass binder was used to connect porous filler grains. Preference of liquid glass binder as a matrix for a composite material is due to the high binding ability of liquid glass; ability to control rheological properties of moulding sand; and reliability of adhesion with filler particles having a related origin with the matrix.

A liquid glass binder was obtained by mixing liquid glass with filler, which was used as a substance of various origins. The materials investigated are conditionally divided into the following groups. The first group is formed by materials, the firing of which is accompanied by dehydration and the formation of water vapour (clay, flask, bauxite, expanded clay dust, volcanic glass). Fillers of the second group contain minerals (pyrite, calcite, dolomite), which emit a gas phase during thermal transformations. Fillers of the third group (oil shale, wood flour, coal-bearing rocks, ash from coal combustion, expanded clay dust) contained a burnable component.

Liquid glass binders containing 40 – 45% additives of the first and third groups are evenly distributed between the filler grains and provide the necessary viscosity of moulding mass. Binding compositions with first group fillers form thin shells around porous filler grains. This ensures the minimization of the matrix in the lightweight concrete structure (Figure 1). Binding compositions with 30 – 35% fillers from all groups exhibit the ability to swell at 200 – 300^{o}C.

Moulding sands were prepared in the following order: liquid glass was mixed with filler (overburdened rocks of the coal basin); granular filler was introduced into the resulting liquid glass suspension. Moulding sand of moderate mobility was placed in cube moulds with a 70 mm edge. To accelerate hardening and ensure water resistance, the samples were subjected to heat at 250^{o}C for 40 min. The strength of samples of composite materials was determined by testing on a hydraulic press. Electron microscopy was used to study the composition of composite materials structure.

As a result of preliminary experiments, approximate ratios between the porous filler and the liquid glass binder were determined, which ensures low-density composite materials production. The mathematical planning method was used to optimize the composition of moulding mass. The conditions of the experiment are shown in Table 2. The moulding sands consisted of pellets fired at 350°C; liquid glass and filler were from coal mining waste. The following factors were taken as the factors studied: the proportion of grains of coarse filler fraction; the ratio between the liquid glass and the filler. Coarse filler is represented by grains 9 – 10 mm in size, fine filler consisted of grains 6 – 7 mm in size.

The planning matrix and the results of the experiment are shown in Table 3.

After statistical processing of experimental data, mathematical models were obtained.

Mathematical model reflecting dependence of composite materials' density, ρ (kg/m^3), on the studied factors as follows:

$$\rho = 635.857 - 0.377 \cdot x_1 + 0.107 \cdot x_1^2 - 475.13 \cdot x_2 + \\ + 2.708 \cdot x_2^2 - 1.920 \cdot x_1 \cdot x_2. \quad (1)$$

A geometric illustration of the function is shown in Figure 2.

The dependence of composite materials' strength (R, MPa) on the composition of the moulding material is obtained in the form of a regression equation of the full quadratic model:

$$R = 5.857 + 0.145 \cdot x_1 - 0.002 \cdot x_1^2 - 3.68 \cdot x_2 + \\ + 22.370 \cdot x_2^2 - 0.140 \cdot x_1 \cdot x_2. \quad (2)$$

A geometric illustration of the function is shown in Figure 3.

Table 2 – Conditions of the experiment

Factors		Levels of variation				
Natural	**Encoded**	**– 1.41**	**– 1**	**0**	**+ 1**	**+ 1.41**
Share of coarse filler fraction, %	X_1	0.0	14.5	50.0	85.5	100.0
Liquid glass / Filler	X_2	0.55	0.59	0.70	0.81	0.85

Table 3 – Mathematical planning of the experiment

	Factors researched		**Share of coarse filler fraction, %**	**Liquid glass Filler**	**Density, kg/m3**	**Compressive strength, MPa**
	X_1	X_2	X_1	X_2	ρ	R
1	–1	–1	14.5	0.59	650	6.42
2	+1	–1	85.5	0.59	615	5.84
3	–1	+1	14.5	0.81	485	4.96
4	+1	+1	85.5	0.81	420	4.16
5	–1.41	0	0.0	0.70	570	5.17
6	+1.41	0	100.0	0.70	510	4.05
7	0	–1.41	50.0	0.55	680	6.20
8	0	+1.41	50.0	0.85	480	4.10
9	0	0	50.0	0.70	505	4.87
10	0	0	50.0	0.70	500	4.93

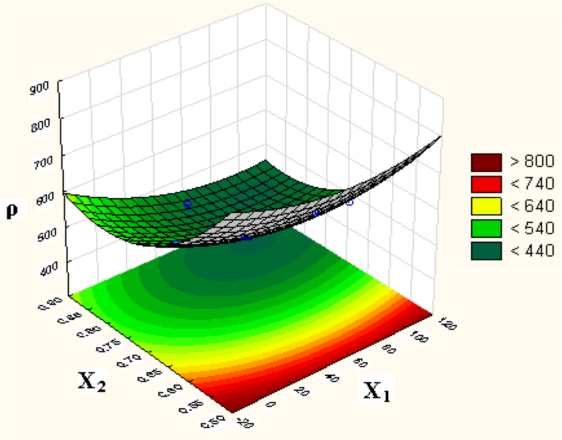


Figure 2– Response surface of the dependence of composite materials' density on moulding mass' composition

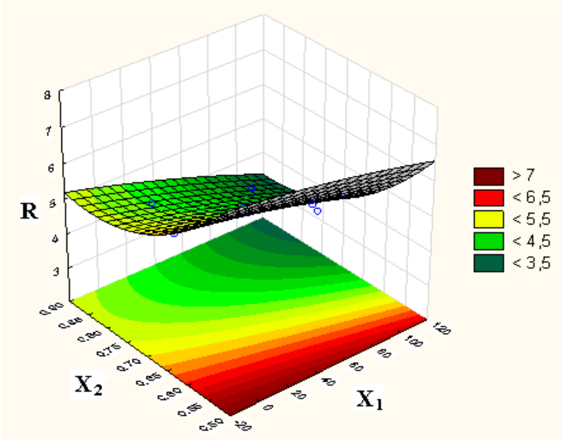


Figure 3 – Response surface of the dependence of composite materials' compressive strength on moulding mass' composition

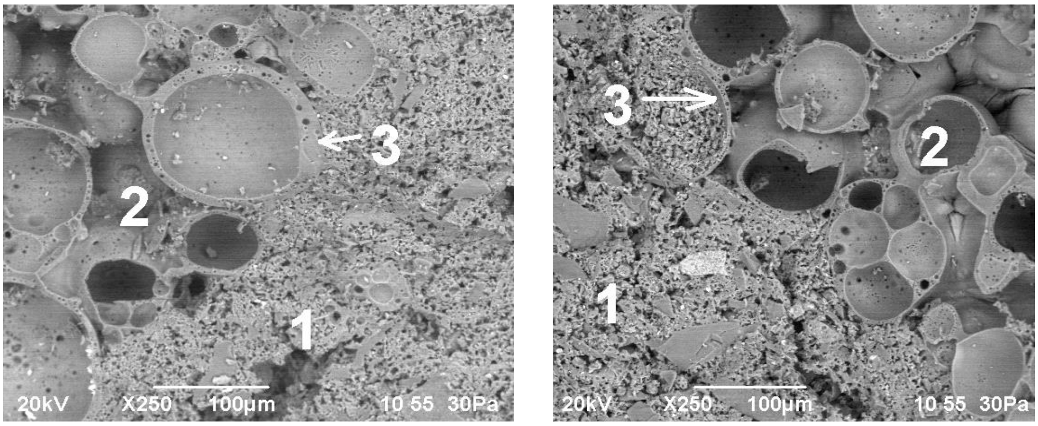


Figure 4 – Microstructure of the composite material: 1 - binder block; 2 - filler; 3 - contact zone

Figure 5 – Composite material sample before testing

Figure 6 – The nature of destruction of the composite material during the strength test

Figure 7– Fragment of a chip of composite material's sample

The obtained mathematical models indicate that the ratio between liquid glass and filler has a decisive influence on the density of composite materials. An increase in the proportion of filler increases the density of composite materials. The influence of the fractional composition of the filler is less significant and is expressed in a decrease in density of the composite as coarse grains of the filler increase. An increase in the strength of composite materials is facilitated by an increase in the proportion of coarse filler, limiting the content of the binder in the moulding sand.

The analysis of mathematical dependences makes it possible to single out the range of compositions of composite materials with density values of not more than 600 kg/m^3. This is ensured when the content of the coarse filler is not less than 20%, and the ratio of liquid glass to filler is not less than 0.65. Requirements for strength indicators of composite materials (not less than 5.5 MPa) thin the area of preferred mixes of composite materials: the proportion of coarse filler is 50 – 80%, the ratio between the binder and the filler is 0.65 – 0.75.

The results of the mathematical model analysis are consistent with the conclusions of numerical studies of the packing of filler in a composite material. A comparison of various porous filler packing schemes showed that the minimum stress and deformation in a composite material are typical for a two-component model that contains 60 – 70% porous filler granules. At the same time, the proportion of large grains in the filler composition is 50 – 60%

The study of the contact zone between the matrix and the surface of the porous filler indicates a close contact of the components (Figure 4). The nature of the destruction of the samples during the strength test confirms the high adhesion strength of the filler and the block of the liquid glass binder (Figures 5 and 6). The fracture of the samples occurs along the binder block and along the filler grain (Figure 7).

In terms of physical and mechanical parameters, liquid glass composite materials are not inferior to cement lightweight concretes of comparable density. Test results testify to the resistance of composite materials under conditions of variable values of humidity and temperature.

Conclusions

Proportions of the composite material based on liquid glass are proposed. The matrix and porous granules of composite materials are synthesized from mixtures of liquid glass and mineral fillers of technogenic origin.

Polarization of liquid glass granules is provided by thermal expansion and the presence of a hollow microsphere.

The range of proportions of the composite material, characterized by a density of 450 – 600 kg/m^3 and compressive strength of at least 5.5 MPa, has been determined. Composite material's proportions with a binder-filler ratio of 0.25 – 0.40 are preferable when large particles of the filler dominate.

Genetic similarity of the raw basis of the matrix and porous granules ensures the reliability of the adhesion of the components and the high technical properties of the composite material.

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

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Сұйық шыны негізіндегі кеуекті композициялық материал

Мирюк О.А.

Рудный индустриялық институты, Рудный, Қазақстан

Мақала келді: *21 қаңтар 2022*
Сараптамадан өтті: *24 наурыз 2022*
Қабылданды: *27 сәуір 2022*

ТҮЙІНДЕМЕ

Мақалада сұйық шыны және техногендік текті минералды толтырғыштар негізінде алынған композициялық материалдың эксперименталды зерттеулерінің нәтижелері берілген. Композиттік материалдың құрылымы сұйық шыны матрицамен бірге ұсталған кеуекті түйіршіктерден тұрады. Кеуекті толтырғыш су шынысының және аралас толтырғыштың (куллет шыны, колбаның үстіңгі қабаты, көмір өндіру қалдықтары, күл микросферасы) қоспасынан синтезделді. Шикізат қоспасындағы толтырғыштың құрамы мен мазмұнын реттеу 270 –330 кг/м^3 көлемді тығыздығы бар кеуекті түйіршіктердің алынуын қамтамасыз етеді. Композиттік материалдың тығыздығы мен беріктігінің қалыптау құмының құрамына тәуелділігін көрсететін математикалық модельдерді талдау сұйық шыны мен толтырғыш, матрица және кеуекті толтырғыш арасындағы ұтымды байланыстарды орнатуға мүмкіндік берді. Композиттік материалдың оңтайлы композициялары 450 – 600 кг / м^3 тығыздықпен және кем дегенде 5,5 МПа қысу күшімен сипатталады. Кеуекті толтырғыштың бетіне сұйық шыны матрицасының күшті жабысуы композиттік материалдың әртүрлі әсерлерге төзімділігін қамтамасыз етеді. Материалдардың құрылымы электронды микроскоп арқылы зерттелді. Композиттік материалды әзірлеу құрылыстың энергия тиімділігін арттыруға бағытталған.

Түйін сөздер: композициялық материал, сұйық шыны, техногендік толтырғыш, кеуекті түйіршіктер, жеңіл бетон

Мирюк Ольга Александровна

Авторлар туралы ақпарат:
техника ғылымдарының докторы, профессор. Құрылыс және құрылыстық материалтану кафедрасының меңгерушісі, Рудный индустриялық институты, Рудный, Қазақстан. E-mail: psm58@mail.ru; ORCID ID: 0000-0001-6892-2763

Поризованный композиционный материал на основе жидкого стекла

Мирюк О.А.

Рудненский индустриальный институт, Рудный, Казахстан

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АННОТАЦИЯ

В статье приведены результаты экспериментальных исследований композиционного материала, полученного на основе жидкого стекла и минеральных наполнителей техногенного происхождения. Структура композиционного материала сформирована пористыми гранулами, скрепленными жидкостекольной матрицей. Пористый заполнитель синтезирован из смеси жидкого стекла и комбинированного наполнителя (стекольный бой, опоковая вскрышная порода, отходы добычи угля, зольная микросфера). Регулирование состава и содержания наполнителя в сырьевой смеси обеспечивает получение пористых гранул с насыпной плотностью 270 – 330 кг/м^3. Анализ математических моделей, отражающих зависимость плотности и прочности композиционного материала от состава формовочной смеси, позволил установить рациональные соотношения между жидким стеклом и наполнителем, матрицей и пористым заполнителем. Оптимальные составы композиционного материала характеризуются плотностью 450 – 600 кг/м^3 и прочностью при сжатии не менее 5,5 МПа. Прочное сцепление жидкостекольной матрицы с поверхностью пористого заполнителя обеспечивает стойкость композиционного материала к различным воздействиям. Структуру материалов исследовали методом электронной микроскопии. Разработка композиционного материала направлена на повышение энергетической эффективности строительства.

Ключевые слова: композиционный материал, жидкое стекло, техногенный наполнитель, пористые гранулы, легкий бетон.

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; ORCID ID: 0000-0001-6892-2763.

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Analysis of Existing Technologies for Depletion of Dump Slags of Autogenous Melting

[1] Kenzhaliyev B.K., [1] Kvyatkovskiy S.A., [1*] Dyussebekova M.A., [1] Semenova A.S., [2] Nurhadiyanto D.

[1] "Institute of Metallurgy and Ore Beneficiation" JSC, Satbayev University, Almaty, Kazakhstan
[2] Faculty of Engineering, Universitas Negeri Yogyakarta, Indonesia

** Corresponding author email: m.dyussebekova@satbayev.university*

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ABSTRACT

Pyro-metallurgy of copper production is characterized by the output of copper slag, which is regarded as a kind of solid waste. Moreover, this slag is identified as hazardous because it contains impurities, like Pb, As, and Cu. Obtaining dump slags in autogenous processes does not always meet the requirements of effective technologies, most often slags contain more than 1.0% of copper and need to be depleted. This work is presented a brief analysis of existing technologies used for copper slag depletion. The analysis of the existing technologies for the depletion of autogenous smelting dump slags showed that the most promising option seems to be the depletion of copper slags in one PV unit since by improving the process itself, by changing the unit design, it is possible to achieve technologically complete production of matte and dump slag with low copper content. There were proposed two technologies of improvement: electro-heating of slag siphon using the graphite electrodes and depletion process in two-zone PV furnace.

Keywords: Copper slag, reduction treatment, depletion, slag siphon, two-zone Vanyukov furnace.

Information about authors:

Kenzhaliyev Bagdaulet Kenzhaliyevich	*Doctor of Technical Sciences, Professor, General Director-Chairman of the Management Board of the JSC "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. Email: bagdaulet_k@satbayev.university; ORCID ID: 0000-0003-1474-8354*
Kvyatkovskiy Sergey Arkad'yevich	*Doctor of Technical Sciences., Chief of Laboratory, JSC "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. Email: s.kvyatkovskiy@satbayev.university; ORCID ID: 0000-0002-9686-8642*
Dyussebekova Maral Adel'bekovna	*Junior researcher, JSC "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. Email: m.dyussebekova@satbayev.university; ORCID ID: 0000-0002-4359-9784*
Semenova Anastassiya Sergeevna	*Master of Engineering Science, Leading Engineer, "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. ORCID ID: 0000-0003-4054-8268. E-mail: a.semenova@satbayev.university*
Didik Nurhadiyanto	*Doctor of Engineering, Lecturer, Faculty of Engineering, Universitas Negeri Yogyakarta, Indonesia. E-mail: didiknur@uny.ac.id; ORCID ID:0000-0003-0643-0776.*

Introduction

Comparative analysis of technical indicators of autogenous processes indicates that slags require several measures to deplete them. For example, in the Norand process, the copper content in slags can reach 15%, KFP - 1.2%, KVP - 1-1.5%, Ausmelt - 0.8-1.0%, Mitsubishi - 0.5%, PV - 0.5-0.6%. The best indicators for dump slags are possible in the Mitsubishi and PV processes, however, a significant deterioration in the composition of concentrates in recent years leads to a violation of the technology and the production of copper-rich slags [[1], [2], [3], [4], [5], [6], [7]]. Slag depletion technologies have two main directions: the improvement of matte smelting itself with the production of dump slags and the use of separate units that allow slag depletion (for example, an electric furnace with several high-power units). The first option is expedient, promising, and economically viable. Improvement of the melting process on matte and the design of the furnace will make it possible to achieve the most significant results in slag depletion [[8], [9]].

Carrying out autogenous smelting of copper raw materials is closely related to the solution of slag depletion issues, which involves the implementation of the following conditions: obtaining a minimum amount of slag with low copper content, while the maximum should be fluidity, slag surface tension, minimum slag density, optimal silicon dioxide content, optimal temperature conditions for the separation of matte and slag [[10], [11], [12]]. Temperature conditions, maintenance of thermal balance due to oxidation of iron sulfides, control of moisture, and silicon oxide in concentrates are of exceptional importance for autogenous smelting. In a certain situation, to maintain the heat balance of the furnace, it is possible, and sometimes necessary, to use additional fuel, for example, natural gas, fuel oil, or coal [[13], [14]].

To compensate for the unsatisfactory heat balance, the insufficient temperature of the melt at the outlet of the furnace, and additional precipitation of the matte phase from the slag melt, it is very important to improve the operation of slag electric mixers on PV furnaces. Analysis of the influence of various factors on the PV process showed that all of them are of decisive importance for the efficient course of the smelting process, the main of which are indicators for the composition of dump slags, which determine the technical and economic characteristics of the entire technology [[14], [15]].

Method

The samples of the slags were obtained from the Vanyukov furnace in Balkhash Copper-Smelting Plant. These samples were analyzed by chemical and X-ray fluorescence analysis. X-ray fluorescence multi-element automated analysis was carried out on a wave-dispersive combined spectrometer Axios.

To simulate the oxidation zone of a two-zone PV furnace the slag was heated to a temperature of 1300 °C in the presence of a reducing agent, then the melt was kept for 1 hour. The consumption of coal was calculated as 2.5 g per 100 g of slag.

Results and discussion

Analysis of existing technologies for copper slag depletion

Depletion of slags when using a technology separate from smelting is possible using various processes such as pyro, hydro, and a combination of pyro-hydrometallurgical methods for metal recovery from copper slag [16]. One of the most promising is the reduction methods using electrothermal furnaces with various methods of supplying the reducing agent. Solid (coke, coal) and gaseous (coal-air mixture, natural and generator gas) substances are used as reducing agents. In world practice, separate or combined with a melting unit electrothermal furnaces, furnaces with a reducing bubbling using coal, natural, or generator gas are most often used [17]. There are known examples of slag depletion in the presence of pyrite, pyrrhotite, calcium sulfide, and cast iron [18]. It is possible to use turbulent mixing of a superheated slag melt for purification from copper with the introduction of CaC_2 into the process as a reducing agent [19]. The effect of an electric field on a slag melt was studied in [20]. It was found that there is a 3-fold increase in the deposition rate of copper drops with a diameter of 5 mm. It is noted that with an increase in the size of the metalized droplet or with an increase in the Cu_2O content in the slag, the effect of the electric field decreases.

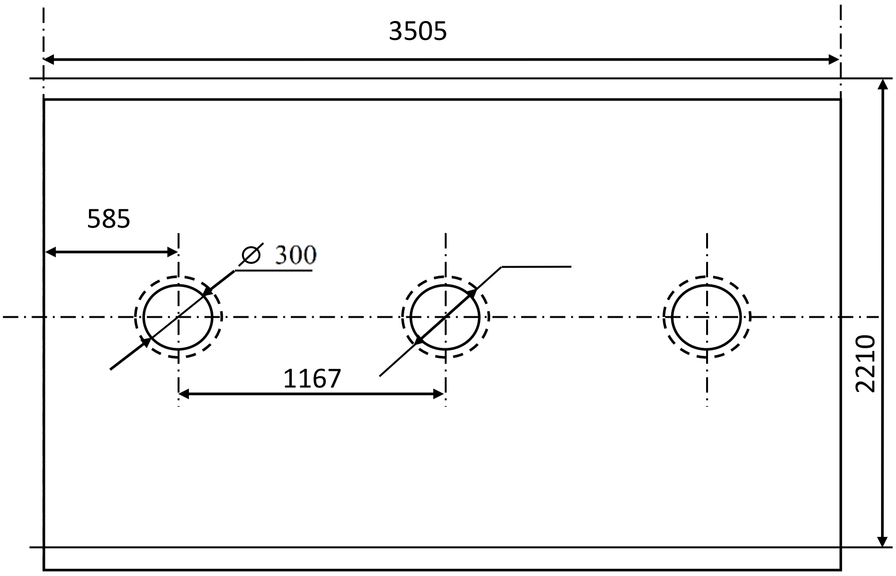
Methods of depletion of slags from copper production using sulfide reagents are seldom used due to environmental pollution with sulfur dioxide and to reduce the number of waste slags. Environmentally friendly methods are hydrometallurgical, in particular, the most common

and industrially implemented is flotation, which includes the preparation of slag by crushing and grinding in several stages, flotation together with ore material (or separate for slag) to obtain sulfide copper concentrate suitable for smelting on matte [21]. This method assumes the availability of the necessary flotation capacity at the concentrator. The disadvantages of such technologies are the relatively low extraction of copper into concentrate and the low quality of these concentrates themselves. Moreover, copper slag wastes after floatation treatment, still contain heavy metals with hazardous properties posing environmental risks, so they needed further utilization [22].

A method has been developed for the depletion of copper slag by leaching using various solvents such as sulfuric acid, hydrochloric acid, ammonia, cyanide, etc. [[23], [24], [25], [26]]. An intensification of the process of leaching of copper slags with the addition of hydrogen peroxide under pressure, as well as with the use of chlorine, has been proposed [[27], [28]]. Improvement of matte smelting itself with the production of dump is more expedient, promising, and economically viable and an additional increase in the slag settling zone, in which depletion occurs with the introduction of a reducing agent, is the most promising direction.

Improvement of slag siphon

The slag siphon structurally is a continuation of the melting zone of the PV, adjacent to the outer part of the slag partition, and in solving the problem of depletion of the slag PV and obtaining the waste slag is of great importance. Improving the operation of the PV slag siphon is expected to take several



Picture 1 – Layout of electrodes in a slag siphon

measures that will affect the processing of copper sulfide concentrates, improve the technical and economic indicators of the process, increase copper recovery, significantly reduce its losses with slag, and eliminate disturbances in the normal operation of PV furnaces. The stable operation of the slag siphon of the PV furnace is often disturbed by deposition processes, which is also facilitated by changes in the composition of the charge, for example, an increase in the content of zinc in concentrates. The continuous discharge of slag from the PV furnace into the electric mixer prevents the formation of build-ups, which are the result of the absence of horizontal movement of the melt and local peroxidation of the melt in the bubbling zones. In the slag siphon, it is necessary to create a regime of free movement of the melt, the possibility of sedimentation of copper sulfide particles, which is possible at a certain temperature regime, the creation of a reducing atmosphere, and the optimal composition of the slag.

A variant is proposed using three graphite electrodes with a diameter of 300 mm and a transformer similar to that used for a slag mixer. The use of electric heating of the slag siphon will allow, when the temperature of the melt in the slag siphon reaches at least 1300 °C, to ensure sufficiently complete separation of slag and matte. The electrodes in the siphon will operate at a relatively constant level of the slag melt with a uniform flow of slag through the slag siphon, which will provide optimal conditions for additional heating of the slag and the most complete separation of the matte phase from the slag and prevention of build-up in the siphon (Picture 1).

Additional heating of the slag in the slag siphon will reduce the power consumption in the slag mixer to maintain the melt temperature at least 1300 °C. The use of graphite electrodes with a diameter of 300 mm will allow for maintaining the existing width of the slag siphon.

Depletion in a 2-zone furnace

This process would be possible by dividing the reaction zone of the furnace into two zones oxidizing and reducing using a water-cooled partition. Slag samples were obtained from the Vanyukov furnace and their content is shown in Table 1.

Activated carbon was used as a reducing agent with the following content wt. %: 74.3 C, 0.16 S, 0.025 P, 1.12 Fe, 0.93 SiO_2, 1.56 Al_2O_3; melting temperature was – 1300 ^{0}C. The reduction treatment was carried out on a laboratory scale.

The slag was heated to a temperature of 1300 °C in the presence of a reducing agent, then the melt

Table 1 - Content of main components in slag before/after reduction treatment

№ of test	Slag content, %					
	Before treatment			After treatment		
	Cu	SiO_2	Fe_3O_4	Cu	SiO_2	Fe_3O_4
11	0.93	32.05	7.80	0.43	33.1	2.5
12	0.97	31.90	7.90	0.47	32.9	2.6
13	1.033	31.30	7.95	0.50	32.9	2.6

was kept for 1 hour. The consumption of coal was calculated as 2.5 g per 100 g of slag. At the end of the reduction process - slag and the bottom phase were obtained. The bottom phase had a similar composition to the matte obtained during smelting in a PV furnace.

Table 1 also shows the results of reduction processing, and it's seen that during the melting process the destruction of magnetite took place, its content had dropped by 5.3-6.5 % from 7.8 -7.95% to 2.5-2.6%, and this consequently had a positive effect on prevention of copper losses with slags. The presented results of analysis of slag samples after interaction with activated carbon indicate a decrease in copper content in the range of 0.43-0.50%, in comparison with its content in slags before reduction treatment in the range of 0.93-1.03%. Such a decrease in the copper content is associated with the process of destruction of magnetite, and the transition of iron oxides to fayalite.

Conclusion

All the proposed solutions for slag depletion, for the implementation of which industrial installations of operating units are required, occupying vast territories, consuming significant material and energy resources, are economically and ecologically unprofitable. The most promising option seems to be the option of depletion of copper slag in one PV unit since by improving the process itself, by changing the unit design, it is possible to achieve a technologically complete production of matte and dump slag with low copper content. The use of graphite electrodes for additional heating of the slag in the slag siphon will reduce the power consumption in the electrical mixer and at the same time will allow maintaining the existing width of the slag siphon. On the other hand, in comparison with similar developments, the proposed technology for melting copper sulfide concentrates in a two-zone PV furnace will make it possible to obtain slags with a copper content of 0.7% or less, with minimal costs for equipment reconstruction.

Conflict of interests

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

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[1] Кенжалиев Б.К., [1] Квятковский С.А., [1] Дюсебекова М.А., [1] Семенова А.С., [2] Нурхадиянто Д.

[1] «Металлургия және кен байыту институты» АҚ, Сәтбаев университеті, Алматы, Қазақстан
[2] Инженерия факультеті, Джокьякарта мемлекеттік университеті, Индонезия

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ТҮЙІНДЕМЕ

Мыс өндірісінің пирометаллургиясы қатты қалдықтарға жататын мыс қождарының бөлінуімен сипатталады. Сонымен қатар, бұл қож қауіпті болып саналады, өйткені оның құрамында Pb, As және Cu сияқты қоспалар бар. Автогендік процестерде үйінді қождарын алу әрдайым тиімді технологиялардың талаптарына сәйкес келмейді, көбінесе қождар құрамында 1,0% - дан астам мыс бар және оларды жұтаңдату қажет. Бұл жұмыста мыс қождарын азайту үшін қолданылатын қолданыстағы технологияларға қысқаша талдау берілген. Автогенді балқытудың үйінді қождарын жұтаңдатудың қолданыстағы технологияларын талдау нәтижесінде ең перспективалы нұсқа ПВ-ның бір агрегатында мыс қождарын жұтаңдату екендігі анықталды, өйткені процестің өзін жақсарту, қондырғының дизайнын өзгерту арқылы технологиялық тұрғыдан аяқталған, штейн мен мыстың мөлшері аз болатын үйіндіні өндіруге қол жеткізуге болады. Жұмыста жетілдірілген екі технология ұсынылған, олар: қож сифонын графит электродтар арқылы электр тогымен жылыту және екі аймақтық ПВ пешінде жұтаңдату процесі.

Түйін сөздер: Мыс қожы, қалпына келтіру, сарқылу, қож сифоны, Ванюковтың екі аймақтық пеші.

	Авторлар туралы ақпарат:
Кенжалиев Багдаулет Кенжалиевич	*Т.ғ.д.., «Металлургия және кен байыту институты» АҚ - ның бас директоры, Алматы, Қазақстан. Email: bagdaulet_k@satbayev.university; ORCID ID: 0000-0003-1474-8354*
Квятковский Сергей Аркадьевич	*Т.ғ.д.., «Металлургия және кен байыту институты» АҚ, зертхана меңгерушісі, Алматы, Қазақстан. Email: Email: s.kvyatkovskiy@satbayev.university; ORCID ID: 0000-0002-9686-8642*
Дюсебекова Марал Адельбековна	*Т.ғ. магистрі, «Металлургия және кен байыту институты» АҚ, кіші ғылыми қызметкер, Алматы, Қазақстан. Email: m.dyussebekova@satbayev.university; ORCID ID: 0000-0002-4359-9784*
Семенова Анастасия Сергеевна	*Т.ғ. магистрі, «Металлургия және кен байыту институты» АҚ, жетекші инженер, Алматы, Қазақстан. E-mail: a.semenova@satbayev.university; ORCID ID: 0000-0003-4054-8268*
Дидик Нурхадиянто	*И.ғ. докторы, Лектор, Инженерия факультеті, Джокьякарта мемлекеттік университеті, Индонезия. E-mail: didiknur@uny.ac.id; ORCID ID:0000-0003-0643-0776*

Анализ существующих технологий обеднения отвальных шлаков автогенной плавки

[1] Кенжалиев Б.К., [1] Квятковский С.А., [1] Дюсебекова М.А., [1] Семенова А.С., [2] Нурхадиянто Д.

[1] АО «Институт металлургии и обогащения», Satbayev University, Алматы, Казахстан
[2] Инженерный факультет, Государственный университет Джокьякарты, Индонезия

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АННОТАЦИЯ

Пирометаллургия медного производства характеризуется выходом медных шлаков, которые относят к твердым отходам. Кроме того, этот шлак считается опасным, так как содержит такие примеси, как Pb, As и Cu. Получение отвальных шлаков в автогенных процессах не всегда соответствует требованиям эффективных технологий, чаще всего шлаки содержат более 1,0% меди и нуждаются в обеднении. В данной работе представлен краткий анализ существующих технологий, используемых для обеднения медных шлаков. Анализ существующих технологий обеднения отвальных шлаков автогенной плавки показал, что наиболее перспективным вариантом является обеднение медных шлаков в одном агрегате ПВ, так как путем совершенствования самого процесса, изменением конструкции агрегата можно добиться технологически завершенного производства штейна и отвального шлака с низким содержанием меди. Предложены две технологии совершенствования: электрообогрев шлакового сифона графитовыми электродами и процесс обеднения в двухзонной печи ПВ.

Ключевые слова: Медный шлак, восстановительная обработка, обеднение, шлаковый сифон, двухзонная печь Ванюкова.

	Информация об авторах:
Кенжалиев Багдаулет Кенжалиевич	*Д.т.н., Генеральный директор-Председатель Правления АО «Институт Металлургии и Обогащения», Алматы, Казахстан. Email: bagdaulet_k@satbayev.university; ORCID ID: 0000-0003-1474-8354*
Квятковский Сергей Аркадьевич	*Д.т.н., заведующий лабораторией, АО «Институт Металлургии и Обогащения», Алматы, Казахстан. Email: s.kvyatkovskiy@satbayev.university; ORCID ID: 0000-0002-9686-8642*

Дюсебекова Марал Адельбековна	*М.н.с., АО «Институт Металлургии и Обогащения», Алматы, Казахстан. Email: m.dyussebekova@satbayev.university; ORCID ID: 0000-0002-4359-9784*
Семенова Анастасия Сергеевна	*Магистр технических наук, ведущий инженер, АО «Институт металлургии и Обогащения», Алматы, Казахстан. E-mail: a.semenova@satbayev.university; ORCID ID: 0000-0003-4054-8268*
Дидик Нурхадиянто	*Доктор инженерных наук, Лектор, Инженерный факультет, Государственный университет Джокьякарты, Индонезия. E-mail: didiknur@uny.ac.id; ORCID ID:0000-0003-0643-0776*

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Additive for improving the quality of foam concrete made on the basis of micro silica and quicklime

[1*]Lukpanov R.E., [1] Dyussembinov D.S., [1] Yenkebayev S.B., [1] Yenkebayeva A.S., [2]Tkach E.V.

[1] L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan
[2] National Research Moscow State University of Construction, Moscow, Russia

** Corresponding author email: rauan_82@mail.ru*

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ABSTRACT

The article presents studies of the use of plasticizing additives in combination with fine aggregate (microsilica) and CaOH quicklime for the production of foam concrete. The research will determine the effect of plasticizing additives and active fillers on the properties of foam concrete during their production. The main issue in the production of foam concrete is the time of setting, as their increase leads to shrinkage of foam concrete mixture and as a consequence of the uneven structure of the material. Therefore, the use of plasticizer additives in the production of foam concrete is not recommended. Plasticizer, as a surface-active substance, increases the setting time of the cement binder. However, examining the features of micro silica in combination with caustic lime and plasticizer was found to reduce the time setting. Laboratory studies have shown that the use of these components will produce foam concrete with the projected density, with a uniformly distributed pore structure, high strength, and frost resistance. According to the results of the study, the influence of the number of additives components on the qualitative characteristics of foam concrete was determined, and the optimal composition of the components, plasticizer additives, micro silica, and caustic lime was selected.

Keywords: Concrete maturity, surface strength, shock-pulse method, operational control, sensor.

	Information about authors:
Lukpanov Rauan Ermagambetovich	*Ph.D., Professor, Director of the Research and Production Center "ENU LAB", L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan. Email: rauan_82@mail.ru; ORCID ID: 0000-0003-0085-9934*
Dyussembinov Duman Serikovich	*C.t.s., Assistant Professor of the Department of Technology of Industrial and Civil Construction, L.N.Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan. Email: dusembinov@mail.ru; ORCID: 0000-0001-6118-5238*
Yenkebayev Serik Beysengalievich	*Ph.D., Assistant Professor, Senior researcher of the Research and Production Center "ENU LAB", L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan. Email: yenkebayev-serik@mail.ru; ORCID: 0000-0002-5984-9346*
Yenkebayeva Aigerim Seksembaykyzy	*Ph.D. student, L.N. Gumilev Eurasian National University, Nur-Sultan, Kazakhstan. Email: aikowa_21@mail.ru; ORCID: 0000-0003-1036-9621*
Tkach Evgeniya Vladimirovna	*Dr.t.s., Professor of National Research Moscow State University of Construction, Moscow, Russia. E-mail: ev_tkach@mail.ru; ORCID ID: 0000-0003-2132-4971*

Introduction

Construction refers to one of the important areas of industry, so the solution of the issues related to the creation of new or upgraded effective building materials becomes a fundamental factor in its development [1]. In this regard, the most important task is to develop new building materials with improved performance properties [2].

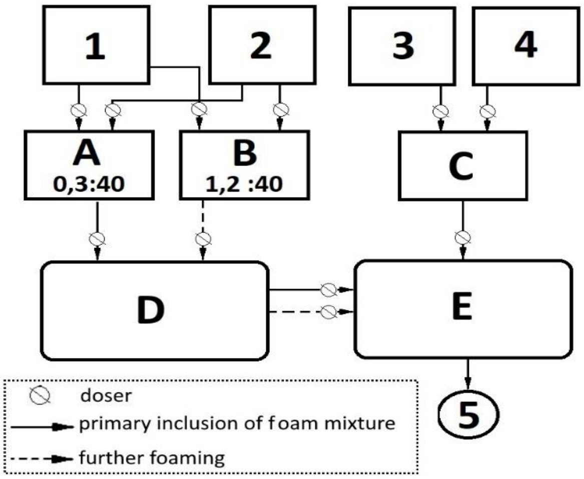
One of the directions for obtaining effective building materials is the use of additives modifiers, which significantly improve the properties of the material, allowing the expansion of the field of their application. The use of additives to improve the physical and mechanical properties of building materials is common practice in modern urban planning [3]. To develop modifier additives both quality raw materials and industrial wastes are used, which is also quite effective. Today, specialized concrete additives used both in industrial-scale production of concrete mixture and in the order of individual construction are in great demand in the market [4]. The use of additives modifiers in concrete is a standard measure, but their use in cellular concrete is not always justified, because with the receipt of certain qualitative characteristics are often lost other, not insignificant indicators. For example, the use of plasticizers and hydrophobic additives increases strength and reduces water absorption, but has a negative effect on increasing the setting time of the mortar, which leads to shrinkage and the development of uneven density [5].

When studying cellular concrete, they should be divided into two types foam concrete and aerated concrete. The main distinguishing characteristic of foam concrete and aerated concrete is the technology of obtaining the pore structure. Gas concrete is obtained through the use of gas-forming additives, such as aluminum powder and hydrogen peroxide technical [6]. In the process of chemical reaction, gas is released, which contributes to the swelling of the gas concrete solution, due to which a communicating pore structure of gas concrete is formed. The use of modifier additives increases the time of setting, which negatively affects the structure formation of aerated concrete mortar. Foamed by gas-forming additives solution should hold the structure until the end of the process of setting, otherwise, if the solution does not have time to set (as a consequence of this may serve plasticizers and hydrophobizing additives, containing in their composition surfactants), shrinkage of the material and violation of geometric parameters and structural characteristics occur [7]. Foam concrete is also a cellular concrete, the distinguishing feature from aerated concrete is the process of formation of the pore structure. To obtain the pore structure of foam concrete, a blowing agent is used, from which quality foam of the required multiplicity is obtained [8]. The foam is then injected into the mortar and swells it. The foamed mortar acquires a cellular structure with closed pores [9]. As with aerated concrete, the main problem is to increase the setting time, so the use of plasticizers and hydrophobic additives becomes impossible [10].

The research is aimed at the development of new additives that do not affect the time of setting, but on the contrary, contribute to their reduction. The research aims to determine the complex influence of plasticizing additives of micro silica and caustic lime on structural and qualitative characteristics of foam concrete made by the two-stage introduction of foam.

Experimental technique

An important condition was to maintain the same composition of components and ingredients (additives) of prototypes for each method, as well as their dimensionality. The technological process of specimen preparation by two-stage foam injection is shown in Figure 1.



1 - water; 2 - foam concentrate; 3 - cement; 4 - sand; 5 - finished product; A - the container for the low-concentrated solution of plasticizing additive of a foam concentrate in water 0,3:40 l, B - the container for a solution of the modified foam concentrate in water 1.2:40 l, C - the cement-sand mixer, D - the foam generator, E - the mortar mixer

Figure 1 – Technology of foam concrete preparation by the method of two-stage foam injection

The technological process consists of three stages. During production, a strict sequence of components must be followed (Figure 1):

Stage 1: in a container (A) the foam concentrate (1) is thoroughly mixed with water (2), in ratio to water - 0.3:40 l; in parallel (independently) in a container (B) the foam concentrate (1) is thoroughly mixed with water (2), in ratio to water - 1.2:40 l; in parallel in a container (C) the cement (3) is mixed with sand (4), in the ratio of cement to sand (1:3).

Stage 2: obtained in a container (A) mortar through the foam generator (C) is converted to foam and combined with cement and sand mixture from the container (D), in a mortar mixer (E).

Stage 3: The mortar obtained in a container (B) is converted to foam by means of the foam generator (C) and introduced into the mortar mixer (E).

Table 1 - Compositions of the compared samples

Type of sample	Cement, kg	Sand, kg	Foamer, l	Plasticizer C-3, kg	Quicklime, kg	Microsilica (MC), kg	Water, l
Type 1 Reference sample	300	300	1.5				150
Type 2	300	300	1.5	5			120
Type 3	267	267	1.5	5	6	60	99
Type 4	270	270	1.5	5		60	94
Type 5	300	300	1.5	5	6		99
Type 6	267	267	1.5		6	60	140

After careful mixing in a mortar mixer, the resulting mortar (5) is poured into forms.

To study the effect of the complex of additives on the qualitative characteristics of foam concrete there was taken as a control comparative sample - foam concrete grade D600 without using any additives. The composition of the compared samples is presented in Table 1.

To determine the qualitative indicators of foam, concrete the following laboratory tests and methods were used:

- Determining the density of the samples was performed according to the GOST 12730.1-78 "Concretes. Methods for determination of density.

- Determination of water absorption is performed according to the procedure of GOST 12730.378 "Concretes. Method for determination of water absorption.

- Determination of thermal conductivity and thermal resistance of the material was carried out according to the method of GOST 7076 "Method for determining the thermal conductivity and thermal resistance under steady-state thermal conditions". The measurements were carried out on the device ITP MG-4 on the principle of generation of heat flow stationary, passing through a flat sample and directed perpendicularly to the front faces of the sample.

- Determination of the strength of foam concrete is performed according to the method of GOST 10180-2012 "Concretes. Methods for Determining Strength by Reference Samples". Testing in compression was carried out on an automatic press CONTROLS (Pilot) 500 kN.

All tests were performed on cube-shaped specimens of 10x10x10 cm.

Results and Discussion

The density. The density study allowed us to objectively assess the uniformity of the pore structure of foam concrete. Figure 2 shows the results of the average values of the densities of the different parts of the foam concrete samples: the upper, middle, and lower parts.

According to the statistical data all partial values have a close relationship and high convergence within the control measurements: for type 1 the maximum quadratic deviation is 20.42 (lower segment) and the coefficient of variation is 3.42%; for type 2 the same values are - the maximum quadratic deviation (QD) is 25.72 (middle segment), the coefficient of variation (CV) is 4. 21%; for type 3, the QD is 14.11 (lower segment) and the CV is 2.32%; for type 4, the QD is 32.73 (upper segment) and the CV is 5.34%; for type 5, the QD is 20.31 (upper segment) and the CV is 3.33%; for type 6, the QD is 23.32 (middle segment) and the CV is 3.78%.

The results of the study showed that in all cases, the density in different areas has different values. The control sample showed an increase in density of the lower sample by 4.0% as opposed to the upper sample, indicating that during the setting process, part of the pore structure breaks down and settles, thereby compacting the structure of the lower layer of the material. The sample with plasticizer has the highest difference in density: the lower sample showed an increase in density of 4.6% compared to the upper sample. The samples where a complex combination of plasticizer, caustic lime, and micro-silica was used in the mixture showed a relatively equal density of the lower and upper sections.

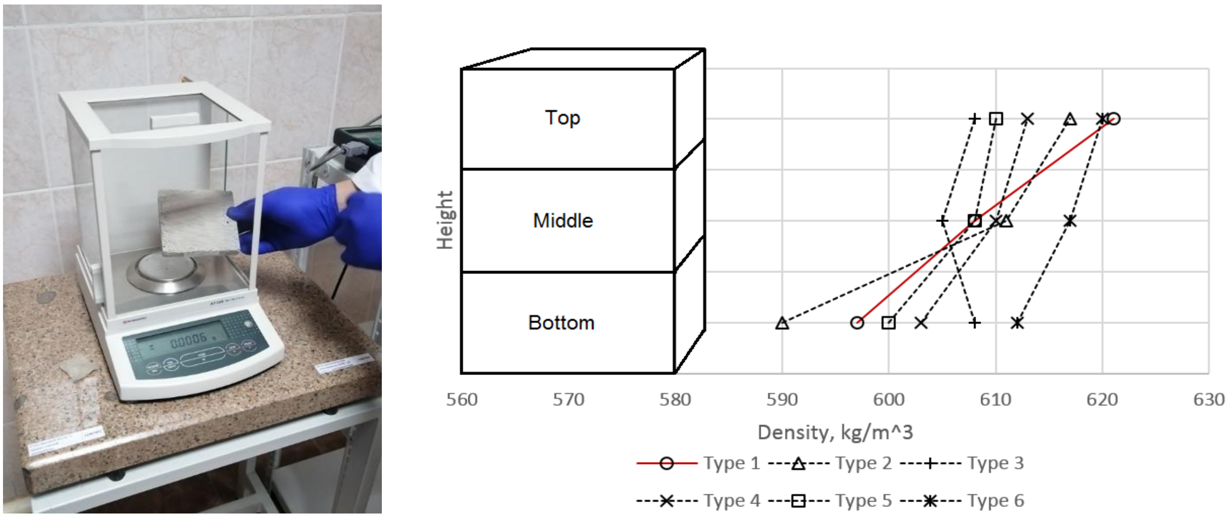


Figure 2 – Results of determining the density of foam block

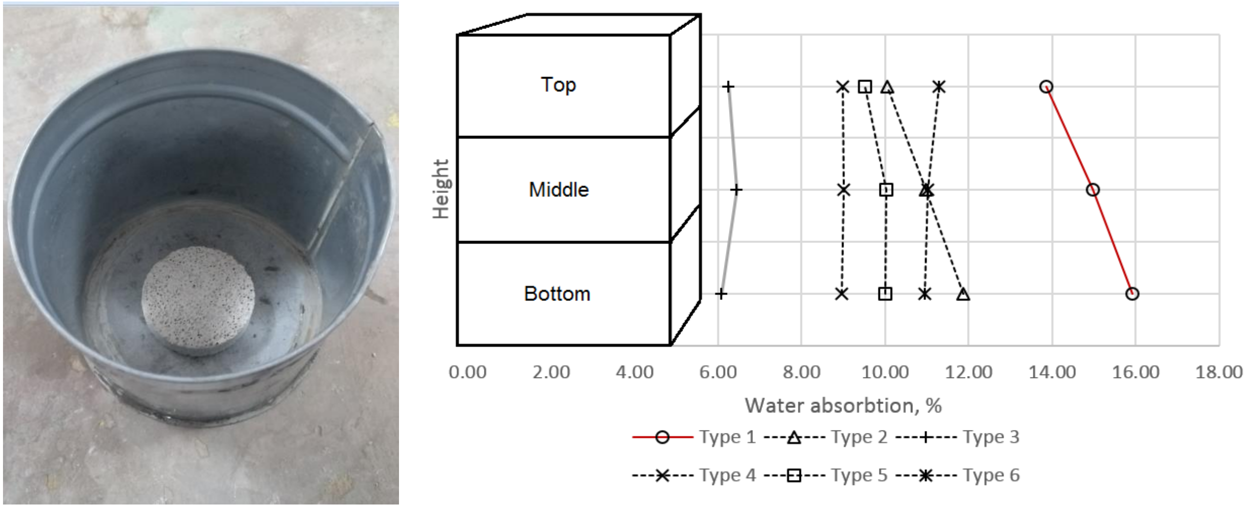


Figure 3 – Results of water absorption measurements

The water absorption. Water absorption of foam concrete was carried out by measuring the density, the results of the study are presented in Figure 3. Assessment of water absorption was also determined for different sections of the samples.

The obtained private values have from the average then a close relationship: for type 1 the maximum quadratic deviation is 1.60 (middle segment), and the coefficient of variation is 10.7%; for type 2 the same values are - the maximum QD is 0.52 (upper segment), the CV is 5.2%; for type 3 - QD is 0. 24 (lower segment), the CV is 3.9%; for type 4 - QD is 0.19 (lower segment), the CV is 3.2%; for type 5 - QD is 0.37 (middle segment), the coefficient of variation is 3.7%; for type 6 - QD is 0.52 (middle segment), the CV is 4.7%.

According to the studies, high (less favorable) rates of water absorption were shown by the control samples of the traditional composition, without the use of additives.

According to the results of the control sample, we see a difference in water absorption between the upper and lower samples, which is 12%. In general, a certain pattern of changes in water absorption capacity according to the height of the sample was not revealed. Nevertheless, there is an obvious effect of plasticizers on the reduction of water absorption (by 21.4% of the control sample), due to the reduction of micropores in the walls of the cells. Samples with the addition of plasticizer, hydrated lime, and micro-silica showed the lowest water absorption, with an average of 6.3%. This figure is a high-quality result for foamed concretes, which is obtained by reducing the time of setting and reducing the formation of micropores in the walls of the cells. In samples of types 3,4,5, the most uniform distribution of water absorption over the

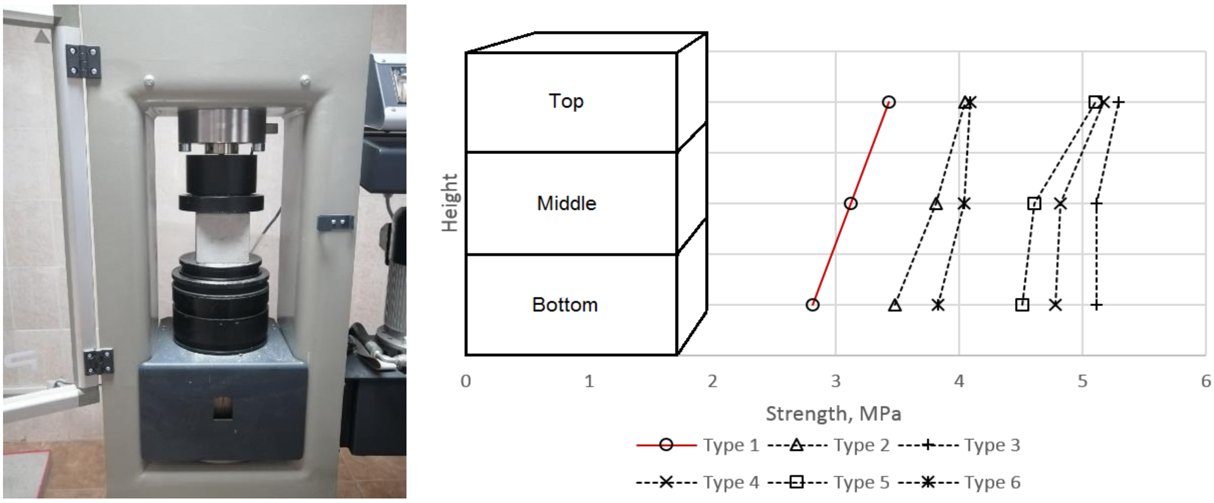


Figure 4 - Results of strength measurements

height of the sample is observed, which together with the results of densities indirectly indicates a relatively uniform porous structure.

The strength. The strength studies were also carried out on samples obtained from different sections of the foam concrete material (foam block). The results are presented in Figure 4.

The partial values obtained have a high degree of convergence: for type 1 the maximum QD is 0.107 (upper segment) and the CV is 3.42%; for type 2 the same values are - the maximum QD is 0.15 (lower segment), the CV is 4.21%; for type 3 the QD is 0. 12 (middle segment), the CV is 2.32%; for type 4 - QD 0.25 (middle segment), the CV is 5.34%; for type 5 - QD 0.17 (middle segment), the CV is 3.33%; for type 6 - QD 0.15 (middle segment), the CV is 3.78%.

The difference in the strength of the upper and lower sections of the foam concrete made by the traditional composition without the use of additives was high 22.1 %, and the coefficient of variation by height is 10%. The obtained result indicates the uneven distribution of strength characteristics along with the height of the sample. The difference between the same indices of samples with additives is from 3.5 to 16.4%, and the coefficient of variation by height is from 1.7 to 7.6%. Thus the use of additives gives a positive effect in increasing the strength characteristics of foam concrete.

Thermal conductivity. The results of the thermal conductivity study are presented in Table 2.

All partial values of all compared sample types have a very close relationship and convergence: the maximum coefficient of variation ranges from 1.18 to 2.08%, and quadratic deviations do not exceed 0.005.

According to the results of thermal conductivity of control samples, it is possible to see the difference in the values of the upper sample and the lower sample, which in percentage ratio is 13.4 %. The large variation in values within a single test sample indicates the conditional reliability of the thermal conductivity indicators, which must be taken into account in the design. Thermal conductivity of

Table 2 - The results of the thermal conductivity

Sample	**Thermal conductivity coefficient λ_0 W/m ×°C**		
	Top samples	***Middle samples***	***Bottom samples***
Type 1 Reference sample	0.15	0.17	0.17
Type 2	0.16	0.17	0.17
Type 3	0.16	0.16	0.16
Type 4	0.15	0.16	0.16
Type 5	0.17	0.17	0.17
Type 6	0.15	0.15	0.16

sample Type 3, where all complex additives was used showed the maximum quality result, thermal conductivity in all areas (both upper and lower) was the same value of 0.16 W/m × °C. The same uniform thermal conductivity in all sections is shown by the sample of Type 4 - 0.17 W/m × °C. Samples of Types 1, 3, and 5, showed practically the same result, which was a difference in values of 6.1-6.7%.

Conclusions

Presented composition of the additive intended for the production of foam concrete, which includes the following components: plasticizing additives in combination with fine filler (microsilica) and hydrated lime CaOH. The relative uniformity of the composition was confirmed by the results of the assessment of the density of the material, measured at different heights of the samples (top, middle, and bottom). The maximum density difference by height observed in specimens of type 2, was 4.5%, and the minimum in specimens of type 3 with the full complexity of the components of the proposed additive, was 0.5%. The most unfavorable rates of water absorption corresponding to the samples of traditional composition, the difference of data on the height of the samples, on average, was 12%. In general, for the samples with the use of plasticizers, there is an obvious decrease in water absorption up to 21.4 %. The results of comparisons of strength characteristics of samples showed minimum values for samples of traditional composition, and maximum for samples with the use of the additive. The maximum difference in strength by height was revealed in the samples of traditional composition, amounting to 22.1%. The samples with additives showed varying degrees, but a naturally smaller scatter, ranging from 3.5 to 16.4%. The results of thermal conductivity also showed less stability of the samples of traditional composition, the difference of private values on the height of which was 13.4%. Samples using the entire set of additives showed the most stable result, and samples with partial use of components showed high convergence with a scatter of data from 6.1 to 6.7% in height.

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

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Көбік бетонының сапасын жақсартуға арналған микрокремнезем және сөндірілген әк негізінде жасалатын қоспа

[1]Лукпанов Р.Е., [1] Дюсембинов Д.С., [1] Енкебаев С.Б., [1] Енкебаева А.С.,[2] Ткач Е.В.

[1] *Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Нұр-Сұлтан, Қазақстан*
[2] *Ұлттық зерттеу Мәскеу мемлекеттік құрылыс университеті, Мәскеу, Ресей*

Мақала келді: *15 ақпан 2022*
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Қабылданды: *28 сәуір 2022*

ТҮЙІНДЕМЕ

Мақалада көбік бетонын өндіру үшін жұқа дисперсті толтырғышпен (микрокремнезем) және $Ca(OH)_2$ әкімен біріктірілген пластификациялық қоспаларды қолдану туралы зерттеулер келтірілген. Зерттеулер пластиктендіретін қоспалар мен белсенді толтырғыштардың көбік бетонының қасиеттеріне әсерін оларды өндіру процесінде анықтауға мүмкіндік береді. Көбік бетон өндірісіндегі негізгі мәселе – орнату уақыты, өйткені олардң артуы көбік бетон қоспасының шөгуіне әкеледі, соның әсерінен материалдың құрылымы біркелкі болмайды. Сондықтан көбік бетон өндірісінде пластиктендіретін қоспаларды қолдану ұсынылмайды. Пластификатор, беттік белсенді зат бола отырып, цемент байланыстырғышын орнату уақытын арттырады. Алайда, сөндірілген әк және пластификатормен бірге микрокремнеземнің ерекшеліктерін зерттей отырып, орнату уақытын қысқартуға мүмкіндік беретін ерекшелік табылды. Зертханалық зерттеулер көрсеткендей, бұл компоненттерді қолдану біркелкі бөлінген құрылымы, жоғары беріктігі және аязға төзімділігі бар көбік бетонын алуға мүмкіндік береді. Зерттеу нәтижелері бойынша қоспалар компоненттері санының көбік бетонының сапалық сипаттамаларына әсері анықталды, компоненттердің оңтайлы құрамы, пластификатор, микрокремнезем және гидратталған әк қоспалары таңдалды.

Түйін сөздер: пенобетон, екі сатылы көбік енгізу, микрокремнезем, пластификатор, беріктік, аязға төзімділік.

Авторлар туралы ақпарат:

Лукпанов Рауан Ермагамбетович	*PhD, профессор, «ENU LAB» ғылыми-өндірістік орталығының директоры, Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Нұр-Сұлтан, Қазақстан. Email: rauan_82@mail.ru, ORCID: 0000-0003-0085-9934*
Дюсембинов Думан Серикович	*т.ғ.к., «Ғимараттар және имараттарды жобалау» кафедрасының доценті, Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Нұр-Сұлтан, Қазақстан. Email: dusembinov@mail.ru, ORCID: 0000-0001-6118-5238*
Енкебаев Серик Бейсенгалиевич	*PhD, доцент, "ENU LAB" ғылыми-өндірістік орталығының бас маманы, Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Нұр-Сұлтан, Қазақстан. Email: yenkebayev-serik@mail.ru, ORCID: 0000-0002-5984-9346*
Енкебаева Айгерим Сексембайкызы	*PhD докторанты, Л.Н. Гумилев атындағы Еуразия ұлттық университеті, Нұр-Сұлтан, Қазақстан. ORCID: 0000-0003-1036-9621; Email: aikowa_21@mail.ru*
Ткач Евгения Владимировна	*т.ғ.д., Ұлттық зерттеу Мәскеу мемлекеттік құрылыс университеті профессоры, Мәскеу, Ресей. E-mail: ev_tkach@mail.ru, ORCID ID: 0000-0003-2132-4971*

Добавка для улучшения качества пенобетона, изготавливаемая на основе микрокремнезема и гашеной извести

[1]Лукпанов Р.Е., [1] Дюсембинов Д.С., [1] Енкебаев С.Б., [1] Енкебаева А.С.,[2] Ткач Е.В.

[1] Евразийский национальный университет им. Л.Н. Гумилева, Нур-Султан, Казахстан
[2] Национальный исследовательский Московский государственный строительный университет, Москва, Россия

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АННОТАЦИЯ

В статье приведены исследования применения пластифицирующих добавок в комплексе с тонкодисперсным наполнителем (микрокремнеземом) и гашенной известью CaOH для производства пенобетона. Исследования позволят определить влияние пластифицирующих добавок и активных наполнителей на свойства пенобетона в процессе их производства. Основным вопросом при производстве пенобетона являются сроки схватывания, так как их увеличение приводит к усадке пенобетонной смеси и как следствие неравномерности структуры материала. Поэтому применение пластифицирующих добавок в производстве пенобетона не рекомендуется. Пластификатор, являясь поверхностно активным веществом, увеличивает сроки схватывания цементного вяжущего. Однако исследовав особенности микрокремнезема в комплексе с гашенной известью и пластификатором была обнаружена особенность, позволяющая сократить сроки схватывания. Лабораторные исследования показали, что применение данных компонентов позволят получить пенобетон с проектируемой плотностью, с равномерно распределенной поровой структурой, высокой прочностью, и морозостойкостью. По результатам исследования, определено влияние количества компонентов добавок на качественные характеристики пенобетона, выбран оптимальный состав компонентов, добавки пластификатора, микрокремнезема и гашенной извести.

Ключевые слова: пенобетон, двухстадийное введение пены, микрокремнезем, пластификатор, прочность, морозостойкость.

Информация об авторах:

Лукпанов Рауан Ермагамбетович	*PhD, Профессор, Директор научно-производственного центра «ENU LAB», ЕНУ им. Л.Н.Гумилева, Нур-Султан, Казахстан. Email: rauan_1982@list.ru; ORCID ID: 0000-0003-0085-9934*
Дюсембинов Думан Серикович	*К.т.н., Доцент кафедры «Проектирование зданий и сооружений», ЕНУ им. Л.Н.Гумилева, Нур-Султан, Казахстан. Email: dusembinov@mail.ru; ORCID: 0000-0001-6118-5238*
Енкебаев Серик Бейсенгалиевич	*PhD, доцент, старший научный сотрудник научно-производственного центра «ENU LAB», ЕНУ им. Л.Н.Гумилева, Нур-Султан, Казахстан. Email: yenkebayev-serik@mail.ru; ORCID: 0000-0002-5984-9346*

Енкебаева Айгерим Сексембайкызы	*докторант PhD, ЕНУ им. Л.Н. Гумилева, Нур-Султан, Казахстан. Email: aikowa_21@mail.ru; ORCID: 0000-0003-1036-9621*
Ткач Евгения Владимировна	*Д.т.н, профессор, Национальный исследовательский Московский государственный строительный университет, Москва, Россия. E-mail: ev_tkach@mail.ru; ORCID ID: 0000-0003-2132-4971*

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Thermophysical properties of synthetic slags of the FeO – MnO – CaO – Al_2O_3 — SiO_2 system

[1*]Yessengaliyev D.A., [2]Baisanov A.S., [3]Dossekenov M.S., [1]Kelamanov B.S., [1]Almabekov D.M.

[1] K. Zhubanov Aktobe regional university, Aktobe, Kazakhstan
[2] Abishev Chemical-Metallurgical Institutes, Karaganda, Kazakhstan
[3] LLP "Research and engineering center ERG" Aktobe, Kazakhstan

Corresponding author email: dauralga@mail.ru

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ABSTRACT

In the electrometallurgy of manganese alloys, viscosity has an important effect on the production indicators from the physicochemical properties of slag. During the smelting of manganese alloys, the main amount of heat spent on reduction reactions is released due to the current passing through the liquid slag phase, since the resistance of the latter, depending on the composition, affects the completeness of the reduction of manganese from melts. In the case of refined ferromanganese by the silicothermic method, the vast majority of silicon of silicomanganese is refined with higher manganese oxides or it is burned out due to oxygen in the air. The paper presents the results of thermophysical properties of slags representing the FeO - MnO - CaO - Al_2O_3 - SiO_2 system. Laboratory experiments were carried out on synthetic slags by varying the slag basicity CaO / SiO_2 = 1.5 - 1.9 and the concentration of Al_2O_3 = 5 - 15%. As a result, graphs of the dependence of these properties on temperature values are constructed, the activation energies of the viscous flow are calculated and the phase compositions of the experimental slags are determined using a mathematical model of the diagram of the FeO - MnO - CaO - Al_2O_3 - SiO_2 system. Thus, an increase in the concentration of aluminum oxide against its usual level, changing the basicity of the slag, significantly affected the physicochemical properties of the slag and thereby contributes to the adjustment of the parameters of the electric melting process. At the same time, it is advisable to study the interaction of some Physical chemical properties of slags on the melting conditions of manganese ferroalloys in relation to the composition of slags.

Keywords: viscosity, slags of manganese alloys, crystallization temperature, activation energy, phase composition.

Information about authors:

Yessengaliyev Dauren Amangeldievich	*Ph.D., senior lecturer of the Department metallurgy and mining technical faculty of K. Zhubanov Aktobe regional university, Aktobe, Kazakhstan. Email: dauralga@mail.ru, ORCID ID: 0000-0003-0792-0822*
Baisanov Alibek Sailaubaevich	*Candidate of technical sciences, head of the laboratory of pyrometallurgical processes of the Abishev Chemical-Metallurgical Institutes, Karaganda, Kazakhstan. Email: alibekbaisanov@mail.ru, ORCID ID: 0000-0002-3025-7267*
Dossekenov Murat Sagitzhanovich	*Engineer of LLP "Scientific and research engineering center ERG" Aktobe, Kazakhstan. Email: dossekenov.ms@mail.ru, ORCID ID: 0000-0003-2483-8118*
Kelamanov Bauyrzhan Satybaldyuly	*Candidate of technical sciences, docent of the Department metallurgy and mining technical faculty of K. Zhubanov Aktobe regional university, Aktobe, Kazakhstan. Email: kelamanov-b@mail.ru, ORCID ID: 0000-0001-7646-9153*
Almabek Dias Maratuly	*Student in the specialty 6B07203 - Metallurgy of the technical faculty of K. Zhubanov Aktobe regional university, Aktobe, Kazakhstan. Email: almabekov@04list.ru*

Introduction

In metallurgy, the final slags of manganese alloys, namely for refined grades of ferromanganese, represent the FeO – MnO – CaO – Al_2O_3 - SiO_2 system. The reduction processes during the smelting of refined grades of ferromanganese pass through the slag phase, so the study of the viscous properties of slags is obvious. As is known, the viscosity of the slag in the desired limit should contribute to the rapid runoff of metal droplets into the alloy, the rapid mutual diffusion of oxides and reducing agent, and consequently, the rapid flow of the process, and, finally, allow optimal distribution of the temperature gradient in the melt [1].

In some cases, the viscosity of the slag determines the performance of metallurgical units, such as the interaction of slag with refractory materials, and metal losses with slag. Viscosity is one of the main parameters characterizing the physical properties of oxide melts. The viscosity of a liquid is related to its structure and is determined by interparticle interaction, therefore, its study, along with other physicochemical properties, allows us to evaluate the structure of metal and slag melts, the nature, and magnitude of the interaction between their components.

The thermophysical properties of synthetic slags of the FeO – MnO – CaO – Al_2O_3 – SiO_2 system were investigated.

Experimental part

To study the physical properties of slags (viscosity and temperature of the beginning of crystallization), pre-prepared synthetic mixtures were used, since metal remains and foreign impurities are present in industrial slags.

Slag samples for the study were prepared from reagents of the brand purely for analysis by fusing mixtures in a graphite crucible in a Tamman resistance furnace.

Synthetic materials were calcined to a constant weight at 800 – 850 C before fusion. The suspension of powdered synthetic materials was thoroughly mixed beforehand and then melted in a furnace. After fusion, the resulting slags were submitted for chemical analysis. As a result, the composition of the resulting slags was close to the industrial slags of the process of obtaining manganese alloys (Table 1).

The studied slag samples were characterized by a ratio of CaO/SiO_2 = 1.5; 1.7; 1.9 and different content of Al_2O_3. Such dynamics of composition variation made it possible to trace the influence of alumina and magnesium oxide on the viscosity and crystallization temperature of slags.

The viscosity of the slag was measured with an electro vibration viscometer in molybdenum crucibles with a current of purified argon. The installation diagram is shown in Figure 1.

The high sensitivity of the vibrating viscometer is due to the fact that it operates on resonant vibrations, and the viscosity of the melt violates the resonance conditions [[2], [3], [4]]. To determine the thermophysical properties of the slags of the FeO – MnO – CaO – Al_2O_3 - SiO_2 system, a pre-crushed slag weight (15-20 g) was immersed in a molybdenum crucible with an inner and outer diameter of 17 mm and 30 mm, respectively, and a height of 60 mm. After melting the slag sample (1550-1650 ° C), the contents in the crucible were mixed with molybdenum rods to average the composition. In the center of the crucible, a molybdenum spindle with a diameter of 2 mm and a length of 40 mm was introduced to a depth of 10 mm from the melt surface using a screw lift, then cooling measurements were made at a speed of 3 degrees/min until complete crystallization. Then the hardened slag was melted again to extract the spindle of the viscometer and remove the slag from the crucible by freezing on a molybdenum wire. The temperature in the furnace was measured with a tungsten-rhenium thermocouple TR 5/20, the hot junction of which in a corundum cover was fed through a recess to the bottom of the crucible. The viscosity was recorded by the value of the electromotive force (mV) on a digital millivoltmeter.

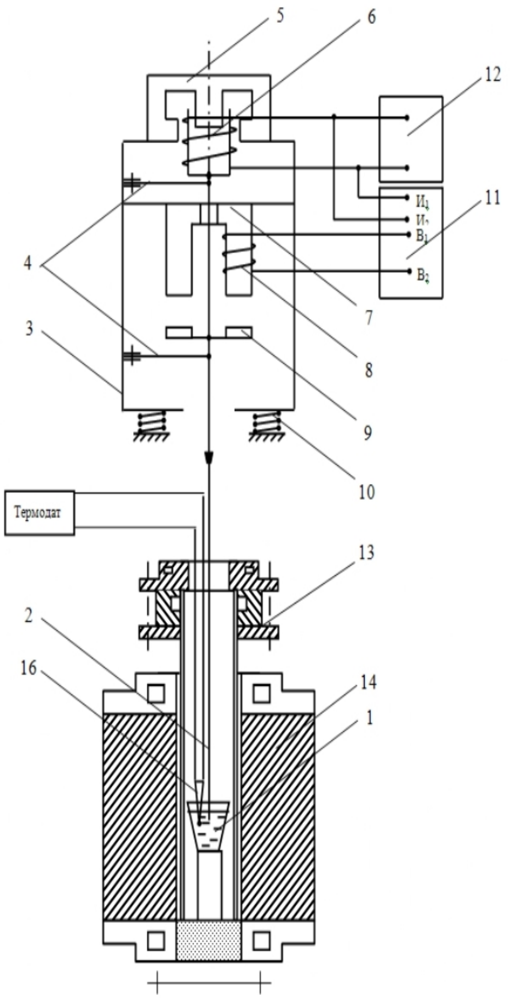

Figure 1 - Diagram of an electro vibration viscometer

1 - crucible; 2 - vibrating rod; 3 - viscometer housing; 4 - flat springs; 5 - ring magnet; 6 - measuring coil; 7 - vibrator core; 8 - vibrator coil; 9 - vibrator armature; 10 - shock-absorbing springs; 11 - auto generator; 12 - digital voltmeters; 13 – lid; 14 - Tamman furnace; 15 - inert gas supply tube; 16 – thermocouple

Table 1 - Chemical composition of the slag

№	Composition, %											
	Chemical						Phase					
	FeO	MnO	CaO	SiO_2	Al_2O_3	CaO/SiO_2	F	M	M_2S	C_2AS	C_2S	CA
1	8.9	19.65	39.01	25.92	6.52	1.51	8.90	7.79	16.86	17.53	48.92	-
2	4.86	16.07	40.35	26.89	11.83	1.50	4..86	3.62	17.70	31.80	42.00	-
3	2.68	15.48	39.32	26.2	16.32	1.50	2.68	3.36	17.24	43.87	32.84	-
4	8.65	15.68	44.42	26.19	5.06	1.70	8.65	10.05	8.00	13.6	59.69	-
5	4.28	14.72	44.66	26.42	9.94	1.69	4.28	8.85	8.34	26.72	51.82	-
6	3.91	15.22	42.45	24.96	13.46	1.70	3.91	10.00	7.42	36.18	42.48	-
7	5.56	15.28	47.12	24.79	7.25	1.90	5.56	15.28	15.22	61.45	-	2.48
8	3.36	13.66	46.45	24.43	12.12	1.90	3.36	13.65	28.33	52.17	-	2.48
9	1.77	14.36	44.01	23.12	16.74	1.90	1.77	14.36	40.77	40.60	-	2.49

Discussions results

Experimental data on the viscosity of slags, the compositions of which are given in Table 1, are shown in Figure 2. The effect of Al_2O_3 concentration on the viscosity of slag with basicity of 1.5; 1.7; 1.9 is shown here.

According to experimental data, the crystallization temperature of the slags was also calculated. It can be determined based on the known exponential dependence of viscosity on temperature [[5], [6]]:

$$\eta = A \cdot e^{-\frac{E}{RT}} \tag{1}$$

where η - the viscosity coefficient; E - the activation energy; T - the absolute temperature; R - the universal gas constant; A - the pre-exponential multiplier. Logarithmic form of expression (1):

$$ln\eta = ln\,A + \frac{E}{RT} \cdot \frac{1}{T} \tag{2}$$

where *lnη* - the segment cut off on the ordinate axis; *E/R* - the angular coefficient of the straight line.

Figure 3 shows the dependence of the logarithm of viscosity (lnη) on the inverse temperature (1/T). As can be seen, an increase in the CaO/SiO_2 ratio in slags affects an increase in the crystallization temperature.

As practice shows, for a homogeneous structural state of slag, the graphical dependence in the coordinate's *ln η - 1/T* must be rectilinear at a certain constant value of E_η. The deviation from the straight line of the dependence of *lnη* from *1/T* indicates the appearance of structural changes in the melt during its cooling. With the development of the crystallization process, a fracture is observed on the graph in the coordinate's *lnη - 1/T*, followed by an increase in viscosity. With the development of the crystallization process, a fracture is observed on the graph in the coordinate's *lnη - 1/T*, followed by an increase in viscosity.

The temperature corresponding to the fracture point determines the crystallization temperature of the studied oxide melt. It can be found from the graph or by solving the equations of the lines together before and after the fracture. In general, they can be written as follows:

$y_a = c + ax$ – for a straight line to a fracture (3)

$y_b = c_1 + a_1 \cdot x$ – for a straight line after a fracture (4)

where ln is denoted by «y» lnη, 1/T is denoted by «x», and «c» and «a» represent the free term (lnA) and the angular coefficient (E/R) of equation (2).

The coordinates of the intersection point of two straight lines are as follows (Figure 3):

$$x = -\frac{c_1 - c}{a - a_1} \tag{5}$$

$$y = \frac{c \cdot a_1 - c_1 \cdot a}{a - a_1} \tag{6}$$

Table 2 shows the above-mentioned equations calculated by processing experimental data using the least-squares method, showing the crystallization temperatures ($t_{cr.}$˚C) and the activation energies of the viscous flow of the studied slags (T).

Increasing the concentration of aluminum oxide reduces the viscosity and crystallization temperature of slags in the entire range of the studied basicity. However, the nature of the influence and the absolute values of the decrease in these values, depending on the basicity of the slags, are different, and this is primarily due to the processes of phase formation.

Table 2 - Crystallization temperature and activation energy of viscous flow

CaO/SiO_2	Slags	Equations	$T_{KR.}$,˚C	E, kJ/mol
1.5	1	$\ln_a = -200.97+36.271/T$ $\ln_b = -109.30+19.709/T$	1534	3015.68 1638.67
	2	$\ln_a = -106.86+19.05/T$ $\ln_b = -83.13+14.807/T$	1515	1583.87 1231.10
	3	$\ln_a = -192.67+33.39/T$ $\ln_b = -123.73+21.39/T$	1468	2776.14 1778.43
1.7	4	$\ln_a = -112.38+20.311$ $\ln_b = -105.91+19.107$	1588	1688.72 1588.61
	5	$\ln_a = -114.22+20.023$ $\ln_b = -95.422+16.644$	1524	1664.77 1383.83
	6	$\ln_a = -123.41+21.162$ $\ln_b = -111.13+19.018$	1473	1759.47 1581.21
1.9	7	$\ln_a = -101.03+18.593$ $\ln_b = -73.306+13.373$	1610	1545.88 1111,87
	8	$\ln_a = -161.74+28.987$ $\ln_b = -105.12+18.562$	1568	2410,07 1543.30
	9	$\ln_a = -70.124+12.341$ $\ln_b = -35.36+6.117$	1517	1026.07 508.59

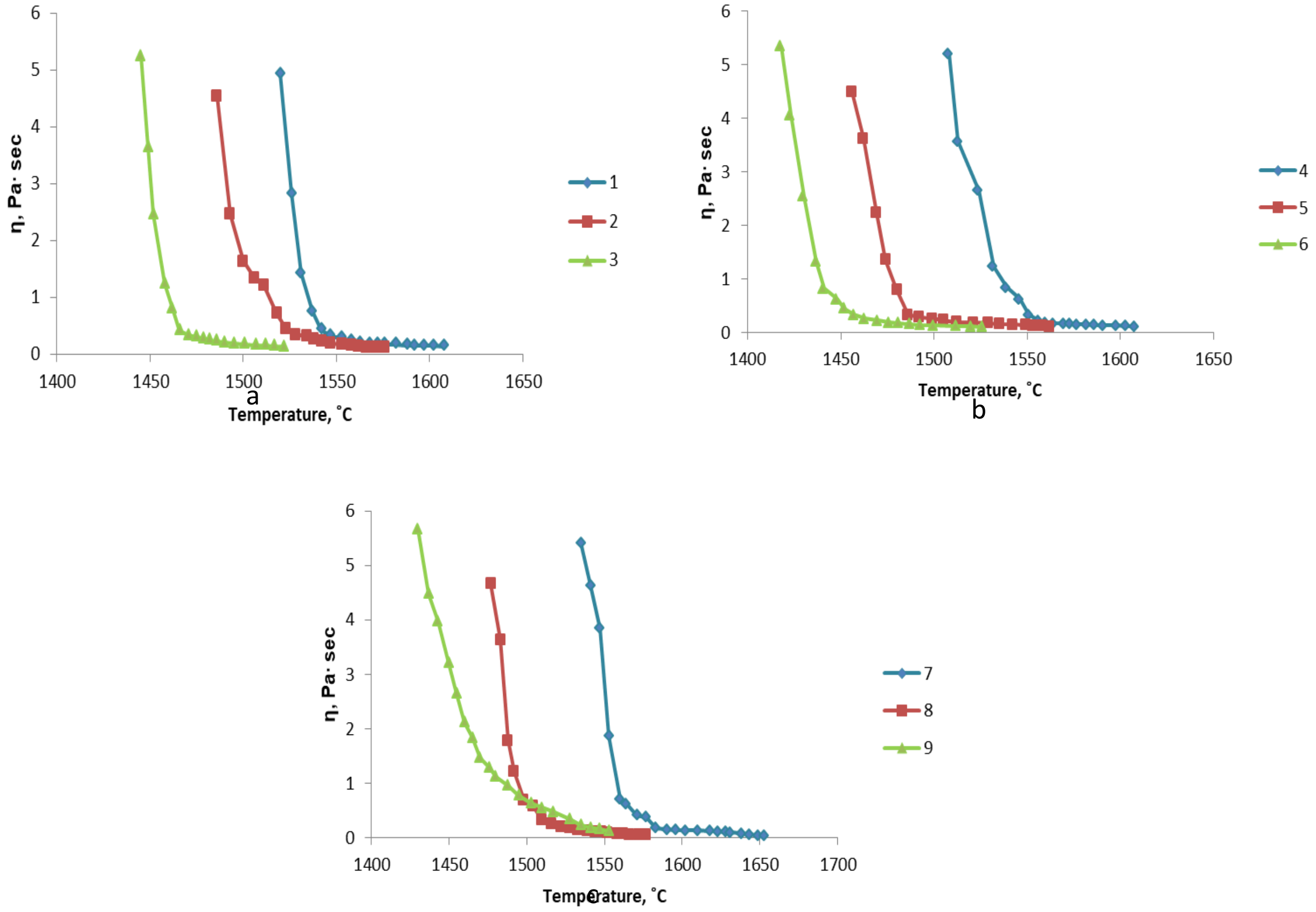

Figure 2 - Dependence of slag viscosity on the temperature at basicities, a - 1.5; b - 1.7; c - 1.9 (figures in the picture of slag numbers according to Table 1)

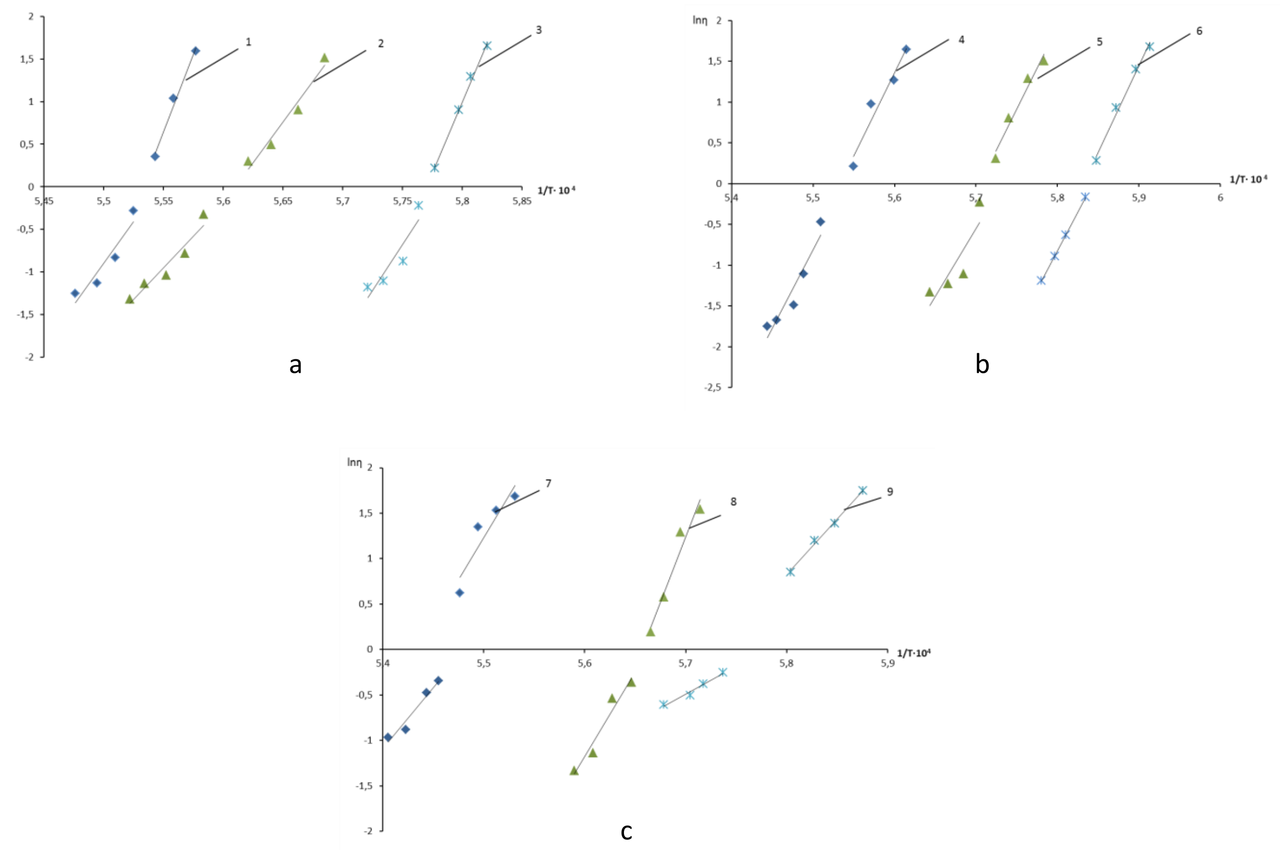

Figure 3 - Dependence of the logarithm of viscosity on the inverse temperature

The phase composition of the experimental slags was estimated using a mathematical model of the diagram of the FeO - MnO - CaO - Al_2O_3 - SiO_2 system [[7], [8]].

It was found that the slags presented in Table 1 numbered 1-6 have the following phase composition: iron oxide - FeO (indicated in the table as F), manganese oxide - MnO (M), tephroite - $2MnO·SiO_2$ (M_2S), gelenite - $2CaO·Al_2O_3·SiO_2$ (C_2AS), bicalcium silicate - 2CaO·SiO2 (C_2S) and their normative composition is described by the following expressions:

F = +1·F,
M = -2,367·S+1,268·C+1·M,
M_2S= +3,367·S-1,805·C,
C_2AS= +2,688·A,
C_2S= -1,688·A+1,536·C.

The calculation shows that with an increase in the basicity of slags due to the CaO additive, there is a decrease in the content of tephroite in them. As a result of the reaction, free manganese oxide and bicalcium silicate are formed [[9], [10]]:

$2MnO·SiO_2 + 2CaO = 2MnO + 2CaO·SiO_2$

When the basicity increases to 1.9, the slag composition moves to the pentatope F-M-C_2AS-C_2S-CA, i.e. tephroite is replaced by calcium aluminate (T=1604 °C) [11]. To calculate the phase composition of slags in this pentatope, it is necessary to use the following equations:

F = +1·F,
M = +1·M,
C_2AS = +9,172·S+2,694·A-4,917C,
C_2S = -2,890·S-1,694·A+3,085·C,
CA = -5,282·S+2,831·C.

Conclusions

By tracking the dynamics of changes in the phase composition, it can be seen that an increase in basicity contributes to the release of MnO in free form from tephroite and thereby contributes to improving the conditions for the reduction of manganese. It is also possible to note an increase in the concentration of Al_2O_3 in the melt, where the temperature range of the beginning of crystallization of the studied slags expands, forming aluminosilicate compounds ($Ca_2Al_2SiO_7$ and $CaAl_2O_4$), the melting point of which is 1550 ° C and

1604 ° C, respectively. At the same time, in order to form a high fluidity of the ore-calcareous melt, it is necessary to ensure a ratio CaO/SiO_2 = 1.5 - 1.7 in the slag and an Al_2O_3 content of at least 10%. Further, with an increase in the CaO/SiO_2 ratio of more than 1.7, the content of the refractory phase (larnite – $2CaO{\cdot}SiO_2$) having a temperature of 2130 °C will increase, thereby worsening the slag regime of the smelting process of refined ferromanganese. With an increase in the basicity and content of alumina, aluminum atoms are rearranged from gear coordination into anionic complexes of the $(Al_2SiO_7^{4-})_9$ type.

Thus, alumina as a slag-forming component does not worsen the performance of the technology of smelting manganese ferroalloys, in particular for the production of refined ferromanganese. For the technology of smelting refined ferromanganese, the slag region turned out to be optimal in viscosity: M_2S-C_2S-C_2AS with a ratio of CaO/SiO_2 = 1.5 - 1.7. In any other region, properties very undesirable for smelting ferromanganese are the manifested-a high melting point of slags. This contributes to the intensive reduction of silicon from tephroite and may cause an increase in the silicon content in the resulting ferromanganese.

By doing so, we can conclude that it is necessary to correct the slag regime of current production towards high-alumina slags, which allow for higher technical and economic indicators of the production of refined ferromanganese.

Al_2O_3 additives can be produced using alumina-containing materials (bauxite agglomerates) as part of charge materials or aluminum together with siliceous alloys used in metallothermy. However, as practice shows, the latter option is unacceptable due to the high cost and high carbon monoxide of free aluminum.

In this case, the most optimal option for smelting refined grades of ferromanganese is the use of a complex aluminum-manganese-silicon alloy (AlSiMn) in the form of a reducing agent containing up to 15% aluminum along with silicon (50%). With such an aluminum content in the reducing agent, the amount of Al_2O_3 in the slag will fluctuate between 10 -15%.

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

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$FeO – MnO – CaO – Al_2O_3 — SiO_2$ жүйесіндегі синтетикалық қождың термофизикалық қасиеті

[1]Есенгалиев Д.А., [2]Байсанов А.С., [3]Досекенов М.С., [1]Келаманов Б.С., [1]Алмабеков Д.М.

[1] Қ.Жұбанов атындағы Ақтөбе өңірлік университеті, Ақтөбе, Қазақстан
[2] Ж.Әбішев атындағы Химия-металлургия институты, Қарағанды, Қазақстан
[3] «ERG-дің ғылыми-зерттеу және инжиниринг орталығы» ЖШС

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ТҮЙІНДЕМЕ

Марганец қорытпаларының электрометаллургиясында қождың физика-химиялық қасиеттерінен тұтқырлықтың өндіріс көрсеткіштеріне әсері маңызды. Марганец қорытпаларын балқыту кезінде жылудың негізгі мөлшері тотықсыздану реакцияларына жұмсалады, ол сұйық шлак фазасынан өтетін ток есебінен жүреді, өйткені соңғысының кедергісі қож құрамына байланысты марганецтің балқымалардан толық тотықсыздануына әсер етеді. Тазартылған ферромарганецті силикотермиялық әдісімен балқыту жағдайында силикомарганец кремнийінің басым бөлігі марганецтің жоғары тотықтарымен тазартылады немесе ауаның оттегі есебінен күйіп кетеді. Жұмыста $FeO – MnO – CaO – Al_2O_3 – SiO_2$ жүйесі негізіндегі қождардың термофизикалық қасиеттерінің нәтижелері келтірілген. Зертханалық тәжірибелер синтетикалық қожды қолдану арқылы қож негізділігі CaO/SiO_2 = 1,5 - 1,9 және қождағы Al_2O_3 концентрациясы 5-15% аралығында жүргізілді. Нәтижесінде көрсетілген қасиеттердің температуралық шамаларға тәуелділік графигі салынды, тұтқыр ағынның активтену энергиясы есептелді және FeO – MnO – CaO – Al_2O_3 – SiO_2 жүйесіндегі диаграммасының математикалық моделін қолдана отырып, тәжірибелік қождардың фазалық құрамы анықталды. Осылайша, қождың негізділігін өзгерте отырып, алюминий оксидінің әдеттегі деңгейінен концентрациясының жоғарлауы арқылы қождардың физика-химиялық қасиеттеріне айтарлықтай әсер етті, бұл өз кезегінде электр балқыту процесінің параметрлерін түзетуге ықпал етеді. Сонымен қатар, қождардың кейбір физикалық химиялық қасиеттерінің марганец ферроқорытпаларын балқыту жағдайларына әсер етуі қождардың құрамымен байланысты зерттелуі қажет.

Түйін сөздер: тұтқырлық, марганец қорытпаларының қождары, кристалдану температурасы, активтендіру энергиясы, фазалық құрамы.

Авторлар туралы ақпарат:

Есенгалиев Даурен Амангельдиевич	*PhD доктор, Қ.Жұбанов атындағы Ақтөбе өңірлік университетінің металлургия және тау-кен ісі кафедрасының аға оқытушысы, Ақтөбе, Қазақстан. Email: dauralga@mail.ru, ORCID ID: 0000-0003-0792-0822*
Байсанов Алибек Сайлаубаевич	*т.ғ.к., профессор, Ж.Әбішев атындағы Химия-металлургия институтының пирометаллургиялық үрдістер зертханасының меңгерушісі, Қарағанды, Қазақстан. Email: alibekbaisanov@mail.ru, ORCID ID: 0000-0002-3025-7267*
Досекенов Мурат Сагитжанович	*«ERG-дің ғылыми-зерттеу және инжиниринг орталығы» ЖШС инженер-технологы, Ақтөбе, Қазақстан. Email: dossekenov.ms@mail.ru, ORCID ID: 0000-0003-2483-8118*
Келаманов Бауыржан Сатыбалдыұлы	*т.ғ.к., қауымдастырылған профессор, Қ.Жұбанов атындағы Ақтөбе өңірлік университетінің металлургия және тау-кен ісі кафедрасының доценті, Ақтөбе, Қазақстан. Email: kelamanov-b@mail.ru, ORCID ID: 0000-0001-7646-9153*
Алмабеков Диас Маратұлы	*Қ.Жұбанов атындағы Ақтөбе өңірлік университеті 6В07203 – Металлургия мамандығының студенті, Ақтөбе, Қазақстан. Email: almabekov@04list.ru*

Термофизические свойства синтетических шлаков системы FeO – MnO – CaO – Al_2O_3 –- SiO_2

[1] Есенгалиев Д.А., [2] Байсанов А.С., [3] Досекенов М.С., [1] Келаманов Б.С., [1] Алмабеков Д.М.

[1] Актюбинский региональный университет им. К.Жубанова, г. Актобе, Казахстан
[2] Химико-металлургический институт им. Ж.Абишева, г. Караганда, Казахстан
[3] ТОО «Научно-исследовательский инжиниринговый центр ERG», г. Актобе, Казахстан

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АННОТАЦИЯ

При электрометаллургии марганцевых сплавов на показатели производства из физико-химических свойств шлака важное значение оказывает вязкость. Поскольку при выплавке марганцевых сплавов основное количество тепла, затрачивается на восстановительные реакции, выделяется за счет тока, проходящего через жидкую шлаковую фазу, поскольку сопротивление последней в зависимости от состава влияет на полноту восстановления марганца из расплавов. В случае рафинированного ферромарганца силикотермическим способом подавляющая часть кремния силикомарганца рафинируется высшим оксидами марганца или же выгорает за счет кислорода воздуха. В работе приведены результаты термофизических свойств шлаков представляющую систему FeO – MnO – CaO – Al_2O_3 — SiO_2. Лабораторные опыты проводились на синтетических шлаках, путем варьирования основности шлака $CaO/SiO_2 = 1{,}5$-$1{,}9$ и концентрации Al_2O_3 в шлаке в пределах 5-15%. В результате построены графики зависимости указанных свойств от температурных величин, рассчитаны энергии активации вязкого течения и определены фазовые составы опытных шлаков с использованием математической модели диаграммы системы FeO – MnO – CaO – Al_2O_3 – SiO_2. Таким образом, повышение концентрации оксида алюминия против его обычного уровня, меняя основность шлака, существенно повлияло на физико-химические свойства шлаков, и тем самым способствует корректировки параметров процесса электроплавки. При этом взаимодействие некоторых физико-химических свойств шлаков на условия плавки марганцевых ферросплавов целесообразно изучать во взаимосвязи с составом шлаков.

Ключевые слова: вязкость, шлаки марганцевых сплавов, температура кристаллизации, энергия активации, фазовый состав.

Информация об авторах:

Есенгалиев Даурен Амангельдиевич	*PhD доктор, старший преподаватель кафедры металлургии и горного дела технического факультета Актюбинского регионального университета им. К. Жубанова, Актобе, Казахстан. Email: dauralga@mail.ru, ORCID ID: 0000-0003-0792-0822*
Байсанов Алибек Сайлаубаевич	*к.т.н., профессор, заведующий лабораторией пирометаллургических процессов Химико-металлургического института им. Ж. Абишева, Караганда, Казахстан. Email:*

	alibekbaisanov@mail.ru, ORCID ID: 0000-0002-3025-7267
Досекенов Мурат Сагитжанович	*инженер-технолог ТОО «Научно-исследовательский инжиниринговый центр ERG», Актобе, Казахстан. Email: dossekenov.ms@mail.ru, ORCID ID: 0000-0003-2483-8118*
Келаманов Бауыржан Сатыбалдыулы	*к.т.н., ассоц. профессор, доцент кафедры металлургии и горного дела технического факультета Актюбинского регионального университета им. К. Жубанова, Актобе, Казахстан. Email: kelamanov-b@mail.ru, ORCID ID: 0000-0001-7646-9153*
Алмабеков Диас Маратулы	*студент по специальности 6В07203 – Металлургия технического факультета Актюбинского регионального университета им. К. Жубанова, Актобе, Казахстан. Email: almabekov@04list.ru*

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Promising methods for hydrometallurgical processing of copper slag

[1*]Kurmangaliyev D.B., [1]Abdulina S.A., [2] Mamyachenkov S.V.

[1] D.Serikbayev East Kazakhstan technical university, Ust-Kamenogorsk, Kazakhstan
[2]Federal State Autonomous Educational Institution of Higher Education «Ural Federal University named after the first President of Russia B.N.Yeltsin», Ekaterinburg, Russia

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

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ABSTRACT

Metals are important in many modern industries. Due to the depletion of their natural resource base, it is necessary to adapt, which means developing new and optimizing existing methods of extraction of valuable components from ore materials. Only comprehensive processing of copper metallurgical slags will solve the problem of resource recovery and the creation of low-waste technology, which has great economic, environmental, and social importance. Hydrometallurgical technologies take into account the specific conditions of the system and the physical and chemical properties of metals when developing and selecting the method of extraction. This article provides a review of the current state and prospects of development technologies used for base metal extraction by leaching with the use of inorganic acids and environmentally safe reagents, the methods are conditionally divided into two groups. The listed studies have made a significant contribution to solving the problem of processing metallurgical slags, however, none of the technologies has gone beyond the scope of laboratory and semi-industrial tests. Noted a tendency to reduce the concentrations of leaching agents by certain pre-treatment of raw material, as well as the transition to ubiquitously use "green technologies": such as bioleaching and organic acid leaching. Directions are suggested to solve the problem of rational use of raw materials and increase the sustainability of the future material cycle.

Keywords: hydrometallurgy, metallurgical slag, leaching, organic acid, bioleaching.

	Information about authors:
Kurmangaliyev Damir Bolatovich	*Ph.D. student of School of Metallurgy and Mineral Processing, D. Serikbayev East Kazakhstan technical university, Ust-Kamenogorsk, Kazakhstan. Email: kurmangaliyev_d@mail.ru, ORCID ID: 0000-0002-5022-696X*
Abdulina Saule Amangeldyevna	*Ph.D., Assistant professor of School of Metallurgy and Mineral Processing, D. Serikbayev East Kazakhstan technical university, Ust-Kamenogorsk, Kazakhstan. Email: abdulina.saule@mail.ru, ORCID ID: 0000-0001-6328-8652*
Mamyachenkov Sergey Vladimirovich	*Doctor of Technical Sciences, Senior Researcher of Federal State Autonomous Educational Institution of Higher Education «Ural Federal University named after the first President of Russia B.N.Yeltsin», Ekaterinburg, Russia. Email: s.v.mamiachenkov@urfu.ru, Scopus Author ID 6507625972*

Introduction

The problem of processing mining and metallurgical slag dumps is one of the most complicated and unresolved problems in modern nonferrous metallurgy. These wastes occupy a large territory and have a negative impact on the environment. Each ton of copper produced about 2.2 tons of copper slag [1]. On average, the annual production of copper-melting slags in the world is about 25 million tons, which usually contain a significant amount of valuable components, the concentration of which often far exceeds their concentration in the extracted raw materials. The growing value of non-ferrous metals and reduction of the mineral resource base do not allow their irretrievable losses and make the processing of such material economically attractive.

Copper smelting slags of different enterprises vary in their chemical composition and structure and usually contain about 1% of copper and 40% of iron, depending on the type of processing and elemental composition of ores, concentrates, and fluxes. Significant amounts of oxides of aluminum, magnesium, calcium, barium, etc., and minor amounts of other elements (e.g., zinc, titanium, and lead) are also associated with copper slag. The main components of copper slag are iron oxide and SiO_2, which are present in copper slag mainly in the form of fayalite ($2FeO - SiO_2$).

Recently, scientists around the world have paid special attention to hydrometallurgical processes for the extraction of valuable components from metallurgical slags, and many technologies have been developed. In these studies, the efforts were mainly focused on leaching processes with the use of inorganic acids and environmentally safe reagents (organic acids and microorganisms), according to the same principle the methods have been classified in this review, but it should be noted that this division is conventional.

The first group includes technologies of leaching with the use of inorganic acids.

In the work, Banza A.N. et al [2] performed an extraction of non-ferrous metals using three different methods (sulfuric acid leaching, leaching at a constant hydrogen peroxide flow rate, and leaching at a constant Eh potential) with samples of milled slag from Lubumbashi, Democratic Republic of Congo. Metal recoveries of about 60% Cu, 90% Co, 90% Zn, and 90% Fe were obtained after 2 hours using only H_2SO_4. Using a combination of H_2SO_4 and H_2O_2, resulted in better metal recovery: 80% Cu, 90% Co, 90% Zn, and 5% Fe.

Yang, Z. et al [3] investigated the leaching of copper smelting slag from Guangdong province in China using the same acid (H_2SO_4) with $NaClO_3$ oxidizer and $Ca(OH)_2$ neutralization to accelerate sludge filtration. The overall leaching and selective precipitation process recovered about 98% Co, 97% Zn, and 89% Cu from this slag, with only 3.2% Si and 0.02% Fe dissolved.

By another technology [4] the authors studied the extraction of copper and cobalt from converter slag obtained at Zhongtiaoshan Nonferrous Complex metallurgical plant, China. Pre-dried slag was treated with H_2O_2 and H_2SO_4 (120% stoichiometric amount), and then solidified slag was leached with water, and as a result, was extracted more than 95% Co and up to 90% Cu.

In the method developed at Firat University, Turkey [5] was shown that roasting with $Fe_2(SO_4)_3$ at 500°C, duration of 120 minutes and ratio ($Fe_2(SO_4)_3 \cdot xH_2O$: slag = 1: 1) followed by water leaching resulted in copper, cobalt, nickel and zinc recovery respectively: 93%; 38%; 13% и 59%. Copper converter slag from Ergani Copper Plant, Maden, Elazig, Turkey was investigated.

In the work of the previously mentioned university [6], the extraction characteristics of copper, cobalt, zinc, and iron from converter slag obtained at Ergani Copper Plant, Maden, Elazig, Turkey were investigated. Studies were carried out by oxidative leaching with a leaching agent based on potassium dichromate ($K_2Cr_2O_7$) and sulfuric acid (H_2SO_4). Experimental results showed that the presence of dichromate has a great influence on the extraction of base metals. The process extracted 81.15% Cu, 12.0% Co, 3.15% Fe and 10.27% Zn.

Arslan and Arslan [7] focused on the recovery of copper, cobalt, and zinc from smelter and converter slags by sulfuric acid roasting. This study used leaching experiments to investigate the effect of firing time, acid: slag ratio, and firing temperature on the degree of metal dissolution. In 2 hours of firing at 150°C and acid: slag ratio = 3: 1, the metals recovered were: 88% Cu, 87% Co, 93% Zn and 83% Fe. Moreover, increasing the firing time to 4 hours increased the copper recovery to 95%.

In work [8] the influence of the degree of grinding of copper smelting slags Kazakhmys Smelting, Balkhash, Kazakhstan on the degree of extraction of non-ferrous metals by sulfuric acid at room temperature in the presence of potassium dichromate was studied. Grinding in a planetary ball mill and an abrasion mill was used for mechanical activation of copper extraction. Figure 1 compares SEM images of slag subjected to dry grinding in a planetary (Fig. 1a) and an abrasion mill (Fig. 1b) for 20 minutes at 600 rpm, a ball : powder ratio = 20 : 1. The figure shows that the planetary grinding produces finer particles.

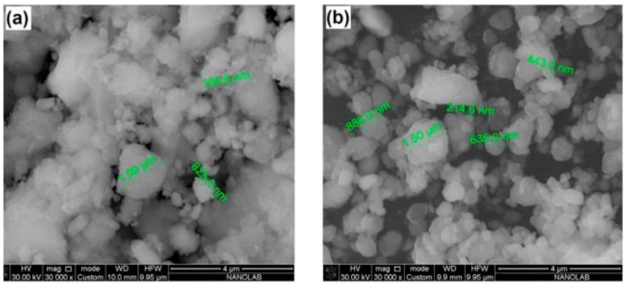

Figure 1 - SEM images of crushed slag samples [8]

When conducting leaching experiments under optimal conditions for milled slag, and with optimal parameters for copper extraction and copper selectivity, the maximum copper extraction was 87.3%, and the maximum copper selectivity was 97.9%.

The second group includes technologies using environmentally safe reagents.

Sukla et al [9], described a leaching process, using a strain of Aspergillus niger, copper converter slag from M/S Hindustan Copper Limited, Gatsila, India, isolated from Sukinda laterite nickel ore. The bacteria were pre-enriched with 2% - potato dextrose broth and the pulp density was varied by dextrose concentration from 2 to 10%. At the same time, good results were obtained by trial experiments with oxalic, acetic, and succinic acids (1M) for 72 hours on a rotary vibrator at 37°C. The maximum recoveries of copper, cobalt, and nickel were 47%, 50%, and 23%, respectively.

Mehta et al [10] investigated the recovery of copper, cobalt, and nickel from converter slag at room temperature by biological leaching using Thiobacillus ferrooxidans, and iron-oxidizing bacteria from two copper converter slag samples from the Indian Copper Complex (ICC) in Gatsil, India on a laboratory scale. The slag treatment optimized parameters such as the degree of grinding of the material, acidity of the medium, solid: liquid ratio, Fe(II)/Fe(III) ratio, and the amount of Fe(II) and additives. Metal recovery from slag under sterile and biological leaching conditions was 80.0% and 99.0% Cu (80 days), 18.0% and 22.0% Ni (70 days), and 16.0% and 30.0% Co (50 days).

Selective leaching of lead and copper by citric acid solutions from the slag of suspended copper smelting was proposed in the work [11]. In the work, the optimal conditions for the transition of lead into solution (85%) were determined, while the leaching of copper into solution was minimal (26%). In the next step, the solid residue could be treated using H_2SO_4 solutions to extract the copper.

In another paper [12], an environmentally friendly hydrometallurgical process for the recovery of copper, nickel, and cobalt from copper-enriched converter slag using organic acids was proposed. In order to optimize copper leaching, the authors of the work varied such parameters as acid concentration, slurry density, temperature, and process time. Optimal extraction of 99.1% Cu, 89.2% Ni, 94% Co and 99.2% Fe was achieved in 9-10 hours at 35°C, pulp density 15% using 2N citric acid, and particle size <45 μm.

The authors of [13] studied the characteristics of Cu, Co, Zn, and Fe extraction from Küre-Kastamonu Historical Copper Slag (KHS) by oxidative leaching under pressure using a sulfuric acid-based leaching additive. The samples used in the leaching tests averaged 0.84% Cu, 0.34% Co, 0.23% Zn, 2.90% Al, 0.70% Ca, 1.30% S and 42.80% Fe. It was found that metal recovery increased with increasing temperature and sulfuric acid concentration. However, high acid concentrations led to gel formation, which caused filtration problems. Under optimal conditions, the recovery efficiency of cobalt, copper, and zinc from KHS was 96.82, 92.85, and 93.44%, respectively.

S.N. Vinogradov Institute of Microbiology of the Russian Academy of Sciences proposed the process of non-ferrous metals leaching [14] from slag by trivalent iron sulfate obtained with the help of iron-oxidizing chemolithotrophic bacteria, which allowed fully enough convert non-ferrous metals to the liquid phase for 1.0 hour at 70°C. At the same time extraction of copper in the solution reached 90%, nickel - 88%, cobalt - 67%, and extraction of iron in the solution was only about 30%.

As a result of the analysis of studies in the field of technologies aimed at extraction of valuable components from copper production slags by hydrometallurgical methods the following was revealed:

- in recent years, domestic and foreign scientists have proposed a large number of promising methods for extracting valuable components from copper slag, but none of them has gone beyond the laboratory and semi-industrial tests;
- the main trend in the processing of copper slag with inorganic acids is a certain pretreatment of the material, which will ensure the use of low concentrations of leaching agents, which is intended to make the process more environmentally friendly;
- much emphasis is now being placed on introducing "green technologies" into production: this is an environmentally safe and economically competitive approach to the extraction of non-ferrous metals from copper slag, in which organic acids and microorganisms are preferred to inorganic acids.

Conflict of interest

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

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Мыс қождарын гидрометаллургиялық өңдеудің перспективті әдістері

[1] Курмангалиев Д. Б., [1] Абдулина С.А., [2] Мамяченков С.В.

[1] Д. Серікбаев атындағы Шығыс Қазақстан техникалық университеті, Өскемен қ, Қазақстан
[2] Ресейдің тұңғыш президенті Б.Н. Ельцин атындағы Орал федералдық университеті, Екатеринбург, Ресей

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ТҮЙІНДЕМЕ

Қазіргі замандағы барлық салаларда металдардың маңызы өте зор. Минералдық-шикізат базасының сарқылуына байланысты кендерден құнды компоненттерді алудың жаңа әдістерін әзірлеу және қолданыстағы әдістерді оңтайландыру қажет. Мыстың металлургиялық қождарын кешенді қайта өңдеу ғана ресурстарды қалпына келтіру және қалдығы аз технологиялар жасауға мүмкіндік береді, бұның орасан зор экономикалық, экологиялық және әлеуметтік маңызы бар. Гидрометаллургиялық технологиялар металды өндіру әдісін әзірлеу және таңдау кезінде жүйенің ерекше жағдайларын және металдардың физика-химиялық қасиеттерін ескереді. Бұл мақалада бейорганикалық қышқылдар мен экологиялық таза реагенттерді қолдана отырып, ерітінділеу (шаймалау) арқылы мыс алу үшін қолданылатын технологиялардың қазіргі жағдайы мен даму перспективаларына шолу жасалады. Әдістер шартты түрде екі топқа бөлінген. Айтылған зерттеулер металлургиялық қожды өңдеу мәселесін шешуге айтарлықтай үлес қосты, дегенмен технологиялардың ешқайсысы зертханалық және жартылай өнеркәсіптік сынақтар шеңберінен шыққан жоқ. Қазіргі кезде материалды алдын ала белгілі бір өңдеу кезінде қолданылатын ерітінділеу агенттерін пайдалануының төмендеу үрдісі, сонымен қатар "жасыл технологияларды" кең түрде пайдалану байқалады. Мұның бәрі кен шикізатын ұтымды пайдалану проблемасын шешуге және материалдардың айналымының тұрақтылығын арттыруға бағытталған.

Түйін сөздер: гидрометаллургия, металлургиялық қож, сілтілеу, органикалық қышқыл, биосілтілеу

	Авторлар туралы ақпарат:
Курмангалиев Дамир Болатович	*Докторант, Металлургия және пайдалы қазбаларды байыту мектебі, Д. Серікбаев атындағы Шығыс Қазақстан техникалық университеті, Өскемен қ., Қазақстан. Электрондық пошта: kurmangaliyev_d@mail.ru, ORCID ID: 0000-0002-5022-696X*
Абдулина Сауле Амангельдыевна	*PhD, Металлургия және пайдалы қазбаларды байыту мектебі Металлургия және пайдалы қазбаларды байыту мектебің қауымдастырылған профессоры, Д. Серікбаев атындағы Шығыс Қазақстан техникалық университеті, Өскемен қ., Қазақстан. Электрондық пошта: abdulina.saule@mail.ru, ORCID ID: 0000-0001-6328-8652*
Мамяченков Сергей Владимирович	*Техникалық ғылымдар докторы, Ресейдің тұңғыш президенті Б.Н. Ельцин атындағы Орал федералдық университетінің аға ғылыми қызметкері, Электрондық пошта: s.v.mamiachenkov@urfu.ru, Scopus Author ID 6507625972*

Перспективные методы гидрометаллургической переработки медных шлаков

[1]Курмангалиев Д. Б., [1] Абдулина С.А., [2] Мамяченков С.В.

[1] Восточно-Казахстанский технический университет им. Д. Серикбаева, Усть-Каменогорск, Казахстан
[2] Уральский федеральный университет имени первого Президента России Б.Н. Ельцина, Екатеринбург, Россия

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АННОТАЦИЯ

Металлы важны во многих современных отраслях. По причине истощения их минерально-сырьевой базы, необходимо адаптироваться, значит разрабатывать новые и оптимизировать существующие методы извлечения ценных компонентов из рудных материалов. Только комплексная переработка медных металлургических шлаков позволит решить задачу восстановления ресурсов и создания малоотходных технологий, имеющую огромное экономическое, экологическое и социальное значение. Гидрометаллургические технологии, при разработке и выборе метода извлечения, учитывают специфические условия системы и физико-химические свойства металлов. В данной статье представлен обзор современного состояния и перспектив развития технологий, используемых для извлечения меди выщелачиванием с применением неорганических кислот и экологически безопасных реагентов, методы условно поделены на две группы. Перечисленные исследования внесли серьезный вклад в решение проблемы перерабоки металлургических шлаков, однако ни одна из технологий не вышла за рамки лабораторных и полупромышленных испытаний. Отмечается тенденция снижения концентраций применяемых выщелачивающих агентов, путём определенной предварительной обработки материала, а также повсеместное внедрение «зеленых технологий». Всё это направлено на решение проблемы рационального использования рудного сырья и повышения устойчивости будущего круговорота материалов.

Ключевые слова: гидрометаллургия, металлургический шлак, выщелачивание, органическая кислота, биовыщелачивание

	Информация об авторах:
Курмангалиев Дамир Болатович	*Докторант, Школа металлургии и обогащение полезных ископаемых, Восточно-Казахстанский технический университет им. Д. Серикбаева, Усть-Каменогорск, Казахстан. Email: kurmangaliyev_d@mail.ru, ORCID ID: 0000-0002-5022-696X*
Абдулина Сауле Амангельдыевна	*PhD, Ассоциированный профессор Школы металлургии и обогащение полезных ископаемых, Восточно-Казахстанский технический университет им. Д. Серикбаева, Усть-Каменогорск, Казахстан. Email: abdulina.saule@mail.ru, ORCID ID: 0000-0001-6328-8652*
Мамяченков Сергей Владимирович	*Доктор технических наук, Старший научный сотрудник Уральский федеральный университет имени первого Президента России Б.Н. Ельцина, Екатеринбург, Россия. Email: s.v.mamiachenkov@urfu.ru, Scopus Author ID 6507625972*

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Studying the characteristics of iodine sorption in synthetized ion-exchangers

[1]Konyratbekova S.S., [1]Baikonurova A.O., [1]Usoltseva G.A., [2,3]Surimbayev B.N.*, [1]Eskalina K.T.

[1]Satbayev University, Almaty, Republic of Kazakhstan
[2]Kazmekhanobr State Scientific Production Association of Industrial Ecology, Almaty, Republic of Kazakhstan
[3]Al-Farabi Kazakh National University, Almaty, Republic of Kazakhstan

** Corresponding author email: surimbaev@gmail.com*

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ABSTRACT
Iodine is an essential micronutrient for humans and animals due to its important role as a component of thyroid hormones. Kazakhstan is a country, most regions of which suffer from a natural deficiency of iodine. At the same time, the country has a rich resource base for obtaining iodine and its compounds. These are formation waters of oil fields under development containing 0.001–0.005% iodine. To extract iodine from natural oil-field brines, we have proposed ion-exchange materials obtained from the waste of the oil refining industry. The article presents the results of studying the characteristics of iodine sorption in the synthesized ion exchangers. The synthesis of ion exchangers was carried out by polycondensation of dihydric phenols (1,3 dioxybenzene, 1,2 dioxybenzene, 1,4 dioxybenzene), hexamethylenediamine, and formaldehyde. The following sorption characteristics of iodine by the synthesized ion exchangers were studied: the influence of the pH of a solution on iodine sorption; kinetic curves of iodine sorption; iodine sorption isotherms; mechanism of iodine sorption. It has been established that the sorption of iodine on the synthesized samples is essentially independent of the pH of a medium, and the degree of its extraction in the entire area under study is 94–100%. Studies have been carried out on the dependence of the degree of extraction and the logarithm of the iodine distribution coefficient on the duration of the process. The sorption capacity of the synthesized ion exchangers with respect to iodine was estimated depending on the structure of the ion exchanger and sorption conditions. It has been established that sorbents based on 1,4 dioxybenzene, which are distinguished by high kinetic abilities and static exchange capacity (SEC = 2283.88 mg/g), are most preferable for iodine extraction. The mechanism of sorption of iodine by synthesized ion exchangers has been determined.

Keywords: *iodine sorption, sorption capacity, synthesis of ion exchangers, sorption isotherm, iodide leaching, iodine.*

	Information about authors:
Konyratbekova Saltanat Sabitovna	*Candidate of Technical Sciences, Senior lecturer, Department of Metallurgical Processes, Heat Engineering and Technology of Special Materials, Satbayev University, Almaty, Kazakhstan, E-mail: s.konyratbekova@satbayev.university, salta_7504@mail.ru;ORCIDID: https://orcid.org/ 0000-0003-2148-035X*
Baikonurova Aliya Omirkhanovna	*Doctor of Technical Sciences, Professor, Department of Metallurgical Processes, Heat Engineering and Technology of Special Materials, Satbayev University, Almaty, Kazakhstan. Email: a.baikonurova@satbayev.university; a.baikonurova@yandex.kz; ORCID ID: ttps://orcid.org/0000-0002-1052-3505*
Usoltseva Galina Alexandrovna	*Candidate of Technical Sciences, Assistant Professor, Department of Metallurgical Processes, Heat Engineering and Technology of Special Materials, Satbayev University, Almaty, Kazakhstan. Email: g.ussoltseva@satbayev.university, nota-vesna@yandex.kz; ORCID ID: ttps://orcid.org/0000-0003-0155-5094*
Surimbayev Bauyrzhan Nurzhanovich	*PhD, Senior Researcher, Laboratory of precious metals, Kazmekhanobr State Scientific Production Association of Industrial Ecology, Almaty, Kazakhstan; Senior Lecturer, Chair of Analytical, Colloid Chemistry and Technology of Rare Elements, Department of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty, Kazakhstan; E-mail: surimbaev@gmail.com, bauyrzhan.surimbayev@kaznu.kz; ORCID ID: https://orcid.org/0000-0002-3988-8444*
Eskalina Kuralay Tulegenkyzy	*PhD student, Department of Metallurgical Processes, Heat Engineering and Technology of Special Materials, Satbayev University, Almaty, Kazakhstan, E-mail: kuralai_eskalina@mail.ru; ORCID ID: https://orcid.org/0000-0002-2804-7076*

Introduction

Iodine is an essential micronutrient for humans and animals due to its important role as a component of thyroid hormones [1]. Kazakhstan is a country, most regions of which suffer from a natural deficiency of iodine. This is due to natural and climatic conditions, due to which iodine can scarcely be found in foods of plant and animal origin [[2], [3]]. At the same time, the country has a rich resource base for obtaining iodine and its compounds. These are formation waters of oil fields under development containing 0.001–0.005% iodine [4].

Interest in iodine sorption was caused by the possibility of using natural iodine-containing raw materials for processing, as well as the prospect of using iodide solutions in the technology of gold recovery [[4], [5]].

The implementation of the iodide method of gold leaching is possible in the development of effective, including sorption methods for extracting iodine from iodine-containing natural solutions. The efficiency of sorption strongly depends on soil types and their characteristics. While sorption of iodide dominates in mineral soils with a low content of organic carbon, soils rich in organic matter are more favorable for the sorption of iodate [6].

Various ion exchangers from activated carbons [[7], [8], [9], [10]] to synthesized ion exchangers [11, 12] are used for sorption recovery.

Thus, the organization of regeneration of iodine-containing solutions, as well as replenishment of irretrievable losses of iodine due to its extraction from natural sources by highly efficient sorption methods, is an important scientific and practical task.

Experimental Part

To extract iodine from natural oil-field brines, we have proposed ion-exchange materials obtained from the waste of the oil refining industry.

Sorption of iodine from aqueous iodine-containing solutions was carried out on synthesized ion exchangers.

The method for obtaining synthesized ion exchangers. The synthesis of amine-containing ion exchangers with a spatial structure of mixed basicity was carried out by polycondensation of dihydric phenols (1,3 dioxybenzene, 1,4 dioxybenzene, 1,2 dioxybenzene), hexamethylenediamine, and formaldehyde [13].

The method for obtaining synthesized ion exchangers. The synthesis of amine-containing ion Hexamethylenediamine was used in the synthesis process as a hardener for the resulting resins, and formaldehyde was used as a crosslinking agent. Ammonium hydroxide, nitric and phosphoric acids, and hydrogen peroxide were used as catalyzing and modifying additives. The latter are involved in the process not only as catalysts but also as reagents that facilitate the introduction of additional ionogenic groups into the polymer structure. The following sorption characteristics of iodine by the synthesized ion exchangers were studied: the influence of the pH of a solution on iodine sorption; sorption kinetics; sorption isotherms; mechanism of iodine sorption.

Results and Discussion

Influence of the pH of a solution on the results of iodine sorption.

The sorption of iodine was studied from aqueous solutions with a concentration of ~200 mg/dm^3 in a wide range of pH values for 24 hours.

The results of the sorption of iodine from its solutions by synthesized ion exchangers depending on the pH of the medium are shown in Table 1 and Figure 1.

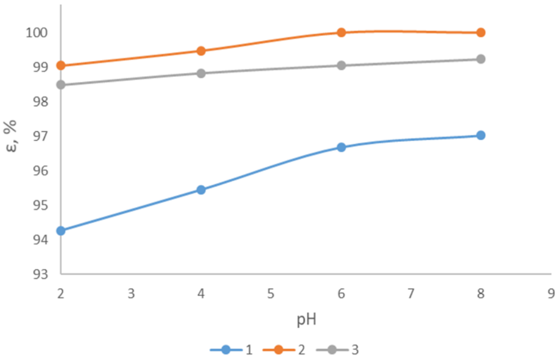
Studies have shown that the sorption of iodine on the synthesized samples is essentially independent of the pH of the medium, and the degree of its extraction in the entire area under study is 94–100% (Table 1, Figure 1).

Influence of the duration of the sorption process on the extraction of iodine.

Sorption of iodine (kinetic curves of iodine sorption) was conducted under the following conditions: C_{I_2} = 200.58 mg/dm^3; $V_{Solution}$= 500 cm^3; $m_{Ion\text{-}Exchanger}$ = 0.0998 g; pH 7.4. The results of the influence of the duration of the sorption process on the extraction of iodine are shown in Table 2 and Figure 2.

Table 1 – Influence of the pH of the solution on the results of iodine sorption by amine-containing ion exchangers

Ion exchanger code	pH of the initial solution	C Equilibrium, mg/dm^3	Kp, mL/g	lg K_p	Static Exchange Capacity, mg/g	ε, %
1	2.25	11.48	82199.95	4.92	943.66	94.27
	4.04	9.11	104884.03	5.02	955.49	95.45
	5.11	6.65	145531.01	5.16	967.78	96.68
	7.85	5.97	162676.35	5.21	971.18	97.02
2	2.25	1.90	521846.05	5.72	991.51	99.05
	4.04	1.04	957503.07	5.98	995.80	99.48
	5.11	–	–	–	1001.00	100.00
	7.85	–	–	–	1001.00	100.00
3	2.25	3.02	326461.29	5.51	985.91	98.49
	4.04	2.34	422781.92	5.63	989.31	98.83
	5.11	1.90	521846.05	5.72	991.51	99.05
	7.85	1.54	645003.70	5.81	993.31	99.23
Note: polymeric ion exchangers are synthesized on the basis of: 1 – 1,3 dioxybenzene, 2 – 1,4 dioxybenzene, 3 – 1,2 dioxybenzene						

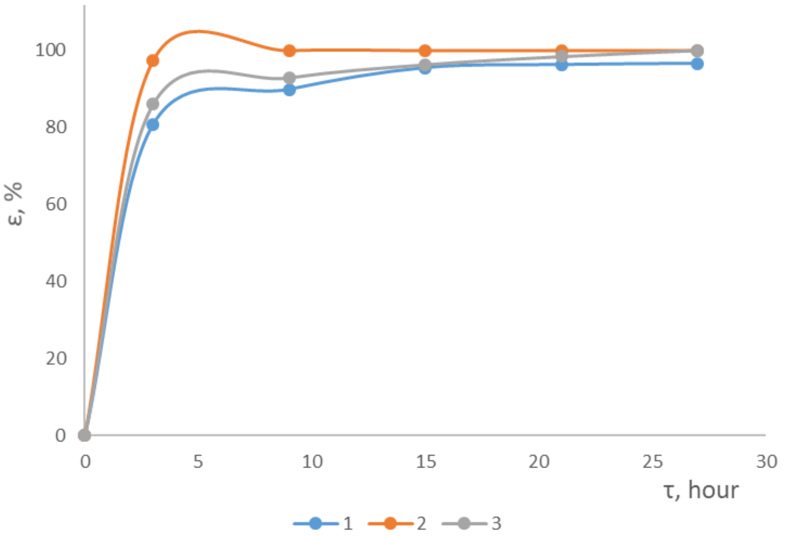


1 – 1,3 dioxybenzene; 2 – 1,4 dioxybenzene; 3 – 1,2 dioxybenzene

Figure 1 – Influence of the pH of stock solutions on the sorption of iodine by amine-containing ion exchangers

Table 2 – Dependence of the results of iodine sorption by synthesized ion exchangers on the duration of the process

Ion exchanger code	τ, hour	C Equilibrium , mg/dm^3	Kp, mL/g	lg K_p	Static Exchange Capacity, mg/g	ε, %
1	3	38.71	20949.85	4.32	810.97	80.7
	9	20.46	44105.63	4.64	902.40	89.8
	15	9.23	103863.86	5.02	958.66	95.4
	21	7.62	126614.17	5.10	964.80	96.2
	27	7.02	138138.97	5.14	969.74	96.5
2	3	5.22	187500.68	5.27	978.75	97.4
	9	–	–	–	1004.91	100.0
	15	–	–	–	1004.91	100.0
	21	–	–	–	1004.91	100.0
	27	–	–	–	1004.91	100.0
3	3	28.08	30777.24	4.49	864.23	86.0
	9	14.24	65559.23	4.82	933.56	92.9
	15	7.42	130422.04	5.12	967.73	96.3
	21	3.21	308044.76	5.49	988.82	98.4
	27	–	–	–	1004.91	100.0
Note: polymeric ion exchangers are synthesized on the basis of: 1 – 1,3 dioxybenzene, 2 – 1,4 dioxybenzene, 3 – 1,2 dioxybenzene.						



1 – 1,3 dioxybenzene; 2 – 1,4 dioxybenzene; 3 – 1,2 dioxybenzene

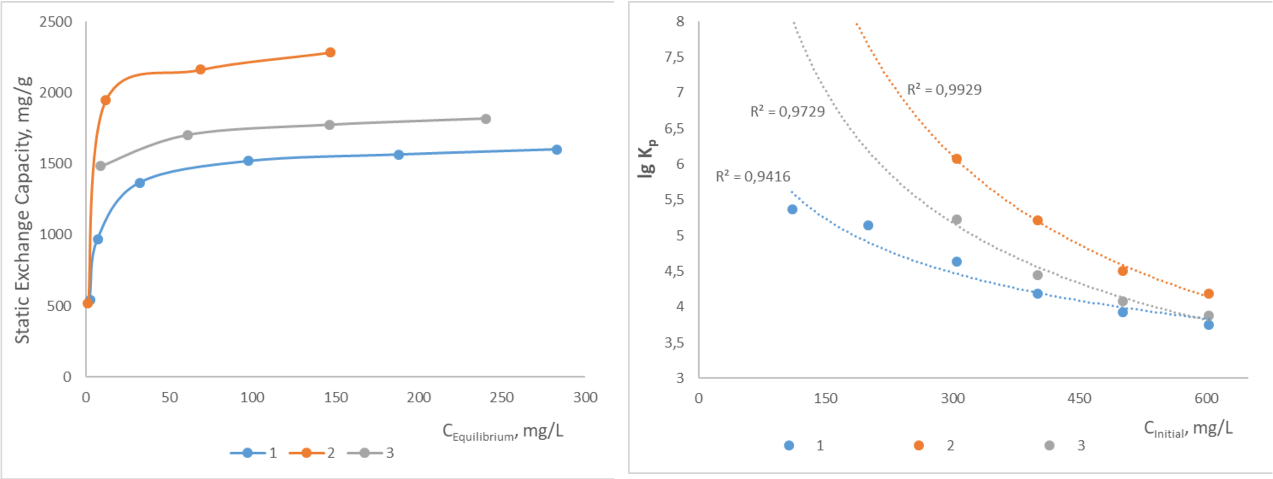
Figure 2 - Dependence of the degree of iodine extraction on the duration of the process

Table 2 and Figure 3 show that preference should be given to the ion exchanger based on 1,4 dioxybenzene, whose sorption kinetic curves are the highest. The maximum extraction of iodine by sorption by the ion exchanger based on 1,4 dioxybenzene is achieved in 9 hours, while it takes 27 hours or more to obtain the same result with 1,3 dioxybenzene, 1,2 dioxybenzene ion exchangers.

Ion exchange isotherms. Ion exchange isotherms were built by the method of variable concentrations using the same volumes of iodine-containing solutions (0.5 dm^3) and weighed portions of ion exchangers (0.1 g) for 27 hours. The pH value of the solutions was maintained in the found optimal range. Sorption isotherms and dependences of the logarithm of the iodine distribution coefficient are presented in Table 3 and Figure 3.

Table 3 - Results of iodine sorption by synthesized ion exchangers depending on its initial concentration

Ion exchanger code	$C_{Initial}$, mg/L	$C_{Equilibrium}$, mg/L	K_p, mL/g	lg K_p	Static Exchange Capacity, mg/g	ε, %
1	110.41	2.32	233185.8	5.37	540.99	97.9
	200.58	7.02	138139.0	5.14	969.74	96.5
	305.32	32.15	42526.2	4.63	1367.22	89.5
	401.13	97.48	15590.6	4.19	1519.77	75.7
	500.88	188.06	8325.4	3.92	1565.67	62.5
	603.24	283.14	5658.3	3.75	1602.10	53.1
2	110.41	–	–	–	552.60	100.0
	200.58	–	–	–	1003.60	100.0
	305.32	1.26	1207795	6.08	521.82	99.6
	401.13	11.90	163705.7	5.21	1948.10	97.0
	500.88	68.78	31443.2	4.50	2162.66	86.3
	603.24	146.92	15545.1	4.19	2283.88	75.6
3	110.41	–	–	–	552.60	100.0
	200.58	–	–	–	1003.60	100.0
	305.32	8.76	169438.4	5.23	1484.28	97.1
	401.13	60.90	27961.5	4.45	1702.85	84.8
	500.88	146.54	12102.3	4.08	1773.47	70.7
	603.24	240.32	7558.3	3.88	1816.42	60.2
Note: polymeric ion exchangers are synthesized on the basis of: 1 – 1,3 dioxybenzene, 2 – 1,4 dioxybenzene, 3 – 1,2 dioxybenzene, $pH_{initial}$ ~ 7.4						



1 – 1,3 dioxybenzene; 2 – 1,4 dioxybenzene; 3 – 1,2 dioxybenzene

Figure 3 - Isotherms of iodine sorption by amine-containing ion exchangers

It can be seen from the data obtained that the isotherms of sorption of iodine on ionites have a convex ($C_{Equilibrium} > 1$) shape. The slopes of the logarithmic dependences of the distribution coefficients of iodine on its initial concentration in an aqueous solution slightly differ from each other, which allows us to make an assumption that the mechanism of halogen sorption by all synthesized ion exchangers is identical. The apparent equilibrium constants for iodine can be arranged in the following series:

$$C_{\text{Equilibrium } 2} > C_{\text{Equilibrium } 3} > C_{\text{Equilibrium } 1},$$

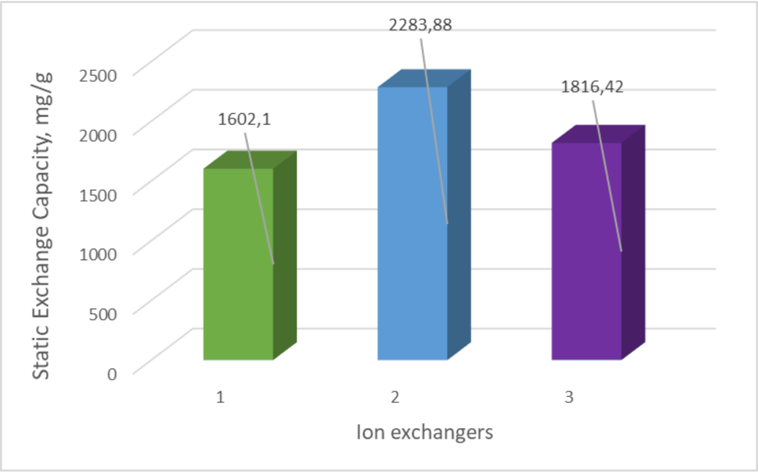
where indices 1–3 denote the corresponding codes of the synthesized ion exchangers.

Figure 4 shows the comparative sorption characteristics of the synthesized ion exchangers.

It can be seen that the sorption capacity of all synthesized ion exchangers for iodine is high and exceeds 1600 mg/g. The ion exchanger synthesized on the basis of 1,4 dioxybenzene has the best sorption characteristics (Static Exchange Capacity = 2283.88 mg/g).

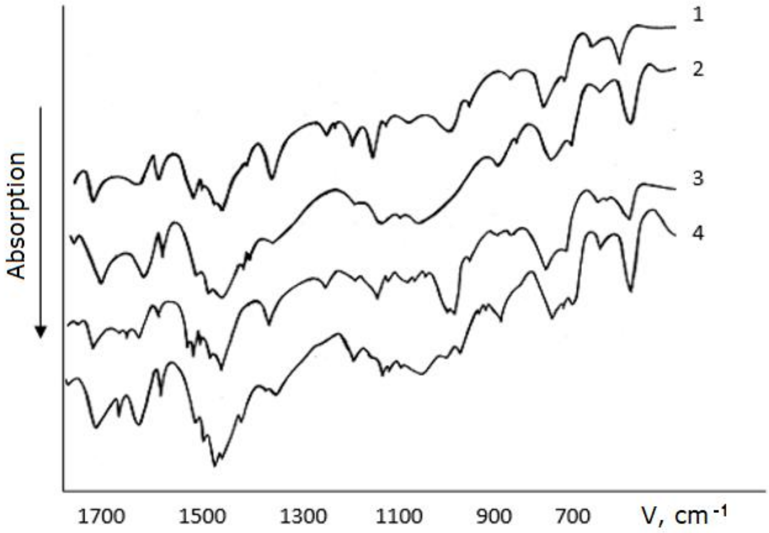
The results obtained significantly exceed the sorption rates of the highly basic anion exchanger AV-17 (Static Exchange Capacity = 300 mg/g), which is widely used in the iodine-bromine industry, as well as those of EDE-10P (Static Exchange Capacity = 500 mg/g) [13].

To establish the mechanism of iodine sorption, the IR spectra of sorbents were studied (Figure 5).



1 – 1,3 dioxybenzene; 2 – 1,4 dioxybenzene; 3 – 1,2 dioxybenzene

Figure 4 - Sorption characteristics of synthesized ion exchangers in relation to iodine



1,4 dioxybenzene saturated with water (1) and iodine (2);
1,2 dioxybenzene saturated with water (3) and iodine (4)

Figure 5 - IR spectra of sorbents

After the contact of ion exchangers with a sulphate solution of potassium iodide, the spectra show changes at 1700–1300 cm^{-1}, where C=C valence bonds and deformation –C–H groups appear.

The increase in the intensities of the absorption bands of bending vibrations of $-CH_3$ and $-CH_2$ groups (3000–2800 cm^{-1}) is also associated with iodine sorption. The coordination of iodine to the nitrogen of the amino group is shown by changes in the spectra at 1100–1200 cm^{-1}.

Thus, it can be concluded that the sorption of iodine by ion exchangers is carried out through a mixed mechanism: ion exchange mechanism, i.e. the extraction of iodide ion, and the coordination one, i.e. the sorption of elemental iodine, which leads to a significant increase in the capacitive properties of sorbents compared to known industrial ion exchangers.

Conclusions

The results obtained made it possible to draw the following conclusions:

– the sorption of iodine on the synthesized samples is essentially independent of the pH of the medium, and the degree of its extraction in the entire area under study is 94–100%.

– sorption kinetic curves of the synthesized ion exchange resin based on 1,4 dioxybenzene are the highest in comparison with 1,2 dioxybenzene and 1,3 dioxybenzene ion exchangers. The maximum extraction of iodine by sorption with an ion exchanger based on 1,4 dioxybenzene is achieved in 9 hours.

– the sorption capacity of all synthesized ion exchangers for iodine is high and exceeds 1600 mg/g. The ion exchanger synthesized on the basis of 1,4 dioxybenzene has the best sorption characteristics (Static exchange capacity = 2283.88 mg/g).

– the sorption of iodine by ion exchangers is carried out through a mixed mechanism: ion exchange mechanism, i.e. the extraction of iodide ion, and the coordination one, i.e. the sorption of elemental iodine, which leads to a significant increase in the capacitive properties of sorbents compared to known industrial ion exchangers.

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

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Синтезделген иониттердегі иод сорбциясының сипаттамаларын зерттеу

[1]Қоңыратбекова С.С., [1]Байқоңырова Ә.Ө., [1]Усольцева Г.А., [2,3]Сүрімбаев Б.Н., [1]Есқалина Қ.Т.

[1]Сәтбаев университеті, Алматы, Қазахстан
[2]«Қазақстан Республикасының минералдық шикізатты кешенді қайта өңдеу жөніндегі ұлттық орталығы» РМК «Қазмеханобр» мемлекеттік өнеркәсіптік экология ғылыми-өндірістік бірлестігі» филиалы, Алматы, Қазақстан, Алматы, Қазақстан
[3]Әл-Фараби атындағы Қазақ Ұлттық Университеті

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ТҮЙІНДЕМЕ

Иод адам және жануарлардың қалқанша безінің маңызды компоненті ретінде маңызды микроэлемент болып табылады. Қазақстанның көптеген аймақтарында йодтың табиғи тапшылығы байқалады. Әйтседе, республикада йод пен оның қосындыларын алудың бай ресурстық базасы бар – бұл құрамында 0,001–0,005% йод бар өндірілетін мұнай кен орындарының қабат сулары. Табиғи бұрғылау суларынан йод алу үшін біз мұнай өңдеу өнеркәсібінің қалдықтарынан алынған ион алмастырғыш материалдарды ұсындық. Мақалада синтезделген иониттердегі иод сорбциясының сипаттамаларын зерттеу нәтижелері келтірілген. Ион алмастырғыштардың синтезі екі атомды фенолдарды (1,3 диоксибензол, 1,2 диоксибензол, 1,4 диоксибензол), гексаметилендиамин және формальдегидті поликонденсациялау арқылы жүзеге асырылды. Синтезделген ион алмастырғыштармен иодтың келесі сорбциялық сипаттамалары зерттелді, олар: иодтың сорбциялануына ерітіндінің pH әсері; иодтың сорбциялануының кинетикалық қисықтары (сызықтары); иодтың сорбция изотермалары; иодтың сорбциялану механизмі. Синтезделген үлгілердегі йодтың сорбциясы іс жүзінде ортаның pH-на тәуелді емес екені, ал оның бүкіл зерттеу аймағындағы бөліп алу дәрежесі 94–100% құрайтыны анықталды. Йодтың бөліп алу дәрежесінің және таралу коэффициентінің логарифмінің процесс ұзақтығына тәуелділігі зерттелді. Синтезделген ион алмастырғыштардың йодқа қатысты сорбциялық қабілеттілігі ионалмастырғыштың құрылымына және сорбция жағдайларына байланысты бағаланды. Йодты бөліп алу үшін жоғары кинетикалық және статикалық алмасу қабілеттілігіімен (САҚ = 2283,88 мг/г) ерекшеленетін 1,4 диоксибензол негізіндегі сорбенттер қолайлы болатыны анықталды. Синтезделген ион алмастырғыштармен иодты сорбциялау механизмі анықталды.

Түйін сөздер: иод сорбциясы, сорбциялық сыйымдылық, ионалмастырғыштардың синтезі, сорбция изотермасы, иодидті шаймалау, иод.

	Авторлар туралы ақпарат:
Қоңыратбекова Салтанат Сәбитқызы	*Техника ғылымдарының кандидаты, «Металлургиялық процестер, жылутехникасы және арнайы материалдар технологиясы» кафедрасының сениор-лекторы, Сәтбаев университеті, Алматы, Қазақстан, E-mail: s.konyratbekova@satbayev.university, salta_7504@mail.ru; ORCID ID: https://orcid.org/0000-0003-2148-035X*
Байқоңырова Әлия Өмірханқызы	*Техника ғылымдарының докторы, «Металлургиялық процестер, жылутехникасы және арнайы материалдар технологиясы» кафедрасының профессоры, Сәтбаев университеті, Алматы, Қазақстан. , Email: a.baikonurova@satbayev.university, a.baikonurova@yandex.kz; ORCID ID: https://orcid.org/0000-0002-1052-3505*
Усольцева Галина Александровна	*Техника ғылымдарының кандидаты, «Металлургиялық процестер, жылутехникасы және арнайы материалдар технологиясы» кафедрасының профессор ассистенті, Сәтбаев университеті, Алматы, Қазақстан, Email: g.ussoltseva@satbayev.university, nota-vesna@yandex.kz; ORCID ID: https://orcid.org/0000-0003-0155-5094*
Сүрімбаев Бауыржан Нұржанұлы	*PhD, Асыл металдар зертханасының аға ғылыми қызметкері, «ҚР МШКҚӨ ҰО» РМК «Қазмеханобр» мемлекеттік өнеркәсіптік экология ғылыми-өндірістік бірлестігі» филиалы, Алматы, Қазақстан; Аға оқытушы, Аналитикалық, коллоидтық химия және сирек элементтер технологиясы кафедрасы, Химия және химиялық технология факультеті, Әл - Фараби атындағы Қазақ ұлттық университеті, Алматы, Қазақстан, E-mail: surimbaev@gmail.com, bauyrzhan.surimbayev@kaznu.kz; ORCID ID: https://orcid.org/0000-0002-3988-8444*
Есқалина Құралай Түлегенқызы	*«Металлургиялық процестер, жылутехникасы және арнайы материалдар технологиясы» кафедрасының докторанты, Сәтбаев университеті, Алматы, Қазақстан, E-mail: kuralai_eskalina@mail.ru; ORCID ID: https://orcid.org/0000-0002-2804-7076*

Изучение характеристики сорбции иода в синтезированных ионитах

[1]Коныратбекова С.С., [1]Байконурова А.О., [1]Усольцева Г.А., [2,3]Суримбаев Б.Н., [1]Ескалина К.Т.

[1]НАО «Казахский национальный исследовательский технический университет имени К.И. Сатпаева»
[2]Филиал РГП «Национальный центр по комплексной переработке минерального сырья Республики Казахстан» Государственное научно-производственное объединение промышленной экологии «Казмеханобр»
[3]Казахский национальный университет им. аль-Фараби

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АННОТАЦИЯ

Иод является важным микроэлементом для людей и животных из-за его важной роли в качестве компонента гормонов щитовидной железы. Казахстан является страной, в большинстве регионов которого наблюдается природный дефицит иода. В то же время республика обладает богатой сырьевой базой для получения иода и его соединений – это пластовые воды разрабатываемых нефтяных месторождений, содержащие 0,001–0,005 % иода. Для извлечения иода из природных буровых вод нами были предложены ионообменные материалы, полученные из отходов нефтеперерабатывающей промышленности. В статье приводятся результаты изучение характеристики сорбции иода в синтезированных ионитах. Синтез ионитов осуществляли поликонденсацией двухатомных фенолов (1,3 диоксибензол, 1,2 диоксибензол, 1,4 диоксибензол), гексаметилендиамина и формальдегида. Были изучены следующие сорбционные характеристики иода синтезированными ионитами: влияние pH раствора на сорбцию иода; кинетические кривые сорбции иода; изотермы сорбции иода; механизм сорбции иода. Установлено, что сорбция иода на синтезированных образцах практически не зависит от pH среды, и степень извлечения его во всей исследуемой области составляет 94–100 %. Проведены исследования зависимости степени извлечения и логарифма коэффициента распределения иода от продолжительности процесса. Оценена сорбционная способность синтезированных ионитов по отношению к иоду в зависимости от структуры ионита и условий сорбции. Установлено, что при извлечении иода наиболее предпочтительны сорбенты на основе 1,4 диоксибензола, отличающиеся высоким кинетическими способностями и статической обменной емкостью (СОЕ = 2283,88 мг/г). Определен механизм сорбции иода синтезированными ионитами.

Ключевые слова: сорбция иода, сорбционная емкость, синтез ионитов, изотерма сорбции, иодидное выщелачивание, иод.

Информация об авторах:

Коныратбекова Салтанат Сабитовна	*Кандидат технических наук, сениор-лектор кафедры «Металлургические процессы, теплотехника и технология специальных материалов», НАО «Казахский национальный исследовательский технический университет имени К.И. Сатпаева», Алматы, Казахстан, E-mail: s.konyratbekova@satbayev.university, salta_7504@mail.ru; ORCID ID: https://orcid.org/0000-0003-2148-035X*
Байконурова Алия Омирхановна	*Доктор технических наук, профессор кафедры «Металлургические процессы, теплотехника и технология специальных материалов», НАО «Казахский национальный исследовательский технический университет имени К.И. Сатпаева», Алматы, Казахстан, Email: a.baikonurova@satbayev.university, a.baikonurova@yandex.kz; ORCID ID: https://orcid.org/0000-0002-1052-3505*
Усольцева Галина Александровна	*Кандидат технических наук, ассистент профессора кафедры «Металлургические процессы, теплотехника и технология специальных материалов», НАО «Казахский национальный исследовательский технический университет имени К.И. Сатпаева», Алматы, Казахстан, Email: g.ussoltseva@satbayev.university, nota-vesna@yandex.kz; ORCID ID: https://orcid.org/0000-0003-0155-5094*
Суримбаев Бауыржан Нуржанович	*PhD, Старший научный сотрудник лаборатории благородных металлов, Филиал РГП «НЦ КПМС РК» Государственное научно-производственное объединение промышленной экологии «Казмеханобр», Алматы, Казахстан; Старший преподаватель кафедры аналитической, коллоидной химии и технологии редких элементов, Факультет химии и химической технологии, Казахский Национальный Университет имени Аль-Фараби, Алматы, Казахстан, E-mail: surimbaev@gmail.com, bauyrzhan.surimbayev@kaznu.kz; ORCID ID: https://orcid.org/0000-0002-3988-8444*
Ескалина Куралай Тулегенкызы	*Докторант кафедры «Металлургические процессы, теплотехника и технология специальных материалов», НАО «Казахский национальный исследовательский технический университет имени К.И. Сатпаева», Алматы, Казахстан, E-mail: kuralai_eskalina@mail.ru; ORCID ID: https://orcid.org/0000-0002-2804-7076*

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Investigation of the microstructure of the oil pipeline pipes destroyed as a result of corrosion

***Suleimenova F.E., El Sayed Negim, Sharipov R.H., Suleimenov E.N.**

Scientific and Educational Center of Materials Science and Corrosion Problems Kazakh-British Technical University,
Almaty, Kazakhstan

** Corresponding author email: fariza.suleimenova@mail.ru*

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ABSTRACT

It is shown that the complexity of Kazakhstan's oils requires specific ways to protect oil pipelines from damage caused by metal corrosion. Even the presence of only paraffin in oil can cause sedimentation effects in the volume of liquid (Dorn effect). And the complexity in the molecular composition of oil causes electrophoretic impacts that lead to increased corrosion rate. All this should be considered when developing corrosion protection. The physical and mathematical analysis of possible mechanisms of electrophoretic mobility of components with the participation of liquid systems was carried out. In such a system with ions content, the macroscopic object will move as a charged particle having the same charge sign as the skeleton. The triboelectric effects on the metal/organic liquids (oil, fuel oil, etc.) boundary have been analyzed to determine their influence on the corrosion of pipeline metals. There are many methods used for temperature-strength control of reinforced concrete structures globally. Their majority is associated with the significant challenges of being time-consuming, costly, and prone to errors. Therefore, this study investigated the potential applicability of the surface-strength approach of specimens using non-destructive testing methods to derive temperature-strength relationships as an alternative approach to the currently widely used methods.

Keywords: Corrosion, oil pipeline pipes, electrical, conductivity, diesel, fuel.

	Information about authors:
Suleimenova F.E.	*Student of Master Degree, Kazakh-British Technical University, Almaty, Kazakhstan. Email: fariza.suleimenova@mail.ru*
El Sayed N.A.	*Ph.D. in chemistry, professor, Kazakh-British Technical University, Almaty, Kazakhstan. Email: a.negim@kbtu.kz*
Sharipov R.Kh.	*Master of Technical Sciences, Head of the Scientific and Educational Center for Materials Science and Corrosion Problems. Email: freedom.k@mail.ru*
Suleimenov E.N.	*Chief Researcher of the Scientific and Educational Center for Materials Science and Corrosion Problems. Email: metallaim@mail.ru*

Introduction

In the scientific and technical literature, there are many points of view on determining the number of metals and liquid particles. However, the micromechanism of this reaction is not fully restored. But knowledge of this mechanism is necessary to create adequate internal protection of pipelines from the collision. An analysis of the current state of science shows that it is dominated by electrochemical and chemical approaches to the problems of assimilation of oxygen atoms and the composition of other liquid phases in a stable and often chemically very stable structure of metals and alloys. In the world literature, there is a huge amount of experimental data on redox processes, which leads to the conclusion that it is necessary to somewhat rethink the mechanism of oxygen incorporation into stable structures. In addition, there is a need to take generalizing conclusions from the works of M. Faraday as a theoretical basis for research in this scientific direction, which are now beginning to play a decisive role in the development of ideas about the nature of the chemical bond and the practical application of electrochemical processes.

In the 20th century, a huge amount of experimental material was accumulated, which confirms the correctness of M. Faraday's views on the effect of electric current on chemical reactions. Key points and main theses of the works of M. Faraday:

1. Identity of energy manifestations in the interaction of material objects.
2. Discrete nature of the electric current.

The statement about the identity of energy manifestations in the interaction of material objects provides a basis for revising scientific statements about the mechanism of heat exchange (and, in general, energy exchange) between material objects. There is reason to believe that it is necessary to have an idea about the features of the microstructure of condensed systems and the influence of the liquid microstructure on the transport of electric current in the system. Obviously, there is a need for a more detailed study of the microstructure of alloys and other solid objects to increase the effectiveness of technical solutions for protecting metals from corrosion.

Especially many questions arise when considering the problems of corrosion. According to scientific and technical literature, the following types of corrosion are known:

- continuous corrosion: Corrosion covering the entire surface of the metal;
- uniform corrosion: Continuous corrosion proceeding at the same rate over the entire surface of the metal;
- non-uniform corrosion: Continuous corrosion proceeding at different speeds on different parts of the metal surface;
- local (local) corrosion: Corrosion covering certain parts of the metal surface;
- pitting corrosion (Pitting): Local corrosion of the metal in the form of individual pitting.

The term "corrosion mechanism" means a combination of factors that are both of a chemical nature (corrosion mechanism in the "classical" sense - carbon dioxide, hydrogen sulfide, mixed, etc.) and related to the technological features of pipeline operation (speed and flow structure, various disturbances in the flow characteristics associated with any technological processes at associated objects). "Mechanism of corrosion" defines the causes, corrosion rate of the pipeline, localization and nature of corrosion damage.

The corrosion mechanism is determined by the following factors that need to be evaluated before developing corrosion protection methods.

Chemical composition of transported products:
- pH value (pH);
- the concentration of carbon dioxide;
- hydrogen sulfide concentration;
- oxygen concentration;
- ionic composition of the aqueous phase;
- bio injection;
- component composition of the gas phase;

component composition of the liquid hydrocarbon phase [1].

Phase composition of products:
- the proportion of water;
- share of gas;
- the concentration of mechanical impurities [1].

Flow characteristics:
- product consumption;
- flow rate;
- flow structure;
- the presence of an extended water sublayer;
- the existence of local water accumulations;
- the possibility of alternate wetting [1].

Technological characteristics:
- Temperature;
- Pressure;
- Possibility of contact with process fluids.

Corrosion characteristics:
- accident rate due to internal corrosion;
- corrosion rate according to non-destructive testing data;
- corrosion rate from corrosion monitoring results;
- design corrosion rate;
- localization of corrosion defects along the pipe section and the pipeline route [1].

Joint consideration of the classification of types of corrosion and the factors necessary to determine methods of protection against corrosion lead to the following conclusion: the formulation of the concept of "corrosion mechanism", the classification of types of corrosion, and factors affecting the corrosion process, do not apply to the analysis of the mechanism of a chemical reaction leading to the introduction of atoms oxygen and other chemical elements into the metal microstructure. The results of metal corrosion destruction and technological factors influencing the destruction rate are considered.

About 4% of the connecting pieces used in the construction of oil pipelines in the 1950s–1970s were manufactured in the field. Despite the fact that in recent years the number of such parts has significantly reduced, failures associated with their lack of reliability occupy a noticeable share in the total number of failures in the system of oil trunk pipelines. The purpose of this work is to analyze the typical causes of failure of connecting parts using the example of a tee bend with a reinforcing plate. The authors carried out structural and fractographic studies of the defective structure [4]. On the basis of information about the operating conditions and the actual characteristics of the bent metal, as well as data on the centers of destruction and the nature of crack propagation, computer modeling of the stress-strain state of the part was carried out. Based on the results of metallurgical studies and computer modeling, it was established that the cause of the formation through a crack in the weld at the junction of the main oil pipeline and the reserve branch was excess stresses in the area of welding of the reinforcing plate to the branch, exceeding the tensile strength of the material of the tee branch pipe [2].

An analysis of the current state of research on the development of methods for protecting metals from corrosion of oil pipelines shows that much attention in these studies is paid to electrochemical methods of protecting metals from environmental influences [3]. However, in multicomponent systems, combined electrochemical reactions require in-depth study. This is because when exposed to aggressive media on steel structures, many corrosions occur together. This leads to severe accidents on industrial oil pipelines. For example, an underwater fire occurred in the Pemex offshore pipeline in the Gulf of Mexico [5].

An analysis of our studies of chemical processes at the phase boundary of multicomponent systems showed that in some cases, the onset of chemical reactions is influenced by triboelectric effects that occur when individual parts of the system move relative to each other. Therefore, this article discusses some aspects of this phenomenon when pumping oil through main pipelines [6].

Experimental technique

We have shown that substances' physical and chemical properties are determined by the structure of primary elements of the microstructure - "chemical individuals". And thanks to a detailed study of changes occurring in the microstructure, which is reflected in changes in the properties of the macroscopic formation, tribology allows us to calculate the amount of heat generation, durability, and wear and tear of structures, model interacting surfaces, solve the problems of boundary hydrodynamics and in the future to obtain materials with the given properties. In addition, the study of the tribolic effect will allow the causes of various undesirable processes, such as the destruction of materials due to corrosion and others [7].

It is known that tribolytic effects electrify and generate heat, which requires clarification of heat transfer processes at the micro-micro level. To determine the tribolytic impacts of oil and oil products, the oil composition of the Mangystau field in the Ozenmunaigas field was determined [8].

In this respect, oil and oil products have a special place, which differs in physical and chemical characteristics. The elemental composition of the investigated oils is summarized in Table 1. By sulfur content, the oil belongs to the second class. In terms of elemental composition, oils differ in sulfur content. In oil, the oxygen content increases from 2.6 to 9.4% mass, nitrogen from 0.3 to 2.2% mass. The elemental composition of Ozenmunaigas JSC oil is given in the table. The main components of oil are: carbon 84-85.8%, hydrogen 12.0-13.6%, nitrogen 0.2-0.4, sulfur 1.4-2.0, oxygen 1.1-1.4 % and others. In this case, the light fraction is made up of alkanes

Table 1 - Elemental composition of oil "JSC" Ozenmunaigas

Oil samples	Contents of elements, %					Others,%
	C	H	N	S	O	
Sample A	84.1	13.6	0.4	1.8	1.4	**2.1**
Sample B	85.0	12.8	0.2	2.0	1.1	**0.3**
Sample C	84.8	12.0	0.2	1.4	1.1	**0.5**

Table 2 - Physicochemical characteristics of oil in the Mangystau region

Name	Oil 1	Oil 2	Oil 3
View	Dark Brown	Dark	Dark Brown
Density at 200C, g/cm3	0.816	0.844	0.864
Water Content,%	0.6	0.7	0.8
The concentration of chlorides, mg/l	450	560	600
Kinematic viscosity, mm2/s(20^{0}C)	56	60	64
Solidification temperature,^{0}C	15- 20	18-21	14-18
Flashing point in the closed crucible,^{0}C	58	56	60
Coking,%	4.6	4.8	5.0
Residual after overclocking 320^{0}C, including. (%):	54.0	57.0	58.4
Paraffin-Naphtens	46.0	43.5	41.4
Arena	36.0	34.5	34.6
Resins	6.0	7.0	7.0
Asphaltenes	4.0	5.0	6.0
Others	8.0	10.0	11.0

with the number of carbon atoms C1-C11 (normal alkanes 40-50%). Paraffins with carbon atoms C12-C17 make up 20-25% of oil. The content of naphthenic hydrocarbons ranges from 25 to 55%. Resins and asphaltenes contain solids, including porphyrins and other undeciphered substances. [8]

Although oil and products are derived from petroleum fuels, oils are dielectrics under normal conditions. When their fractions move relative, electrostatic charges arise. The experimental values of the specific electrical conductivity of oil and oil products in laboratory conditions allow us to judge their dielectric nature (Table 2) [9].

Electrophysical properties of oils and petroleum products are currently insufficiently studied, especially regarding the movement of individual liquid components relative to each other. In the transportation process in the volume of oil and petroleum products, due to the complex microstructure and certain heterogeneity of the macrostructure, electrostatic charges can be formed. In this case, the potential difference between the individual sections of the fluid volume may be quite significant. The accumulation of electrostatic charges can ultimately be realized as a spark discharge, a chemical process, etc. This leads to ignition of oil products, destruction of pipelines, and premature failure of equipment parts. [[10], [11], [12]].

Functional analysis of these complex systems is necessary to determine the influence of the oil structure on their physical and chemical characteristics. IR spectra of some samples of oils in Kazakhstan have been taken. Below infrared spectra of initial highly paraffinic oil samples and asphalt-resinous paraffinic deposits are presented. Asphalt-paraffin component is manifested in infrared spectra of initial oil. Therefore, this component plays a decisive role in the physical and chemical transformations that occur during oil movement in the pipeline. The following functional groups in the range 2916.70 have been revealed -2848.81 см$^{-1}$ -(CH$_2$)-; 1461.75 см$^{-1}$ – CH$_3$-; 719,44 см$^{-1}$ - (CH); 2916.70 -2848.81 см$^{-1}$ -(CH$_2$)-; 1461.75 см$^{-1}$ – CH$_3$-. [13].

Table 3 - Values of specific electrical conductivity of oil and oil products

Oil and petroleum products	**Specific Electroconductivity, См·м.** $^{-1}$
Oil Uzenmunaigas	$1\cdot10^{-5}$ - $4\cdot10^{-5}$
Mazut	$1\cdot10^{-7}$ - $2\cdot10^{-9}$
Gasoline (N.K. - 140^0C)	$4\cdot10^{-11}$ - $6\cdot10^{-12}$
Kerosene (fr. 140- 180^0C)	$1\cdot10^{-10}$ - $4{,}6\cdot10^{-12}$
Aerial gasoline (fr. 40- 180^0C)	$1{,}1\cdot10^{-11}$ - $4{,}6\cdot10^{-11}$
Jet fuel (fr.180- 260^0C)	$1\cdot10^{-10}$ - $1\cdot10^{-12}$
Diesel (fr.220- 280^0C)	$3\cdot10^{-11}$ - $5\cdot10^{-11}$
Gasoil (fr.240- 350^0C)	$2\cdot10^{-8}$ - $4\cdot10^{-9}$

Results and Discussion

Oil and petroleum products are a source of fire hazards, including those caused by electric charges caused by triboelectric effects. These circumstances require a more detailed study of these systems. The mechanism of occurrence of electrostatic charges between surfaces of two moving liquids, liquid-solid surfaces of bodies, is still insufficiently studied and requires a fundamental solution to the problem [14]. Experimental values of specific electrical conductivity of oil and petroleum products under laboratory conditions have been obtained, allowing us to judge their dielectric character. The values of electrical conductivity of oils and petroleum products have been established [15].

Oil and petroleum products are bad conductors. According to literature data, specific electrical conductivity is 10-5-10-8 Om-1m-1 for crude oil. However, even an insignificant content of impurities in the movement of these liquids causes the formation of electrostatic charges. A material object is able to produce positive or negative charges, which are characterized by a triboelectric scale. At the mechanical movement of oil components relative to each other, the polarization of hydrocarbon molecules occurs, which results in interphase potential difference [[16], [17]].

Electrophysical properties of oil products (gasoline, kerosene, etc.) were determined to determine triboelectric effects at the boundary between metal/organic liquids (oil, fuel oil, etc.) to determine their influence on the corrosion of pipeline metals. As a parameter of electrical characteristics of oil products, current forces were measured and the results are summarized in the table [18].

Table 4 - Influence of gasoline pumping speed on electrification current values

No.	Pumping speed, m/s	Measured current strength, µA	Relative error, %
1	1.0	0.901	5.0
2	2.0	1.044	7.0
3	3.0	1.216	6.0
4	4.0	1.645	5.0
5	5.0	1.735	5.0
6	6.0	1.971	7.0
7	7.0	2.105	6.0
8	8.0	2.403	5.0

Table 5 - Influence of kerosene pumping speed on electricization current values

No	Pumpingspeed, m/s	Measuredcurrentstrength, µA	Relativeerror, %
1	1.0	0.706	6.0
2	2.0	0.978	5.0
3	3.0	1.045	6.0
4	4.0	1.119	6.0
5	5.0	1.265	5.0
6	6.0	1.339	7.0
7	7.0	1.827	6.0
8	8.0	1.951	5.0

Table 6 - Influence of diesel fuel pumping speed on current electrification values

No.	Pumping speed, m/s	Measured current strength, μA	Relative error, %
1	1.0	0.617	5.0
2	2.0	0.781	7.0
3	3.0	0.899	6.0
4	4.0	1.103	5.0
5	5.0	1.266	5.0
6	6.0	1.322	7.0
7	7.0	1.474	6.0
8	8.0	1.537	5.0

As the pumping rate of petroleum products increases, the value of current strength increases due to the appearance of triboelectrification in the systems studied. The appearance of the triboelectrization effect is caused by electrification, i.e. occurrence of electric potential in oil products, which causes corrosion [19].

Any disturbance of this equilibrium state leads to polarizations of "electromagnetic matter" on the surface of substances and creates a triboelectric effect. During friction and deformation of materials, "electromagnetic matter" is polarized, the electromagnetic interaction changes, and "electromagnetic matter" is released in the form of heat, and at the places of rupture of the bond simultaneously appears electric charges with the corresponding potentials [20].

Conclusions

In the case of system stationarity disorders, depending on the nature of the process, "electromagnetic matter" manifests itself in heat, light, electromagnetic field, bias current, etc. Friction and deformation of materials lead to polarizations of "electromagnetic matter", which changes the electromagnetic interaction of the system and releases "electromagnetic matter" in the form of heat. In the places of rupture of communication simultaneously, there are electric charges with corresponding potentials causing triboelectric effects.

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

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Коррозия нәтижесінде қираған мұнай құбырының құбырларының микроқұрылымын зерттеу

Сулейменова Ф.Е., Эль Сайед Н., Шарипов Р.Х., Сулейменов Э.Н.

Материалтану және коррозия мәселелері жөніндегі ғылыми-білім беру орталығы
Казақ-Британ Техникалық университеті, Алматы қ., Қазақстан

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ТҮЙІНДЕМЕ:

Бұл жұмыста Қазақстан мұнайының күрделі болу себебінен мұнай құбырларын металл коррозиясынан болатын зақымданудан қорғаудың ерекше тәсілдері қажет болатыны көрсетілген. Мұнайда тек парафиндердің болуының өзі сұйықтықтың негізгі бөлігінде шөгу әсерін тудыруы мүмкін (Дорн эффектісі). Ал мұнайдың молекулалық құрамының күрделілігі электрофоретикалық әсерлер туғызып, коррозия жылдамдығының артуына әкеледі. Мұның бәрін коррозиядан қорғауды әзірлеу кезінде ескеру қажет. Сұйық жүйелердің қатысуымен компоненттердің электрофоретикалық қозғалғыштығының мүмкін механизмдерінің физикалық-математикалық талдауы жүргізілді. Құрамында иондар бар мұндай жүйеде макроскопиялық нысан қаңқа сияқты заряд белгісімен зарядталған бөлшек ретінде қозғалады. Металл/органикалық сұйықтық шекарасындағы (мұнай, мазут және т.б.) трибоэлектрлік әсерлерді талдау, олардың құбыр металдарының коррозиясына әсерін анықтау үшін жүргізілді. Бүкіл әлемде темірбетон конструкцияларын температуралық және беріктік жағынан сынау үшін қолданылатын көптеген әдістер бар және олардың көпшілігі айтарлықтай қиындықтармен, уақытты қажет ететін, шығындармен және қателіктермен байланысты. Осылайша, бұл зерттеуде қазіргі уақытта кеңінен қолданылатын әдістерге балама тәсіл ретінде температура-беріктік қатынасын алу үшін бұзбайтын сынау әдістерін пайдалана отырып, үлгілердің бетінің беріктігін анықтау әдісінің әлеуетті қолдану мүмкіндігі зерттелді.

Түйін сөздер: коррозия, мұнай құбырлары, электрөткізгіштік, дизель отынын айдау жылдамдығы, электрлену тоғының мәндері.

	Авторлар туралы ақпарат:
Сулейменова Фариза Ержанкызы	*Қазақ-Британ Техникалық университетінің магистранті, Алматы қ., Қазақстан. Email: fariza.suleimenova@mail.ru*
Эль-Сейед Негим	*Химия ғылымдарының кандидаты, профессор, Қазақ-Британ Техникалық университеті, Алматы қ., Қазақстан Email: a.negim@kbtu.kz*
Шарипов Рустам Хасанович	*Техника ғылымдарының магистрі, Материалтану және коррозия мәселелері жөніндегі ғылыми-білім беру орталығының жетекшісі. E-mail: freedom@mail.ru*
Сулейменов Эсен Нургалиевич	*Материалтану және коррозия мәселелері жөніндегі ғылыми-білім беру орталығының бас ғылыми қызметкері. E-mail: metallaim@mail.ru*

Исследование микроструктуры труб нефтепровода, разрушенных в результате коррозии

Сулейменова Ф.Е., Эль Сайед Н., Шарипов Р.Х., Сулейменов Э.Н.

Научно-образовательный центр материаловедения и проблем коррозии
Казахстанско-Британский технический университет, г.Алматы, Казахстан

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АННОТАЦИЯ

Показано, что сложность казахстанских нефти требует особых способов защиты нефтепроводов от повреждений, вызванных коррозией металлов. Даже присутствие в нефти только парафинов может вызвать эффекты седиментации в объеме жидкости (эффект Дорна). А сложность молекулярного состава масла вызывает электрофоретические эффекты, приводящие к увеличению скорости коррозии. Все это следует учитывать при разработке защиты от коррозии. Проведен физико-математический анализ возможных механизмов электрофоретической подвижности компонентов с участием жидких систем. В такой системе с содержанием ионов макроскопический объект будет двигаться как заряженная частица, имеющая тот же знак заряда, что и скелет. Проведен анализ трибоэлектрических эффектов на границе металл/органические жидкости (нефть, мазут и др.) для определения их влияния на коррозию металлов трубопроводов. Существует множество методов, используемых для температурно-прочностного контроля железобетонных конструкций во всем мире, и большинство из них связаны со значительными трудностями, требующими много времени, затратами и подверженными ошибкам. Таким образом, в этом исследовании изучалась потенциальная применимость метода определения поверхностной прочности образцов с использованием методов неразрушающего контроля для получения соотношений температуры и прочности в качестве альтернативного подхода к широко используемым в настоящее время методам.

Ключевые слова: коррозия, нефтепроводы, электропроводность, скорость впрыска дизельного топлива, значения тока электризации

	Информация об авторах:
Сулейменова Фариза Ержанкызы	*Магистрант Казахстанско-Британского Технического Университета, Алматы, Казахстан. Email: fariza.suleimenova@mail.ru*
Эль-Сейед Негим	*Доктор химических наук, профессор Казахстанско-Британского Технического Университета, Алматы, Казахстан. Email: a.negim@kbtu.kz*
Шарипов Рустам Хасанович	*Магистр технических наук, руководитель научно-образовательного центра и материаловедения и проблем коррозии. Email: freedom.k@mail.ru*
Сулейменов Эсен Нургалиевич	*Главный научный сотрудник Научно-образовательного центра материаловедение и проблем коррозии. E-mail: metallaim@mail.ru*

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Porosity and non-metallic inclusions in cast iron produced with a high proportion of scrap

***Panichkin A.V., Korotenko R.Yu., Kenzhegulov A.K., Kshibekova B.B., Alibekov Zh.Zh.**

Institute of Metallurgy and Ore Beneficiation JSC, Satbayev University, Almaty, Kazakhstan

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

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ABSTRACT
The work is devoted to the problem of an increase in the proportion of scrap metal in castings smelted and produced from wear-resistant chromium cast irons. Castings obtained with more than 60% of armor scrap and cracked during solidification and subsequent heat treatment were selected as research objects. Castings of similar mill armor after operation characterized with different wear resistance were selected to compare the characteristics of the structure and properties. The composition, structure, amount of non-metallic inclusion and porosity of samples cut from identical places of castings were studied with the help of the methods of optical and scanning microscopy, metallographic analysis, X-ray fluorescence analysis, and measurement of Vickers hardness. The characteristic localization of non-metallic inclusions of various types in the structure of cast iron samples was considered. An increase in the proportion of non-metallic inclusions in cast irons obtained using a high proportion of scrap was found, and it was shown that non-metallic oxide inclusions with a loose structure had the most negative effect. Along with porosity and primary crystals of carbide (CrFe)3Ctheydo not prevent the propagation of cracks caused by internal stresses arising during crystallization and subsequent polymorphic transformations in castings.

Keywords: wear-resistant chromium cast iron, casting, non-metallic inclusions, cracking, structure.

Information about authors:

Panichkin Alexander Vladimirovich	*Candidate of Technical Sciences, Head of the National Scientific Collective Use Laboratory of JSC "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. Email: a.panichkin@satbayev.university, ORCID ID: 0000-0002-2403-8949*
Korotenko Roman Yuryevich	*Engineer, JSC "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. Email: r.y.korotenko@yandex.ru*
Kenzhegulov Aidar Karaulovich	*Ph.D., Researcher, JSC "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. Email: a.kenzhegulov@satbayev.university, ORCID ID: 0000-0001-7001-2654*
Kshibekova Balzhan Bulatovna	*Researcher, JSC "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. Email: b.kshibekova@satbayev.university, ORCID ID: 0000-0002-5944-7865*
Alibekov Zhassulan Zhanuzakovich	*Engineer, JSC "Institute of Metallurgy and Ore Beneficiation", Almaty, Kazakhstan. Email: zh.alibekov@satbayev.university, ORCID ID: 0000-0003-3213-5420*

Introduction

Currently, there is an increase in the proportion of scrap metal used in the iron foundry [[1], [2], [3], [4], [5]]. It is primarily due to economic and environmental considerations and is especially important in the case of products obtained from expensive wear-resistant high-alloy cast irons. Such products include parts of mills and crushers that can be remelted after their operational life to obtain similar products. It should be noted that the metal loss because of wear of such parts does not exceed 10%in some cases, especially if the destruction of the grinding body or armor occurs due to the formation of a crack. The amount of such scrap generated is large and its processing with the purpose to obtain similar products is relevant to the enormous amounts of such equipment annually used in the world.

It is known that it is recommended to use not more than 30% of scrap by the charge weight when cast iron is smelted [[6], [7]]. It is due to the need to reduce the contamination of the resulting castings with various impurities, including non-metallic inclusions and dissolved gases. An increase in porosity and the proportion of non-metallic inclusions results in a decrease in the resistance of castings to crack propagation caused by both shock loads and stresses that occur in the casting during the cooling stage and often lead to the formation of hot cracks. Hot cracks result in the rejection of a large number of castings. So, it is relevant to study the problem of the porosity formation and the accumulation of non-metallic inclusions and to evaluate their role in the cracking of castings obtained using a high proportion of scrap. For this purpose, it is required to estimate the quantity, composition, the sizes of pores and non-metallic inclusions and the place of their localization in the structure of such cast irons, and to compare them with the results of the study of cast iron obtained without the use of scrap metal.

Experimental part

A series of crusher armor samples made with a scrap proportion of more than 60% at a domestic enterprise and samples taken from similar parts obtained by various enterprises without the use of scrap were studied in this regard. All castings were made with sand casting molds. Samples of castings obtained with a high proportion of scrap were deliberately taken from castings damaged during the manufacture of products. The characteristics of the samples studied are shown in Table 1. They were taken from identical places of castings.

The composition of the castings was determined with an Axios X-ray fluorescence wave-dispersive combined spectrometer; the content of sulfur and carbon was determined with a Bruker G4 ICARUS TF analyzer. Metallographic analysis was performed using an inverted Leica DM IRM microscope and the VideoTest-Metal software package. Non-metallic inclusions were studied before etching; the structure of the phases forming cast irons was studied after etching. The number and proportion of non-metallic inclusions were determined under Interstate standard 1778-80 by method P1. The composition was studied with a JEOL JXA-8230 microprobe analyzer. The structure was found with a reagent having the following composition: 3% FeCl3 + 3% HCl in ethanol. Hardness was determined under the Vickers scale with an HBV-30A multifunctional stationary hardness tester.

Table 1 - Characteristics of armor casting samples

Sample No.	Characteristics of cast iron products	Characterization of alloy structure and matrix	Share of carbides, vol.%	Hardness, HV30
1	Crusher armor casting burst after heat treatment (HT). The share of scrap is over 60%	Hypereutectic P+A	48.6	746
2			39.2	671
3			31.4	752
4	Crusher armor casting burst after installation		26.7	698
5	High wear-resistance. Armor completed a full cycle		22.5	641
6	Low wear-resistance. Armor wears out quickly		34.3	436
7	Armor with high wear resistance. Worked full cycle	Hypereutectic P+A+M	22.4	665
8	Armor is characterized by the greatest wear resistance. Worked full cycle	Hypereutectic P+A	27.0	676
9	Armor with increased impact strength. Worked full cycle	Hypoeutectic P+A+M	22.2	710
10	Armor of the European manufacturer. Average wear resistance	Eutectic P+A	29.1	681

Table 2 - Composition of castings samples from wear-resistant chromium iron

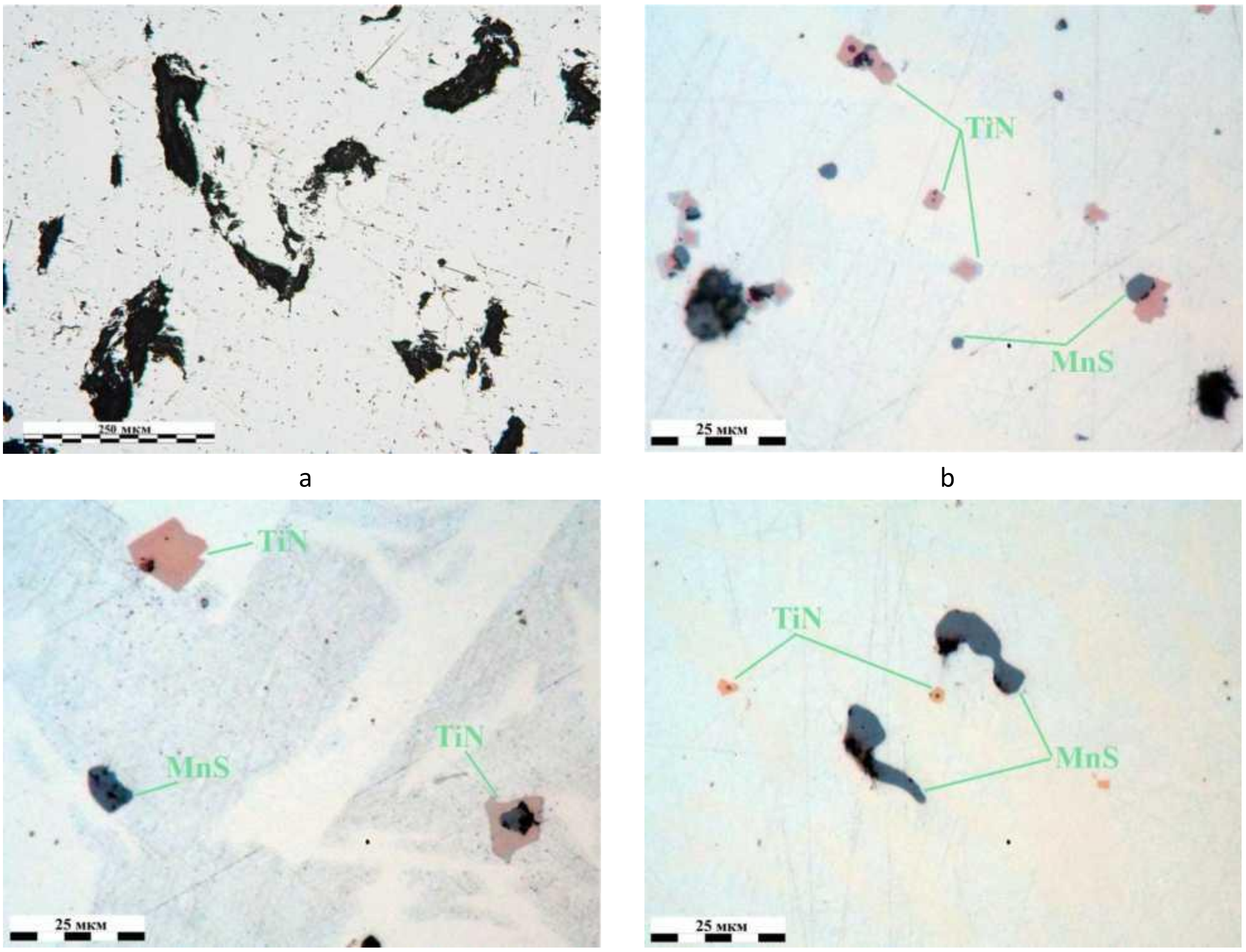
Sample No.	**Chemical composition, wt.%**										
	Fe	**Cr**	**Mo**	**C**	**Ni**	**Mn**	**Si**	**V**	**Co**	**Cu**	**Ti**
1	~70	21.8	0.74	4.05	0.62	1.14	0.7	0.15	0.12	0.16	0.23
2	70.2	19.63	0.56	3.26	0.38	2.2	0.85	0.09	0.13	0.26	0.32
3	70.3	21.7	0.65	3.81	0.33	1.39	0.56	0.1	0.09	0.18	0.04
4	69.5	23.04	0.29	3.35	0.38	0.67	0.66	0.13	0.15	0.07	0.26
5	69.1	22.79	0.33	2.96	0.37	0.86	1.48	0.1	0.14	-	0.27
6	69.1	22.97	0.31	3.23	0.46	0.82	1.18	0.12	0.14	0.07	0.19
7	67.3	24.89	0.59	3.20	0.69	0.61	0.24	0.12	0.10	0.16	0.05
8	65.5	27.08	0.41	3.34	0.74	0.87	0.4	0.07	0.11	0.1	0.08
9	75.5	16.5	1.27	2.83	0.28	1.02	0.43	0.07	0.2	0.12	0.04
10	67.9	25.7	0.23	3.0	0.54	1.14	0.58	0.04	0.14	0.16	-
	P	**Pb**	**S**	**Al**	**Mg**	**Zr**	**Ge**	**Nb**	**W**	**Zn**	**As**
1	-	0.012	0.04	0.08	-	-	-	-	-	-	-
2	0.032	-	0.042	0.6	0.31	0.01	0.01	0.007	0.05	-	-
3	0.034	-	0.049	0.19	0.15	-	-	0.005	-	0.01	-
4	0.030	-	0.054	0.2	0.28	-	-	-	-	-	0.027
5	0.026	-	0.031	0.14	0.09	-	-	-	-	0.08	-
6	0.026	-	0.044	0.08	0.09	-	-	-	-	0.16	-
7	0.017	-	0.027	0.43	0.19	-	-	0.048	0.27	-	-
8	0.025	-	0.058	0.24	0.09	-	-	-	-	-	-
9	0.03	-	0.05	0.17	0.2	-	-	0.005	-	-	-
10	0.035	-	0.036	0.055	0.08	-	-	0.06	-	-	-

The composition of Samples 2 and 4-7 is close (19.6-24.9 wt.% Cr and 2.96-3.35 wt.% C) according to the content of the main alloying elements (Table 2). Samples 7 and 9 contain more and less chromium, respectively (Table 2). Samples 1-7 can be attributed to ChKh22 cast iron, Sample 8 to ChKh28P cast iron, and Sample 9 to ChKh16M2 cast iron according to the chromium content under Interstate standards 7769-82. However, Samples 1-7 deviate from ChKh22cast iron according to the content of carbon (2.4-3.6 wt.%), manganese (1.5-2.2 wt.%), silicon (0.2-1.0), vanadium (0.15-0. 35 wt.%) and titanium (0.15-0.35 wt.%). Similarly, Samples 8 and 9 do not correspond to the specified grades under the content of other alloying elements. Besides, all samples contain micro additives of alloying elements - Al, Mo, Mg, Ni, Co, Ti, Zr, Nb, W. It enables us to conclude that the studied cast iron samples are made under the internal standards of enterprises and, probably, are foreign brands. The content of impurity elements, such as sulfur and phosphorus, in the studied samples, does not exceed the permissible level under Interstate standards 7769-82 (S<0.08%, P<0.1%).

The cast iron microstructure study shows that non-metallic inclusions are represented by manganese and iron sulfides, titanium nitrides, and oxides of the complex composition and confirmed by the microprobe analysis results. In some cases, nitrides and sulfides are found in intergrowths (Figure 1). The shape is predominantly polyhedral equiaxed. Samples 1-7 are characterized by inclusions shown in Figures 1 b and c. The sizes of non-metallic inclusions, both nitride and sulfide ones, are close and vary from 1 to 25 µm in the studied cast iron samples. The shape of sulfide inclusions differs in Samples 8-10 where they have a rounded surface (Figure 1d) not characteristic of the emerging crystal. It allows us to conclude that such inclusions crystallized after the alloy solidification. Oxide inclusions, predominantly with a loose structure, are found in the form of large inclusions associated with primary chromium carbide crystals (Figure 1 a).

The distribution of non-metallic inclusions of various types is not uniform (Figure 2). So, manganese sulfide inclusions are mainly localized in the places of eutectic crystallization (Figure 2 b) and are found intergrown with the surface of primary carbide crystals (CrFe)$_7$C$_3$ in some cases. Often, (CrFe)$_3$C crystals are formed on the surface of this compound that precipitates during the eutectic crystallization. MnS inclusions are also found in conjunction with ligature fragments showing that the melt was contaminated with them during alloying. TiN inclusions are formed both in the structure of primary carbides (CrFe)3C and in the eutectic as independent phases (Figure 2c). The formation of such inclusions is caused by alloying cast iron with titanium that binds nitrogen diffusing into the melt from the atmosphere during the melting process.

Inclusions of undissolved ferromolybdenum were found in the studied cast iron samples besides non-metallic inclusions (Figure 3). It proves the fact that the melt exposure duration after the ligature inclusion is insufficient for its complete dissolution. The mapping made to find the composition for the localization areas of ferromolybdenum inclusions shows that molybdenum alloys (CrFe)7C3 crystals when it is dissolved. At the same time, molybdenum dissolves in the cast iron matrix very little.

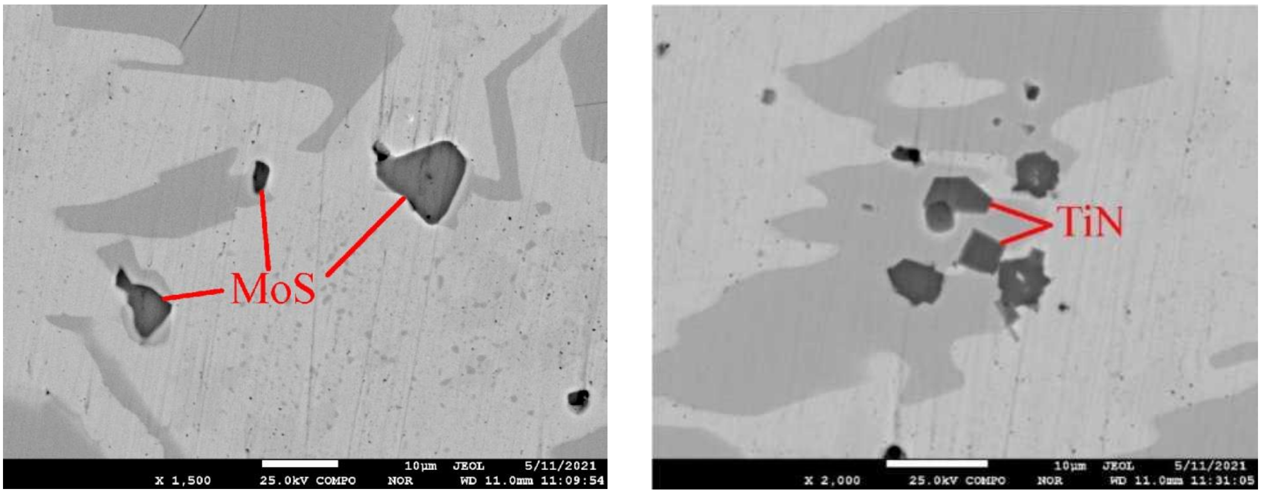


a b

c d

a - Sample No. 1 oxide inclusions (dark areas); b - Sample No. 2; c - Sample No. 6; d - Sample No. 8

Figure 1 - Typical shape and dimensions of non-metallic inclusions in samples of wear-resistant chromium cast irons



a b

Figure 2 - The structure of various non-metallic inclusions in wear-resistant chromium cast iron

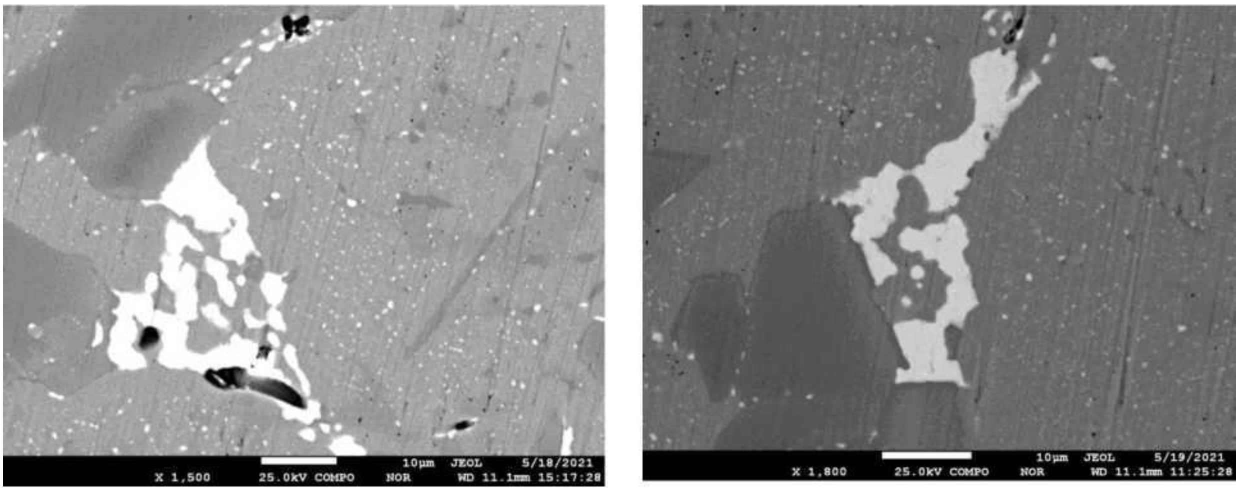


Figure 3 - Inhomogeneous distribution of molybdenum (light areas) in the cast ironstructure caused by incomplete dissolution of ferromolybdenum

Table 3 - Porosity and volume proportion of non-metallic inclusions and a group of inclusions in samples

Sample No.	Porosity, vol.%	Distribution density of non-metallic inclusions (NMI), pcs/mm2	Non-metallic inclusions, vol.%	Inclusion group							
				1	2	3	4	5	6	7	8/9
1	6.5	165	6.13	46.7	25.5	13.4	7.5	3.9	-	0.7	-
2	1.4	259	0.534	59.9	27.4	9.6	4.2	0.4	0.39	-	-
3	0.59	180	0.342	53.3	33.3	8.3	2.8	1.1	1.11	-	-
4	0.45	138	0.516	36.2	23.9	18.8	15.2	5.8		-	-
5	0.38	155	0.493	45.2	25.8	16.1	8.4	3.2	1.3	-	-
6	0.56	119	0.715	32.8	17.6	21.8	17.6	8.4	1.6	-	-
7	0.63	192	0.359	58.3	27.6	8.9	5.2	-	-	-	-
8	0.73	170	0.525	54.1	20	14.7	6.5	4.7	-	-	-
9	0.44	79	0.54	24.1	10.1	8.9	11.4	17.7	12.6	11	3.8/1.2
10	0.09	32	0.65	21.9	28.1	21.9	21.9	6.25	-	-	-

a b

Figure 4 - Formation of cracks in Casting No. 1

The discussion of the results

The analysis of the metallographic study results of samples suggests that an increase in the proportion of scrap in the production of castings results in an increase in the amount and dispersion of non-metallic inclusions in their structure. Only inclusions traditional for this type of cast iron are predominantly formed in this case. The formation of cracks in the volume of castings is not directly related to the presence and amount of non-metallic inclusions. A net of cracks was found near the surface (in 10-13 mm) in Castings 1, 2, and 3 obtained using a large proportion of scrap and destroyed at the cooling stage after crystallization and during subsequent heat treatment (Figure 4 a). The study of crack propagation suggests that they mainly pass through oxide inclusions, pores, and primary crystals of chromium carbide $(CrFe)_7C_3$, propagating between them along with the matrix alloy (Figure 4 b). Sulfide and nitride non-metallic inclusions rarely get into a crack, and in some cases, cracks stop on titanium nitride inclusions changing direction. It is due to the high hardness of the TiN compound. Besides, cracks in a smaller number and of a shorter extent were also found inside other studied castings. It suggests that their formation is primarily associated with the properties of such cast irons and, in particular, with the cooling modes for castings and the amount of carbon in their composition. It is known that an increase in the cooling rate and the availability of primary chromium carbides in the structure of alloys contribute to the occurrence of stresses exceeding the ultimate strength of the metal causing hot or cold cracking of the casting [[8], [9], [10], [11], [12], [13], [14]].

Thus, the study of samples of wear-resistant chromium cast irons cut from large-sized castings obtained in the factory by casting into a sand mold showed that the use of a high proportion (≥60%) of scrap metal in their production can increase the amount, dispersion and volume proportion of non-metallic inclusions in their structure, as well as porosity. The main non-metallic inclusions for such cast irons are crystals of manganese sulfide MnS (2-10 µm), and titanium nitride TiN (4-7 µm) typical for chromium cast irons, and oxide inclusions are introduced along with scrap metal. Meanwhile, internal stresses arising from violations of cooling regimes and a higher proportion of primary chromium carbide crystals are the main reasons for the increase in porosity, the formation of cracks, and accelerated wear of such castings [[15], [16], [17], [18], [19]].

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Сынықтардың жоғары үлесін пайдалану арқылы алынған шойындардағы кеуектілік және металл емес қосындылар

Паничкин А.В., Коротенко Р.Ю., Кенжегулов А.К., Кшибекова Б.Б., Алибеков Ж.Ж.

«Металлургия және кен байыту институты» АҚ, Satbayev University, Алматы, Қазақстан

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ТҮЙІНДЕМЕ

Жұмыс тозуға төзімді хромды шойындарды балқыту және құю кезінде металл сынықтарын пайдалану үлесін арттыру мәселесіне арналған. Зерттеу объектілері ретінде құрыш сынықтарының 60% - дан астамын пайдалана отырып алынған, сонымен қатар қатаю және кейіннен термиялық өңдеу кезінде жарылған құймалар таңдалды. Құрылымы мен қасиеттерінің сипаттамаларын салыстыру үшін қолданыстан кейінгі диірмендердің ұқсас құрыштарының құймалары таңдалды және олар әртүрлі тозу төзімділігімен сипатталады. Оптикалық және растрлық микроскопия, металлографиялық талдау, рентгенофлуоресценттік талдау, Виккерстік қаттылықты өлшеу әдістерін қолдана отырып, құймалардың ұқсас орындарынан кесілген үлгілердегі металл емес қосындылардың құрамы, құрылымы, саны және кеуектілігі зерттелді. Шойын үлгілерінің құрылымындағы әртүрлі типтегі металл емес қосындылардың сипаттамалы локализациясы қарастырылды. Сынықтардың жоғары үлесін пайдалану арқылы алынған шойындардағы металл емес қосындылар үлесінің артуы анықталды және тығыз емес құрылымы бар металл емес оксидті қосылыстардың өте теріс әсер беретіндігі көрсетілді. Олар кеуектілік пен $(CrFe)_3C$ карбидтің бастапқы кристалдарымен бірге құймаларда кристалдану және кейінгі полиморфты өзгерістерден туындаған ішкі кернеулердің әсерінен пайда болатын жарықтардың таралуына кедергі келтірмейді.

Түйін сөздер: хромды тозуға төзімді шойын, құйма, металл емес қосындылар, сызаттану, құрылым.

Авторлар туралы ақпарат:

Паничкин Александр Владимирович	*Техникалық ғылымдардың кандидаты, Ұлттық ғылыми зертханасының меңгерушісі, «Металлургия және кен байыту институты» АҚ, Алматы, Қазақстан. Email: a.panichkin@satbayev.university; ORCID ID: 0000-0002-2403-8949*
Коротенко Роман Юрьевич	*Инженер, «Металлургия және кен байыту институты» АҚ, Алматы, Қазақстан. Email: r.y.korotenko@yandex.ru*
Кенжегулов Айдар Караулович	*PhD, Ғылыми қызметкер, «Металлургия және кен байыту институты» АҚ, Алматы, Қазақстан. Email: a.kenzhegulov@satbayev.university; ORCID ID: 0000-0001-7001-2654*
Кшибекова Балжан Булатовна	*Ғылыми қызметкер, «Металлургия және кен байыту институты» АҚ, Алматы, Қазақстан. Email: b.kshibekova@satbayev.university; ORCID ID: 0000-0002-5944-7865.*
Алибеков Жасулан Жанузакович	*Инженер, «Металлургия және кен байыту институты» АҚ, Қазақстан. Email: zh.alibekov@satbayev.university; ORCID ID: 0000-0003-3213-5420.*

Пористость и неметаллические включения в чугунах, полученных с использованием высокой доли лома

Паничкин А.В., Коротенко Р.Ю., Кенжегулов А.К., Кшибекова Б.Б., Алибеков Ж.Ж.

АО «Институт металлургии и обогащения», Satbayev University, Алматы, Казахстан

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АННОТАЦИЯ

Работа посвящена проблеме увеличения доли использования металлического лома при выплавке и получении отливок из хромистых износостойких чугунов. В качестве объектов исследований выбраны отливки, полученные с использованием более 60% лома броней и растрескавшиеся при затвердевании и последующей термической обработке. Для сравнения характеристик структуры и свойств были выбраны отливки аналогичной брони мельниц после эксплуатации и характеризующиеся различной износостойкостью. С применением методов оптической и растровой микроскопии, металлографического анализа, рентгенофлуоресцентного анализа, измерения твердости по Виккерсу был изучен состав, структура, количество неметаллических включений и пористость образцов, вырезанных из идентичных мест отливок. Рассмотрено характерная локализация неметаллических включений различных типов в структуре образцов чугуна. Выявлено увеличение доли неметаллических включений в чугунах, полученных с использованием высокой доли лома, и показано, что наиболее отрицательное влияние оказывают неметаллические оксидные включения с неплотной структурой. Они наряду с пористостью и первичными кристаллами карбида (CrFe)3C не препятствуют распространению трещин, вызываемых внутренними напряжениями, возникающими при кристаллизации и последующих полиморфных превращениях в отливках.

Ключевые слова: износостойкий чугун, отливка, неметаллические включения, растрескивание, структура.

	Информация об авторах:
Паничкин Александр Владимирович	*Кандидат технических наук, заведующий Национальной научной лабораторией, АО «Институт металлургии и обогащения», Алматы, Казахстан. Email: a.panichkin@satbayev.university; ORCIDID: 0000-0002-2403-8949*
Коротенко Роман Юрьевич	*Инженер, АО «Институт металлургии и обогащения», Алматы, Казахстан. Email: r.y.korotenko@yandex.ru*
Кенжегулов Айдар Караулович	*PhD, Научный сотрудник, АО «Институт металлургии и обогащения», Алматы, Казахстан. Email: a.kenzhegulov@satbayev.university; ORCID ID: 0000-0001-7001-2654*
Кшибекова Балжан Булатовна	*Научный сотрудник, АО «Институт металлургии и обогащения», Алматы, Казахстан. Email: b.kshibekova@satbayev.university; ORCID ID: 0000-0002-5944-7865*
Алибеков Жасулан Жанузакович	*Инженер, АО «Институт металлургии и обогащения», Алматы, Казахстан. Email: zh.alibekov@satbayev.university; ORCID ID: 0000-0003-3213-5420*

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Flotation studies of the middling product of lead-zinc ores with preliminary sulfidizing roasting of oxidized lead and zinc compounds

[1] **Chepushtanova T.A.,** [1*] **Motovilov I.Yu,** [1] **Merkibayev Y.S.,** [2] **Polyakov K.V.,** [3]**Gostu S.**

[1]Satbayev University, Almaty, Kazakhstan
[2] Metallurgical Complex, Kazzinc LLP, Ust-Kamenogorsk, Kazakhstan
[3] Hydrometallurgy Air Liquide, USA, Newark, DE

** Corresponding author email: i.motovilov@satbayev.university*

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ABSTRACT

The development of combined enrichment technologies becomes more significant due to the decreasing of the processed ores quality and involvement in the processing of poor, refractory ores. The difficulty in the flotation enrichment of mixed and oxidized polymetallic ores and intermediate products lies in the effective sulfidization of the surface of oxidized minerals. The sodium sulfide reagent used in flotation does not always provide complete sulfidization of the mineral surface. On the intermediate product of lead-zinc ores related to the phase composition of mixed ores, flotation studies were carried out on the original product and after preliminary sulfidization by the pyro-metallurgical method. It was found that in the pre-sulfidizied product, the extraction of zinc increased to 17.23 %, and lead to 10.07 %, compared with the original product without pre-treatment.

Key words: lead-zinc ore, phase analysis, sulfidization, yield, content, extraction.

Information about authors:

Chepushtanova Tatyana Aleksanrovna	*PhD doctor, Associate professor, head of department of the JSC "Satbayev University", Almaty, Kazakhstan. Email: t.chepushtanova@satbayev.university; ORCID ID: 0000-0002-6526-0044*
Motovilov Igor Yurievich	*PhD doctor, Associate professor of the JSC "Satbayev University", Almaty, Kazakhstan. Email: i.motovilov@satbayev.university; ORCID ID: 0000-0002-0716-402X*
Merkibayev Yerik Serikovich	*Master's degree, head of laboratories of the JSC "Satbayev University", Almaty, Kazakhstan. Email: y.merkibayev@satbayev.university; ORCID ID: 0000-0003-3869-6835*
Polyakov Konstantin Vladimirovich	*Chief Specialist, Ust-Kamenogorsk Metallurgical Complex, Kazzinc LLP, Ust-Kamenogorsk, Kazakhstan. Email: kostya.polyakov.89@internet.ru; ORCID ID: 0000-0003-2005-9416*
Sumedh Gostu	*Research Scientist – Hydrometallurgy, American at Air Liquide, USA, Newark, DE. Scopus 56310039900, Email:Sumedh.gostu@airliquide.com*

Introduction

In the process of beneficiation of mixed polymetallic ores, a significant amount of intermediate products and beneficiation tailings are formed, the flotation processing of which is ineffective. At the same time, in addition to oxidized Zn and Pb compounds, a significant amount of pyrite is concentrated in the chamber flotation products [[1], [2], [3]].

The processing of large masses of ores, which are complex, hard-to-dress mineral raw materials, with the production of conditioned concentrates, in many cases, cannot be solved in the classical sequence "concentration plant - metallurgical plant". This fact naturally led to combined enrichment schemes, including operations of mechanical, pyro-metallurgical, and hydrometallurgical processing in a single technology implemented at the processing plant [4].

The use of combined enrichment technologies for the processing of refractory ores, combining the actual enrichment and mainly hydrometallurgical (rarely pyro-metallurgical) processes in a single technological scheme of the enrichment enterprise is a general global trend.

A promising technological approach to the processing of refractory ores, which at the enrichment stage provides for the partial extraction of valuable metals into conditioned monometallic flotation concentrates, as well as additional extraction of valuable metals and substandard polymetallic intermediate products. The intermediate products mainly contain oxidized mineral particles of valuable metals that are not sufficiently contrasting in terms of technological properties. The complex intermediate substandard product is processed separately using chemical-metallurgical processes [[5], [6]].

An analysis of the practice of concentration plants shows that for additional extraction of metals from tailings rich in Zn and Pb of flotation enrichment of polymetallic ores, as well as for tailings from the processing of copper sulfide ores, flotation enrichment methods are used, with preliminary preparation of tailings for flotation [[7], [8], [9], [10]]. However, for the processing of tailings poor in Zn and Pb, flotation re-enrichment according to the flotation scheme of selective flotation is ineffective due to low recovery rates of metals [[11], [12], [13]]. Collective flotation of tailings does not give a positive result due to the presence of a high content of metal oxides [[14], [15], [16], [17]]. During flotation, most of these compounds remain in the chamber product. Even with fine grinding and high consumption of reagents during flotation, no more than 10% of zinc is extracted into the sulfide product [[18], [19], [20]].

Thus, the use of combined methods, including the sulfidation of oxidized surfaces of valuable minerals with their further flotation enrichment, is promising for the processing of oxidized and mixed refractory polymetallic ores and intermediate products [[20], [21], [22], [23]].

This work is devoted to the study of the flotation of the intermediate product of lead-zinc ores subjected to preliminary sulfidization of valuable minerals by the pyro-metallurgical method.

Materials and research methods

The object of the study was the intermediate product of lead-zinc ores. The sample cutting of the original sample is shown in Figure 1.

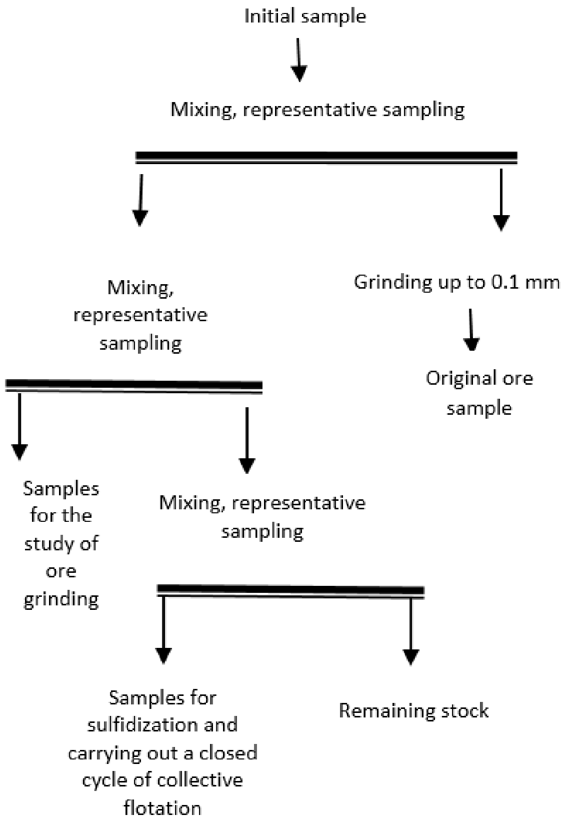

Figure 1 - Scheme of sample cutting of the initial sample

The study of the material composition of the intermediate product of lead-zinc ore: the determination of the initial content of lead and zinc was carried out by chemical analysis, the determination of the components that make up the sample by X-ray fluorescence analysis, the study of the material composition by X-ray phase analysis. Phase analyzes were performed to establish the forms of occurrence of lead and zinc minerals.

Surface sulfidization of oxidized minerals by the pyro-metallurgical method: sulfiding roasting of lead-zinc flotation tailings was carried out in a vacuum. Experiments were carried out in a fixed bed in an eclectic oven by Zhengzhou Brother

Furnace Co. Ltd (BR-17 AM-5) in a vacuum, pressure of -0.05 MPa. The holding time of the weighed samples in the oven ranged from 15 to 60 min; the temperature varied from 400 to 900 ºC. The sample was cooled under a vacuum.

Flotation enrichment: laboratory studies were carried out using the following laboratory equipment:

3) ore grinding was carried out in a laboratory ball mill at a ratio of T:W:W = 1: 0.5: 9;

4) flotation was carried out in mechanical flotation machines with chamber volumes, dm3: 1.5; 1.0; 0.5.

When conducting research on flotation, the reagent mode was used using the following reagents:

medium pH regulator - soda (Na2CO3); collectors - butyl xanthate (BKK), Aeroflot (Aero); activator - copper sulfate (CuSO4); foaming agent - T-80.

Flotation tests in a closed cycle were carried out on a sample of the original ore and a sample subjected to sulfiding roasting.

Results and discussion

After taking representative samples, chemical analysis determined the content of metals in the initial product, which amounted to 0.77% lead and 1.91% zinc. The results of X-ray fluorescence analysis of the initial sample are shown in Table 1.

Table 1 - X-ray fluorescence analysis of the original sample

Element	*Content, %*	*Element*	*Content, %*
O	51.166	Cr	0.010
Mg	0.153	Mn	0.097
Al	2.682	Fe	3.514
Si	32.048	Cu	0.076
P	0.018	Zn	1.585
S	2.515	As	0.043
Cl	0.032	Sr	0.018
K	0.583	Ba	1.487
Ca	2.991	W	0.033
Ti	0.194	Pb	0.756

From the results of X-ray fluorescence analysis, it follows that the main host elements of the sample are silicon, aluminum, calcium, sulfur, iron, and barium.

The results of studying the material composition by X-ray phase analysis are shown in Tables 2, 3 and in Figure 2.

Table 2 - Interplanar distances and phase composition of the intermediate product sample

d, Å	*I %*	*mineral*	*d, Å*	*I %*	*mineral*
4.25170	25.1	quartz	2.23549	7.1	quartz
3.34305	100.0	quartz	2.21069	6.2	quartz
3.12404	11.5	sphalerite, pyrite	2.12596	8.5	quartz
3.02886	13.1	calcite	1.97744	6.9	quartz
2.70701	8.1	pyrite	1.91221	8.4	pyrite, sphalerite
2.45524	10.3	quartz	1.81716	11.9	quartz
2.42171	6.5	pyrite	1.67099	6.6	quartz
2.27992	11.1	quartz	1.65840	5.1	quartz

Table 3 - Results of semi-quantitative X-ray phase analysis of the middling product sample

Mineral	*Formula*	*Concentration, %*
quartz	SiO_2	74.3
pyrite	FeS_2	12.5
sphalerite	ZnS	7.5
calcite	$Ca(CO_3)$	5.6

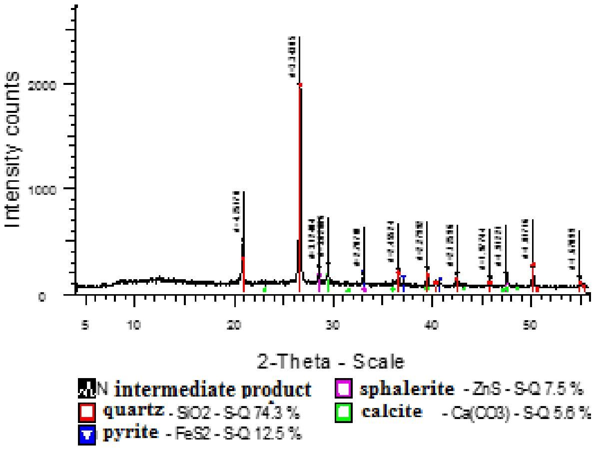

Figure 2 - X-ray diffraction pattern of an intermediate sample

It follows from the results of X-ray phase analysis that the main host minerals of the sample are quartz, pyrite, sphalerite, and calcite.

The results of phase analysis established the percentage ratio of oxidized and sulfide minerals of lead and zinc in the sample. The results of the phase analysis are shown in Table 4.

Table 4 - Results of phase analysis of lead and zinc in the sample of the intermediate product

Value	*Forms of finding / mass fraction, %*					
	Lead			*Zinc*		
	Total	*Oxidized*	*Sulfide*	*Total*	*Oxidized*	*Sulfide*
Abs	0.76	0.27	0.49	1.93	0.46	1.47
Rel	100.00	35.90	64.10	100.00	23.58	76.42

Phase analysis found that lead in the sample of the intermediate product is 64.10% sulfide, 35.90% oxidized, zinc is 76.42% sulfide, 23.58% oxidized.

Based on the results of mineralogical, phase analysis, the sample of the intermediate product belongs to the mixed type of lead-zinc ores.

Further studies were carried out on the flotation of the initial sample and the sample after sulfiding roasting.

Figure 3 shows a graph of the dependence of the content of the class minus 0.074 mm on the grinding time from the results of which it follows that in order to achieve a fineness of the crushed product of 90% class less than 0.074 mm in a laboratory mill, the time is 40 minutes.

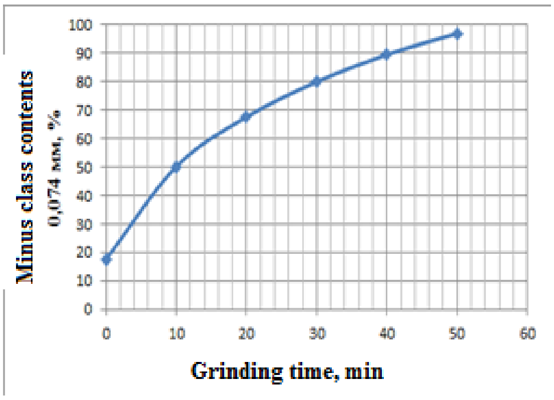

Figure 3 - Graph of class content minus 0.074 mm from grinding time for a sample of an industrial product

The consumption of reagents, flotation time and the degree of ore grinding before flotation is taken from the practice of processing similar ores and is presented in Table 5.

Table 5 - Reagent consumption, time and degree of ore grinding

The name of the operation	***Time, min***	***Reagent consumption, g/t***				
		Na_2CO_3	***БКК***	***Аэро***	***$CuSO_4$***	***T-80***
Grinding 90% class less than 0.074 mm	40	-	-	-	-	-
Main collective flotation	12	800	150	-	-	50
Control bulk flotation	15	-	50	50	700	-
I cleaning	10	-	-	-	-	-
II cleaning	8	-	-	-	-	-

Flotation experiments were carried out according to the collective scheme shown in Figure 4 and the reagent regime shown in Table 6.

Table 6 shows the results of the experiment on collective flotation on the original sample.

Table 6 - Results of the experiment on bulk flotation on the initial sample of the intermediate product

Products	***Output, %***	***Content, %***		***Recovery, %***	
		Pb	***Zn***	***Pb***	***Zn***
Collective concentrate	12.34	2.97	11.20	47.60	72.36
Tails	87.66	0.46	0.60	52.40	27.64
Nutrition	100.00	0.77	1.91	100.00	100.00

From table 6 it follows that according to the collective scheme of flotation of the initial sample of the intermediate product, the following were obtained:

- collective concentrate with a lead content of 2.97%, zinc 11.20%, with the extraction of lead 47.60%, zinc 72.36%. The concentrate yield is 12.34%.

- tailings with a lead content of 0.46%, zinc 0.60% with a yield of 87.66%. Losses are lead 52.40%, zinc 27.64%.

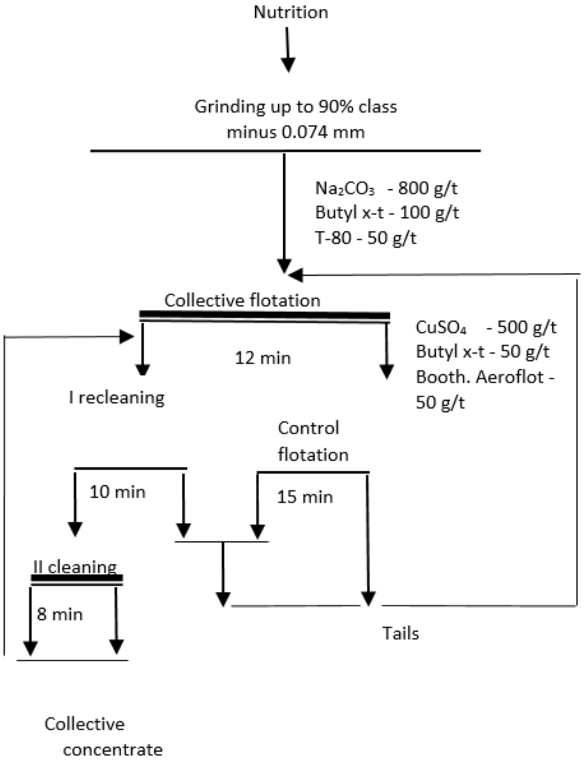

Figure 4 - Collective flotation scheme

Table 7 shows the results of a bulk flotation test on a sample of the intermediate after the sulfiding roast.

From table 7 it follows that according to the collective flotation scheme, samples of the intermediate product with preliminary sulfiding roasting were obtained:

- collective concentrate with a lead content of 3.05%, zinc 11.97%, with the extraction of lead 57.67%, zinc 89.59%. The concentrate yield is 14.37%.

- tailings with a lead content of 0.38%, zinc 0.23% with a yield of 85.63%. Losses are lead 42.33%, zinc 10.41%.

Using the method of preliminary sulfidization of the surface by the pyro-metallurgical method, the extraction of zinc into the bulk concentrate increased by 17.23%, and lead by 10.07%.

Table 7 - Results of the experiment on collective flotation on a sample of the intermediate product subjected to sulfiding roasting

Products	***Output, %***	***Content, %***		***Extraction, %***	
		Pb	***Zn***	***Pb***	***Zn***
Collective concentrate	14.37	3.05	11.97	57.67	89.59
Tails	85.63	0.38	0.23	42.33	10.41
Nutrition	100.00	0.76	1.92	100.00	100.00

Conclusion

Preliminary sulfidization of oxidized lead and zinc minerals by a pyro-metallurgical method improves the efficiency of the flotation enrichment process. The extraction of zinc into the collective concentrate increases on average by 17.23% from 72.36 to 89.59%, and lead by 10.07% from 47.60 to 57.67%.

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Қорғасын мен мырыштың тотыққан қосылыстарын алдын ала сульфидтеу арқылы күйдіре отырып қорғасын-мырыш кендерінің аралық өнімін флотациялық зерттеу

[1]Чепуштанова Т.А., [1]Мотовилов И.Ю., [1]Меркибаев Е.С., [2]Поляков К.В, [3]Gostu S.

[1]Satbayev University, Алматы қ., Қазақстан
[2]УК МК ЖСС «Казцинк», Өскемен қ., Қазақстан
[3]Гидрометаллургия, Америка Air Liquide Master, Ньюарк қ., АҚШ

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Қабылданды: *18 мамыр 2022*

ТҮЙІНДЕМЕ

Қайта өңделетін кендер сапасының төмендеуіне және кедей, қиын байытылатын кендерді қайта өңдеуге тартуға байланысты байытудың аралас технологияларын әзірлеу өте маңызды болып отыр. Аралас және тотыққан полиметалл кендері мен аралық өнімдерді флотациялық байыту кезіндегі қиындық тотыққан минералдардың бетін тиімді сульфидтеуге байланысты. Флотацияда қолданылатын реагент сульфидті натрий барлық жағдайда минералдың бетінің толық сульфидтенуін қамтамасыз ете алмайды. Фазалық құрамы бойынша аралас кендерге жататын қорғасын-мырыш кендерінің аралық өнімінің бастапқы өнімінде пирометаллургиялық тәсілмен алдын ала сульфидтеуден кейін флотациялық зерттеулер жүргізілді. Алдын ала сульфидтелген өнімде, өңдеуден өтпеген бастапқы өніммен салыстырғанда мырыштың алынуы 17,23%-ға, қорғасын 10,07%-ға артқаны анықталды.

Түйін сөздер: қорғасын-мырыш кені, фазалық талдау, сульфиттеу, шығын, құрылым, бөліп алу.

	Авторлар туралы ақпарат:
Чепуштанова Татьяна Александровна	*PhD докторы, қауымдастырылған профессор, кафедра меңгерушісі «Сәтбаев Университеті», Алматы, Қазақстан. Email: t.chepushtanova@satbayev.university; ORCID ID: 0000-0002-6526-0044*
Мотовилов Игорь Юриевич	*PhD докторы, қауымдастырылған профессор, «Сәтбаев Университеті», Алматы, Қазақстан. Email: i.motovilov@satbayev.university; ORCID ID: 0000-0002-0716-402X*
Меркибаев Ерик Серикович	*Магистр, зертхана меңгерушісі «Сәтбаев Университеті», Алматы, Қазақстан. Email: y.merkibayev@satbayev.university; ORCID ID: 0000-0003-3869-6835*
Поляков Константин Владимирович	*Бас қызметкер, УК МК ЖШС «Казцинк». Өскемен, Қазақстан. Email: kostya.polyakov.89@internet.ru; ORCID ID: 0000-0003-2005-9416*
Sumedh Gostu	*Ғылыми қызметкер, Hydrometallurgy at Air Liquide, Ньюарк, США. Scopus 56310039900, Email:Sumedh.gostu@airliquide.com*

Флотационные исследования промпродукта свинцово-цинковых руд с предварительным сульфидирующим обжигом окисленных соединений свинца и цинка

[1]Чепуштанова Т.А., [1]Мотовилов И.Ю., [1]Меркибаев Е.С., [2]Поляков К.В, [3]Gostu S.

[1]Satbayev University, г. Алматы, Казахстан
[2]УК МК ТОО «Казцинк», г. Усть-Каменогорск, Казахстан
[3]Гидрометаллургия, American Air Liquide Master, г.Ньюарк, США

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АННОТАЦИЯ

В связи со снижением качества перерабатываемых руд, вовлечением в переработку бедных, труднообогатимых руд, становится более значимым разработка комбинированных технологий обогащения. Сложность при флотационном обогащении смешанных и окисленных полиметаллических руд и промежуточных продуктов заключается в эффективной сульфидизации поверхности окисленных минералов. Применяемый во флотации реагент сернистый натрий не всегда обеспечивает полную сульфидизацию поверхности минералов. На промежуточном продукте свинцово-цинковых руд относящегося по фазовому составу к смешанным рудам выполнены флотационные исследования на исходном продукте и после предварительной сульфидизации пирометаллургическим способом. Установлено, что в предварительно сульфидированный продукт извлечение цинка повысилось на 17,23%, а свинца на 10,07%, по сравнению с исходным продуктом без предварительной обработки.

Ключевые слова: свинцово-цинковая руда, фазовый анализ, сульфидизация, выход, содержание, извлечение.

	Информация об авторах:
Чепуштанова Татьяна Александровна	*PhD доктор, ассоциированный профессор, заведующий кафедры НАО «Сатпаев Университет», Алматы, Казахстан. Email: t.chepushtanova@satbayev.university; ORCID ID: 0000-0002-6526-0044*
Мотовилов Игорь Юриевич	*PhD доктор, ассоциированный профессор НАО «Сатпаев Университет», Алматы, Казахстан. Email: i.motovilov@satbayev.university; ORCID ID: 0000-0002-0716-402X*
Меркибаев Ерик Серикович	*Магистр, заведующий лабораторий НАО «Сатпаев Университет», Алматы, Казахстан. Email: y.merkibayev@satbayev.university; ORCID ID: 0000-0003-3869-6835*
Поляков Константин Владимирович	*Главный специалист, УК МК ТОО «Казцинк». г. Усть-Каменогорск, Казахстан. Email: kostya.polyakov.89@internet.ru; ORCID ID: 0000-0003-2005-9416*
Sumedh Gostu	*Научный сотрудник, Hydrometallurgy at Air Liquide, Ньюарк, США. Scopus 56310039900, Email:Sumedh.gostu@airliquide.com*

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Influence of industrial waste on the structure of environmentally friendly cement clinker

[1,2]Zhanikulov N.N., [3*]Kolesnikov A.S., [3]Taimasov B.T., [4]Zhakipbayev B.Y., [3]Shal A.L.

[1]Academician E.A. Buketov Karaganda University, Karaganda, Kazakhstan
[2] M.V. Lomonosov Moscow State University, Moscow, Russian Federation
[3]M. Auezov South Kazakhstan University, Shymkent, Kazakhstan
[4]Bolashak University, Kyzylorda, Kazakhstan

**Corresponding author`s e-mail: kas164@yandex.kz*

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ABSTRACT

The main problem of cement production is to reduce energy consumption and reduce the amount of greenhouse gases CO_2 emitted into the atmosphere. The prerequisite for solving the problem is: the use of man-made waste and unconventional raw materials in the composition of the charge and the reduction of limestone content from 85% to 70-75% as a source of CO2 gas. The article presents the results of the studied technogenic waste and the suitability of non-traditional raw materials such as tefritobazalt, coal mining waste, and lead slag. The chemical and mineralogical composition of the materials and their suitability for obtaining environmentally friendly clinker have been established. The possibility of obtaining cement clinker using low-energy resource-saving technologies is shown. Clinker formation processes in the developed mixtures are completed at a temperature of 1350 °C, which, with the coal contained in the waste, will reduce the consumption of fuel injectors and reduce CO_2 emissions into the atmosphere. In the developed low-energy mixtures, the specific consumption of raw materials for obtaining 1 ton of clinker is reduced to 1516-1525 kg, which is significantly lower than in traditional raw mixtures. Alite crystals are large, reaching 100-140 microns. The content of clinker minerals is C_3S-57.88%, C_2S-18.82%, C_3A-6.46% and C_4AF-11.61%. Disposal of large-tonnage waste will reduce environmental pollution and improve the environmental situation in the region.

Keywords: clinker, microstructure improvement, waste disposal, temperature reduction, mineralizer.

	Information about authors:
Zhanikulov Nurgali Nodiruly	*Doctor of Ph.D., assistant professor, Karagandy university of the name of academician E.A. Buketov, Universitetskaya street, 28, 100028, Karaganda, Kazakhstan; e-mail: nurgali.zhanikulov@mail.ru, ОРСИД: 0000-0002-0750-9753; Scholarship holder of the Bolashak program of the M.V. Lomonosov Moscow State University, Moscow, Russian Federation*
Kolesnikov Alexandr Sergeevich	*Professor, Candidate of Technical Sciences, M. Auezov South Kazakhstan university, Avenue Tauke-Khan, 5, 160012, Shymkent, Kazakhstan, e-mail: kas164@yandex.ru, ОРСИД: 0000-0002-8060-6234*
Taimasov Bahitzhan Tamasovich	*Professor, Doctor of technical sciences, M. Auezov South Kazakhstan university, Avenue Tauke-Khan, 5, 160012, Shymkent, Kazakhstan, e-mail: taimasovukgu@mail.ru, ОРСИД: 0000-0002-1844-4932*
Zhakipbayev Bibol Yermuratovich	*associate professor, Doctor of PhD, Bolashak University, Avenue Abay, 31A, 120000, Kyzylorda, Kazakhstan, e-mail: bibol_8484@mail.ru, ОРСИД: 0000-0002-1412-7796*
Shal Aizhan Leskyzy	*master student, M. Auezov South Kazakhstan university, Avenue Tauke-Khan, 5, 160012, Shymkent, Kazakhstan, e-mail: shalaizhan@mail.ru, ОРСИД: 0000-0002-0291-6894*

Introduction

Much attention is paid to the production of building materials, including Portland cement, in the Republic of Kazakhstan. The production of cement and a number of other building materials is constantly growing. According to the statistical agency of the Republic of Kazakhstan, in 2021 cement production amounted to more than 12.65 million tons, which is 15% more than in 2020 [[1]. [2], [3]].

Exports of cement to neighboring countries increased. The production of mixed binders and dry building mixtures for finishing works is also increasing. At the same time, we must remember that large enterprises in metallurgy, chemical industry, thermal power plants, cement production, etc. cause significant harm to the environment, ecology, and health of the population [[4], [5]].

The Concept for the Transition of the Republic of Kazakhstan to a Green Economy, approved by the Decree of the President of the Republic of Kazakhstan dated May 30, 2013, No.577 [6], lays the foundations for deep systemic transformations in order to transition to a new economy by increasing the welfare, quality of life of the population of Kazakhstan and countries among the 30 most developed countries in the world while minimizing the burden on the environment and degradation of natural resources. The concept of a green economy sets ambitious goals to achieve the level of pollutant emissions at the level of the participating countries of the Organization for Economic Cooperation and Development and other developed countries [[7], [8]].

Cement production refers to facilities that have a significant negative impact on the environment and are required to obtain integrated environmental permits to carry out their activities in accordance with the environmental legislation of the Republic of Kazakhstan [[9], [10]].

Portland cement is a large-tonnage and energy-intensive product.

The production of 1 ton of cement requires about 5 tons of various materials: raw materials, additives, fuel, water, air, refractories, grinding bodies, etc. In the Republic of Kazakhstan, 3 plants are still operating in a wet way. Specific fuel consumption for the wet method per 1 ton of clinker is 220-240 kg, for the dry one - 100-120 kg. Therefore, the issues of energy saving, especially with the wet method of obtaining clinker, remain important and relevant [[11], [12], [13]].

To increase the energy efficiency of the clinker burning process, and reduce fuel consumption, we have developed low-energy-intensive compositions of raw mixtures, where traditional natural raw materials are completely or partially replaced by technogenic ones [[14], [15]].

In this study, we propose to partially replace the traditional carbonate and aluminosilicate components of the raw charge (loess) with waste from coal mines in Lenger, magmatic rock – tephrite basalt of the Daubaba deposit in South Kazakhstan, and lead slags.

Experimental part

Limestone is mainly composed of $CaCO_3$. The content of oxides SiO_2, and Al_2O_3 is low, and the content of Fe_2O_3 is very low - 0.57%. The MgO content is insignificant - 0.88%. The limestone is pure and highly basic, and the CaO content is more than 52%. The alkali content is within the normal range.

Coal mining wastes are composed of clay, carbonate minerals, and carbon. The content of silicon oxide is more than 55%, Al_2O_3 -10.6 %, they can replace the aluminosilicate component of the raw mixture in the raw mixture. The carbon content in coal mining waste is more than 15%.

Tephrite basalt contains SiO_2 - 45.54 %, Al_2O_3 - more than 10 %, Fe_2O_3 - about 8.5%. The magnesium content is increased - 6.95 %, which is undesirable. It contains a significant amount of alkalis: (K_2O + Na_2O) is 2.54%, which is also a lot.

Lead slags consist mainly of fayalite Fe_2SiO_4, melilite, wustite, small amounts of iron, lead and copper sulfides, and zinc spinel. Lead slag contains up to 37-40% iron oxides and can replace a corrective additive. In addition, lead slags contain up to 15% CaO and partially replace the carbonate component [[16], [17]].

For the preparation of the raw batch for low-energy clinkers, we used limestone of the Sastobe deposit, tephrite basalt, technogenic raw materials - lead slags, and coal mining waste, the chemical composition of which is given in Table 1.

Table1 - Chemical composition of mineral and technogenic raw materials

Natural and technogenic raw materials	Chemical composition, wt%							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	loss on ignition	Sum
Limestone	3.87	1.04	0.57	52.83	0.88	0.10	40.71	100.0
Cinders	17.81	4.25	62.23	4.21	3.71	-	7.79	100.0
Lead slag	25.94	6.44	37.25	14.71	6.15	0.04	0.1	90.63
Tephrite basalt	45.54	10.7	8.53	10.66	6.95	0.2	7.92	90.50
Coal mining waste	55.50	10.6	2.01	3.21	0.7	0.79	24.08	96.89

Table 2 - Composition of low-energy raw mixes and clinkers based on technogenic and non-traditional raw materials

Mixes	Composition of the raw mixture, wt%					Specific consumption of raw materials, t/t of clinker					SC	Modules		Mineralogical composition of clinker, wt%			
	Lime stone	coal mining waste	tephrite basalt	cinders	lead slag	Lime stone	coal mining waste	tephrite basalt	cinders	lead slag		n	p	C_3S	C_2S	C_3A	C_4AF
1	75.76	11.69	11.68	0.86	-	1.158	0.179	0.178	0.013	-	0.85	2.7	1.50	48.85	30.29	6.44	11.55
2	76.67	10.92	10.91	1.50	-	1.174	0.167	0.167	0.023	-	0.90	2.5	1.26	58.61	19.05	3.11	16.38
3	76.94	11.13	11.12	0.81	-	1.182	0.171	0.171	0.012	-	0.90	2.7	1.51	59.62	19.38	5.19	13.0
4	76.64	10.34	10.33	2.69	-	1.171	0.158	0.158	0.041	-	0.92	2.2	0.97	60.90	19.81	7.76	8.72
5	77.12	10.21	10.2	1.47	-	1.183	0.164	0.165	0.023	-	0.92	2.5	1.26	61.99	14.86	1.47	18.88
6	77.39	10.92	10.91	0.79	-	1.191	0.336	0.168	0.168	-	0.92	2.7	1.51	62.85	15.07	3.1	16.17
7	76.22	19.61	-	-	4.17	1.186	0.305	-	-	0.065	0.85	2.7	1.31	48.43	30.03	6.65	11.28
8	76.93	18.03	-	-	5.05	1.196	0.280	-	-	0.078	0.90	2.5	1.13	59.00	19.19	5.41	12.67
9	77.38	18.67	-	-	3.95	1.209	0.292	-	-	0.062	0.90	2.7	1.32	59.69	19.41	6.49	10.88
10	76.56	16.54	-	-	6.90	1.181	0.255	-	-	0.106	0.92	2.2	0.89	61.97	14.80	3.48	15.65
11	77.37	17.68	-	-	4.94	1.204	0.275	-	-	0.077	0.92	2.5	1.13	63.27	15.18	5.38	12.49
12	77.82	18.32	-	-	3.87	1.218	0.287	-	-	0.061	0.92	2.7	1.33	64.00	15.35	6.43	10.7
13	74.34	10.36	10.37		4.93	1.119	0.156	0.156		0.074	0.85	2.2	0.98	45.97	28.49	4.58	15.35
14	75.56	11.47	11.48	-	1.49	1.152	0.175	0.175	-	0.023	0.85	2.7	1.51	47.43	29.41	7.73	10.18
15	76.32	10.55	10.55	-	2.57	1.164	0.161	0.161	-	0.039	0.90	2.5	1.27	57.88	18.82	6.46	11.61
16	76.75	10.93	10.93	-	1.39	1.176	0.167	0.168	-	0.021	0.90	2.7	1.52	58.50	19.03	7.57	9.82
17	76.01	9.68	9.68	-	4.63	1.152	0.147	0.147	-	0.070	0.92	2.2	0.99	60.89	14.60	4.46	14.65
18	76.78	10.35	10.35	-	2.52	1.173	0.158	0.158	-	0.039	0.92	2.5	1.28	62.08	14.89	6.41	11.46
19	77.20	10.72	10.72	-	1.36	1.185	0.164	0.165	-	0.021	0.92	2.7	1.52	62.75	15.06	7.47	9.70

Results and Discussion

We have developed various options for low-power compositions of raw materials, designed for the production of clinkers of various mineralogical composition, including sulfate-resistant and road Portland cements using limestone from the LLP Standard Cement (Table 2).

Calculations of charge compositions were made according to the formulas of S.D. Okorokov [18]. Several series of calculations of raw materials charges with natural limestone, unconventional and technogenic raw materials, located in close proximity (5-40 km) to the existing cement plants in South Kazakhstan, have been performed. Delivery of waste to the plant can be carried out by road and rail.

Based on the calculations, the compositions of the three- and four-component charges were selected:

- Limestone + coal mining waste + tephrite basalt + cinders;
- Limestone + coal mining waste + lead slag;
- Limestone + coal mining waste + tephrite basalt + lead slag.

When selecting the compositions of the raw mixtures, the saturation coefficient (SC) was changed from 0.85 to 0.92, and the silicate modulus (n) from 2.2 to 2.7. In this case, the value of the alumina modulus (p) varies depending on the type of components, silicate modulus, and SC from 0.97 to 1.52 [19].

Regularities of changes in modular characteristics and mineral composition of clinker from the type and amount of technogenic raw materials in the composition of the charge have been established. At SC= 0.92, with an increase in silicate modulus from 2.2 to 2.7, the content of lead slag in the charge decreases from 4.63 to 1.36%, and the alumina modulus increases from 0.99 to 1.52, the content of alite and C_3A increases, and the proportion of C_4AF decreases. The strength and speed of hardening of such cement will be higher.

Table 3 - Influence of mixture compositions and temperature on the process of binding calcium oxide

Raw mix composition, wt%				SC	Modules		Content of CaO free,%, at burning temperature, °C			
Limestone	coal mining waste	tephrite basalt	lead slag		n	p	1300	1350	1400	1450
77.02	9.79	9.78	3.41	0.92	2.2	1.15	3.4	2.1	1.9	0.6
76.72	9.10	9.11	5.06	0.94	2.0	0.95	1.3	0.2	-	-

In the 1st series of raw mixtures "Limestone + coal mining waste + cinders" the content of coal waste is 20-23%. In this case, 3-4% of coal is added to the composition of the raw mixture. This will reduce the fuel consumption for burning clinker in the kiln. The cinder content is 0.86-2.69%. An increase in the silicate modulus from 2.2 to 2.7 leads to a gradual decrease in the proportion of pyrite cinders from 2.69 to 0.49%. The magnitude of the p modulus increases from 0.89 to 1.52. The resulting clinkers contain 3.1-7.76% tricalcium aluminate. These clinkers are suitable for the manufacture of low-aluminate sulfate-resistant clinkers and cement.

In the second batch of charges, scarce pyrite cinders were replaced by lead slags. The iron content in slags is slightly lower than in cinders. Therefore, the content of lead slag in the charge increases and reaches 3.95-6.9%. Similarly to series 1 of mixtures, an increase in the modulus n leads to a gradual increase in the alumina modulus from 0.89 to the optimal 1.12-1.33. The specific consumption of lead slag increases to 78-106 kg per 1 ton of clinker.

In the third series, coal mining waste and tephrite basalt are used as the aluminum-containing component, lead slags are the correcting additive. Slags, together with tephrite basalt, add a sufficient amount of iron oxides to the charge composition.

In the developed low-energy-intensive mixtures, the specific consumption of raw materials for obtaining 1 ton of clinker is reduced to 1516-1525 kg, which is much lower than in traditional raw mixtures. The mass of the material that must be heated in the furnace to the clinker formation temperature of 1300-1350°C is reduced, which makes it possible to further reduce fuel consumption. The content of lead slag in the mixture is from 70 to 106 kg, due to which from 10 to 15 kg of non-carbonate lime is added per 1 ton of clinker, which improves the heat balance of the burning process.

The effect of temperature on the clinker burning process is shown in Table 3.

As can be seen from the data in Table 3, depending on SC, n, and the content of lead slag, the processes of clinker formation in the developed low-energy-intensive raw mixtures are completed at 1300 or 1350°C. The content of unbound CaO is 1.3 and 2.1%, respectively. A raw mixture with a higher silicate modulus n=2.2 and a lower lead slag content of 3.41% is burned more difficult - the content of CaO free at 1300°C is 3.4%. An increase in the content of lead slag to 5.06% leads to a decrease in the silicate modulus to 2.0, an acceleration of the clinker formation process, and an improvement in sintering.

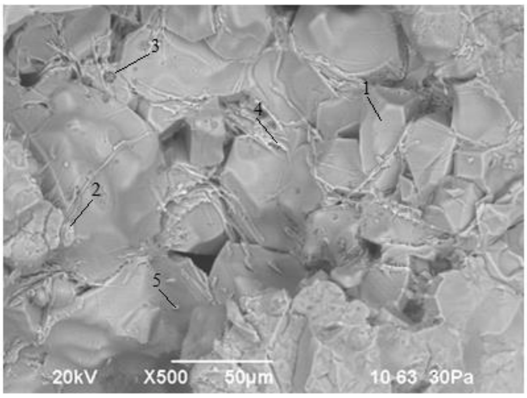
The lead slag contains 4.34% ZnO, 0.52% PbO, 1.1% CuO, which have a mineralizing effect on the sintering of the charge. Zinc oxide is a catalyst for the formation of minerals in the production of clinker. Zn^{2+} ions replace Ca^{2+} in the crystal lattices of minerals with the formation of solid solutions. The solubility of zinc oxide in C_3S is slightly more than 2% [20]. Differential thermal analysis of limestone with additions of 3-10% lead slag showed that the maximum of the $CaCO_3$ decarbonization process decreases by 30-50°C. The above will allow completing the processes at low temperatures, reducing the heat costs for clinker burning, increasing the furnace productivity, and reducing the consumption of nozzle fuel [21].

The developed raw mixes contain two technogenic products - coal mining waste and lead slag, as well as a low-melting igneous rock – tephrite basalt. Their total content is about 23-26% [22].

The synthesized clinker was subjected to microscopic examination. Using an electron microscope in the field of binders, one can study the following issues: the shape and size of individual crystals: the processes of growth and destruction of crystals, processes occurring at the grain boundary, and a number of other more particular problems [23].

The dissertation studied the microstructure of synthesized clinkers. Samples for research were cleaved from synthesized clinker.

Analysis of micrographs from a clinker chip obtained from the traditional raw mix "Limestone + coal mining waste + cinders" is shown in Figure 1.



1 - C_3S; 2 – C_2S; 3 – C_3A; 4 - C_4AF; 5 – CaO.

Figure 1 - Micrograph of a clinker chip obtained from traditional raw materials

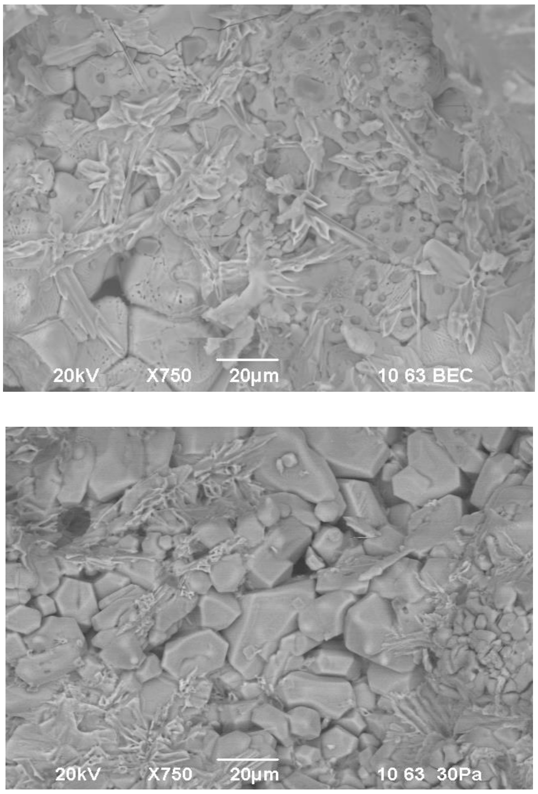


Figure 2. Micrographs from clinker chips obtained from the raw mixture Limestone + coal mining waste + tephrite-basalt + lead slag

Micrograph of clinker allows us to conclude that crystallization is relatively clear, the distribution of minerals is not uniform. Along with areas of relatively well-formed alite crystals, there are areas with crystals of an indefinite shape, passing into intergrowths of alite crystals.

Belite inclusions are observed in large crystals of alite. Belite is represented by small round and oval crystals. The amount of belita is much less than that of alita. The micrograph also shows a slight accumulation of crystals of free calcium oxide (dark rounded crystals). On the surface of crystals and between them, an alumoferite phase (light intermediate substance) is clearly visible. The presence of the aluminate phase in this micrograph is not determined [24].

Analysis of micrographs from a clinker chip obtained from an unconventional energy-saving raw mixture of Limestone + coal mining waste + tephrite-basalt + lead slag (Figure 2).

Figure 2 shows a photomicrograph from cleavage of clinker. Analysis of micrographs allows us to conclude that the crystallization of minerals is clear, but their distribution is uneven. Along with areas where alite has a regular geometric shape, there are areas with an indefinite crystal shape. Belite is represented by crystals of round and oval shape; cracks are observed on the surface of belite granules.

Alite crystals of large size, reaching 100-140 microns. A small amount of lead slag (2.57%) introduced into the mixture has a mineralizing effect. This, together with basalt tephrite, reduces the burning temperature from 1450 °C to 1350 °C, the CaOf content decreases to 1.39%. There is a lot of intermediate phase and it is represented mainly by calcium aluminoferrite. Calcium alumoferrites are represented by light needle-like crystals. The content of clinker minerals is C_3S — 57.88%, C_2S — 18.82%, C_3A — 6.46%, and C_4AF — 11.61%.

The presence of three cement plants in the South Kazakhstan region: LLP Standard Cement, JSC Shymkentcement and LLP Sastobe Technologies with a total capacity of ~ 3.5 million tons would allow for a short period of time to completely utilize lead slag and coal waste in cement production. This would help to reduce the anthropogenic load on the environment, eliminate major sources of its pollution [25].

Conclusions

1. Experiments have shown the possibility of using technogenic waste as part of the charge: coal mining waste - 9.79%, lead slag - 3.41-5.06%, and tefrito bazalt - 9.78%, that is, to dispose of up to 25%.

2. To improve the clinker formation process and the microstructure of the main minerals of alite

due to the introduction of lead slag. In the composition of lead slag, zinc oxide performed the task of a mineralizer and accelerated the process of clinker formation at 1350°C. The free calcium oxide in the composition of clinker was 0.2 % at a temperature of 1350°C.

3. With coal mining waste, from 2 to 3.5% of coal is introduced into the incinerated charge, which made it possible to reduce heat costs and nozzle fuel consumption for clinker combustion. Significantly reduced greenhouse gas CO_2.

Thus, the developed low-energy resource-saving compositions of raw materials for the production of cement clinkers using man-made raw materials will increase the efficiency of cement production, reduce environmental pollution and improve the ecology of the region.

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

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Экологиялық таза цемент клинкерінің құрылымына өндірістік қалдықтардың әсері

[1,2]Жаникулов Н.Н., [3*]Колесников А.С., [3]Таймасов Б.Т., [4]Жакипбаев Б.Е., [3]Шал А.Л.

[1]Академик Е.А. Букетов атындағы Қарағанды университеті, Қарағанды, Қазақстан
[2]М.В. Ломоносов атындағы Мәскеу мемлекеттік университеті, Мәскеу, Ресесй Федерациясы
[3]М.Әуезов атындағы Оңтүстік Қазақстан университеті, Шымкент, Қазақстан
[4]Болашақ университеті, Қызылорда, Қазақстан

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ТҮЙІНДЕМЕ

Цемент өндірісінің негізгі проблемасы - энергия шығынын төмендету және атмосфераға шығарылатын CO_2 парниктік газдар мөлшерін азайту. Мәселені шешудің алғышарты: техногендік қалдықтар мен дәстүрлі емес шикізатты шикіқұрамның құрамында қолдану және CO_2 газын шығару көзі әктастың мөлшерін 85% - дан 70-75% - ға дейін төмендету. Мақалада техногенді қалдықтарды және тефритобазальт, көмір өндірісінің қалдықтары және қорғасын шикіқұрамы сияқты дәстүрлі емес шикізат материалдарын физика-химиялық зерттеу нәтижелері келтірілген. Материалдардың химиялық және минералогиялық құрамы және олардың экологиялық таза клинкер алуға жарамдылығы анықталды. Энергияны аз қажет ететін ресурстарды үнемдейтін технологияларды қолдана отырып, цемент клинкерін алу мүмкіндігі көрсетілген. Әзірленген қоспалардағы клинкер процестері 1350°C температурада аяқталады, бұл қалдықтардағы көмірмен бірге бүріккішті (форсунка) отын шығынын азайтады және атмосфераға CO_2 шығарындыларын азайтады. Әзірленген аз энергиялы қоспаларда 1 тонна клинкер алуға арналған шикізаттың меншікті шығыны 1516-1525 кг дейін төмендейді, бұл дәстүрлі шикізат қоспаларына қарағанда айтарлықтай төмен. Алынған клинкердің минералогиялық құрамы C_3S — 57,88%, C_2S — 18,82%, C_3A — 6,46% және C_4AF -11,61%. Көп тоннажды қалдықтарды кәдеге жарату қоршаған ортаның ластануын азайтуға және өңірдегі экологиялық жағдайды жақсартуға мүмкіндік береді.

Түйін сөздер: клинкер, микроқұрылымды жақсарту, қалдықтарды жою, температураны төмендету, минерализатор.

	Авторлар туралы ақпарат:
Жаникулов Нургали Нодырұлы	*PhD докторы, профессор ассистенті, Академик Е.А. Букетов атындағы Қарағанды университеті, Қарағанды, Қазақстан; e-mail: nurgali.zhanikulov@mail.ru; ОРСИД: 0000-0002-0750-9753; Болашақ бағдарламасының стипендиаты, М.В. Ломоносов атындағы Мәскеу мемлекеттік университеті, Мәскеу, Ресей Федерациясы*
Колесников Александр Сергеевич	*профессор, техника ғылымдарынң кандидаты, М.Әуезов атындағы Оңтүстік Қазақстан университеті, Шымкент, Қазақстан, e-mail:kas164@yandex.ru; ОРСИД: 0000-0002-8060-6234*
Таймасов Бахитжан Таймасович	*профессор, техника ғылымдарынң докторы, М.Әуезов атындағы Оңтүстік Қазақстан университеті, Шымкент, Қазақстан, e-mail: taimasovukgu@mail.ru, ОРСИД:0000-0002-1844-4932*

Жакипбаев Бибол Ермуратович	*Қауымдастырылған профессор м.а., PhD докторы, Болашақ университеті, Қызылорда, Қазақстан, e-mail: bibol_8484@mail.ru; ОРСИД: 0000-0002-1412-7796*
Шал Айжан Лесқызы	*магистрант, М.Әуезов атындағы Оңтүстік Қазақстан университеті, Шымкент, Қазақстан, e-mail: shalaizhan@mail.ru, ОРСИД: 0000-0002-0291-6894*

Влияние промышленных отходов на структуру экологически чистого цементного клинкера

[1,2]Жаникулов Н.Н., [3*]Колесников А.С., [3]Таймасов Б.Т., [4]Жакипбаев Б.Е., [3]Шал А.Л.

[1]Карагандинский университет имени академика Е.А. Букетова, Караганда, Казахстан
[2] Московский государственный университет им. М.В. Ломоносова, Москва, Российская Федерация
[3]Южно-Казахстанский университет им. Ауэзова, Шымкент, Казахстан
[4]Университет Болашак, Кызылорда, Казахстан

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АННОТАЦИЯ

Основной проблемой производства цемента является снижение энергозатрат и снижение количества парниковых газов CO_2, выбрасываемых в атмосферу. Предпосылкой решения проблемы является: применение техногенных отходов и нетрадиционного сырья в составе шихты и снижение содержания известняка с 85% до 70-75% как источника выделения газа CO_2. В статье представлены результаты физико-химических исследований техногенных отходов и пригодность нетрадиционных сырьевых материалов таких, как тефритобазальт, отходы угледобычи и свинцовый шлак. Установлен химический и минералогический состав материалов для получения экологического чистого клинкера. Показана возможность получения цементного клинкера с использованием малоэнергоемких ресурсосберегающих технологий. Установлено, что процессы клинкерообразования в разработанных смесях с углесодержащими отходами завершаются при температуре 1350 °С, что, способствует снижению расхода форсуночного топлива и уменьшению выбросов CO_2 в атмосферу. В разработанных малоэнергоемких смесях удельный расход сырья на получение 1 тонны клинкера снижается до 1516-1525 кг, что значительно ниже, чем в применении традиционных сырьевых смесей. Определен минералогический состав получаемого клинкера, который представлен C_3S- 57,88%, C_2S- 18,82%, C_3A- 6,46% и C_4AF- 11,61%. Утилизация крупнотоннажных отходов позволит снизить загрязнение окружающей среды и улучшить экологическую обстановку в регионе.

Ключевые слова: клинкер, улучшение микроструктуры, утилизация отходов, снижение температуры, минерализатор.

Информация об авторах:

Жаникулов Нургали Нодырұлы	*Доктор PhD, ассистент профессор, Карагандинский университет имени академика Е.А. Букетова, Караганда, Казахстан; e-mail:nurgali.zhanikulov@mail.ru, ОРСИД: 0000-0002-0750-975; Стипендиат программы "Болашак", Московский государственный университет имени М.В. Ломоносова, Москва, Российская Федерация*
Колесников Александр Сергеевич	*Профессор, кандидат технических наук, Южно-Казахстанский университет им. М.Ауэзова, Шымкент, Казахстан, e-mail: kas164@yandex.ru; ОРСИД: 0000-0002-8060-6234*
Таймасов Бахитжан Таймасович	*Профессор, доктор технических наук, Южно-Казахстанский университет им. М. Ауэзова, Шымкент, Казахстан, e-mail: taimasovukgu@mail.ru; ОРСИД: 0000-0002-1844-4932*
Жакипбаев Бибол Ермуратович	*И.о. асоц. профессор, доктор PhD, Университет Болашак, Кызылорда, Казахстан, e-mail: bibol_8484@mail.ru; ОРСИД:0000-0002-1412-7796*
Шал Айжан Лесқызы	*Магистрант, Южно-Казахстанский университет им. М. Ауэзова, Шымкент, Казахстан, e-mail: shalaizhan@mail.ru; ОРСИД: 0000-0002-0291-6894*

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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.Ж. Артыкбаев

Институт металлургии и обогащения, Satbayev University

Алматы, Казахстан

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