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**Комплексное
Использование
Минерального
Сырья**

**Complex
Use of
Mineral
Resources**

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Kaolinite clays as a source of raw materials for the aluminum industry of the Republic of Kazakhstan

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ABSTRACT

Kaolinite clays can serve as an additional source of alumina in the Republic of Kazakhstan. The most promising is the Alekseevsky kaolinite deposit. To obtain high-quality kaolinite and quartzite products, it is necessary to develop special enrichment techniques, since no satisfactory results were achieved when using standard methods of gravitational enrichment of kaolinites. The paper presents the results of studies of the effect of preliminary chemical activation during the processing of kaolinite clays of the Alekseevsky deposit. Previously, the method of preliminary chemical activation of raw materials in a solution of sodium bicarbonate has proven itself well in the processing of various mineral raw materials. It was determined that during the preliminary chemical activation in a solution of sodium bicarbonate, changes occurred in the phase composition of the kaolinite fraction: the content of muscovite decreased almost twice; the phase of sodium aluminosilicate was formed. The dependence of the yield of Al_2O_3 in the kaolinite fraction on the temperature of chemical activation, duration, and the ratio of L:S and the concentration of the sodium bicarbonate solution during chemical activation. The optimal mode of preliminary chemical activation of kaolinite clay of the Alekseevsky deposit has been established: the temperature is 150 °C, the duration is 120 minutes and the concentration of sodium bicarbonate solution is 120 g/dm³. A basic technological scheme is proposed for the processing of kaolinite clays.

Keywords: kaolinite, quartzite, silicon module, chemical activation, chemical enrichment, product yield, technology.

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Introduction

The constant decline in the production of high-quality bauxite is an impartial basis for the use of alternative alumina-containing raw materials; however, high operating costs, energy intensity, and low efficiency of the known methods of mining, enrichment, and processing of such raw materials restrain their use in production.

The world production of alumina is based mainly on the processing of high-quality bauxite by the Bayer method [1-4]. According to this method, the processing involves bauxite with a flint modulus of more than 7 units.

The Republic of Kazakhstan has no bauxite deposits that are suitable for direct processing by the Bayer process.

Geological exploration in Kazakhstan has identified various types of aluminum raw materials such as bauxite, nepheline syenite, alunite, and iron-aluminum ore. Only bauxite is used industrially. Bauxite deposits and ore occurrences are grouped in several bauxite-ore regions: West Torgaysky, East Torgaysky, Central Torgaysky, Mugodzarsky, Tselinogradsky, Ekibastuzsky, and Prichimkentsky, differing in geological and morphological features and the scale of mineralization. Commercial deposits are known in the first three regions [5].

The structure of Aluminum of Kazakhstan JSC includes the Pavlodar Aluminum Smelter (PAS) which is the only alumina producer in the Republic of Kazakhstan with an annual capacity of 1,500,000 tons of Al_2O_3 , and the Kazakhstan Electrolysis Plant which produces about 250,000 tons of aluminum in ingots per year. The raw materials used by PAS are mainly low-quality bauxites of the Krasnooktyabrsky deposit, which are located in the Kostanay region, with a low flint modulus and an increased content of iron and carbonates [6, 7].

Currently, the Krasnooktyabrsky deposit has reserves of about 80 million tons of bauxite. Mining is performed at the Ayatsky and Krasnogorsky bauxite mines.

At the beginning of 2021, the total bauxite reserves of the Ayatsky mine and the Krasnogorsky mine were 29.194 million tons and 47.094 million tons, respectively [8-11].

Thus, the available bauxite reserves can be enough for PAS to be operated at the existing capacities for no more than 15 years; given that the bauxite processing technology includes the redistribution of the release of ferrous sand in the amount of 10-12% of the total mass, the period of supply of raw materials will be further reduced. Since the remaining bauxite deposits in Kazakhstan do not have sufficient reserves, it is necessary to switch to alternative sources of aluminum raw materials.

The world practice has experience in the industrial processing of nepheline raw materials in the Russian Federation: Leningrad region, Pikalevo; Krasnoyarsk Krai, Achinsk Alumina Refinery. These enterprises are currently working unstable due to the difficulties in sales of silicate products. The Republic of Kazakhstan has the Kubasadyrskoye deposit, one of the largest deposits of nepheline syenite in the world, located in the Kostanay region and having total forecast resources of up to 1.7 billion tons.

One of the leading places in alternative raw materials sources of alumina belongs to kaolinite ores. The world volume of kaolinite ores is estimated at 16 billion tons [12]. Modern mining and processing of kaolinite raw materials have an established infrastructure, are provided with raw materials and in the future can be adapted to the production of alumina and by-products. Currently, kaolin is mined in the USA, UK, China, Ukraine, Russia, Kazakhstan, the Arab Republic of Egypt, etc. [13].

There are some studies performed to extract alumina from kaolinite by high-temperature firing

and effective separation of alumina and silica minerals.

Work [14] is aimed at studying the effect of thermal reactions of kaolin at different sintering temperatures on the mechanisms of phase transformation and microstructural changes, the mechanism of self-decomposition, as well as the efficiency of extracting aluminum oxide from kaolinite using the lime-agglomeration process.

Agglomerates were obtained at temperatures between 800°C and 1400°C, then subjected to a leaching process (S:L = 1:5) with sodium carbonate solution (120 g/dm³); the final productive solutions contained alumina.

It was found that 1360°C is an optimal sintering temperature for the induction of a solid-phase reaction between clay and carbonate components, which results in maximum alumina recovery equal to 80.49%. Under optimal sintering conditions, kaolinite was dehydroxylated and converted to metakaolinite, while calcite was decomposed to calcium oxide. The new phases formed have reacted to form calcium aluminates, which are considered to be highly efficient and generating precursor phases in the recovery of alumina.

The article [15] describes the process of extracting alumina from aluminum slag using a safe alkaline sintering process.

Aluminum slag which causes numerous disposal problems is a useful resource for extracting alumina.

For slag grinding, aluminum nitride (AlN) decomposition, and salt removal, an experimental unit was developed. Then, the desalted slag was calcined with NaOH and leached under optimal conditions, and the kinetics of dissolution of aluminum oxide and silica was evaluated.

The leach residue was used to produce the mineral ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$) with calcium-based compounds (including CaO and CaSO_4) to avoid problems associated with solid waste disposal during the leaching process.

Aluminum hydroxide $\text{Al}(\text{OH})_3$ precipitated after carbonization was calcined at 900°C for 2 hours to obtain γ -alumina.

It is noted that the activation temperature equal to 1000°C; $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio equal to 1.4; leaching temperature equal to 60°C, process time equal to 40 minutes and liquid/solid ratio in leaching (ml/g) equal to 25/1 are optimal for 86.7% alumina recovery with a purity of more than 98%. The results of studying the leaching kinetics showed that the dissolution of aluminum oxide and silicon dioxide is controlled by the process of diffusion of

layers with an apparent activation energy of $11.4010 \text{ kJ mol}^{-1}$ and $2.0556 \text{ kJ mol}^{-1}$, respectively.

The work [16] studied the effect of different calcination temperatures on the phase transformation of minerals in coal gangue and optimal conditions for alkaline leaching of coal waste after calcination. Based on the results, the following conclusions were drawn.

Phase transformation of kaolinite during high-temperature roasting occurs as follows: kaolinite ($A/S = 0.85$) \rightarrow metakaolin ($A/S = 0.85$) \rightarrow spinel ($A/S = 1.13$) \rightarrow mullite ($A/S = 2.55$), where A/S is the weight percentage of alumina to silica. Phase transformation releases the active silica mineral which can be dissolved in an alkaline solution and separated from the desilicate residue.

The optimum calcination temperature of coal gangue should be maintained at the level of $1050 \pm 50^\circ\text{C}$. Lower calcination temperatures will result in the incomplete release of the active mineral silica and the formation of the cristobalite phase instead of active silica formed at high calcination temperatures.

Under conditions of desilicization with an alkali concentration of $90 \text{ g}\cdot\text{L}^{-1}$ and solid content of $320 \text{ g}\cdot\text{L}^{-1}$, the optimum leaching temperature is 85°C and the leaching time is 60-80 minutes. The modulus of the resulted sodium silicate solution can reach 1.1, the ratio of aluminum oxide to silicon dioxide in the desilicated residue is 1.6-1.7, and the Na_2O content is about 4-5%.

In the Republic of Kazakhstan and near the city of Kokshetau, the Alekseyevskoye kaolinite deposit developed by Arai Pro LLP is the most promising. At the deposit, the balance kaolin reserves of categories B, C_1 , and C_2 are 13.665, 67.228, and 174.261 million tons, respectively. The average stripping ratio is not more than $1 \text{ m}^3/\text{t}$.

At present, Arai Pro extracts about 300 thousand tons of raw kaolin, which is exported to the Russian Federation. The relatively high content of REE reaching 1% is one of the advantages of the kaolinite of the Alekseyevsky deposit, where the bulk is represented by erbium.

We are developing a technology for complex waste-free processing of kaolinite from the Alekseyevsky deposit to obtain alumina concentrate, a wide range of popular kaolinite products for use in the production of fine ceramics, pharmaceuticals, cosmetics, and high-purity quartz products.

To create a cost-effective technology for the processing of kaolinite clays, the proposed method provides for the operation of preliminary chemical

activation of the feedstock at the head of the process. It will allow, with further gravitational enrichment, to effectively isolate high-quality kaolinite and quartz products and significantly reduce the flow of materials supplied for sintering. Preliminary chemical activation is a key operation of the proposed technology. It enables not only to increase the efficiency of gravity concentration but also has a positive effect on further hydrochemical processing. When developing the technology in the research, it was taken into account that the optimal modes of preliminary chemical activation and processing depend on the characteristics of the feedstock.

The purpose of the research was to increase the efficiency of the complex processing of kaolinite clays in Kazakhstan due to the preliminary chemical activation of clay in a sodium bicarbonate solution.

Experimental part

The research used X-ray fluorescence, chemical, X-ray phase, and thermal analyzes. X-ray fluorescence analysis was performed on a Venus 200 wave dispersion spectrometer (PANalytical B.V., Holland).

Samples were chemically analyzed using Optima 2000 DV, an optical emission spectrometer with inductively coupled plasma (USA, Perkin Elmer). Semi-quantitative X-ray phase analysis was performed on a D8 Advance (BRUKER) diffractometer using copper $\text{Cu-K}\alpha$ radiation at an accelerating voltage of 36 kV and a current of 25 mA. Thermal analysis was performed on STA 449 F3 Jupiter, a synchronous thermal analysis instrument. The results obtained from the STA 449 F3 Jupiter were processed using the NETZSCH Proteus software.

Discussion of the results

A representative sample of a kaolinite clay from the Alekseyevsky deposit, provided by Arai Pro LLP and corresponding to the company standard 101240014515-01-2019 was the initial product for the research.

The appearance of a sample of kaolinite clay is loose whitish sand with a density of 2.06 g/cm^3 , bulk density 1.36 kg/cm^3 , pH 7.7, with an average grain size of 2 mm. Chemical composition of the kaolinite clay sample from the Alekseyevsky deposit (wt %): Al_2O_3 26.9; SiO_2 56.6; Fe_2O_3 0.537; Na_2O 0.07; SO_3 0.028; K_2O 1.31; LOI: 14.555, silicon

module (μ_{Si}) 0.47. The silicon modulus (μ_{Si}) is determined by the mass ratio of $Al_2O_3:SiO_2$.

X-ray phase analysis of a sample of kaolinite clay indicates the presence of the following minerals (wt %): kaolinite 31.1; quartz 67.5 and muscovite 1.1.

Figures 1 and 2 show the results of thermal analysis of a sample of kaolinite clay from the Alekseyevskoye deposit.

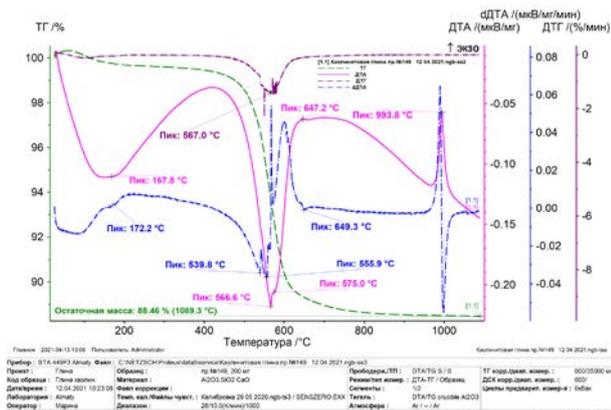


Figure 1 - Heating curves of a kaolinite clay sample from the Alekseyevskoye deposit

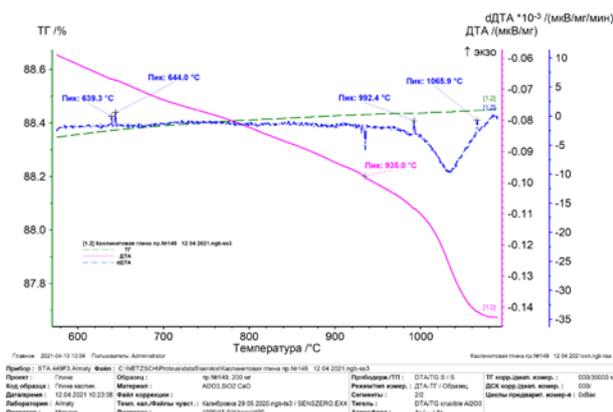


Figure 2 - Cooling curves of a kaolinite clay sample from the Alekseyevskoye deposit

The DTA curve showed an intense endothermic effect with maximum development at 167.8°C. An

even more intense endothermic effect with maximum development at 566.6°C was also noted. On its ascending branch, one more endothermic effect with an extremum at 575°C was noted. They are developed against the background of an intensive decrease in the weight of the sample, which can be seen from the course of the curve. In addition to endothermic effects, strong and weak exothermic effects with peaks at 993.8°C and 647.2°C, respectively, were recorded. Additional endothermic effects with extrema at 172.2°C, 539.8 °C, 555.9°C, 649.3°C can be noted on the dDTA curve.

Kaolinite or hydrated halloysite (endellite, a kaolin group mineral) is the main phase of the sample. Its manifestation is associated with endothermic effects (-)167.8°C, (-)566.6°C, and exothermic effect is (+)993.8°C. The endothermic effect with an extremum at 575°C on the DTA curve and endothermic effects with extrema at 539.8°C, 555.9°C on the dDTA curve can be a manifestation of the dehydration of aluminum hydroxides, may be boehmite, diaspora with various degrees of grinding. In addition, the combination of the endothermic effect with an extremum at 167.8°C and the exothermic effect with a peak at 993.8°C on the DTA curve can be a manifestation of the clay mineral allophane ($mAl_2O_3nSiO_2pH_2O$). The combination of the endothermic effect with an extremum at 167.8°C and an exothermic effect with a peak at 647.2°C can be interpreted as a manifestation of the opal SiO_2nH_2O . In superposition, in the temperature range of 500 - 600°C, the decomposition of the siderite impurity is also possible. These effects may be due to the polymorphic transformation $2CaO:SiO_2$.

Sieve analysis of a representative sample of kaolinite clay from the Alekseyevskoye deposit was performed (table 1).

Table 1 - Chemical composition of various fractions of the kaolinite clay sample from the Alekseyevskoye deposit

Size	Content, %										
	Yield, %	Na ₂ O	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	CaO	TiO ₂	SO ₃	K ₂ O	LOI	μ_{Si}
+0.05	51.97	0.03	23.47	60.85	0.69	0.48	2.5	0.09	0.61	11.28	0.386
-0.05+0.02	44.69	0.068	29.89	46.65	0.597	0.19	0.79	0.028	1.31	20.477	0.641
-20 + 10 μ m	3.05	0.09	32.07	48.09	0.631	0.313	0.57	0.23	1.48	16.526	0.667
-10 μ m	0.29	0.176	30.35	46.59	0.689	0.24	0.53	0.26	1.39	19.775	0.651

For further research, a fine fraction with a particle size of 0.05 mm was isolated by washing with running water at room temperature.

Chemical composition of fine clay fraction (wt %): Al_2O_3 31.2; SiO_2 51.6; Fe_2O_3 0.53; CaO 0.43; Na_2O 0.095; MgO 0.2; SO_3 0.02; K_2O 1.5; TiO_2 1.05; Cl^- 0.02; LoI : 13.355; μ_{Si} 0.6. Content of rare earth elements: Ce 0.44376; Dy 0.00056; Er 0.19488; Eu 0.00298; Gd 0.01049; Ho 0.00125; La 0.00623; Lu 0.00008; Nd 0.00023; Pr 0.02006; Sc 0.00229; Sm 0.00547; Tb 0.00710; Tm 0.00191; Y 0.00048; Yb 0.00034; ΣREM 0.69811. The fines yield was 41.4%.

The phase composition of the fine fraction is presented (wt %) by kaolinite 63.2; quartz 21.6 and muscovite 15.3.

The chemical composition of the coarse fraction + 0.05 mm is as follows, wt%: Al_2O_3 7.65; SiO_2 65.5; Fe_2O_3 0.68; CaO 0.29; Na_2O 0.031; MgO 0.08; SO_3 0.05; K_2O 0.39; TiO_2 0.9; Cl^- 0.016; LoI : 24.413; μ_{Si} 0.12. Content of rare earth elements: Ce 0.65758; Dy 0.00043; Er 0.09495; Eu 0.00195; Gd 0.01485; Ho 0.00076; La 0.00638; Lu 0.00004; Nd 0.00051; Pr 0.02981; Sc 0.00131; Sm 0.0002; Tb 0.00349; Tm 0.00188; Y 0.00253; Yb 0.00018; ΣREM 0.81686.

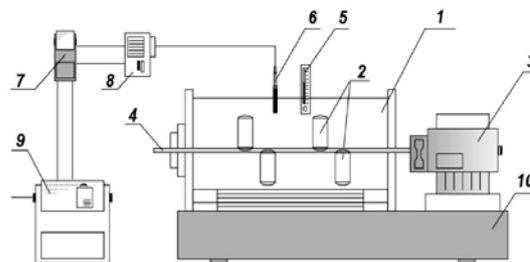
The phase composition of the coarse clay fraction is represented by 100% quartz. To determine the optimal conditions for the preliminary chemical activation of kaolinite clay, the process was performed in a solution containing $40 \div 120 \text{ g/dm}^3 \text{ NaHCO}_3$ at a L:S ratio of $2 \div 10.0$ and temperatures of $90 \div 230^\circ\text{C}$ using a thermostated unit with 6 autoclaves rotating through the head with a working volume of 250 cm^3 (Figure 3); the activation duration was $30 \div 300$ minutes. The maximum content of sodium bicarbonate in the solution was 120 g/dm^3 , taking into account its solubility limit. The initial weight of a kaolinite clay sample was 25.0 g.

X-ray phase analysis of the kaolinite fraction of clay after chemical activation under optimal conditions is represented by kaolinite 54.8%, quartz 28.0%, muscovite 8.0%, sodium aluminosilicate 5.5%, and magnetite 3.7%. The analysis of the results showed that after preliminary chemical activation of the clay:

- the yield of kaolinite fraction increased from 48.03% to 76.39%;

- dispersion increased, the class yield was 0.02 microns (increased from 3.34 to 11.7%);

- the yield of Al_2O_3 in the kaolinite fraction increased by 30.6%. The yield of Al_2O_3 in the quartz fraction was only 5.67% after activation.



1 – thermostat; 2 – autoclaves; 3 – electric motor; 4 – shaft; 5 – control thermometer; 6 – thermocouple; 7 – thermal sensor; 8 – starter; 9 – reducer; 10 – bed

Figure 3 - Thermostated unit with autoclaves

Thus, as a result of preliminary chemical activation, there was a significant increase in the yield of Al_2O_3 in the kaolinite fraction, which will make it possible to efficiently process them using integrated technology to obtain alumina, alumina concentrate and cement.

The amount of alumina concentrate sent for autonomous processing for alumina and cement is determined from the region's demand for commercial Portland cement. The remaining alumina concentrate is sent to the dilution of high-iron red mud to ensure optimal performance of the After preliminary chemical activation, the clay was divided into small (kaolinite) and large (quartz) fractions, and the yield of Al_2O_3 in the kaolinite fraction was determined.

Studies on the release of Al_2O_3 into the kaolinite fraction after preliminary chemical activation, depending on temperature, duration, L:S ratio, the concentration of NaHCO_3 solution, showed that the yield increases with increasing duration, the concentration of NaHCO_3 solution and practically does not depend on a L:S ratio. A temperature of 150°C , a duration of 120 minutes, and a concentration of NaHCO_3 solution of 120 g/dm^3 should be considered the optimal mode for preliminary chemical activation of kaolinite clay. Under these conditions, the yield of the kaolinite fraction was 76.39%.

The basic process flow diagram of complex processing of kaolinite ore was developed (Figure 4).

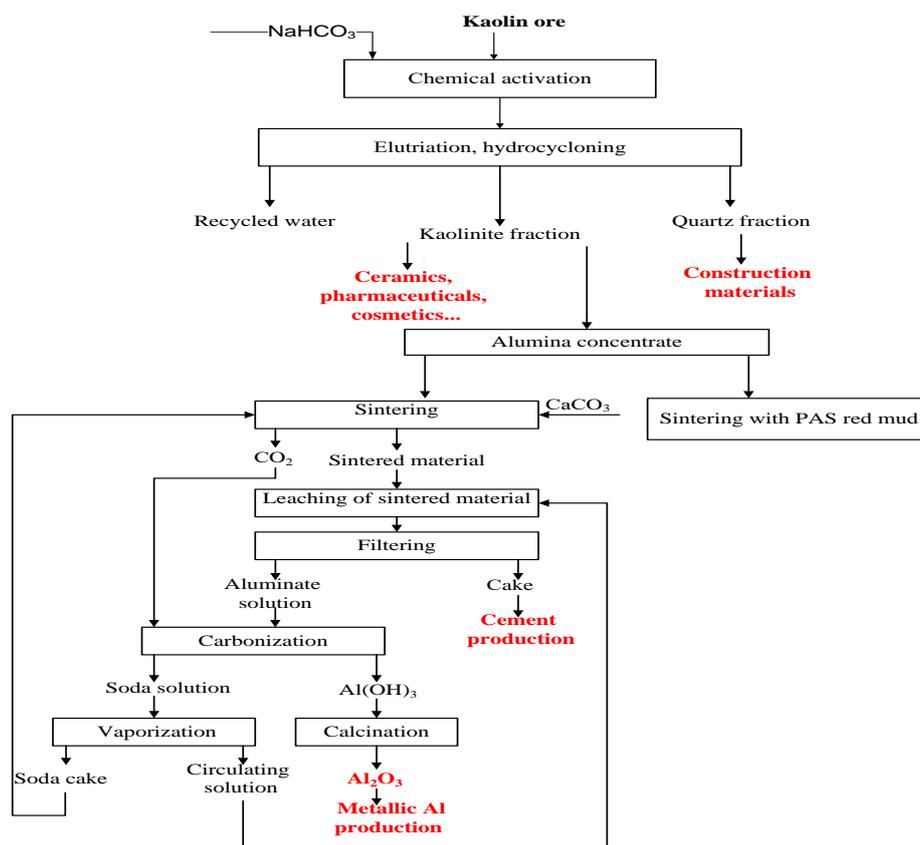


Figure 4 - Basic process flow diagram of complex processing of kaolinite ore

Conclusions

The effect of preliminary chemical activation of kaolinite clays from the Alekseyevsky deposit of the Republic of Kazakhstan in a sodium bicarbonate solution on the qualitative separation of kaolinite and quartz fractions was studied. The yield of the kaolinite fraction after clay activation increased from 48.03% to 76.39%.

As a result of activation, the phase composition of the kaolinite fraction has changed: the percentage of the kaolinite fraction decreased; new phases of muscovite and sodium aluminosilicate

appeared; the amount of quartz increased. A decrease in the content of a chemically stable fraction of kaolinite in clay will increase the efficiency of processing when extracting Al_2O_3 .

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

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Каолинитті саздар Қазақстан Республикасының алюминий саласы үшін шикізат көзі

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ТҮЙІНДЕМЕ

Қазақстан Республикасында сазбалшықты алудың қосымша көзі каолинитті саздар болуы мүмкін. Алексеев каолинит кен орны ең перспективалы болып табылады. Жоғары сапалы каолинит және кварцит өнімдерін алу үшін байытудың арнайы әдістерін жүзеге асыру қажет, өйткені каолиниттерді гравитациялық байытудың стандартты әдістерін қолданған кезде қанағаттанарлық нәтижелерге қол жеткізілген жоқ. Жұмыста Алексеев кен орнының каолинитті саздарын өңдеуде алдын-ала химиялық белсендірудің әсерін зерттеу нәтижелері келтірілген. Бұрын шикізатты натрий гидрокарбонаты ерітіндісінде алдын-ала химиялық белсендіру әдісі әртүрлі минералды шикізатты өңдеуде өзін жақсы көрсетті. Натрий гидрокарбонаты ерітіндісінде алдын-ала химиялық белсендіру кезінде каолинит фракциясының фазалық құрамында өзгерістер болғандығы анықталды: мусковит мөлшері екі есе азайды; натрий алюмосиликатының фазасы пайда болды. Al_2O_3 -тың каолинитті фракцияға шығымының химиялық белсендіру температурасына, ұзақтығына, Ж:Т қатынасына және химиялық белсендіру кезіндегі натрий гидрокарбонаты ерітіндісінің концентрациясына тәуелділігі зерттелді. Алексеев кен орнындағы каолинит сазын алдын-ала химиялық белсендірудің оңтайлы режимі анықталды, олар: температура 150 °С, ұзақтығы 120 минут және натрий бикарбонаты ерітіндісінің концентрациясы 120 г/дм³. Каолинит балшықтарын өңдеудің негізгі технологиялық схемасы ұсынылды.

Түйін сөздер: каолинит, кварцит, кремний модулі, химиялық белсендіру, химиялық байыту, өнім шығымы, технология.

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Каолинитовые глины как источник сырья для алюминиевой отрасли Республики Казахстан

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АННОТАЦИЯ

В качестве дополнительного источника для получения глинозема в Республике Казахстан могут служить каолинитовые глины. Наиболее перспективным является Алексеевское месторождение каолинитов. Для получения высококачественной каолинитовой и кварцевой продукции необходима разработка специальных приемов обогащения, так как при использовании стандартных приемов гравитационного обогащения глин не были достигнуты удовлетворительные результаты. В работе приведены результаты исследований влияния предварительной химической активации при переработке каолинитовых глин Алексеевского месторождения. Ранее способ предварительной химической активации сырья в растворе гидрокарбоната натрия хорошо зарекомендовал себя при переработке различного минерального сырья. Определено, что при проведении предварительной химической активации в растворе гидрокарбоната натрия произошли изменения в фазовом составе каолинитовой фракции: практически в два раза уменьшилось содержание мусковита; образовалась фаза алюмосиликата натрия. Исследована зависимость выхода Al_2O_3 в каолинитовую фракцию от температуры химической активации, продолжительности, отношении Ж:Т и концентрации раствора гидрокарбоната натрия. Установлен оптимальный режим проведения предварительной химической активации каолинитовой глины Алексеевского месторождения: температура 150 °С, продолжительность 120 минут и концентрация раствора гидрокарбоната натрия 120 г/дм³. Предложена принципиальная технологическая схема переработки каолинитовых глин.

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Study of influence of the charge granulometric composition on the quality of burned anodes

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ABSTRACT

Many factors affect the quality of produced anodes: composition and grade of raw materials, recipe, technology, operating parameters, the granulometric composition of charge materials etc. The most significant influence is from the last factor. The article provides research results on the effect of fine fractions on the quality of anodes. The research object is charge of different granulometric composition used to produce anodes at the Kazakhstan Electrolysis plant in Pavlodar. Six types of anode mass with different granulometric composition were prepared for the experiment. The anode mass was made of petroleum coke, pitch, recycled anodes, and dust from filters and grinder produced during coke treatment. Several properties of the specimens were studied. In total, six specimens were made and, specimen № 4 drew particular attention. Its granulometric composition is as following: coarse fractions – 25 %, medium fractions – 20%, fine fractions (grinder dust) – 50 %, and filter dust – 5 %. The results showed that some specifications of anodes, like gas permeability and apparent density that affect anode consumption, are improved as the fineness of dust grinding. For instance, the addition of dust fraction in the charge increases anode density from 1.542 to 1.639 kilogram per cubic decimeters and decreases gas permeability from 1.01 to 0.78 nPm. In addition, the presence of dust fraction minimizes the porosity of the anode block. The results of the investigation help adjust the optimal recipe of anode mass to obtain high-quality anodes.

Keywords: anode mass, production of baked anodes, gas permeability, density, granulometric composition, fine fraction.

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Introduction

Burnt anodes in an aluminium electrolyzer supply current and participate in the electrochemical process by being burned in formed oxygen. Therefore, one of the main specifications of anodes used as reducing agents during electrolysis of cryolite-alumina melts is the consumption rate.

The relevant literature review showed that increase in anodes density causes a decrease in gas permeability. Consequently, the consumption rate of anodes is reduced during electrolysis of cryolite-alumina melts [1-4].

Anode mass and burnt anodes are made of coal pitches, petroleum coke, and stubs (remnants of anodes) mixed with a recipe. “Green” anode blocks are then formed out of the mixture and are calcinated to produce burnt anode blocks.

There are special requirements for an aluminium electrolyzer:

- as a physical object that must withstand mechanical stress at high temperatures and supply high electrical conductivity;
- as a chemically active electrode that undergoes chemical and electrochemical oxidation during electrolysis, it must resist advanced chemical influences.

These requirements could be satisfied if the electrodes’ structure is built with principles of composite materials, i.e. framework made of coke grain (filler) and binding component (matrix) from coal pitch. According to the theory of composite materials, end-product – composite exceeds by properties both its constituents [4].

Nevertheless, compositional properties of the structure determine some peculiarities of anode’s work under conditions of electrolysis of cryolite-

alumina melt. The most significant peculiarities are as following:

1. Due to the different chemical properties of a coke made of fillers and a coke made of binding material, their oxidation occurs at different rates. This leads to uneven (selective) anode oxidation and shedding off some parts of the filler.

2. Uncompensated shrinkage of matrix's materials during burning causes the formation of many defects (microcracks, pores, bundles) in the structure of coke made of a binding component. This, in turn, triggers mechanical shedding of coke particles.

During the development of an anode mass recipe, one should consider including coke as a filler with a strictly regulated value of reactivity. Appropriate calculation of granulometric composition requires steps like taking into consideration dense packing of grains to prevent high porosity of anode and infiltration of oxidation products into intraporous space.

One of the main tasks of technology is to regulate purposefully the structure and properties of raw materials to reduce uncompensated shrinkage. It is possible to achieve desirable results by varying granulometric composition, filling the matrix with a fine dusty fraction, using high temperature pitch and coke with low thermal expansion coefficient values and changing technological parameters of burnt anode production.

Studying the packing of aggregate grains on geometrical models that consist of homogeneous spheres makes it possible to understand that a minimum quantity of spheres in a unit of volume is achieved when centres match cubic lattice nodes. Meanwhile, a maximum amount of spheres happens by rhombohedral packing. If empty spaces are filled with spheres with corresponding diameters, theoretically, it is feasible to obtain a filling factor infinitely close to one. Using materials of several fractions such as coarse, medium, and dust helps achieve maximum packing.

Literature review showed that granulometric composition significantly affects the quality of a produced anode. An increase of coarse fraction content leads to a decrease in electrical resistance and anode shrinkage during burning. On the other hand, an increase in dust fraction quantity improves anode blocks' mechanical strength and density. Intermediate fractions of coke charge mainly crumble during electrochemical anode oxidation and their amount is regulated [1-6].

It is possible, to sum up, a relation between different components of an anode mass recipe:

– Maximum packing (minimum porosity) is achieved in a system developed according to a relatively balanced straightforward principle, when material from the granular composition has a small size enough to ensure intergranular space. At the same time, the porosity of coarse grains has its influence [6-9].

– Gas permeability of anode material is significantly reduced as fineness and dust content are increased [10].

– Resistance to thermal shock grows if the granular composition has a high percentage of coarse fractions.

A fine fraction in an anode structure affects the "elasticity" of the charge. That property improves compression resistance [11]. For all mentioned reasons, adjustment of optimal granulometric composition significant.

Experimental part

An object of research is a charge with different granular composition used for anode production at the Kazakhstan electrolysis plant. Table 1 represents a granulometric composition of the charge.

Table 1 – Granulometric composition of the charge

Sample number	Granulometric composition, %			
	Coarse fraction	Medium fraction	Fine fraction	
			Grinder dust	Filter dust
1	37	40	15	8
2	25	40	25	10
3	30	30	30	10
4	25	20	50	5
5	40	20	22	18
6	40	23	22	15

Equipment used for the research: RDC-161 bench-scale anode production unit; BF12S anode baking furnace; equipment for determination of anode blocks gas permeability; pycnometer.

Six batches of anode mass with different granulometric compositions were prepared for the experiment (Table 1). The fraction classes that were selected are coarse (-14 + 6.3 mm), medium (-6.3 + 0.25 mm), fine fractions (-0.25+0.08 mm), and coke filter dust (-0.074 mm). The coarse fraction consisted of snuff; other fractions were made of coke.

Determination of reactivity to carbon dioxide.

Two test samples with a diameter of (50±1) mm and a length of (60±1) mm were prepared. The samples were dried at (120±5) °C within 12 hours and cooled to room temperature. The initial mass of each test samples was measured by weighing each core (m₀) to an accuracy of ±0.1 g. Then, the muffle furnace was heated to (960±2) °C. The temperature was stabilized by keeping it in the furnace at least for 60 minutes; after, that, the test samples were placed inside. The gaseous flow of carbon dioxide was supplied, and the rate was set at 200 litres per hour through an alumina tube. Mentioned parameters were kept within 7 hours, and the samples were cooled by switching off the gaseous flow. As soon as the furnace temperature cooled to lower than 550 °C, remnants of the test samples (core) and produced dust were taken out, cooled to room temperature, and weighed to an accuracy of ±0.1 g. Each remaining test sample was placed in a separate camera of tripping apparatus with 50 steel balls and was left to turn over for 20 minutes to remove any loose particles. As soon as turning over finished, the camera's content was emptied into a 4 mm sieve, balls were taken out, and remnants of the samples (core) were weighed to an accuracy of ±0.1 g.

Determination of anode density in xylene by pycnometric method. Cylindrical specimens of anode mass 50 mm high and 30 mm in diameter were ground up to a particle size of 63 µm, dried in the furnace at 120°C ± 2°C for 8 hours, and cooled with silica gel in a drying cabinet. A dry clean pycnometer without a stopper with 5 g ± 0.1 g of that specimen was placed in a degassing container. Xylene was added drop by drop inside the pycnometer until the content was covered by it to a maximum of 20 mm. After that, the pycnometer was put in a thermostat and heated to a temperature of 25 ± 0.05 °C. As soon as all water was removed, the pycnometer reached test temperature; it was taken out, thoroughly dried and weighed. The experiment was repeated three times with every recipe.

The equation determines density ρ of burned anode expressed in grams per millilitre:

$$\rho = \frac{m_3}{V - \frac{m_4 - (m_0 + m_3)}{\rho_x}} \quad (1)$$

where V – pycnometer volume, ml;

m₀ – a mass of clean, dry, empty pycnometer, g;

ρ_x – xylene density, g/ml;

m₃ – sample mass, g;

m₄ – a mass of pycnometer with a sample and xylene, g.

Density calculation of sample № 1:

$$\rho = \frac{24.3}{25 - \frac{58.815 - (25 + 24.3)}{1.21}} = 1.418,$$

$$\rho = \frac{23.8}{25 - \frac{58.315 - (25 + 23.8)}{1.21}} = 1.388,$$

$$\rho = \frac{25}{25 - \frac{59.515 - (25 + 25)}{1.21}} = 1.458.$$

Similarly, densities of other samples were determined.

Determination of gas permeability. Calculation of gas permeability of the anodes is done using data from measurements:

$$W_{RCR} = \frac{m_0 - m_1}{m_0} \times 100 \quad (2)$$

where m₀ – initial mass the test sample (core), g;

m₁ – a mass of the remaining test sample (core) after tripping, g.

Calculation of gas permeability of burnt anodes prepared with different compositions:

$$W_{RCR (P1)} = \frac{25 - 24.525}{25} \times 100 = 1.9$$

$$W_{RCR (P2)} = \frac{23 - 22.6}{23} \times 100 = 1.73$$

$$W_{RCR (P3)} = \frac{27.3 - 26.8}{27.3} \times 100 = 1.83,$$

$$W_{RCR (P4)} = \frac{21.3 - 21.133}{21.3} \times 100 = 0.78$$

$$W_{RCR (P5)} = \frac{23.23 - 22.951}{23.23} \times 100 = 1.2$$

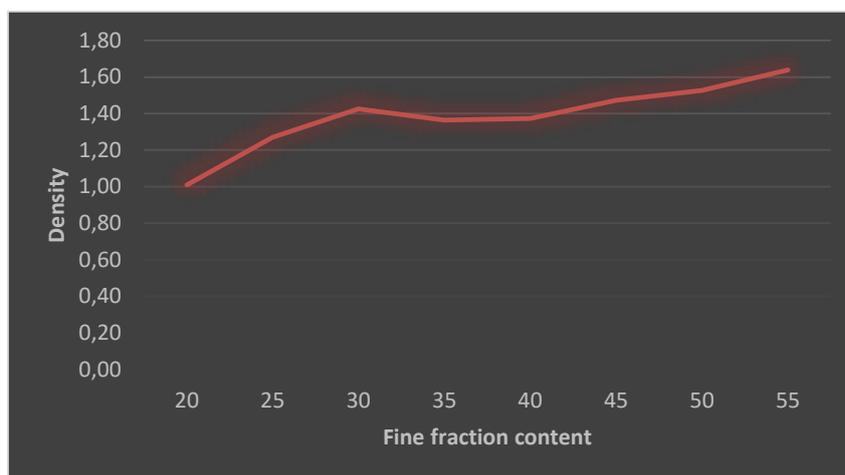
$$W_{RCR (P6)} = \frac{26.33 - 25.915}{26.33} \times 100 = 1.58.$$

Results and discussion

The results of the experiment showed that granulometric composition affects the density of anodes significantly. It seems that an increase of

Table 2 – Density of anodes with different granulometric compositions

Sample number	Density 1, kg/dm ³	Density 2, kg/dm ³	Density 3, kg/dm ³	Mean value, kg/dm ³
1	1.418	1.388	1.458	1.421
2	1.307	1.388	1.400	1.365
3	1.458	1.488	1.517	1.487
4	1.633	1.587	6.88	1.639
5	1.517	1.587	1.476	1.526
6	1.418	1.388	1.310	1.373

**Figure 1** – Plot relationship between anode density and fine fraction content

fine fractions contents increase density of the anode.

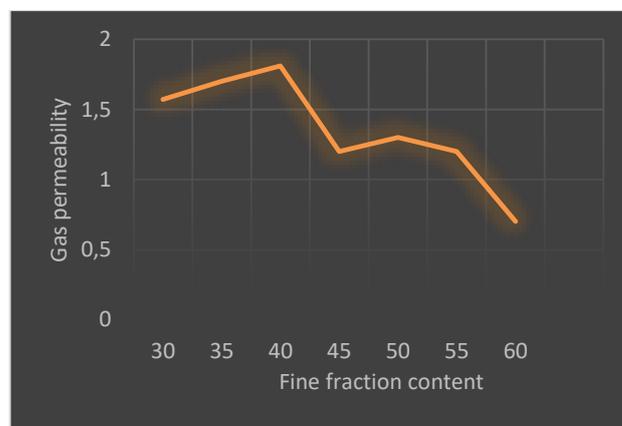
Table 2 shows the result of the experiments related to determination of anode density in xylene by pycnometric method.

Table 3 represents the obtained data from the experiment related to gas permeability of the anodes.

Table 3 – Gas permeability of burnt anodes with different coke granular compositions

Samples	Sample mass, g	Gas permeability, nPm
Sample № 1	25	1.9
Sample № 2	23	1.73
Sample № 3	27.3	1.83
Sample № 4	21.3	0.78
Sample № 5	23.23	1.2
Sample № 6	26.33	1.58

Based on the calculated values, the plot that represents the dependence of gas permeability on the content of a fine fraction was drawn. The experiment results revealed that an increase of fine fraction content leads to a significant decrease in anode gas permeability.

**Figure 2** – Plot relationship between anode gas permeability and fine fraction content

The results showed that the highest density value has a test sample № 4 (with the highest content of fine fractions). Figures 1 and 2 represent the tendency that an increase in fine fraction content reduces anodes' gas permeability. Further increase in fine fraction content is unacceptable. According to production experience, there is an upper limit of fine fraction content above which deterioration of mechanical properties is observed. The mentioned limit is determined by fineness of applied dust as well [4-5]. High content of fine fractions and dust reduces coarse fraction

Table 4 – Specification of burned anodes

<i>Present granulometric composition of charge</i>	<i>Density, kg/dm³</i>	<i>Gas permeability, nPm</i>	<i>Suggested granulometric composition of charge</i>	<i>Density, kg/dm³</i>	<i>Gas permeability, nPm</i>
Coarse fraction (-14 + 3.5 mm) - 26 %	1.542	1.01	Coarse fraction (-14 + 3.5 mm) – 25 %	1.639	0.78
Medium fraction (-3.5 + 0.25 mm) – 35 %			Medium fraction (-3.5 + 0.25 mm) – 20 %		
Fine fraction (-0.25+0.0 mm) – 39%			Fine fraction (-0.25 +0.0 mm) – 50 %		
			Filter dust (-0.074 mm <) – 5%		

content in anode frame that in turn causes weakening of cohesion between particles. As a result, anodes may undergo deformation after molding or during burning [3, 5].

Granulometric composition of charge for production of higher quality anode masses was chosen based on the research results (Table 4).

Thus, according to the proposed method for producing anode mass, adding an extra fraction of coke – filter dust caught from filters to existing fractions.

Developed recipe will increase anode density from 1,542 kg/dm³ to 1,639 kg/dm³ and reduce gas permeability from 1,01 to 0,78 nPm.

Conclusions

The influence of fine fraction content on the quality of produced anodes was studied experimentally. An increase of anode density was observed as more fine fractions were added to the charge recipe. Moreover, gas permeability was reduced with the addition of fine particles. Gas permeability affects the consumption of anodes during electrolysis of cryolite-alumina melt.

A better option of granulometric composition of coke for production of higher quality anodes at JSC Kazakhstan electrolysis plant was suggested.

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

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Шихтаның гранулометриялық құрамының күйдірілген анод сапасына әсерін зерттеу

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ТҮЙІНДЕМЕ

Алынатын анодтың сапасына көптеген факторлар әсер етеді, олар: шикізаттың сапасы, рецептура, технология, режимдік параметрлер, шихтаның гранулометриялық құрамы және т.б. Олардың ішінде шихтаның гранулометриялық құрамы ең негізгі орын алады. Бұл мақалада ұсақ фракциялардың анод сапасына әсерін зерттеу нәтижелері келтірілген. Зерттеу объектісі Қазақстан электролиз зауытындағы (Павлодар қ.) әртүрлі гранулометриялық құрамдағы шихта болды. Зерттеу жұмыстары үшін әртүрлі гранулометриялық құрамды анод массасының 6 партиясы дайындалды. Анодты массаны дайындау үшін мұнай коксі, пектер, істен шыққан анод қалдықтары және коксты ұсату кезінде пайда болған фильтрдегі кокс шаңдары мен диірмендегі ұсақ кокстер қолданылды. Зерттеулер барысында осы үлгілердің кейбір қасиеттері зерттелді. Дайындалған үлгілердің ішінен гранулометриялық құрамы келесілерден тұратын: ірі фракциясы – 25 %, орташа фракциясы – 20 %, кішігірім фракциясы (диірмендегі ұсақ кокстер) -50 % және фильтрлердегі ұсақ бөлшектер – 5 % болатын № 4 үлгіге ерекше мән берілді. Зерттеулер нәтижесінде, анод өндірісінің шикізатына кокстың кішкентай (ұсақ) бөлшектерін қосқанда, оның шығынына әсер ететін кейбір қасиеттерінің тығыздығы мен газөткізгіштігінің өзгергені байқалды. Шаң-тозаңдық фракцияны қосқан кезде,

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анодтың тығыздығы 1,542 кг/дм³ –тен 1,639 кг/дм³ дейін жоғарылағаны, ал газеткізгіштігінің 1,01-ден 0,78 нРт дейін төмендегені байқалды. Сонымен қатар шикізатқа шаң-тозаңдық фракцияны қосқан кезде анод блоктарының кеуектіліктері төмендейді. Зерттеулер нәтижесі сапалы анод өндіру үшін, анод массасының оңтайлы рецептурасын таңдауға мүмкіндік береді.

Түйін сөздер: анодты масса, күйдірілген анод өндірісі, газеткізгіштік, тығыздық, гранулометриялық құрам, ұсақ фракция.

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Исследование влияния гранулометрического состава шихты на качество обожженных анодов

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АННОТАЦИЯ

На качество получаемых анодов влияют многие факторы: состав и качество сырьевых материалов, рецептура, технология, режимные параметры, гранулометрический состав шихтовых материалов и т.д. Особое место среди них занимает гранулометрический состав шихты. В данной статье представлены результаты исследования влияния тонкой фракции на качество анодов. Объектом исследования являлась шихта различного гранулометрического состава для получения анодов на базе КЭЗ (Казахстанский электролизный завод, г.Павлодар). Для эксперимента были приготовлены 6 партий анодной массы с разным гранулометрическим составом. Для приготовления анодной массы использовались нефтяной кокс, пек, оборотные аноды и пыль с фильтров и мельницы, которые образуются при измельчении кокса. Было определено и исследовано некоторые свойства этих образцов. Из приготовленных шести проб особое внимание привлекло проба № 4, где содержание крупной фракций – 25 %, средней – 20 %, мелкой (мельничная пыль) -50 % и фильтровая пыль -5 %. Результаты показывают, что с увеличением тонины помола пыли улучшаются некоторые характеристики анода, в частности газопроницаемость и кажущаяся плотность, которые влияют на расход анодов. Так, при добавлении пылевой фракций в шихту, плотность анодов увеличивается от 1,542 до 1,639 кг/дм³, а газопроницаемость снижается от 1,01 до 0,78 нРт. Так же добавление пылевой фракций минимизирует пористость анодного блока. Результаты исследования позволяют подобрать более оптимальную рецептуру анодной массы, для получения более качественного анода.

Ключевые слова: анодная масса, производство обожженных анодов, газопроницаемость, плотность, гранулометрический состав, тонкая фракция.

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Investigation of degradation processes in perovskite under the influence of external factors

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ABSTRACT

The article describes a number of new fundamental knowledge about mechanisms of degradation processes occurring in photoactive perovskite materials based on complex lead halides and solar cells based on them, modern methods and approaches to increasing the operational stability of perovskite photovoltaic devices are considered. The revealed paths of degradation processes occurring in complex metal halides (lead and tin) under the influence of light and elevated temperatures are important for further developments in the field of creating highly efficient and stable perovskite solar cells of a new generation. The investigated models of degradation are described both under the action of moisture and as a result of radiation ionization processes. The importance of solving the Dexter-Varley paradox, which takes into account the competition between the processes of displacement of ISO states, as well as the delocalization of the resulting hole in the valence band, is emphasized. It was shown that by changing the force of pressure of the tape on the perovskite film, it was possible to achieve the maximum values of the light conversion efficiency of about 12.7%. It was found that the presence of charge carriers in the form of polarons can significantly affect the assessment of the degradation efficiency towards its increase. The data obtained can radically change the traditional ideas about the efficiency of photochemical reactions.

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Introduction

The development of hybrid complex lead halides with a perovskite structure is the most promising area of research in the field of creating a new generation of thin-film phototransformers. The modern approach to the processing of mineral raw materials should be based on the use of effective technological methods that ensure the integrated use of raw materials and the environmental friendliness of the processing process [1]. These materials demonstrate impressive optoelectronic properties, and solar cells based on them – record growth rates of light conversion efficiency. A significant disadvantage of hybrid perovskites is their low resistance to various external (oxygen, moisture) and internal (electric field, temperature, light) factors. It should be emphasized that the influence of external factors is the least dangerous

for these materials, which is eliminated by isolating the photoactive layer of the solar battery with special encapsulating materials. The same approach of PSC stabilization by encapsulation is practically not applicable to protect devices from the influence of internal factors. In this regard, the researchers are faced with the task of finding ways to prevent the degradation of perovskite materials caused by internal factors. Various approaches have been proposed for the stabilization of devices based on complex lead halides, from optimizing the chemical composition of perovskite films by introducing modifying additives into the perovskite layer to optimizing the architecture of perovskite solar cells. However, for the targeted development of effective approaches to improving the stability of perovskite systems and solar batteries based on them, a deeper understanding of the processes of photochemical and thermal degradation of various

types of complex metal halides is necessary. At the same time, to obtain reliable data, it is necessary to study the degradation processes of perovskite materials under strictly controlled conditions in an inert atmosphere.

The problem of stability of perovskite solar cells. For the production of efficient and at the same time cheap solar panels based on perovskites, it is necessary that the solar panels have long-term operational stability. To date, the warranty period of silicon solar cells is 20-25 years. If the efficiency of a perovskite solar battery is reduced by 1% every year, then in 20 years it will degrade by 20%, which is quite an acceptable indicator in the field of photovoltaics [2]. Just like organic solar panels, devices based on perovskite materials have significant stability problems. This is due both to the true instability of the perovskite material itself, and to external factors that have a detrimental effect on the device as a whole.

External factors contributing to the degradation of perovskite materials. Despite the enormous advantages of perovskite solar cells over other photo-converters, these types of devices, unfortunately, are still far from practical implementation. The main problem is the extremely low stability of complex lead halides. Halide (especially iodide) complexes of lead are rapidly destroyed under conditions of elevated temperatures, as well as under the influence of moisture and oxygen in the air [3,4]. In addition, perovskite materials based on lead halides are characterized by low photochemical and electrochemical stability [5,6]. In real-world operating conditions, the efficiency of solar cells based on MAPbI_3 drops to almost zero in just a few hours, which makes it impractical to use them in practice.

Experimental part

Degradation effects in perovskites. The problem of degradation of solar cells based on organic-inorganic perovskites is very acute in two respects. First, like every salt, the interaction with moisture is very significant here. Secondly, the ionic nature of the lattice and the large value of the Madelung energy open up specific pathways for photochemical reactions. Let us briefly consider these two features. In the infusional hypothetical scheme of the influence of moisture on the decomposition of perovskite has now been elucidated (see Figure 1).

Figure 1 shows that when one water molecule interacts with n "molecules" of perovskite, one water molecule and one PbI_2 molecule are separated in several successive stages. This scheme goes back to the Grothaus mechanism [7], so that the molecules HI and CH_3NH_2 are still isolated along the path of the complete reaction.

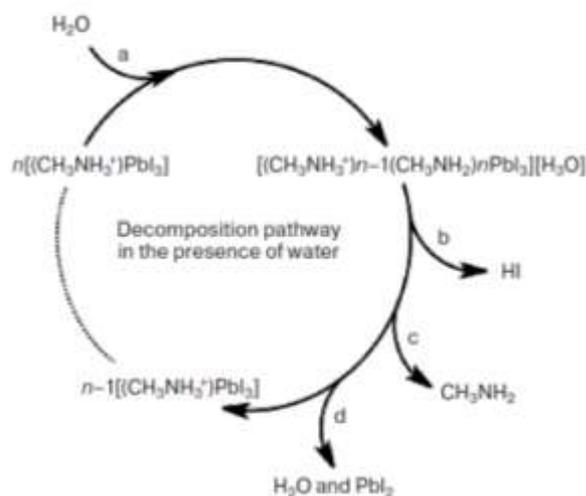


Figure 1 - Possible decomposition pathway of hybrid halide perovskites in the presence of water

One water molecule is required to initiate this process, with the decomposition being driven by the phase changes of both hydrogen iodide (soluble in water) and the methylammonia (both volatile and soluble in water) [8].

Apparently, it is still not clear how to change the composition of perovskite to reduce degradation under the influence of moisture, both in the presence and in the absence of photoexcitation of the material.

It is necessary, however, to keep in mind that there are other (without moisture) channels of degradation of perovskite under the influence of radiation. One such path is indicated in [9], who believes that after the generation of a hole on the iodine ion, this hole migrates to the surface, after which it is on the surface that the reaction of neutral iodine with one of the surface negative iodine ions occurs. This position is the originator of a whole sequence of reactions, resulting in the disintegration of the perovskite structure. However, when analyzing this scheme, an extremely important circumstance is not taken into account: the passage of the reaction between neutral iodine and a negatively charged iodine ion is prevented by the delocalization of the hole, which in the zone scheme is the neutral iodine atom. Taking into

account this circumstance requires a special analysis (namely, the resolution of the Dexter-Varley paradox), which is particularly clearly manifested in the problems of subthreshold defect formation and has been studied since the late 50s of the XX century. In our recent work on the ionization-stimulated degradation of perovskite, this problem was studied in some detail [10]. Indeed (Fig. 2), if a photon tears an electron from any nodal atom of an iodine ion, this means the simultaneous manifestation of two circumstances: first, if we proceed from the band structure, the ionization of iodine means the appearance of a hole in the valence band; second, from the point of view of crystal chemistry, the neutralization of iodine immediately leads to the elimination of a potential Modelung pit for it (the depth of this pit was calculated earlier (see Table 1).

Table 1 - Calculated properties of four hybrid lead halide perovskites from density functional theory

Cation	D, D	a, nm	$\Delta P, \mu C / cm^2$	$E_{rot}, kJ / mol$	$E_{dip}, kJ/mol$
NH ₄	0	0.621	8	0.3	0
CH ₃ NH ₃	2.29	0.629	38	1.3	4.6
CF ₃ NH ₃	6.58	0.635	48	21.4	42
NH ₂ CH ₃	0.21	0.634	63	13.9	0.03

Note. The electron polarization of the lattice (ΔP) and the rotational barrier energy (E_{rot}) were calculated by PBEsol in VASP. The nearest neighbor dipole interaction (E_{dip}) was estimated from the point dipole calculation (source: [8]).

After the elimination of the Modelung pit, the neutral iodine atom appears on the hump of the crystal potential and tends to slide into the neighboring internode.

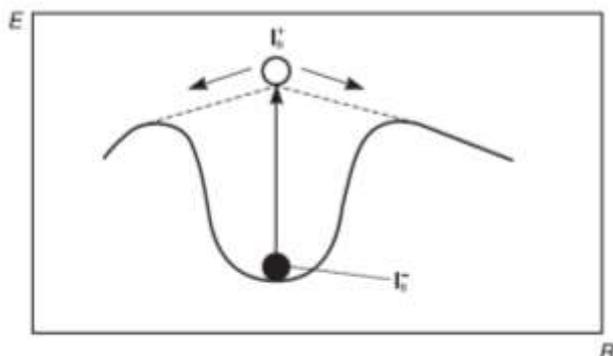


Figure 2 - The formation of dynamic Coulomb instability in the I-sublattice of perovskite [10]

This takes a time of $\tau_+ \approx 5 \cdot 10^{-14}$ s. However, the hole is localized at the node also during the finite time τ_e . If τ_e is much less than τ_+ , then the Dexter displacement of the iodine atom in the internode does not have time to occur, so there will be no defect formation (degradation). However, the situation is much subtler: the motion of the hole is a quantum process, which means that there are both faster and slower cases of delocalization of the hole (for τ_e is the average value). Therefore, to find the probability of displacement of iodine atoms in the internode, despite the competition of hole delocalization, it is necessary to do a quantum calculation. This gives for the probability of displacement of internode ions the probability of the following type: $n = \exp(-\tau_+ / \tau_e)$. The estimation of the value of τ_e is possible on the basis of the uncertainty ratio: $\tau_e = h / \Delta E_v$, where ΔE_v is the width of the valence band formed from the P states of iodine. For the parameters of perovskite (CH₃ – NH₃)PbI₃, the characteristic value of the probability of displacement of the iodine atom in the internode is $n \approx 10^{-4}$, which means that after ionization of the iodine ion, one of 10,000 ionizations changes this determines the degradation ability of the crystal. Obviously, it is by a factor of this order that the entire Schumann scheme is reduced.

Encapsulation as an effective method of protecting the photoactive layer of solar cells from external factors. Encapsulation is a technology for protecting solar cell components from the influence of aggressive environments (O₂, H₂O) by using an impermeable capsule. Typically, thin plates of glass and epoxy glue are used for encapsulation, which hardens under the influence of ultraviolet light (Figure 3) [11-13]. Han and colleagues investigated two different methods of encapsulation of perovskite solar cells. [14]. The first method was to use a UV-curable adhesive between the top silver electrode of the device and a regular slide. In the second method, a technique was used in which the insulation of the active layer was carried out using a special glass "lid", in the niche of which a desiccant was located, which acts as an adsorbent of moisture, in the case of its penetration through the epoxy glue [15].

This approach has further improved the efficiency and stability of the devices. Figure 3. Schematic illustration of perovskite solar cell encapsulation. However, such types of encapsulation are unlikely to be applied on an industrial scale. For perovskite solar cells, the protection methods used for organic solar cells



Figure 3 - Schematic illustration of perovskite solar cell encapsulation

manufactured by roll technologies can be very effective. In 2009, Krebs et al. developed a technology for the production of fully encapsulated flexible polymer solar cells [16].

The substrate in such batteries is polyethyleneterephthalate (PET), and the encapsulation was carried out by laminating a thin film of 25 microns of the same PET with an acrylic adhesive applied. As a result, this technique has led to a significant increase in the stability of devices in real-world operating conditions of solar panels. The disadvantage of the developed method was the degradation of the manufactured devices in the places of the roll cut. But this problem is easily eliminated by treating the edges with a special sealant. Another interesting and inexpensive way to increase the stability of devices by encapsulation was to use a copper tape instead of the usual sputtered top electrodes.

The conductive copper adhesive tape is pasted over the photoactive layer using a conventional glass rod. By varying the pressure force of the tape on the perovskite film, it was possible to achieve the maximum values of the light conversion efficiency of about 12.7%. Devices obtained by this method also showed higher stability in air compared to devices with sputtered electrodes. However, it is worth emphasizing that

encapsulation protects the active layer of a perovskite solar cell only from the effects of aggressive environments, but cannot prevent the influence of internal factors such as electric field, elevated temperature, and sunlight. Therefore, the study of the influence of these factors on the stability of perovskite solar cells requires serious and detailed consideration.

Conclusions

The article describes in detail the degradation models (both under the influence of moisture and as a result of radiation ionization processes). The role of solving the Dexter-Varley paradox (taking into account the competition between the processes of ISO state displacement and delocalization of the resulting hole in the valence band) is emphasized; it is shown that the latter circumstance can radically change the ideas about the efficiency of photochemical reactions. It should be noted in this connection that the existence of charge carriers in the form of polarons can have a significant impact on the assessment of the efficiency of degradation in the direction of its increase.

The publications of recent years not only reflect the state and problems, but also reasonable hopes that the future of alternative energy sources lies with perovskite-based cells.

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

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Сыртқы факторлардың әсерінен болатын перовскиттегі деградациялық процестерді зерттеу

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<p>Мақала келді: 06 мамыр 2021 Сараптамадан өтті: 07 маусым 2021 Қабылданды: 05 қазан 2021</p>	<p>ТҮЙІНДЕМЕ</p> <p>Мақалада күрделі қорғасын галогенидтері мен оларға негізделген күн батареялары негізінде фотоактивті перовскит материалдарында болатын деградация процестерінің механизмдері туралы бірқатар жаңа іргелі білім келтірілген. Перовскиттік фотоэлектрлік қондырғылардың жұмыс тұрақтылығын арттырудың заманауи әдістері мен тәсілдері қарастырылған. Жарық пен жоғары температураның әсерінен металдардың кешенді галогенидтерінде (қорғасын мен қалайы) жүретін деградация процестерінің анықталған жолдары жаңа бұйындық жоғары тиімді және тұрақты күн батареяларын құру саласында жаңа зерттеулерді одан әрі дамыту үшін маңызды. Ыдыраудың зерттелген модельдері ылғалдың әсері кезінде де, радиациялық иондалу процестерінің нәтижесі арқылы да суреттеледі. ISO күйлерінің орын ауыстыру процестері арасындағы бәсекелестікті, сондай-ақ валенттік диапазонында пайда болған тесіктің делокализациясын ескеретін Декстер-Варли парадоксын шешудің маңыздылығына баса назар аударылады. Перовскит пленкаға таспаның қысым күшін өзгерту арқылы жарық конверсиясының ПӘК -нің максималды мәніне шамамен 12,7 % жетуге болатындығы көрсетілді. Полярон түріндегі заряд тасымалдаушылардың болуы оның жоғарылауына қарай деградация тиімділігін бағалауға айтарлықтай әсер етуі мүмкін екендігі анықталды. Алынған мәліметтер фотохимиялық реакциялардың тиімділігі туралы дәстүрлі идеяларды түбегейлі өзгерте алады.</p> <p>Түйін сөздер: перовскит материалдары, деградациялық процестер, инкапсуляция.</p>
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Исследование деградационных процессов в перовските при воздействии внешних факторов

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<p>Поступила: 06 мая 2021 Рецензирование: 07 июня 2021 Принята в печать: 05 октября 2021</p>	<p>АННОТАЦИЯ</p> <p>В статье описан ряд новых фундаментальных знаний о механизмах деградационных процессов, протекающих в фотоактивных перовскитных материалах на основе комплексных галогенидов свинца и солнечных батареях. На их основе, рассмотрены современные методы и подходы к повышению эксплуатационной стабильности перовскитных фотовольтаических устройств. Выявленные пути деградационных процессов, протекающих в комплексных галогенидах металлов (свинца и олова) под действием света и повышенных температур, имеют важное значение для дальнейших разработок в области создания высокоэффективных и стабильных перовскитных солнечных батарей нового поколения. Исследованные модели деградации описаны как под действием влаги, так и в результате процессов радиационной ионизации. Подчеркивается значение решения парадокса Декстера-Варли, где учитывается конкуренция между процессами смещения ISO-состояний, а также делокализация образующейся дырки в валентной зоне. Показано, что изменяя силу давления ленты на перовскитную пленку, можно было достичь максимальных значений эффективности преобразования света около 12,7 %. Установлено, что наличие носителей заряда в виде поляронов может существенно повлиять на оценку эффективности деградации в сторону ее увеличения. Полученные данные могут коренным образом изменить традиционные представления об эффективности фотохимических реакций.</p> <p>Ключевые слова: перовскитные материалы, деградационные процессы, инкапсуляция.</p>
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Prospects for use of chlorine-containing leaching solutions for extraction of associated useful components from spent ores of uranium deposits

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ABSTRACT

Work aimed at diversification of production through the additional extraction of associated useful components at uranium mines. The peculiarity of the work carried out is the additional processing of spent uranium mines at the existing ones using the existing production infrastructure for the extraction of associated useful components. The technology of underground leaching is well developed for uranium deposits. The leaching of associated useful components differs from the leaching of uranium only in the reagents used, and they are fundamentally similar to the method of underground-borehole leaching. Even if there are associated components in the uranium-bearing sands with a content of less than 1 g/t, up to 0.1 g/t production can be profitable. The use of ready-made infrastructure of uranium mines on spent blocks of deposits allows us to expect positive economic profitability in the future.

Keywords: uranium mines, associated valuable metals, associated useful components, underground well leaching, productive solution, chlorine-containing solutions.

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Introduction

Today, sodium cyanide is the main reagent in the industrial hydrometallurgical process for extracting gold from ores.

Increasing requirements for environmental protection, especially in relation to the in situ leaching method, determine the relevance of the search for less toxic reagents - gold solvents. One of these reagents can be solutions containing active chlorine, both in the form of free halogen and in the form of hypochlorites. In this work, studies have been carried out on core samples obtained during the drilling of an exploration well at the Semizbay uranium deposit.

Literature review

Leaching of ores in situ, that is, by the PV method, excludes any ore preparation and imposes

high environmental requirements, therefore, the use of cyanides in underground leaching is practically excluded. In the case of mining placer deposits containing large, hardly soluble in cyanides gold, the use of cyanides is also ineffective in the technological aspect.

In this regard, chlorine, iodine and bromine-containing reagents, which are environmentally safer than cyanide reagents, can be used as leaching agents. In the case of using the in situ leaching method, capital costs can be reduced by 2-4 times, therefore, the in situ leaching process can be cost effective with a higher chlorine consumption, with a duration of mining of ore deposits of several months, as well as when mining poor off-balance ores [1].

It is important to emphasize that in situ leaching of gold is carried out without cyanide, using hydrochloride technology, which makes it possible to ensure the environmental safety of the

work. Potassium and sodium hypochlorite obtained by electrolysis and gaseous chlorine are used as a solvent in the Ural deposits. [2].

In work [3], the results of studies on the leaching of gold from crushed ore to a size of $-12 + 0$ mm are given. The use of sodium acetate as a chemical additive in leaching gold on bottle dough from crushed ore to a particle size of $-12 + 0$ mm increases gold recovery by $\sim 4\%$ and improves the kinetics of gold dissolution.

According to the method [4], the efficiency of leaching both gold and silver is achieved by the fact that at the first stage of gold extraction, a weak chlorine solution (0.2-0.7%) is used, having a $\text{pH} > 1.8$, and at the second stage, a weak solution sodium thiosulfate (0.2-0.7%), having a pH of 7.5-8.5. Oxidation and dissolution of gold thus proceeds in a weakly acidic medium at a high oxidation potential (> 1200 mV). At the same time, sulfides, oxides, carbonate minerals, feldspars, organic compounds are exposed, which contributes to both the most complete gold recovery and an increase in the filtration permeability of the formation, in particular, due to the dissolution of carbonate cement. There is also no swelling of clays, which is characteristic of the alkaline medium, which is distinguished by the cyanide method.

Simultaneously with the leaching of gold, silver is oxidized and re-precipitated in the form of chloride, which facilitates its leaching with thiosulfate at the subsequent stage of mining.

The novelty of the proposed method consists in regulating the concentration of chlorine in the solution so that $\text{pH} > 3$ is maintained in the evacuated solution. This ensures the purity of the productive solution from the presence of iron, aluminum, zinc, copper due to their hydrolysis and reprecipitation in the formation. The oxidation potential in this mode remains high enough and ensures the retention of gold in solution.

When leaching ore from the Tas-Yuryakh deposit under normal conditions ($T = 20^\circ \text{C}$), with agitating the ore with chlorine water, a productive solution was obtained with $\text{pH} = 6$ and $\text{EMF} = 1230$ mV. At the same time, the degree of gold extraction was 98%. The productive solution was then treated with ammonia, as a result of which only traces of chlorine were found in it, while the pH increased and the redox potential decreased.

From productive gold-bearing solutions, gold was almost completely precipitated by cementation on zinc powder.

The method [5] includes preparing a leaching solution of hydrochloric acid and feeding it

into the ore. The novelty is that immediately before feeding into the ore, the hydrochloric acid solution is neutralized by adding a solution of commercial alkaline sodium or potassium hypochlorite to it. Used sodium hypochlorite (TU-6-15-746-87) or obtained by electrolysis. A solution of sodium hypochlorite (TU-6-15-746-87) is served in an amount of 0.6 volumes with 1-4 volumes of hydrochloric acid solution.

The aim of the invention is to increase the efficiency of gold extraction, reduce the acidity of the process, ensure the selectivity of the process and eliminate the dangers associated with the preparation and use of chlorine water and the transition to arsenic solution.

This goal is achieved by the fact that gold leaching is carried out without preliminary acidification and washing of arsenic and iron with a neutral solution prepared immediately before feeding into the ore from commercial alkaline sodium hypochlorite (for example, sodium hypochlorite TU 6-15-746-87) and hydrochloric acid solution, with the following ratio of ingredients, g/l by volume.

A solution of sodium hypochlorite alkaline TU 6-15-746-87 (sodium hypochlorite 30-40) is served in an amount of 0.6 volumes with 1-4 volumes of hydrochloric acid solution.

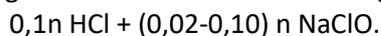
As it was found experimentally, the decrease in the leaching efficiency with acidic chlorine chloride solutions (according to the prototype), when going into an iron solution, is due to the low redox potential of the medium: $+ 700-800$ mV, which does not ensure the stability of complex gold ions $(\text{AuCl}_4)^-$. The decrease in efficiency is also due to the sedimentation of gold by iron.

The efficiency of leaching according to the proposed method is ensured by the fact that the neutralization of the acid solution with an alkaline solution of hypochlorite is carried out immediately before feeding into the ore. Atomic chlorine, which is released when mixing solutions and did not have time to combine into a Cl_2 molecule, is very aggressive towards gold. Excess acid is neutralized with alkali from a commercial solution of alkaline hypochlorite.

In order to increase the recovery of gold in the method [6], leaching is carried out with a solution of hydrochloric or sulfuric acid with the addition of hypochlorite at the following ratio: $0.1 \text{ n HCl} + (0.02-0.1) \text{ n NaClO}$, prepared immediately before its injection into the ore. Preliminary acidification of ores is carried out until the level of

iron concentration in the output solution decreases below 600 mg/l.

In order to increase gold recovery and eliminate the dangers associated with the preparation and use of chlorine water, the following solutions are used for leaching:



pH of the medium is 1.3-2.5, Eh = from +900 to +1300 mV.

In the claimed composition, HCl can be replaced by H_2SO_4 and other acids.

A method for extracting gold from ores, including preliminary acidification of ore with an acid solution, preparation of a leach solution and leaching with an acid solution containing active chlorine in the form of Cl_2 , differs in that, in order to increase gold recovery, reduce the consumption of chemical reagents and eliminate and using chlorine water, the preparation of the leaching solution is carried out immediately before its injection into the ore, while hypochlorite is added to the acid solution at a pH of 1.3-2.5, Eh from +900 to +1300 mV.

The use of aqueous solutions of chlorine for the opening and leaching of gold (hydrochlorination) is becoming more widespread in the practice of enrichment of refractory ores and concentrates [7–13].

In [14], the leaching of the concentrate was carried out for 10 hours at a ratio of S: L = 1:10 and a current density on the electrodes of 50 A / m². As a result of the experiments, it was found that the rational concentration of NaCl salt in the solution is 250 g / dm³, since a subsequent increase in its concentration to 300 g / dm³ leads to a slight (by 1.1%) increase in gold recovery from 34.6% to 35.7%. A flotation gold-bearing concentrate with a size class of 74 μm, containing 60–65% arsenopyrite and 52.5 g / t gold, was used as the test product.

In [15], an alternative non-cyanide method of gold leaching from oxidized ores of the Malmyzh deposit (Khabarovsk Territory) was investigated. The initial gold content in the ore is 0.8-0.95 g / t. The initial gold content in the ore is 0.8-0.95 g / t. The solution was prepared by electrolysis of a sodium chloride (NaCl) solution with a concentration of 20 g / l with the addition of 0.1 N hydrochloric acid (HCl). The optimal conditions for obtaining a solution with the maximum concentration of active chlorine required for gold leaching have been determined. A study of gold extraction by agitation with preliminary action on the pulp by preoxidation and cavitation (ultrasound) was carried out. Analysis of samples of

the liquid phase of the pulp for gold was carried out using atomic absorption spectroscopy. Direct hypochlorite leaching resulted in 23.0% gold recovery in 4 hours and 72.7% in 24 hours. After preoxidation followed by leaching with hypochlorite, gold recovery was 80.2% and 98.8% in 4 and 24 hours, respectively. After ultrasonic treatment, the yield of gold in the liquid phase of the pulp was 36.7-66.5% for 4 hours of agitation. The process of re-precipitation of the extracted gold into the solid phase and a decrease in its yield during prolonged agitation after preliminary ultrasonic treatment of both the initial hypochlorite and the pulp were revealed. Re-precipitation occurs due to the transition of the pH of the medium to the neutral region. Consequently, the process of extracting gold with a chloride-hypochlorite solution must take place in an acidic environment.

Experimental part

Based on the analysis of scientific sources, a chlorine-containing solution of the following composition was selected for experimental work on the leaching of associated useful components:

$\text{Ca}(\text{ClO})_2 + \text{HCl}_{(c)}$ (hydrochloric acid with calcium hypochlorite), pH = 3.00.

Laboratory experimental work on agitational leaching was carried out on samples of core material from ores of the "Semizbay" deposit from the supra-ore, ore and sub-ore intervals.

After agitational leaching of ores, the productive solutions were analyzed to determine the concentration of associated elements by the atomic absorption method and are presented in Table 1.

According to the data obtained, the highest yield of components into solution was achieved in the ore interval. Iron concentration - 514.80 mg/dm³, aluminum - 148.81 mg/dm³, scandium - 0.068 mg/dm³, lanthanum - 0.23 mg/dm³.

Recovery of gold (Au) in pooled technological samples.

Studies to determine the content of gold in technological samples were carried out in the laboratory "Technologies for the hydrocarbon and mining and metallurgical sectors and related service industries" of JSC "IMiO" in Almaty. Analyzes in solutions were performed according to the method (MVI reg. No. KZ 07.00.01996-2014) on a Varian AA240 atomic absorption spectrometer and the assay method was used to determine gold in core samples. The results of analyzes of

Table 1 - Concentration of accompanying elements of technological solutions

No.	No. samples	Fe _{total} , mg/dm ³	Al, mg/dm ³	La, mg/dm ³	Sc, mg/dm ³	Leaching solution concentration, g/l	Rock interval
1	AP-4-1(C)	27,79	20,74	0,063	0,00095	12	Supra-sternum interval
2	AP-5-1(C)	71,84	71,98	0,10	0,047		
3	AP-6-1(C)	514,80	50,34	0,14	0,031		
4	AP-4-2(C)	243,98	72,82	0,13	0,046	24	Ore interval
5	AP-5-2(C)	446,79	148,81	0,23	0,068		
6	AP-6-2(C)	133,79	38,48	0,077	0,021		
7	AP-4-3(C)	1,19	0,64	0,0081	0,00088	48	Breast interval
8	AP-5-3(C)	0,02	14,26	0,035	0,0013		
9	AP-6-3(C)	0,020	2,26	0,023	0,0014		

Table 2 - The result of the chemical analysis of prefabricated core samples by the assay method for gold

No.	No. samples	Au g/t	Interval
1	A-6-1(C)	0,34	Supra-sternum
2	A-6-2(C)	0,34	Ore
3	A-6-3(C)	0,34	Breast

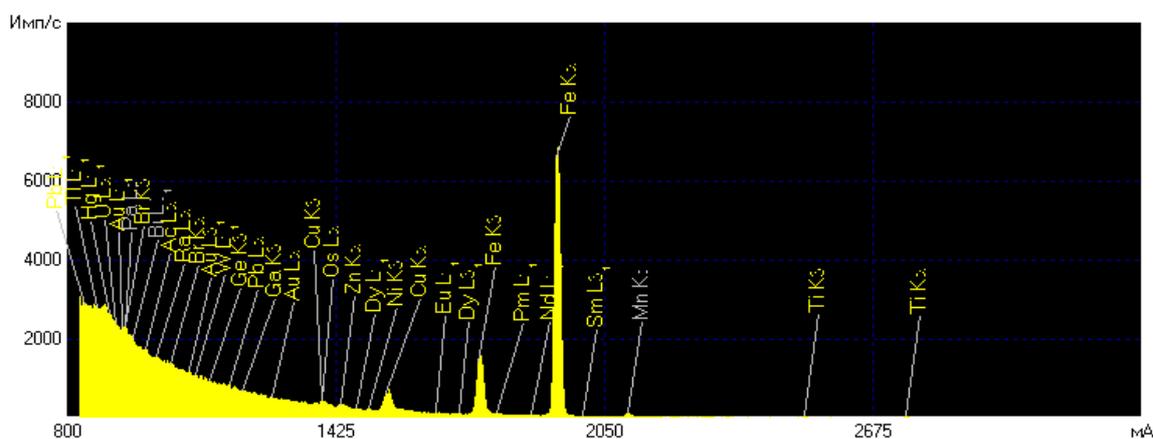
Table 3 - Comparison of gold recovery from ore samples at different concentrations

No.	No. samples	Au mg / dm ³	Leaching solution concentration, g / l
1	A-6-1(C)	0,006	12 (Supra-sternum)
2	A-6-2(C)	0,0167	24 (Ore interval)
3	A-6-3(C)	0,046	48 (Breast spacing)

technological samples for gold are presented in Tables 2 and 3.

The results of X-ray phase analysis are shown in Figure 1. In the range from 800 to 2050 nm, the decomposition spectrum exhibits pronounced fluctuations of the main peaks of uranium - U, iron-Fe, copper-Cu, manganese-Mn, zinc-Zn. Also in the decomposition spectrum there are vibrations of rare earth elements such as osmium-Os, rhenium-Re, neodymium-Nd, actinium-Ac, scandium-Sc, cesium-Ce, bismuth-Bi, etc. It is worth noting that the decomposition spectra contain spectral lines of mercury-Hg and implicit vibrations of gold-Au.

With the formation of uranium ores in chemical composition, sulfide minerals arise along with which mercury is formed, since they are genetically related in chemical nature. Mercury, in turn, forms compounds with gold in the amalgamation reaction. Therefore, the presence of implicit reflections of gold and pronounced spectra of mercury indicates the probable finding of gold.

**Figure 1** - Results of X-ray phase analysis of a core sample

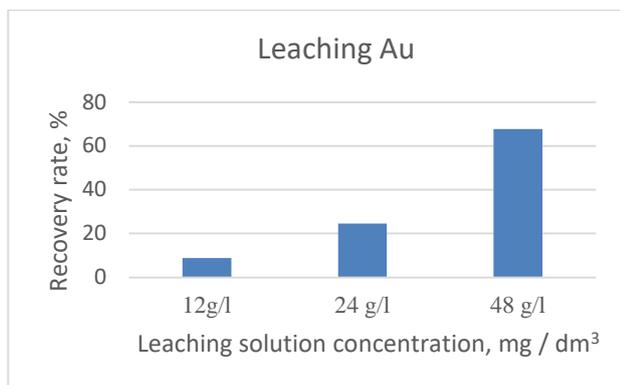


Figure 2 - The degree of extraction of Au during agitational leaching with a CaClO solution with the introduction of oxidants at various concentrations

The Au recovery is shown in Figure 2. The result obtained characterizes a solution of the composition HCl + CaClO + H₂O with a concentration of 48 g/l as more effective for Au than a solution with a concentration of 24 g/l and 12 g/l. The recovery of Au at a concentration of 48 g/l reached 67%.

Conclusions

The laboratory and experimental work on agitational leaching on samples of core material from ores of the Semizbay deposit of the supra-ore,

ore and sub-ore intervals showed that a chlorine-containing solution of the composition Ca (ClO)₂+ HCl_(c) (hydrochloric acid with calcium hypochlorite) at pH = 3.00.

The highest gold yield into solution was achieved in the under-ore interval. The gold recovery rate is 67%. The highest yield of accompanying components is observed in the ore interval. The concentration of iron - 514.80 mg/dm³, aluminum - 148.81 mg/dm³, scandium - 0.068 mg/dm³, lanthanum - 0.23 mg/dm³, which is possibly a consequence of the effect of acid treatment in the extraction of uranium.

To date, the use of the method of leaching with calcium hypochlorite in combination with hydrochloric acid has not found application in industry for the extraction of gold on an industrial scale. In this work, the experiments were carried out directly on the ore material and the result was achieved allowing the application of this method on an industrial scale.

Thus, in-situ leaching of spent uranium deposits for the extraction of associated useful components is a promising area of research.

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

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Уран кен орындарының пайдаланылған кендерінен ілеспе пайдалы компоненттерді өндіру мақсатында құрамында хлор бар шаймалайтын ерітінділерді пайдаланудың клешегі

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ТҮЙІНДЕМЕ

Жұмыс уран кеніштерінде ілеспе пайдалы компоненттерді қосымша алу есебінен өндірісті әртараптандыруға бағытталған. Жүргізілетін жұмыстың ерекшелігі ілеспе пайдалы компоненттерді өндіру үшін қолданыстағы өндірістік инфрақұрылымды пайдалана отырып, жұмыс істеп тұрған уран кеніштерінде пайдаланылған блоктарды қосымша қайта өңдеуден тұрады. Жерасты шаймалау технологиясы уран кен орындары үшін жақсы дамыған. Ілеспе пайдалы компоненттерді шаймалау уранды шаймалаудан қолданылатын реагенттер бойынша ғана ерекшеленеді және олар жер асты – ұңғымалық шаймалау әдісімен түбегейлі ұқсас. Құрамында ≤ 1 г/т бар ілеспе компоненттер болса да, 0,1 г/т дейін өндіріс үнемді болуы мүмкін. Кен орындарының пайдаланылған блоктарында уран кеніштерінің дайын инфрақұрылымын пайдаланудан

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келешекте оң экономикалық рентабельділікті күтуге мүмкіндік береді.

Түйін сөздер: уран кеніштері, ілеспе бағалы металдар, ілеспе пайдалы компоненттер, жер асты ұңғылап шаймалау, өнімді ерітінді, хлорлы ерітінділер.

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Перспективы использования хлор содержащих выщелачивающих растворов с целью добычи попутных полезных компонентов из отработанных руд урановых месторождений

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АННОТАЦИЯ

Работа нацелена на диверсификацию производства за счет дополнительного извлечения попутных полезных компонентов на урановых рудниках. Особенность проводимой работы состоит в дополнительной переработке отработанных блоков на действующих урановых рудниках с использованием существующей производственной инфраструктуры для добычи попутных полезных компонентов. Технология подземного выщелачивания хорошо отработана для урановых месторождений. Выщелачивание попутных полезных компонентов отличается от выщелачивания урана только по используемым реагентам, и они принципиально схожи методом подземно – скважинного выщелачивания. Даже при наличии в ураноносных песках попутных компонентов с содержанием ≤ 1 г/т, вплоть до 0,1 г/т производство может быть рентабельно. Использование готовой инфраструктуры урановых рудников на отработанных блоках месторождений позволяет ожидать положительную экономическую рентабельность в перспективе.

Ключевые слова: урановые рудники, попутные ценные металлы, попутные полезные компоненты, подземное скважинное выщелачивание, хлорсодержащие растворы.

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Pitting resistance evaluation of ternary Ni-Cr-Mo alloys in flue gas environment

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ABSTRACT

After the appearance of pitting corrosion, the corrosion rate reaches very high values, which leads to a deterioration in the quality of the product in a short time. It may happen that the pitting does not continue its penetrating effect: if there are no necessary conditions for its growth, a pitting of greater activity is not formed, which will absorb all the current supplied from the area surrounding the cathode. Results of potentiodynamic investigations of four Ni-base alloys are presented. The tests were conducted in 1 percent sulphuric acid, containing 0.2 percent chlorides at temperature 353K. Gravimetric test, performed in the same conditions, revealed excellent properties of alloy signed A3. Pitting corrosion of alloy A4 at the test conditions after long exposure at 353K was observed and was confirmed by the applied tests. The multiple anodic polarization (MAP) method is proposed to control alloys' susceptibility to pitting corrosion.

Keywords: pitting, alloy, anodic polarization.

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Introduction

High performance nickel alloys have been applied during the years at critical zones of flue gas desulphurization (FGD) units. Among them alloys A1 and A2 have a number years of proven service, alloy A3 is the newest one with superior corrosion resistance and nitrogen enhanced alloy A4 presents. acidic corrosion resistance with reduced cost [1-3]. The composition of the alloys is shown in table 1.

Table 1 - Composition of investigated alloys

	Ni	Cr	Mo	W	Si	C	Fe
(A1)	57,5	15,85	16,15	3,6	0,05	0,004	5,70
(A2)	66,6	15,75	15,70	-	0,04	0,003	1,10
(A3)	59,0	22,50	15,90	-	0,02	0,002	0,23
(A4)	31,0	26,60	6,30	-	0,04	0,008	bal

There has been short experience with alloy A3 FGD applications mainly in the USA but not much has been reported on alloy A4. Nickel super alloys have been used for lime / limestone FGD systems not only for scrubbers but also at critical locations with more aggressive environments, such as out let ducts, repeaters, stacks and dampers Failure of an alloy occurs usually due to pitting corrosion, but also general corrosion, crevice corrosion, erosion n- corrosion or stress corrosion cracking may be involved.

Lately there has been some doubt emphasized on the differences of alloys properties when laboratory tests and field FGD practice has been considered. It was also stated that in diluted sulfuric-hydrochloric acid mixtures the resistance of alloys depends on the ratio of both acids. The high Mo alloy A1 has been announced to be usually superior to alloy C-22 in such an environment [4-7].

Experimental part

The alloy samples were supplied by one of the world best producer of Ni-base alloys and used in delivery condition for tests. They had plate shapes. At least 2 samples having dimensions 35 x 100 mm were used for corrosion tests. The exposure was carried out in 1 % H₂SO₄ (pH 1) solution at 353±2K. The test solution and the elevated exposure temperature simulated corrosion conditions of absorber upper zones, outlet ducts, reheat mixing zones and stacks in FGD plants. The solution formula was chosen from a number of electrolytes used for laboratory experiments simulating chosen FGD conditions. The polarizations were carried out using GAMRY INSTRUMENTS card for DC electrochemical measurements. Passive properties of alloys were checked by means of potentiokinetic standard anodic polarization (SAP). Resistance of alloys against pitting corrosion was investigated by means of cyclic polarization (CP) and five anodic polarizations finished with return polarization (MAP). Fifteen minutes break was used after each single anodic polarization within MAP had been finished. Each anodic polarization started from the corrosion potential. The potential scan rate was 10 mV/60s. A saturated calomel electrode was used as a reference.

The anodic polarization was performed from the corrosion potential until the current density achieved a value of about 1 mA/cm² for CP at that point the polarization direction was reversed. A reversed polarization was finished when the current density was close to the zero value. The weight loss

was determined after corrosion exposure carried out in glass vessels with air coolers situated in a sand bath. A scale on alloy A4 was removed by boiling in an alkaline solution with zinc dust. A weight change checked with unexposed sample showed no necessity for corrections. Pitting corrosion photographs of alloy A4 were taken using an optical microscope [8-10].

Results and discussion

From the SAP carried out at 353 K (figure 1, a-d) one can deduce that both A1 and A2 alloys behaviour was similar at these conditions and their passive state current was higher compared to alloy A3. At the end of the return polarization the potential of alloy A3 and alloy A4 was much more noble than the corrosion potential and this must be connected with the character of passive films. Such phenomena were not registered in the case of A1 and A2 alloys [11-13].

After MAP a high corrosion current was registered for alloy A4. Nearly no change of alloy A1 cyclic polarization curves was found after MAP (Fig.2 A, B). Circular small pits in the case of alloy A4 were observed after the test. The breakdown of the passive film occurs during the dynamic process of its growing. The pit formation depends probably on different phases in the alloy, like on the composition and morphology of the passive film. No pit was displayed when the alloy A4 sample was kept in the, transpassive state for the time equivalent to the MAP test period.

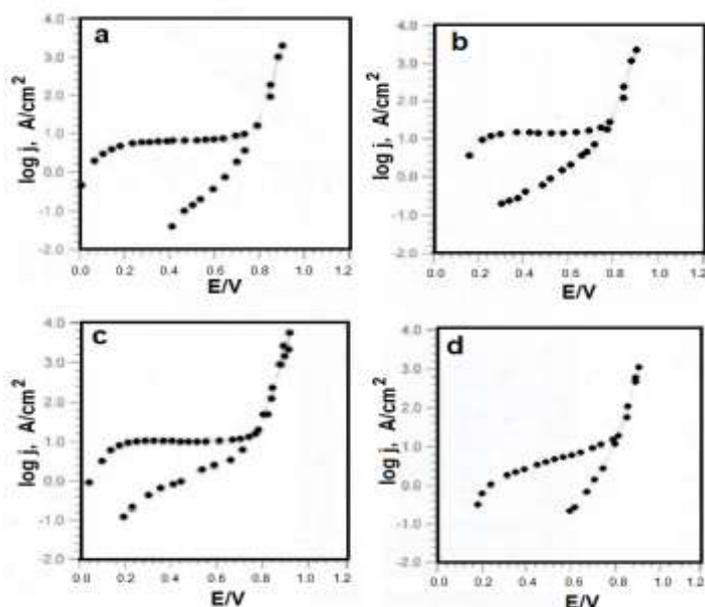


Figure 1 - Potentiokinetic anodic polarization of Ni-alloys: a - A1, b - A2, c - A3, d - A4

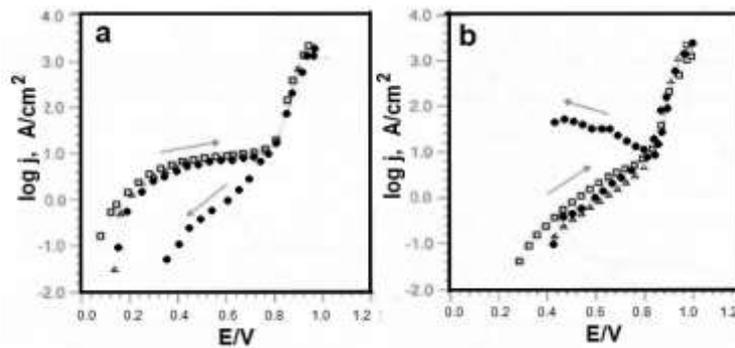


Figure 2 - Multiple potentiokinetic polarization (MAP) of Ni-alloys: a - A1, b - A4

Gravimetric test results after an exposure at 298 K gives an impression about good performance of alloy A4 in comparison with others. This has been confirmed after 21 days of exposure at 353 K because alloy A4 seems to be better than A1 and A2 alloys.

Nevertheless, when a yellow deposit was removed from the alloy A4 sample after 280 days of exposure the lowest durability of that alloy was demonstrated. Alloy A3 is least sensitive to the acidic solution in all gravimetric tests.

Alloy A1 is less susceptible to dissolution than alloy A2. The passive layer durability was controlled during long term corrosion exposure in the test solution at 353 K. No pitting corrosion was observed for high Mo alloys (A1, A2, A3) due to their high pitting resistance equivalent.

Pitting corrosion was observed with the naked eye on the surface of alloy A4 after 280 days of exposure [14-15]. It is obvious that the nitrogen content is not high enough to balance lower concentration of molybdenum in this alloy. The passive layer formed is not resistant enough to the environment, possibly due to passive film composition or defects.

The problem has to be studied more for an explanation. Mainly small diameter pits at the alloy surface could be seen, sometimes with caverns under the passive layer.

Conclusions

The alloy 59 proved its best corrosion resistance compared to C-276, C4 and 31 alloys in 1% sulfuric-hydrochloric (0,2%Cl-) acid solution simulating a chosen FGD environment at 353 K.

In such an environment pitting corrosion of alloy 31 occurs after a quite long incubation time. Alloy 31 demonstrates a high tendency to passivation in the test environment forming a protective layer with high dielectric properties. Nevertheless, the passive film cannot survive for a long time without a breakdown in the test conditions. The multiple potentiokinetic anodic polarization finished with cyclic polarization (MAP) can be applied to find the sensitivity of an alloy to pitting corrosion. There are limitations when short tests like cyclic polarization are applied to predict pitting corrosion of high performance nickel alloys.

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

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Түтін газдарында Ni-Cr-Mo үштік қорытпалардың нүктелік коррозияға төзімділігін бағалау

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ТҮЙІНДЕМЕ

Нүктелік коррозия пайда болғаннан кейін коррозия өте жылдам жүреді, бұл өнім сапасының қысқа мерзімде нашарлауына әкеледі. Питтинг өзінің ену әрекетін келесі жағдайларда жалғастырмауы мүмкін: оның өсуіне қажетті жағдайлар болмағанда катодта қоршаған аймақтан келетін барлық тоқты сіңіретін үлкен белсенділік пайда болмайды. Жұмыста Ni негізіндегі төрт қорытпаның потенциодинамикалық зерттеулерінің нәтижелері келтірілген. Сынақтар 0,2% хлоридтен тұратын 1% күкірт қышқылында 353К температурада жүргізілді. Сол жағдайларда жүргізілген гравиметриялық сынақтар А3 қорытпасының өте жақсы қасиеттерін көрсетті. 353К-де ұзақ жүргізілген сынақтарда А4 қорытпасының нүктелік коррозиясы байқалды және қолданылған сынақтармен расталды. Қорытпалардың нүктелік коррозияға сезімталдығын бақылау үшін көп анодты поляризация (MAP) әдісі ұсынылды.

Түйін сөздер: қорытпа, питтинг, анодты поляризация.

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Оценка устойчивости к питтингу тройных сплавов Ni-Cr-Mo в среде ДЫМОВЫХ ГАЗОВ

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АННОТАЦИЯ

После появления точечной коррозии скорость коррозии достигает очень высоких значений, что в короткие сроки приводит к ухудшению качества изделия. Может случиться так, что питтинг не продолжит свое проникающее действие: если нет необходимых условий для его роста, не образуется питтинг большей активности, который поглотит весь ток, подаваемый из области, окружающей катод. Представлены результаты потенциодинамических исследований четырех сплавов на основе Ni. Испытания проводились в 1-процентной серной кислоте, содержащей 0,2 процента хлоридов, при температуре 353 К. Гравиметрические испытания, проведенные в тех же условиях, показали отличные свойства сплава, подписанного А3. Наблюдалась точечная коррозия сплава А4 в условиях испытаний после длительной выдержки при 353 К и была подтверждена примененными испытаниями. Предложен метод множественной анодной поляризации (MAP) для контроля восприимчивости сплавов к точечной коррозии.

Ключевые слова: питтинг, сплав, анодная поляризация.

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Horizontal wells as a means of intensification of oil production

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ABSTRACT

Numerous experimental and field studies have established that during the development of oil and gas fields, there are deformations of rocks that occur due to changes in reservoir pressure. It is established that with a drop in reservoir pressure, the volume of the pore space of the formation decreases due to the elastic expansion of the rock grains and an increase in compressive forces transmitted to the skeleton from the masses of the overlying rocks. As a result, there is a change in the deformation processes in the porous medium, accompanied by a decrease in its porosity and permeability, and a more significant change, compared with the porosity of the formation, is the permeability under one and the same pressure change. The manifestation of these anomalies in reservoir conditions, which cause nonlinear effects, can significantly affect the entire process of reservoir development and lead to various qualitative and quantitative discrepancies between the observed facts and the indicators that were calculated.

Keywords: horizontal wells, productive formation, drilling, horizontal trunk.

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Introduction

The search for ways to solve the problem of meeting the public's need to increase the productivity of each of the drilled wells has always been in many directions, starting from the correct choice of the well laying point, preserving and improving the permeability of rocks in the bottom-hole zone of the wellbore, developing methods of influencing the productive reservoir itself, creating effective oil-displacing agents and methods for regulating their movement through productive reservoirs, etc.

Each direction, as well as their rational combination, gave a technical effect in the form of an increase in well productivity, but in many cases this increase was insufficient to ensure an economically acceptable profitability of the methods used.

As is known, the main directions of intensification of the development of oil and gas fields are to increase the pressure gradient in the

reservoir using the most intensive methods of maintaining reservoir pressure, as well as to reduce filtration resistances in the bottom-hole zones of production and injection wells.

Along with such methods as "hydraulic fracturing" and various physico-chemical methods of processing bottom-hole zones of wells, the "method of reducing filtration resistances" in bottom-hole zones of wells by drilling with an increased surface of opening the productive reservoir has great opportunities. Such wells include inclined-directional (NNS), horizontal (GS) and branched-horizontal wells (CSG).

For a long time, the idea of increasing the productivity of wells by significantly increasing the contact area of the borehole with the rocks of the productive formation did not receive its development. The first attempts to implement it were made in the former USSR back in 1937 at the Yarega field [1]. However, the pre-war situation and the lack of appropriate technical means and technologies, which caused the high cost of drilling

horizontal wells, led to the suspension of work in this direction. The discovery of highly productive fields in Western Siberia has again reduced interest in the development of deposits by horizontal wells, which was resumed in the 50s of the last century.

However, the global trend observed in recent decades of a significant increase in the share of proven oil reserves in low-yield reservoirs, the development of which by vertical wells is obviously unprofitable, has again brought to the fore the need for practical implementation of ensuring a large area of contact between the wellbore and the productive reservoir.

Currently, the development of oil and gas fields using inclined and horizontal wells is relevant and is considered one of the most important recent achievements in the oil and gas industry. Horizontal drilling, in the world practice of oil and gas production, has become a standard technology and is considered an important method of increasing oil and gas production. In this regard, there is an increased interest in the study of issues related to the use of horizontal and branched-horizontal wells in the development of natural hydrocarbon deposits all over the world.

Horizontal wells are used in depleted productive formations, as well as in fields with difficult-to-recover oil reserves, when widespread methods of developing oil and gas fields do not allow achieving a high level of oil production. The development of oil fields by horizontal wells is a new version of the technology for increasing productivity, as well as a new method of development, gradually replacing the methods of operation by vertical wells. However, at present, methods for predicting production, designing and optimizing systems for developing deposits opened by horizontal and branched-horizontal wells are not sufficiently developed.

Currently, horizontal well drilling is successfully used in most oil-producing countries of the world. It has received special development in the USA, Canada, France, Denmark, Norway and other countries.

A horizontal shaft running along the productive horizon for tens and hundreds of meters connects with each other the areas of heterogeneous, low-permeable, poorly drained, cavernous and fractured sections of the formation that were not previously involved in development. This technique not only increases the filtration rate in the inter-well space, but also increases the degree of reservoir coverage, increasing the final oil recovery. Most often, horizontal trunks are used when

cutting the side trunk. The cutting of the side trunk is this new life of a low-yield well.

Currently, production workers and scientists have accumulated a huge statistical material based on the experience of working horizontal wells at various fields. The length of the horizontal section of wells varies from 100-200 m to 1.4 km and depends on the skill of the drilling company and the equipment used. The practice of directional drilling of horizontal wells is currently owned by several drilling foreign companies (Gorvel, Exxon, Amoko, Philips, etc.) and enterprises in the former USSR.

Therefore, the process of creating and rapidly improving the technique and technology of drilling horizontal wells, which led to a sharp decrease in their cost, cannot be considered spontaneous, but should be considered as a natural consequence of the need that has arisen. Demand, as always, caused supply and, in turn, stimulated the development of research on the quantitative refinement of known and identification of new opportunities for using wells with horizontal sections of the trunk of various lengths and shapes.

A huge number of publications devoted to the study of various operational parameters of horizontal wells have appeared. To date, a significantly higher productivity of horizontal wells compared to vertical wells, with other equal conditions, is a fact proven theoretically and confirmed by practice.

Based on the conducted research and accumulated practical experience, it is now generally accepted that the greatest effect from using the capabilities of horizontal wells can be useful at operational facilities with the following characteristics [2]:

- sub-gas objects and objects with plantar water;
- collectors with vertical fracturing;
- deposits of high-viscosity oils and bitumen;
- offshore and hard-to-reach productive zones;
- during the operation of gas deposits;
- when using methods to increase oil recovery, especially thermal methods;
- at the viscosity of oil ($\mu > 10$ MPa.c);
- low-efficiency mode of reservoir development;
- the effective thickness of the formation is at least 3m;
- low permeability of collectors ($k < 0.1$ mm²);
- large residual recoverable reserves.

Experimental part and discussion of results

In accordance with the chronology of the study of this issue, we will first review the works

published in the former USSR on the topic related to horizontal wells.

A wide range of studies is devoted to the study of various operational parameters of HS. A number of theoretical and experimental works are devoted to the issues of steady and unsteady fluid inflow to horizontal wells. Let's focus on some of the results of the main studies.

One of the first works on determining the productivity of horizontal oil wells is the work of I. A. Charny on the inflow of incompressible fluid to a horizontal trunk, asymmetrically located relative to the supply circuits with distances R_{k1} , R_{k2} and contour pressures P_{k1} , P_{k2} , respectively. Under the conditions that the distance from the well to the reservoir boundary H is greater than or equal to the thickness h , i.e. $H \geq h$. For the case when the horizontal trunk is located symmetrically to the power supply circuit, I. A. Charny obtained the following expression for determining the flow rate of the HS:

$$Q = \frac{2\pi k(P_k - P_c)}{\mu \left[\frac{2\pi H}{h} + \ln \frac{h}{2\pi R_c} \right]}, \quad (1)$$

Where k is the reservoir permeability, P_k , P_c is the pressure on the supply circuit and at the bottom of the well; μ is the oil viscosity; H is the distance from the well to the reservoir boundary; h is the thickness of the reservoir; R_c is the radius of the well.

Later, A.M. Pirverdyan studied a similar problem for the case when one of the boundaries is closec (impenetrable), for example, at $R_k = R_{k1}$, and the pressure P_{k2} is set at the second boundary $R_k = R_{k2}$. Taking into account this condition, the oil inflow to the horizontal trunk is presented in the form:

$$Q = \frac{2\pi k(P_k - P_c)}{\mu \left[\frac{2\pi k}{h} + \ln \frac{h}{2\pi R_c} + \frac{1}{2} \ln \frac{2}{1 - \cos \frac{\pi(2a - R_c)}{h}} \right]}, \quad (2)$$

Where a is the distance from the axis of the horizontal trunk to the roof or the sole of the formation. With a symmetrical arrangement of the horizontal trunk in thickness $a=h/2$.

The theoretical studies of I. A. Charny and A.M. Pirverdyan are devoted to the issues of fluid inflow to horizontal wells of infinite length in layers of finite thickness. If we use these formulas to determine the flow rate of horizontal wells of finite length, the result will be underestimated, and the error at different well lengths and reservoir thicknesses cannot be strictly determined. In

addition, the obtained formulas are suitable only for a band-shaped deposit.

The possibility of obtaining a solution to the oil inflow by dividing the flow into two zones in the horizontal and vertical planes is also used in the work of S. D. Joshi. With a symmetrical arrangement of the horizontal barrel in thickness, the formula for determining the flow rate is proposed as:

$$Q = \frac{2\pi k h \Delta P}{\mu B \left[\ln \left(A + \frac{\sqrt{A^2 - (L_r/2)^2}}{L_r/2} \right) + \frac{h}{L_r} \ln \frac{h}{2R_c} \right]}, \quad (3)$$

Where B is the volume coefficient of oil; L_r is the length of the horizontal section of the trunk; L_r h and $L_r/20.9 R$. A is the half of the major axis of the ellipse taken as the shape of the drainage zone by a horizontal well determined by the formula:

$$A = \frac{L_r}{2} \left[\frac{1}{2} + \sqrt{\frac{1}{4} + \left(\frac{2R_k}{L_r} \right)^4} \right]^{0.5}, \quad (4)$$

For $L_r h$, the formula of G. I. Renald and J. M. Dupug, which has the form, is more accurate for determining the oil flow rate:

$$Q = \frac{2\pi k h \Delta P}{\mu B \left[\cos h^{-1}(X) + \frac{h}{L_r} \ln \frac{h}{2\pi R_c} \right]}, \quad (5)$$

where $X=24A/L_r$

In the works of 3.S. Aliev et al., formulas for determining the flow rate of an oil horizontal well that has completely opened up strip-shaped homogeneous isotropic and anisotropic formations are proposed. According to this method, it is assumed that the filtration region consists of two zones, in the first of which the layer thickness is considered a function of the radius, i.e. $h=h(r)$ and varies according to the parabola. Under the accepted conditions, the oil flow rate of a horizontal well that has opened an isotropic reservoir is proposed to be determined by the formula [4-6]:

$$Q = \frac{k L_r \Delta P}{\mu B} \frac{1}{\left[1 + \frac{2R_c}{h-2R_c} \ln \frac{2R_c}{h} \right] + \frac{R_k - (h-2R_c)}{2h}}, \quad (6)$$

If the horizontal borehole is located asymmetrically in thickness, the well flow rate will be determined by the sum of the flow rates from

the upper and lower zones, according to the formula:

$$Q = \frac{kL_r \Delta P}{\mu B} \frac{1}{\frac{2}{h_1} \left[h_1 + R_c \ln \frac{R_c}{h_1 + R_c} \right] + \frac{R_k h_1}{(h_1 + R_c)} + \frac{2}{h_2} \left[h_2 + R_c \ln \frac{R_c}{h_2 + R_c} \right] + \frac{R_k h_2}{(h_2 + R_c)}}, \quad (7)$$

where $h_1 = (h-h_2)$ is R_c -the thickness of the formation of the i -th zone minus the radius of the well. Accordingly, for an anisotropic reservoir, taking into account the anisotropy parameter, the oil flow rate is determined by the formula:

$$Q = \frac{2kL_r \Delta P}{\mu B} \frac{1}{\left[\frac{1}{\vartheta h_i} \left(\vartheta h_i + R_c \ln \frac{R_c}{R_c + \vartheta h_i} \right) \right] + \frac{R_k - \vartheta h_i}{R_c + \vartheta h_i}}, \quad (8)$$

where ϑ is the anisotropy parameter determined from the equality: $\vartheta = v(k_{\text{ver}}/k_{\text{pore}})$.

The problem of fluid flow to a well of finite length in an unlimited space and to a well arbitrarily located in a half-space, as well as to a system of similar wells, was solved by P. Ya. Polubarinova-Kochina. The results of these studies are valid only for the case when the reservoir capacity is many times greater than the length of the borehole, otherwise the obtained formulas cannot be used.

The problem of the steady flow of liquid to horizontal and inclined wells was also solved experimentally. The greatest interest in this direction is the work of V. I. Shurov, which was carried out on an electrolytic model [3]. The processing of the experimental results is based on the Dupuy formula, in the denominator of which the term is introduced in the form of an additional parameter "C", which characterizes the value of the hydrodynamic perfection of the well. The value of the parameter "C" is determined by comparing the flow rates of horizontal and inclined wells with the flow rates of vertical wells for different values of lengths, diameters of wells, reservoir capacities and angles of inclination of trunks in the formation. The value of the parameter "C" has a negative value. This indicates that the flow rate of inclined and horizontal wells, all other things being equal, is higher than the flow rate of vertical wells. The results are summarized in tables, on the basis of which graphs are constructed. However, a strict analytical dependence was not obtained. Each specific case requires its own table or series of graphs, on the basis of which calculations can be made. This is the main drawback of V. I. Shurov's work.

The formulas obtained by V. P. Merkulov are semi-empirical. They do not require the use of any graphs or tables to calculate the debits [4]. However, there are certain limits of applicability found on the basis of experimental data. It is impossible to judge the errors of calculations carried out according to the proposed formulas within unspecified limits.

In the works of American researchers, results similar to the results of the works of V. I. Shurov and V. P. Merkulov were obtained, although they were carried out much later. In the work of Yu. P. Borisov et al. [5, 6] for homogeneous and layered formations, when the permeability in the vertical direction is zero, and in the horizontal direction $K = \text{const}$, under a rigid water pressure regime, analytical dependences are obtained for determining the flow of liquid to single horizontal wells of finite length, to inclined and multi-hole wells and to their systems in circular and strip deposits.

When solving these problems, the method of filtration resistances is used. A comparison of the calculation results with the results of electrolytic modeling showed a satisfactory coincidence. In addition, [7] a general hydrodynamic theory of the inflow of a homogeneous liquid in a horizontal infinite reservoir of constant thickness is proposed. In the solution, the method of constructing the Newtonian potential of a point source acting in a reservoir of limited thickness was used. However, the solutions obtained in a strict analytical formulation are very complex and difficult to use even taking into account the capabilities of computer technology. The lack of numerical results for exact formulas did not allow us to assess the reliability of the proposed approximate solutions.

In the work of G. A. Razumov, a study of horizontal wells of finite length and their radial systems in the conditions of an aquifer pressure reservoir of limited capacity with a rectilinear supply circuit is presented [8]. When the approximate calculation formulas are derived, the theoretical linear flow with a constant intensity along the length q is replaced by a "filter" having the shape of the equipotential closest to the well in the form of an ellipsoid of rotation. This method is used for horizontal wells by P. Ya. Polubarinova-Kochina, and before it was used by N. K. Girinsky – for vertical well [9]. The transition from an imaginary equipotential filter to a real tubular well with a radius $r = r_c$ can be performed by equating the areas of the water intake surface of an ellipsoid

with a small semi-axis "b" and a cylinder of equal length $b=1.415 r_c$.

The issues of fluid inflow to a horizontal perfect well, taking into account the influence of the supply circuit, the permeability of the reservoir sole, the location of the filter relative to its roof and the non-stationary filtration, are studied in the works of M. A. Huseynzade. In the work it is indicated that, in relation to horizontal wells, the anisotropy of the formation should be taken into account [10]. The fact is that, as a rule, the vertical permeability is less than the horizontal one. And if for vertical perfect wells the anisotropy of the reservoir has absolutely no effect on the inflow, then for horizontal wells the influence of anisotropy becomes very significant. It is qualitatively clear that the anisotropy of the formation reduces the efficiency of its longitudinal opening. On the basis of what has been said in this work, studies of the flow of liquid to longitudinal (inclined, horizontal) wells along the reservoir under various filtration modes have been carried out.

The lack of accurate analytical solutions significantly complicates the task of establishing the applicability of existing approximate solutions in various conditions.

With this in mind, the paper [11] offers an exact analytical solution to the equation of three-dimensional fluid filtration for determining the productivity of horizontal wells. It is assumed that a limited band-shaped reservoir with an arbitrary thickness, homogeneous in permeability, is opened by a horizontal well with a filter length n and is operated with a constant flow rate q evenly distributed along this length. The roof and the sole of the formation are considered impenetrable. The reservoir under study has a power supply circuit, on which a constant pressure is maintained. In addition, it is assumed that the well can be replaced by a linear source located along its axis. A finite integral Fourier transform is applied to solve the problem. According to the obtained formulas, multivariate calculations were performed for the symmetrical and asymmetric placement of a horizontal well. At the same time, the influence on the filtration resistance of the place, degree and symmetry of the opening by a horizontal well of a homogeneous reservoir, according to reservoir properties, was studied. Further, the same problem is generalized to take into account the anisotropy of the reservoir in terms of permeability [12].

The issues of operation of horizontal wells with gas inflow are investigated in [13]. In this work, it is indicated that with the same depression on the

reservoir, the flow rates of horizontal wells are several times higher than the productivity of vertical ones due to the increased interval of gas inflow. Therefore, for the most accurate justification of the technological mode of operation of horizontal wells, it is necessary to take into account the quadratic law of gas filtration, otherwise significant errors may occur in determining their performance indicators.

Next, an approximate method for schematizing the process of gas inflow to wells is considered. At the same time, in the bottom-hole zone of a horizontal well, a hyperbolic or parabolic dependence between the thickness of the formation and the distance from the well is taken and the equation of one-dimensional nonlinear gas filtration in a reservoir with a variable thickness is used, and plane-parallel filtration is considered outside this zone. This method of schematization of the gas inflow to the horizontal shaft under the conditions of the quadratic filtration law allows us to obtain simple analytical solutions to problems related to the determination of well performance indicators. Comparison of the results of calculations using the proposed method with the results of numerical modeling of three-dimensional non-stationary gas filtration showed their fairly good convergence. It was shown, in particular, that the determination of the well flow rate using the proposed approach can be carried out with an error not exceeding 4%.

Recently, a significant number of works related to the exploitation of fields, mainly oil, by horizontal wells have been published abroad.

In these publications, most of the authors used the results and conclusions obtained by Soviet scientists Yu. P. Borisov, V. P. Pilatovsky, etc. Among such works are the studies of D. K. Bodu, S. D. Dojoshi, J. Comba, A. S. Ode, D. Sparmin, R. Hagen, F. E. Kuchuk, A. E. Roza, R. Ragavan, D. E. Wilkinson, E. Ozkan, etc., [14, 15, 16] who proposed various methods of analytical and numerical solutions to problems of two - and three-dimensional unsteady filtration of compressible fluid to determine the productivity and interpretation of the results of the study of horizontal wells.

The paper [14] presents an analytical solution to the problems of pressure drop and recovery in a horizontal well. The three-dimensional equation of motion is solved by the method of integral transformations. For small, intermediate and large time values, where there are rectilinear sections on the pressure change curves, simplified formulas for

pressure are given. The validity of the method is demonstrated by comparing the results of numerical modeling with a similar analytical solution. The method recommended for the analysis of pressure drop and recovery is illustrated by practical examples. The method allows you to determine the characteristics of the reservoir, including permeability, skin factor and distance to the boundaries.

The study of special flow regimes in the process of an unsteady inflow to a horizontal well has been the object of a significant number of works in the modern literature. For example, this was done in for the Bombay field [17], where simultaneously measuring the pressure drop and flow rate made it possible to identify the modes of pseudo-radial flow at an early and late time, as well as linear flow during the transition period [18].

The analysis of these successive flow modes allows us to estimate the permeability of the anisotropic reservoir and the skin factor. The refined parameters obtained for the field example are compared with the results of extensive conventional studies for the same horizontal well [19].

The detected good agreement for horizontal permeability increases the confidence level for parameters such as vertical permeability and the actual skin factor.

In a mathematical model is given for calculating the pressure in an infinitely conducting horizontal well. At the same time, the following assumptions are made: the reservoir is horizontal, homogeneous and has a constant horizontal and vertical permeability, the product enters through a well represented by an I-linear source, the filtration mode is unsteady, the reservoir is limited by upper and lower impermeable boundaries, the pressure at an infinitely remote distance from the well remains constant and equal to the initial value. The analytical solution is found using the "instantaneous source theory" and the green function.

The work is devoted to the analysis of pressure recovery for horizontal wells in a real fractured formation [20]. A combination of analytical and numerical methods was used to conduct a consistent interpretation of the results of the well analysis, taking into account the possible double porosity of the reservoir [21].

In a method is given for interpreting the results of a study of horizontal wells in an unsteady mode (using the example of the Prudhoe Bay field in the USA). The complex geometry of the flow in a

horizontal well makes it difficult to analyze pressure recovery curves (KVD). The peculiarity lies in the fact that it is impossible to determine the parameters based on pressure and flow rate data for a short study time. It is necessary to get an inflow to the face and achieve an inflow under pressure, and then remove the KVD, which will allow you to determine the parameters accurately.

The work presents the results and a representative data set of a non-stationary study of a horizontal well on the area of the Austin Chalk field (USA). The data set shows the possibility of radial flow in an early period of time, strongly distorted by the storage effect (accumulation of fluid in the wellbore). This is followed by a well-developed period of linear inflow. The data are interpreted in terms of a pseudo-stationary model with double porosity and the range of changes in the permeability of cracks, the volume of pores and the value of the flow coefficient are determined [22, 23].

The partial differential equation describing the filtration of a liquid in a porous medium to a horizontal well is very complex. In its solution for the deposit is proposed. The solution is obtained by the method of separating variables. The slow convergence of the obtained solution is overcome by using certain simplifying formulas. A complex solution is reduced to a form that is convenient for calculating productivity. The form of the expression obtained for it is identical to the well-known expression for a vertical well.

Simple formulas are proposed for determining two parameters:

a) a geometric factor associated with anisotropy in permeability, the location of the well and the relative size of the drained volume;

b) the skin factor caused by the incompleteness of the opening and related to the length of the well.

A fairly general solution is obtained, which is still not accurate, for the most common cases the error does not exceed 3%.

Provides an analysis of pressure changes in a horizontal well or a branch of a vertical well in comparison with a vertical crack that completely opens the deposit. Two types of boundary conditions at the well are considered: constant inflow and infinite conductivity. Analytical expressions and dependencies for the pseudo-skinfactor are obtained.

It is indicated in that the analysis of pressure recovery curves in a well with a horizontal trunk in an unsteady mode should be carried out taking into account the measured inflow profiles, which makes

it possible to estimate the effective length of the horizontal trunk and specify the parameters characterizing the reservoir properties. A specific field example demonstrates the difficulties that arise when interpreting data on pressure recovery in an unsteady mode in a well with a horizontal trunk under constant boundary conditions.

It should be noted that in addition to the above-mentioned articles by foreign authors, there are still many works in Western oil journals devoted to solving both direct and inverse problems related to horizontal wells [24].

Later, various researchers (V. G. Griguletsky, A. Nikitin, A. P. Telkov, V. D. Lysenko, S. D. Joshi, M. Giger, etc.), based on various inflow modes obtained and proposed fairly simple analytic expressions for estimating the flow rates of single-phase wells located in the center of homogeneous layers with elliptical, circular and semi-distinct support circuits.

In the works [25] of M. N. Veliyev, the issues of fluid inflow to the GS battery in the three-dimensional region are considered. For the case when the number of wells in the battery is arbitrary, the problem is solved in an exact formulation and analytical dependencies are obtained in a very convenient form for conducting hydrodynamic calculations. The interference of vertical and horizontal wells was studied. The problem is solved: when vertical and horizontal wells are operated simultaneously in the reservoir. The influence of the distance between wells on the productivity of wells has been studied.

In our review, we touched only on the most important, in our opinion, studies.

Summing up the review done, we can note the following:

- horizontal wells are the most interesting topic discussed in the oil industry these days and have certain advantages over vertical wells, in terms of such parameters as crossing with a large number of faults, the efficiency of reservoir coverage and accelerating the increase in oil production;
- the productivity of a horizontal well in homogeneous non-fractured formations with single-phase filtration is higher than the productivity of a vertical well that has completely opened this formation, if the length of the horizontal trunk is greater than

$$h = \sqrt{\frac{K_z}{K\theta}}, \quad (9)$$

where h is the thickness of the formation, m ; and, respectively, the horizontal and vertical permeability of the formation, microns;

- horizontal wells drilled in a homogeneous naturally fractured formation with a fairly high conductivity of the crack system do not provide increased oil recovery and even accelerated reserve extraction;

- horizontal wells are able to provide increased final oil recovery when implementing a linear flooding mode, as well as in the case of a ring-shaped flooding;

- in the conditions of the manifestation of the effect of the formation of water or gas cones, horizontal wells provide much higher accumulated production (at least 3-4 times).

- in multiphase systems, the equations for the productivity coefficients of horizontal and vertical wells can only be used to estimate the ratio of these coefficients;

- in homogeneous reservoirs operating at depletion, horizontal wells in low-permeable reservoirs provide both higher flow rates and a significant increase in oil recovery, and in high-permeable wells, a significant increase in oil extraction with a moderate increase in final oil recovery;

- increased productivity at the same rate of selection allows one to maintain a reduced depression on the reservoir, contributing to a decrease in water or gas production, as well as significantly reduce the loss of gas condensate from gas in the near-water zone at gas condensate fields;

- in reservoirs with natural vertical fracturing, the recoverable volume of oil increases with the increase in the length of the horizontal trunk in the direction perpendicular to the orientation of the crack system, while reducing the duration of operation;

- reducing the length of the horizontal trunk or its location parallel to the crack system leads to a more significant reduction in oil recovery with a decrease in the permeability of the fractured rock skeleton;

- when developing homogeneous reservoirs by flooding with horizontal production and injection wells, oil production is noticeably accelerated. Throughout the entire period of operation, the accumulated oil production is always greater than during the development of vertical wells, but the water content of the products is higher. Therefore, the profitability of using this method of development may depend on additional costs.

Even this far from complete list of the results of hydrodynamic studies of fluid inflow to horizontal wells indicates that the use of horizontal wells is not only a means of increasing well productivity, but can be an important component of new field development systems (especially low-productivity ones), which allows significantly increasing the final oil recovery coefficients and reducing the time of field development.

Therefore, it is no accident that in recent years dozens of patents have been protected in the USA, Russia, Canada and other countries for systems for the development of hydrocarbon-containing deposits using both their own capabilities of horizontal wells and in combination with traditional methods of influencing formations (flooding, thermal methods, wave action, etc. physical and chemical methods). A comparative analysis, on average, of the economic indicators of the construction and operation of horizontal and vertical wells revealed that:

- GP debits increased from 2.5 (Russia) to 3-4 times (USA, Canada);
- the cost of construction is from 1.1-1.3 (USA, Canada) to 2 times (Russia) and higher;
- technological efficiency ranges from 50% (Russia) to 90% (USA, Canada);
- the profit rate from the introduction of HS was 50% (Russia), 160% (USA), 186% (Canada).

To date, more than 26,000 GS have been drilled in the world, more than 1300 in Russia, including half of them in Tatarstan and Bashkortostan. In Kazakhstan, drilling and development of GS is a promising direction and there are several fields where GS have been drilled.

More than 30 deposits containing industrial oil reserves have been identified on the Mangyshlak

Peninsula [26]. The largest of them-Uzen contains 75% of all oil reserves of the peninsula. The field was discovered in December 1961, and has been in industrial development since 1965. 25 productive horizons (I-XXV) have been identified in the field section. Productive horizons are represented by frequent interbedding of sand-siltstone and clay layers.

The horizons of the I-XII Cretaceous age are gas-bearing, the XIII-XVIII horizons of the Upper and Middle Jurassic age represent the main (>90%) floor of the oil and gas potential of the field. In some areas, the XIX-XXV horizons of the Lower Jurassic age are oil and gas-bearing.

The effective oil-saturated thickness of the horizons (layers) varies within 7-22m. The viscosity of oil is <10 MPa s, the values of permeability vary widely from 0.01-2 mm². Collectors are of the pore type. Oil reserves are 1.054 billion tons [27]. More than 60% of the initial balance oil reserves are concentrated in low-permeable reservoirs and belong to the category of hard-to-recover (table 1). The accumulated production is more than 300 million tons. Despite the long development time of the field, the degree of use of reserves does not exceed the value of 0.32.

Thus, it is established that the fields of the Atyrau region and the low-permeable oil zones of the Uzen field are promising objects for drilling horizontal wells [28, 29].

It should be noted that in the conditions of modern scientific and technological progress, when the technical possibility of drilling deep and ultra-deep wells has increased, there is a real possibility of involving deposits lying at great depths in the development. This leads to the urgent need for a comprehensive study of the flow processes of reservoir fluids and the construction of

Table 1 - The list of operational objects of deposits recommended for the introduction of horizontal wells

Deposit	Effective thickness, m		Dismemberment Kr		Permeability, mkm ²		Initial balance sheet reserves, thousand tons
	h	Gran.	Kp	wounds.	K	Gran.	
XIII	7,8		6,3		0,194	More than 60% of the initial balance oil reserves are concentrated in low-permeability (K ≤ 0.1 mkm ²) reservoirs	225,5
XIV	18	h _{min} >3 m	9,1	Kb>3	0,247		426,5

computational schemes for the development of deep-lying reservoirs (characterized by high reservoir pressures, fracturing and deformability), taking into account changes in physical properties. However, in deep-lying reservoirs, a change in the intra-pore pressure during operation often leads to the fact that the difference between the mountain and non-pore pressures reaches values sufficient to deform the skeleton of many rocks, reduce the number and diameter of open pores, which leads to a significant change in the capacitance and filtration characteristics of reservoir rocks [30].

Naturally, it should be expected that under these conditions, the nature of the flow of fluids to horizontal wells will differ for such in reservoirs lying at shallow depths. In this regard, there is a need to develop modeling of filtration processes in the conditions of development by horizontal wells of deep-lying deposits composed of fractured and deformable rocks.

A list of works devoted to the use of horizontal wells in the development of oil and gas fields can be found in [31].

Conclusions

Thus, it is established that the fields of the Atyrau region and the low-permeable oil zones of the Uzen field are promising objects for drilling horizontal wells.

A mathematical model and its solution for steady-state liquid filtration to CSG in a deformable porous medium are proposed, scientifically substantiated and implemented. The analysis of the derived dependence showed that the flow rate of a well in a deformable formation is less, respectively, than the flow rate of a well draining a non deformable formation ($\alpha=0$) with the same pressure drops and other equal characteristics of the formation. The rate of growth of the well flow rate slows down for multi-barrel horizontal wells, with an increase in the number of trunks.

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Көлденең ұңғымалар - мұнай өндіруді қарқындатудың құралы ретінде

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ТҮЙІНДЕМЕ

Көптеген эксперименттік және коммерциялық зерттеулер мұнай және газ кен орындарын игеру кезінде тау жыныстарының деформациясы бар екенін анықтады. Қойнауқаттық қысымның төмендеуімен қойнауқаттың кеуек кеңістігінің көлемі жыныс түйірлерінің серпімді кеңеюі және қаңқаға жоғары жатқан жыныстардың массасынан берілетін қысатын күштердің артуы салдарынан азаятыны анықталды. Нәтижесінде кеуекті ортадағы деформациялық процестердің өзгеруі оның кеуектілігі мен өткізгіштігінің төмендеуімен бірге жүреді, ал резервуардың кеуектілігімен салыстырғанда едәуір өзгеріс қысымның бірдей өзгеруімен өткізгіштікке ұшырайды. Сызықтық емес әсерлерді тудыратын осы ауытқулардың резервуарлық жағдайдағы көрінісі кен орнын игерудің бүкіл процесіне айтарлықтай әсер етуі мүмкін және байқалған фактілер мен есептелген көрсеткіштер арасындағы әр түрлі сапалық және сандық айырмашылықтарға әкелуі мүмкін.

Түйін сөздер: көлденең ұңғымалар, өнімді қабат, бұрғылау, көлденең оқпан.

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Горизонтальные скважины как средство интенсификации добычи нефти

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АННОТАЦИЯ

Многочисленными экспериментальными и промысловыми исследованиями установлено, что в процессе разработки нефтяных и газовых месторождений имеются деформации пород, происходящие вследствие изменения пластового давления. Установлено, что с падением пластового давления объём порового пространства пласта уменьшается вследствие упругого расширения зерен породы и возрастания сжимающих усилий, передающихся на скелет от масс вышележащих пород. В результате происходит изменение деформационных процессов в пористой среде, сопровождаемое снижением её пористости и проницаемости, причём более значительное изменение, по сравнению с пористостью пласта, претерпевает проницаемость при одном и том же изменении давления. Проявление в пластовых условиях указанных аномалий, вызывающие нелинейные эффекты, может значительно влиять на весь процесс разработки залежи и приводить к различным качественным и количественным расхождениям между наблюдаемыми фактами и теми показателями, которые рассчитывались по обычным методикам.

Ключевые слова: горизонтальные скважины, продуктивный пласт, бурение, горизонтальный ствол.

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Study of rare earth elements in the coals of the Shubarkol deposit

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ABSTRACT

The work studies mineralogical and geochemical features of the Jurassic coals of the Shubarkol deposit. The samples were examined using the method of scanning electron microscopy (SEM-EDX) Hitachi S-3400N, which was carried out at the Uranium Geology Research and Development Center at the Department of Geoecology and Geochemistry of TPU. Coal geochemistry was studied by instrumental neutron activation analysis (INAA) at the nuclear geochemical laboratory of the Department of Geoecology and Geochemistry of National Research Tomsk Polytechnic University (TPU). The choice of this object of study was determined by the tasks of research including the study of the patterns of accumulation of abnormal concentrations of REE, the effect of various factors of the geological environment on the levels of their accumulation in coals, as well as the conditions of its concentration and forms of occurrence in coals to expand the mineral resource base of Kazakhstan for rare earth elements. According to the results of scanning microscopic analysis, aluminosilicates, sulfides and sulfates with inclusions of microparticles of rare and rare earth elements were found in the composition of the Shubarkol deposit coals. According to the INNA results, abnormal concentrations of Sc, Ta, Nb, Hf, Zr, Ba, Sr, Ce and REE were found. Weathering processes led mainly to the loss and redistribution of REE in the coal seams of the Shubarkol deposit, which in turn led to increasing the content of rare earth elements from the bottom up the section. As a result of the action of multiple processes, increased concentrations of rare earth metals, mainly of the yttrium group, were formed. The absence of negative europium anomaly was determined, which confirms the original rocks composition peculiarity. The maximum contents of rare-earth metals are confined to weathered coals; for the medium-heavy group (Nd, PM, Sm, Eu), they are almost a hundredfold higher than the clarkite in the upper continental crust. The tenfold excess of the clarkite for elements from Gd to Lu was found in clayey sandstones and siltstones; for the rest of the rocks of the deposit the excess over the clarkite is significantly lower. It was found that the coals of the deposit belong to the H-type and L-type of REE distribution. During the formation of oxidized H-type coals, clayey matter of terrigenous ash predominated as a carrier of REE, while unoxidized L-type coals were formed with the introduction of REE into the coal accumulation basin mainly in the composition of clay minerals and LREE-phosphates. Here the main source of REE was apparently the weathering crust over acidic rocks.

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

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Introduction

Explored coal reserves in Kazakhstan (according to the BP Review of the World Energy statistics, June 2020) amount to 34 billion tons, which is 4%

of the total world reserves. Despite declining the share of coal in the global energy balance, the demand for this type of fuel in the world market will remain stable for a long time to come. In this regard, it is planned to introduce a number of

innovative projects in the coal industry. In order to develop the coal industry, to take systemic measures to support the industry, as well as to implement new projects, the Roadmap of developing the coal industry of the Republic of Kazakhstan for 2019-2021 was developed and approved. According to it, it is necessary to pay special attention to coals containing industrial concentrations of rare and trace elements such as germanium, gallium, yttrium, tungsten, and others. Some of them are toxic - mercury, arsenic, antimony, beryllium and others. Some of them are toxic, such as mercury, arsenic, antimony, beryllium and others. Comprehensive use of coal and associated minerals increases profitability of developing coal deposits and contributes to solving a number of environmental problems. At present, reliable estimate of the average content of rare earth elements in coals for most of the coal basins and deposits of Kazakhstan needs to be clarified using up-to-date research methods. In the countries with developed economies (USA, Europe, Australia, China), the rare metal composition in organic matter has been partially estimated and published in numerous editions, where it has been shown that waste of the coal use can also contain high, in some cases industrially significant concentrations of impurity elements (Zharov, 2004; Seredin, 2006; Yudovich, 2006, Dai et al, 2010, 2011, 2019 and others).

Coals are considered the main sources of Ge (the Pavlovskoye deposit, the Spetsugli site is the largest one in Russia). In China, germanium and lithium are extracted on an industrial scale from coal. Attempts are being made to extract individual chemical elements (U, Au, Al, Ga, Sc) from coals and their wastes. However, the efficiency of recovery techniques is not high. One of the main reasons for this is the lack of information on the forms of finding elements in coals and their combustion products. Nevertheless, it has been proven that in a number of cases individual coal seams or even deposits can be considered as a potential complex source of rare, rare-earth and noble metals (Seredin, 2003, Arbuzov S.I., 2008, etc.). But at present, there is still no sufficient geological information of the accumulation of rare earth metals in coal seams, of the forms of their occurrence and the mechanisms of concentration of these elements in the coals of Kazakhstan. In this regard, this work is very relevant, since here there are represented the results of studying the content of chemical elements, their mineral form in the coals of the Shubarkol deposit.

Previous studies [1, 2] have shown that the deposit contains significant contents of Ba, Zr, Sr, U, Rb, Th, Co, Fe, Zn, Ce and Sc. Studying the distribution of REEs and the form of their occurrence can provide important information for understanding in what environment of coal formation they appeared, as well as with what diagenetic and epigenetic processes they are associated. Minerals in coals are usually formed due to the influx of the terrigenous material, ground and sea water, fallout of volcanic ash, intrusion of volcanic rocks [3-6]. As some researchers point out [3, 6, 7], igneous rocks are one of the main geological factors that can cause increasing the content of REE and satellite elements in coals.

Experimental part

Within the framework of studying coals and enclosing rocks of the Shubarkol deposit for the content of satellite elements and REE, studies were carried out using instrumental neutron activation analysis (INAA) at National Research Tomsk Polytechnic University (TPU) and inductively coupled plasma at the Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare elements (IMGRE-Moscow), the total number of samples was 45. The samples of the Central and Western sections of the field were taken by the bulk method, the sampling interval was kept within 15-35 m. The rocks of the western wing of the Central section were sampled by the point method. The rocks of the Western section were sampled by the core method, the sampling interval was kept within 5-20 m. Using the primary samples, briquettes of 2cm*3cm were made for scanning electron microscopy. The forms of occurrence of minerals in coal samples were studied using SEM-EDX at the ISEC "Uranium Geology". The chemical content of coal was determined by the INAA method at the nuclear-geochemical laboratory of the Department of Geoecology and Geochemistry (TPU) (analyst A.F. Sudyko).

Discussing the results

Based on the results of scanning microscopic analysis, various micro-mineral impurities were found in the composition of the Shubarkol deposit coals. These are mainly aluminosilicates, sulfides and sulfates with inclusions of microparticles of rare and rare-earth elements, and according to the

results of INAA, abnormal concentrations of Sc, Ta, Nb, Hf, Zr, Ba, Sr, Ce and REE were found.

The specific features of the analytics of lanthanides by the INAA method have identified a group of studied elements in detail: La, Ce, Sm, Eu, Tb, Yb, Lu. Their average contents in the Shubarkol deposit coals were estimated based on 45 samples.

The average content of lanthanides in run-of-mine coals of the deposit are lower (approximately 2 times) than the Clarke ones. The analysis of the distribution maps in the Western and Central areas of the field of a group of studied elements in detail have shown that the elements have a different degree of concentration over the area. Attention is drawn to the spatial discrepancy in the concentrations of the elements. The maximum concentrations within the lower Clarke contents of La, Ce and Sm are found in the coals of both areas, mainly in the Western area: Tb, Yb, Lu and Nd mainly in the Central area. This fact can indicate both the difference in the sources of input and different mechanisms of the concentration of lanthanides in coals.

Above the "coal Clarke" (ytterbium is somewhat lower) are their contents, as well as the number of the above-considered elements, in oxidized coals. Moreover, the La-Yb ratio is noticeably higher than in ordinary coals. This is explained by the peculiarities of the geochemical specialization of the framing rocks, the conditions of peat accumulation and coal formation. It was found that the average La-Yb ratio for the coals of the deposit is higher than for the post-Archean Australian shales (PAAS) and corresponds to that for sandstones according to [8].

The maximum concentrations of elements found in private coal samples are 205 ppm for La, 644 ppm for Ce, 227 ppm for Sm, 79 ppm for Eu, and 97 ppm for Tb, for Yb 358 ppm, for Lu 59 ppm. In coal ash, the content of the total of rare earth elements in some samples can reach 2-3% with the sharp predominance of light lanthanides.

Coal oxidation processes affecting the distribution of REE are manifested in the Western area of the deposit in the near-roof part of the oxidized coal seam.

Oxidation of coal is accompanied by the formation of regenerated humic acids that interact with elements and contribute to their redistribution. It was found that redistribution of lanthanides over the site in the section is uneven. There is a general tendency expressed in increasing the content of rare earth elements from the bottom upward along the section.

It has been established that weathering processes within the Shubarkol deposit have mainly led to the loss and redistribution of REE in coal seams. They are most significant for heavy lanthanides that are relatively mobile under hypergene conditions. The maximum accumulation took place under the mudstone screen, i.e. in the upper part of the section, the coals underwent a "cerium" phase of weathering: the relative contents of lanthanum and cerium decreased, in turn, the contents of yttrium and "heavy" REE increased. As a result of the multiple processes action, increased concentrations of rare earth elements, mainly of the yttrium group, were formed.

The combined concentration and separation of lanthanides in coals are most clearly manifested in the normalized distribution curves (Figure 1).

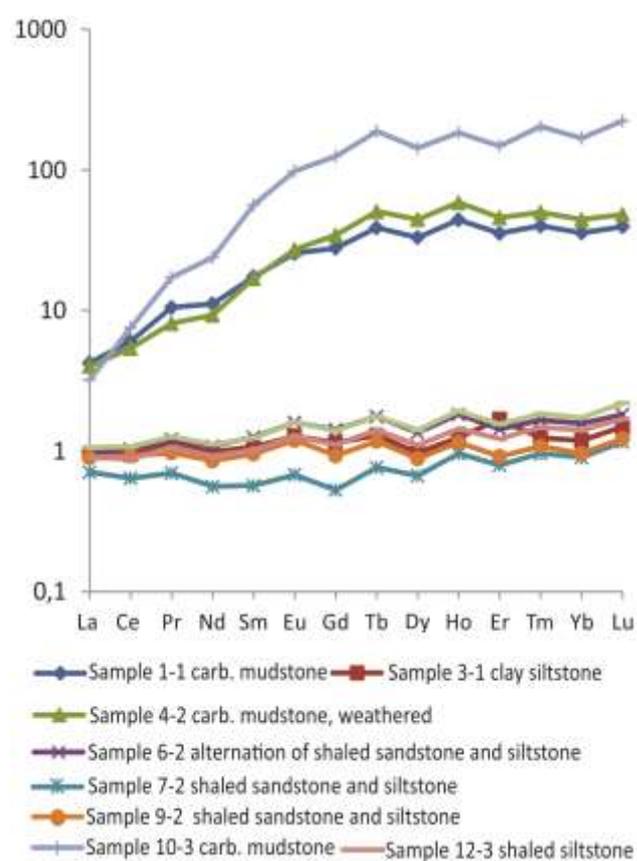


Figure 1 – Pattern of REE distribution in enclosing rocks

The nature of the REE distribution curves in the coals of the Shubarkol deposit normalized to chondrite according to [8], shows that the negative europium anomaly characteristic of most sedimentary rocks is not pronounced. The nature of the distribution curve for coals (Figure 2) is similar to that for the coal-bearing rocks (Figure 1) of the deposit.

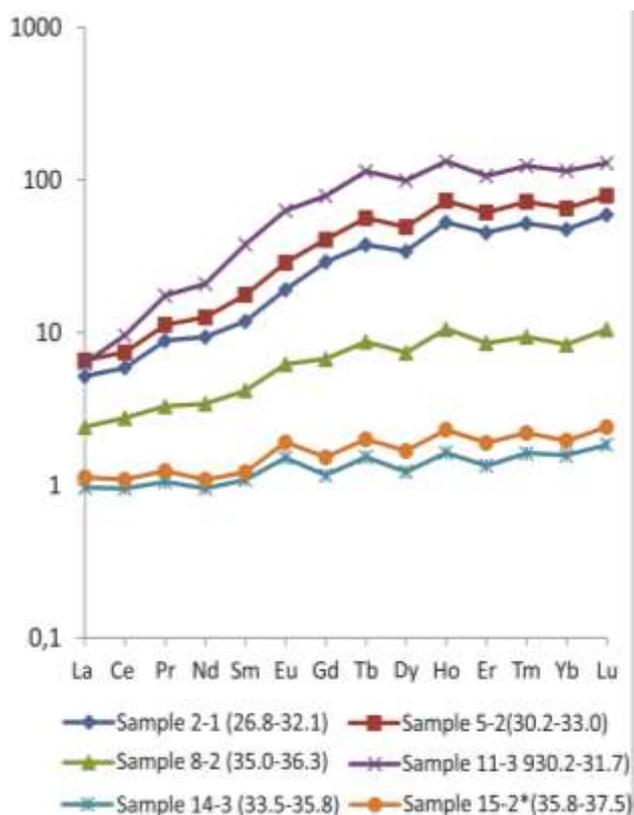


Figure 2 – Pattern of REE distribution in coals (in brackets there are the sampling intervals)

The average spectra of the lanthanides of the Shubarkol deposit normalized according to the chondrite standard [8] are in general characterized by the normal type of distribution.

The lutetium peak is clearly visible in Figure 2. Such peaks are characteristic of the Kuzbass coals and some coals of Australia and the USA.

The absence of the europium minimum can be associated with both the reducing conditions of coal accumulation and the peculiarities of the initial substrate composition. The absence of the europium minimum was noted for some coals of Canada, Far East, and Kuzbass. According to [8], the absence of a negative europium anomaly in well-mixed sedimentary deposits can be explained by only one factor: the feature of the original rocks composition.

With the general increasing the contents up the section, the nature of the distribution curves of rare earth metals with a relative depletion in lanthanum and cerium and enrichment in elements from samarium to lutetium, clearly shows the weathering processes in the upper part of the coal seam with relative enrichment in the groups of medium and heavy rare earth elements.

The maximum REE contents are confined to weathered coals; for the medium-heavy group (Nd, PM, Sm, Eu) they are almost a hundredfold higher than the clark in the upper continental crust. The tenfold excess of clark for elements from gadolinium to lutetium was found in clayey sandstones and siltstones; for other varieties of rocks of the deposit, the excess over clark is significantly lower (Figure 3).

Analyzing the obtained graphs of the average content of rare earth elements in coals normalization to the average content in coals of the world and according to the method of V.V. Seredin [9], the oxidized Shubarkol coals can be classified as H-type coals of the REE distribution.

The formation of H-type coals of the Shubarkol deposit with near-clark REE contents was dominated by the clayey matter of terrigenous ash as the carrier of REE, while the formation of metalliferous coals with record levels of REE accumulation took place upon prolonged discharge of carbonic water into the peat bog with elevated contents of heavy lanthanides with the following organic REE binding by the peat matter.

Lateral variability of the types of REE distribution and the level of their concentrations occur within the Shubarkol deposit. This indicates significant spatial variations in the nature of the processes that determine the REE geochemistry in coals. In unoxidized coals, normalized La/Yb>1 and therefore, the type of REE distribution differs significantly from oxidized weathered coals and belongs to the L-type that differs in relative enrichment with light lanthanides. Association of light REEs with clay matter and the presence of micromineral REE-containing phosphates (monazite, goyacite, gorseixite) in coals make it possible to associate the L-type formation with the input of REE into the coal accumulation basin mainly in the composition of clay minerals and LREE-phosphates. The main source of REEs was apparently the weathering crust over acidic rocks.

Based on the literature data, phosphates concentrating light lanthanides are considered to be the predominant mineral form of REE in coals [10]. Phosphates and carbonates enriched with yttrium and heavy lanthanides are much less common, despite their high contents in coals. However, according to [9, 10], this form is not primary, since a transformation from the organic to the phosphate form occurred in diagenesis.

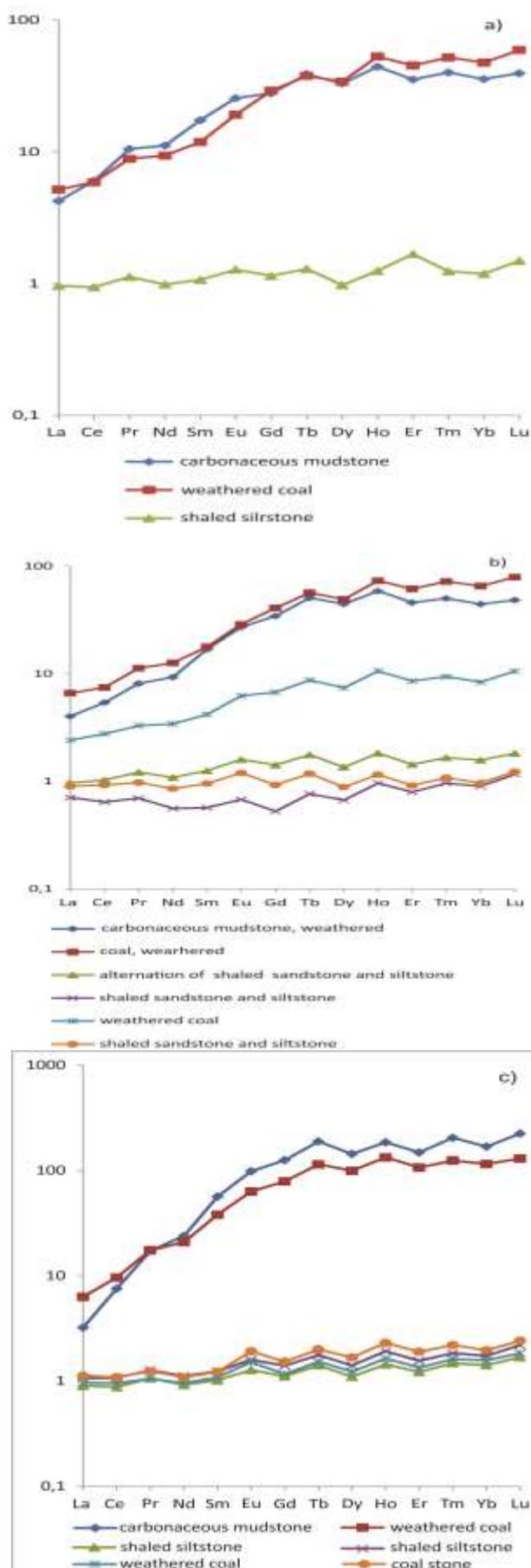


Figure 3 – REE distribution spectra in well No. 1 (a), 2(6), 3(c) normalized to chondrite (Taylor, McLennan)

High-resolution electron microscopy studies of the coals of the deposit under study revealed only a few micron-sized minerals containing REE. Kularit was identified in a sample of oxidized coal (Figure 4a). A cone-shaped particle is located in an aluminosilicate matrix. Its size is about 5 microns.

In a sample of oxidized coal there was found a differentiated micromineral phase of siderophilic Fe and individual REE-Nd in quantities not exceeding the first percent (Figure 4b).

The established extremely small REE minerals precipitates and the peculiarities of their composition allow assuming the authigenic nature of their formation. The formation of the bulk of authigenic minerals occurred in the process of maturation of brown coal and its transformation into stone. In mature coals of the Carboniferous stage, the role of mineral phases increases due to metals released during coalification caused by the loss of carboxyl, hydroxyl, and other functional groups, authigenic minerals are formed.

According to [11], some of the REEs during metamorphism remains in the composition of organometallic complexes in organic matter forming complex aluminum-sulfate-silicophosphate compounds with different rare metal spectra.

The conditions for the accumulation of REEs in coals, like most other trace elements, are still poorly studied.

The analysis of studying geochemistry of the Shubarkol coal deposit allows identifying the main source of REE input into the coal-bearing deposits. This is a complex of folded framing rocks. The predominant importance of the folded framing rocks composition in the accumulation of lanthanides in coals is emphasized by all specialists involved in the coal geochemistry of REEs [12].

The role of framing is also visible in studying modern peatlands [13]. For the Shubarkol deposit, the contribution of the Kokchetav uplift in the north and northwest, the Kaptyadyr, Arganatinsk and Ulutau mountains in the west, which compose the chain of the Kokchetav-North Tien Shan fold system and the Central Kazakhstan (Devonian) volcano-eastern plutonic belt massifs of alkaline-granitoid composition are characteristic. Significant massifs of alkaline rocks in the composition of the folded framing probably caused the formation of positive europium anomalies in coals and coal-bearing rocks, which are clearly visible throughout the coal-bearing section.

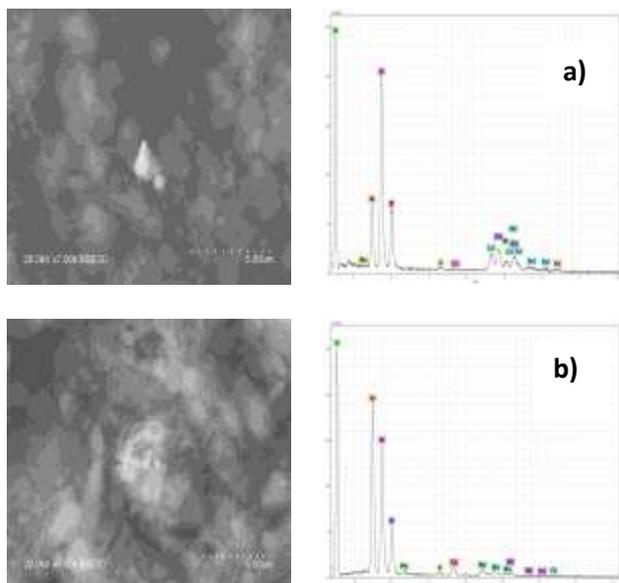


Figure 4 a – kularit, b – complex differentiated micromineral phase Fe-Nd

In this case, the mechanism of transferring the matter from the listed sources and the accumulation of rare earths in coals in the form of clastogene material ensures the accumulation of background concentrations of impurity elements in coals.

Weathering of rocks in the warm, humid Jurassic climate also caused transition of elements to the dissolved state and their transfer in aqueous solutions. Carbonate rocks in the framing structures caused the formation of carbonate and hydrocarbonate waters of varying degrees of alkalinity. The degree of saturation of terrigenous ash with REEs is in direct proportion to the chemical composition of the areas fed by the clastic material of the ancient peat bog. The sharp predominance of coals in the geochemical spectrum indicates the important role of the clastogene component in the accumulation of light lanthanides. Probably, the important role of ultramafic rocks in the framing structures ensured the enrichment of groundwater, suspended matter, and more coarse detrital material with europium. This explains the increased content of this element in the coal-bearing rocks and coals and the absence of the characteristic europium minimum on the normalized curves.

The analysis of the graphs allows concluding that the distribution of REEs formed in the process of peat accumulation, with the removal of cerium and lanthanum characteristic of atmospheric weathering processes, was superimposed on the processes of weathering the coals; increasing the content of rare earth elements in coals in the oxidation zone was caused not by the introduction

of elements into the coal seam but by changing its ash content due to the loss of organic matter as a result of coal oxidation to carbon dioxide, water-soluble humic substances and other mobile compounds, which is also observed in other coal basins (Minussinsky, Kuznetsky and other deposits of Siberia).

Conclusions

Based on the results of scanning microscopic analysis, various micromineral inclusions were found in the composition of the Shubarkol deposit coals: aluminosilicates, sulfides and sulfates with inclusions of microparticles of rare and rare earth elements, and according to the results of INAA, abnormal concentrations of Sc, Ta, Nb, Hf, Zr, Ba, Sr, Ce and REE.

It was found that redistribution of lanthanides over the site in the section is uneven. Within the Shubarkol deposit, weathering processes resulted mainly in the loss and redistribution of REE in coal seams, which led to increasing the content of rare earth elements from the bottom upward along the section. The maximum accumulation took place under the mudstone screen, i.e. in the upper part of the section; the coals underwent the "cerium" phase of weathering: relative contents of lanthanum and cerium decreased, the contents of yttrium and "heavy" rare earth metals in turn increased. As a result of the multiple processes action, increased concentrations of rare earth metals, mainly of the yttrium group, were formed. The absence of negative europium anomaly at this deposit was determined, which confirms peculiarity of the composition of the original rocks.

The maximum contents of rare-earth metals are confined to weathered coals; for the medium-heavy group (Nd, PM, Sm, Eu), they are almost a hundredfold higher than the clarke in the upper continental crust. The tenfold excess of clarke for elements from gadolinium to lutetium was found in clayey sandstones and siltstones; for other varieties of rocks of the deposit, the excess over clarke was significantly lower.

When studying the normalized average content of REE distribution in coals, it was found that the coals of the deposit belong to the H-type and L-type. During the formation of oxidized H-type coals, clayey matter of terrigenous ash predominated as the carrier of REE, while unoxidized L-type coals were formed with

introducing REE into the coal accumulation basin mainly in the composition of clay minerals and LREE-phosphates. Here the main source of REE was apparently the weathering crust over acidic rocks.

An electron microscope revealed single micron-sized rare-earth minerals. Kularit was determined in a sample of oxidized coal: a cone-shaped particle with the size of about 5 microns was located in the aluminosilicate matrix. In a sample of oxidized coal in quantities not exceeding the first percent, a differentiated micromineral phase of siderophilic Fe and individual REE-Nd was found.

The established extremely small precipitates of REE minerals and the peculiarities of their composition allow assuming the authigenic nature of their formation.

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Шұбаркөл кен орнының көмірлеріндегі сирек жер элементтерін зерттеу

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ТҮЙІНДЕМЕ

Мақалада Шұбаркөл кен орнының юра көмірінің минералогиялық және геохимиялық ерекшеліктері зерттелген. Үлгілер ТПУ-дағы геоэкология және геохимия кафедрасына қарасты, «Уран геологиясы» ХЗҒБО-да жүргізілген Hitachi s-3400n сканерлейтін электронды микроскопия (SEM-EDX) әдісін қолдана отырып зерттелді. Көмір геохимиясы Томск ұлттық зерттеу политехникалық университетінің (ТПУ) геоэкология және геохимия кафедрасының ядролық-геохимиялық зертханасында аспаптық нейтрондық-белсендіру арқылы талдау (НАТ) әдісімен зерттелді. Осы зерттеу объектісін таңдау геологиялық ортаның әртүрлі факторларының олардың көмірде жинақталу деңгейлеріне әсер етуінің сирек кездесетін элементтерінің аномальді шоғырлануының жинақталу заңдылықтарын, сондай-ақ оның шоғырлануы шарттарын және сирек кездесетін элементтер бойынша Қазақстанның минералдық-шикізат базасын кеңейту үшін көмірде болу нысандарын зерттеуді қамтитын зерттеу міндеттерімен айқындалды. Сканерлеуші микроскопиялық талдау нәтижелері бойынша Шұбаркөл кен орны көмірінің құрамында алюмосиликаттар, сульфидтер мен сульфаттар сирек және сирек жер элементтері микробөлшектерінің қосындыларымен табылды. НАТ нәтижелері бойынша Sc, Ta, Nb, Hf, Zr, Ba, Sr, Ce және сирек жер элементтерінің аномалды концентрациялары анықталды. Үгілу үрдістерінің әсерінен Шұбаркөл кен орнының көмір қабаттарында сирек жер элементтерінің жоғалатыны және қайта бөлінетіні анықталды, бұл өз кезегінде кеніш бойынша төменнен жоғары қарай сирек жер элементтері құрамының ұлғаюына әкелді. Көптеген процестердің нәтижесінде сирек кездесетін металдардың, негізінен итрий тобының жоғары концентрациясы пайда болды. Теріс еуропийлік аномалия анықталмады, бұл бастапқы тау жыныстары құрамының ерекшелігін растайды. Сирек кездесетін металдардың ең көп мөлшері үгілген көмірлермен шектелген, орташа ауыр топ үшін (Nd, Pm, Sm, Eu) олар жоғарғы континентальды қыртыстағы кларктан жүз есе асады. Gd-ден Lu-ға дейінгі элементтер үшін кларктардың он есе артуы сазды құмтастар мен алевролиттерде анықталған, кларк құрамынан айтарлықтай төмен. Кен орындарының көмірі СЖЭ-нің H-типіне және L-типіне жататыны анықталды. Тотыққан H-типті көмірді қалыптастыру кезінде СЖЭ тасымалдаушысы ретінде терригенді күлдің сазды заты басым болды, ал L-типті қышқылданбаған көмірлер негізінен саз минералдары мен LREE фосфаттарының құрамында көмір жинау бассейніне СЖЭ енгізу арқылы пайда болды. Мұндағы СЖЭ-нің негізгі көзі қышқыл жыныстардағы үгілген қабықтары болған сияқты.

Түйін сөздер: көмір, Шұбаркөл, сирек жер элементтері, минералогия, геохимия.

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Изучение редкоземельных элементов в углях месторождения Шубарколь

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АННОТАЦИЯ

В работе изучены минералогические и геохимические особенности юрских углей месторождения Шубарколь. Образцы исследовались с использованием метода сканирующей электронной микроскопии (SEM-EDX) Hitachi S-3400N, которая проводилась в МИНОЦ «Урановая геология» при кафедре геоэкологии и геохимии ТПУ. Геохимия углей изучена методом инструментального нейтронно-активационного анализа (ИНАА) в ядерно-геохимической лаборатории кафедры геоэкологии и геохимии Национального исследовательского Томского политехнического университета (ТПУ). Выбор данного объекта изучения определялся задачами исследований, включающими изучение закономерностей накопления в них аномальных концентраций РЗЭ, влияния различных факторов геологической среды на уровни накопления их в углях, а также условий его концентрирования и форм нахождения в углях для расширения минерально-сырьевой базы Казахстана по редкоземельным элементам. По результатам сканирующего микроскопического анализа в составе углей Шубаркольского месторождения обнаружены алюмосиликаты, сульфиды и сульфаты с включениями микрочастиц редких и редкоземельных элементов. По результатам ИННА были обнаружены аномальные концентрации Sc, Ta, Nb, Hf, Zr, Ba, Sr, Ce и РЗЭ. Процессы выветривания привели преимущественно к потере и перераспределению РЗЭ в угольных пластах Шубаркольского месторождения, что привело к увеличению содержания редкоземельных элементов снизу вверх по разрезу. В результате действия множественных процессов сформировались повышенные концентрации редкоземельных металлов, преимущественно, иттриевой группы. Определено отсутствие отрицательной европиевой аномалии, что подтверждает особенность состава исходных пород. Максимальные содержания редкоземельных металлов приурочены к выветрелым углям, для средней-тяжелой группы (Nd, Pm, Sm, Eu) они практически стократно превышают кларк в верхней континентальной коре. Десятикратные превышения кларков для элементов от Gd до Lu выявлены в глинизированных песчаниках и алевролитах, для остальных разностей пород месторождения превышения над кларком существенно ниже. Установлено, что угли месторождения относятся к H-типу и L-типу распределения РЗЭ. При формировании окисленных углей H-типа преобладало глинистое вещество терригенной золы как носитель РЗЭ, тогда как неокисленные угли L-типа формировались с привносом РЗЭ в бассейн угленакопления в основном в составе глинистых минералов и LREE-фосфатов. Основным источником РЗЭ, здесь по-видимому, являлись коры выветривания по кислым породам.

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

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On the possibility to process copper-molybdenum ore using a combined flotation reagent

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ABSTRACT

The article presents the results of laboratory studies on ore flotation of copper-molybdenum deposits in the East Kazakhstan region of Kazakhstan using a combined reagent. It is required to use new beneficiation methods and flotation reagents to increase the efficiency of flotation of ore minerals to improve the processing of finely disseminated ores. The problem can be solved by using a combination of different collectors. The objective of the research is to increase the recovery of copper and molybdenum during flotation of copper-molybdenum ore using a combined reagent. The studied ore sample contains 0.42% copper; 0.009% molybdenum. A combination of sodium butyl xanthate, TS-100 thionocarbamate, and reaflo in a ratio, in %: 15: 3: 1, was used as a combined flotation reagent. The combined flotation reagent was preliminarily passed through an ultrasonic homogenizer JY96-IIN to obtain a reagent microemulsion before flotation. The optimum dispersion time for the combined flotation reagent is 60 seconds. At the same time, 99.4% are microemulsion particles with a particle size of fewer than 3.7 microns. The use of a combined reagent microemulsion increases the extraction of copper into the copper-molybdenum concentrate by 3.69%, and the extraction of molybdenum by 6.05%. The copper content in the copper-molybdenum concentrate increases by 1.26%. The copper content in the flotation tailings decreases from 0.07 to 0.056%. The consumption of the combined reagent is reduced by 15% in comparison with the basic butyl xanthate.

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Introduction

It becomes required to improve the reagent modes of beneficiation of copper-bearing ores, the use of additives and reagent compositions, and the use of modernized equipment, as the deposits are depleted, and the need arises to involve poor, finely disseminated ores in the processing. It is required to use new beneficiation methods and flotation reagents to increase the efficiency of

flotation of ore minerals to improve the processing of finely disseminated ores. Particular difficulties are associated with the processing of the slurry part of the crushed ore, which is usually enriched with non-ferrous, rare, and noble metals [1-5]. Improving the efficiency of flotation can be achieved by using a combination of different collectors [6-10]. The modern practice of using collectors in the flotation of sulfide ores in most cases involves the combined use of xanthate and

aerofloats. The use of aerofloats in addition to xanthogenates enables not only to improve the quality of the obtained sulfide concentrates due to the more selective action of aerofloats, but also to increase the recovery of metals due to the ability of aerofloats to efficiently float fine particles.

Scientists conduct researches to create new dialkyldithiophosphates. The flotation properties of dialkyldithiophosphates and reagents containing them can be significantly influenced by the strong surface-active properties of dialkyldithiophosphates. This was established in the study of surface-active properties in the series of dialkyldithiophosphates with a hydrocarbon chain length C_4 - C_{12} . Dialkyldithiophosphate C_{10} corresponds to the maximum recovery of sulfides [11, 12].

Thus, the problem of finding more effective reagents for the flotation of non-ferrous metals from mineral raw materials is still urgent.

Experimental part

Modern research and analytical equipment were used in the study. Chemical analysis of ore samples and concentration products was performed on an Optima 2000 DV optical emission spectrometer with inductively coupled plasma. X-ray fluorescence analysis was performed on a Venus 200 PANalytical B.V spectrometer. We used X-ray phase analysis on a D8 ADVANCE X-ray diffractometer to study the material composition of the ore; spectral analysis on a ThermoNicoletAvatar 370 FTIR Spectrometer; electron-probe microanalysis on a JEOL JXA-8230 electron scanning microscope.

The following technological equipment was used: jaw crusher DMD160/100; ball mill 40ML-000PS; flotation machines FML; photometric sedimentometer FSKh-6K; ultrasonic homogenizer JY96-IIN; laser particle analyzer Winner 2000E; mechanical eraser MM-1.

Copper-molybdenum ore of Kazakhstani deposit and combined flotation reagent were used as objects of research. The combined flotation reagent is a mixture of sodium butyl xanthate, thionocarbamate, and reafлот.

The original ore was crushed for research in a laboratory jaw crusher to a size of $-2.5 + 0$ mm and ground in a laboratory ball mill to 94% of a class of -0.074 mm. A sieve analysis on a set of wire sieves with square holes corresponding to a standard scale was performed to determine the particle size distribution of crushed and milled ore. The weighed

amount of ore was 0.5 kg. Copper and molybdenum content and distribution were determined in each size class. Dispersion analysis was performed on the crushed ore using an FSKh-6K photometric sedimentometer.

Flotation studies were performed on laboratory flotation machines with a volume of 3 chambers; 1.0; 0.5 dm³. The weight of the ore sample was 1 kg. The experiments were performed in open and closed cycles. The flotation scheme included grinding, main flotation, control, and three cleaning operations of the collective copper-molybdenum concentrate. We used 7 weighed portions of ore, 1 kg each in the experiment to achieve a stable distribution of the returned products.

Lime was fed into the grinding process to create a pH of the medium equal to 8.0-9.0; sodium sulfide for the sulfidization of minerals.

The main collective copper-molybdenum flotation was performed for 1020 seconds, the control one for 480 seconds, and the following reagents were used in the basic mode as a collector - sodium butyl xanthogenate; foaming agent - T-92. The liquid glass was added to all of the rewashing treatments to depress the minerals in the waste rock. The total consumption of the basic reagents used is: lime (medium regulator) - up to pH 8.0-9.0; sodium sulfide (sulfidizer) - 200 g/t; sodium butyl xanthate (collector) - 180 g/t; liquid glass (depressor) - 150 g/t; T-92 (foaming agent) - 120 g/t. Lime and sodium sulphide were fed into the process of grinding ore into a ball mill. Sodium butyl xanthate and T-92 were fed to the main and control copper-molybdenum flotation. The liquid glass was fed for cleaning collective copper-molybdenum concentrate.

It was fed into the main and control flotation instead of the basic collector of sodium butyl xanthate during flotation processing of ore using a combined flotation reagent. The combined flotation reagent was a mixture of sodium butyl xanthate, TS-100 thionocarbamate, and reafлот in a ratio of 15: 3: 1. The combined flotation reagent before flotation was passed through a JY96-IIN ultrasonic homogenizer to obtain a microemulsion. The optimum particle size of the microemulsion for the best ore flotation was determined on a Winner2000E laser particle analyzer.

The mineral slurry was placed in a flotation chamber after grinding in a ball mill in the presence of sodium sulfide and adjusting the pH (by adding lime) to 8.0-9.0. Sodium butyl xanthate (or combined flotation agent) and foaming agent T-92 were added to it. The mineral slurry was stirred for

60 seconds without air supply at a rotor speed of 1500 rpm. Flotation treatment of the pulp was performed after atmospheric air supply (3.3 dm³/min) according to the applied beneficiation scheme. Liquid glass was added to the first refining of the collective copper-molybdenum concentrate to depress the waste rock.

Results and discussion

The authors of the article have experience in the development and testing of beneficiation schemes using various modified reagents (foaming agents, collectors, depressants) and additional equipment for intensifying flotation processes. A modified foaming agent (MFA) has been developed, used in the form of a microemulsion obtained in a water-air microemulsion generator. The optimum composition of MFA particles was selected on the PhotocorCompact particle size analyzer: the average particle size of microbubbles is 38 microns, the content (fraction) of these particles is 65.8%. In this case, MFA molecules become compact due to intramolecular interactions, due to which they are more efficiently fixed on the surface of small particles of useful components and improve combined microflotation.

The results of experimental studies of collectors from the class of dialkyldithiophosphates (aerofloat) show that their combined use with xanthogenates in many cases provides an increase in metal recovery by 2-3% [13, 14]. The most effective flotation of minerals that do not have natural hydrophobicity is observed in the optimal ratio.

Mineralogical analysis shows that copper minerals in the ore under study are represented mainly by chalcopryrite, chalcocite and covellite are present in smaller amounts. The main molybdenum mineral is molybdenite. The ore contains pyrite, magnetite, and, to a lesser extent, hematite and ilmenite. In addition, the ore contains a small amount of rutile, galena, sphalerite. The results of the mineralogical analysis are presented in Table 1.

Chalcopryrite exists independently mainly in the form of xenomorphic grains or is associated with pyrite and is unevenly disseminated in vein minerals, sometimes located in the form of veins. Dispersed chalcopryrite grain size varies from 0.001 to 1 mm. Chalcopryrite grain size in veins and nests is generally more than 0.01 mm. Molybdenite is mainly disseminated in quartz in the form of lamellar single crystals or their aggregates. It is

found in calcite, quartz-calcite, and quartz veins. This mineral also forms nests and placers in zones of alteration with potash feldspar.

Table 1 - Results of mineralogical analysis of the initial sample of copper-molybdenum ore

Mineral name	Content, %
Chalcopryrite	1.05
Covellin	0.01
Kholkozin	0.01
Pyrite	0.4
Molybdenite	0.014
Sphalerite	0.04
Galena	0.016
Magnetite	2.1
Hematite	0.1
Ilmenite	0.2
Rutile	0.2
Ti-Fe rutile	0.1
Quartz	20.6
Sodium feldspar	26.0
Calcium Sodium Feldspar	16.0
Potassium feldspar	7.0
Potassium microplagioclase	3.0
Chromite	13.0
Sericite	4.0
Biotite	2.0
Epidote	2.0
Calcite	1.4
Titanite	0.6
Apatite, wollastonite, and others	0.16

Rock-forming minerals are represented by sodium feldspar, quartz, calcium-sodium feldspar, chlorite, and, to a lesser extent, potassium feldspar, sericite, potassium microplagioclase are present. In addition, there is a small amount of biotite, epidote, calcite, wollastonite, titanite, and apatite.

The studied sample of copper-molybdenum ore contains 0.42% Cu; 0.009% Mo; 0.55% S; 5.1% Fe; 0.012% Pb; 0.025% Zn; 0.001% As; 0.02 g/t Au; 2.1 g/t Ag; 2,92 % K₂O; 2,93 % Na₂O; 4,8 % CaO; 14,8 % Al₂O₃; 61,5 % SiO₂; 2,8 % MgO according to the results of chemical analysis.

Phase analysis of initial ore for copper and molybdenum is performed. The results of the analysis showed that the content of primary copper sulfides (chalcopryrite CuFeS₂) in the ore is 95.5%; secondary copper sulfides (chalcocite Cu₂S, covellite CuS) - 2.1%; in the form of copper oxides - 2.4%. The content of molybdenum in the original ore in the sulfide form (molybdenite MoS₂) is 96%; in oxidized form - 4.0%.

An X-ray phase analysis of an ore sample was performed. The diaphragms of the samples were made on a D8 Advance apparatus (Bruker), α -Cu, tube voltage 40/40. The processing of the obtained data of diffraction patterns and the calculation of interplanar distances were performed using the EVA software. The results of the X-ray phase analysis are presented in Table 2.

Table 2 - Results of X-ray phase analysis of the initial sample of copper-molybdenum ore

Compound Name, Formula	S-Q
Quartz, syn SiO_2	35.1
Albite, calcian, ordered, $(\text{Na,Ca})\text{Al}(\text{Si,Al})_3\text{O}_8$	19.7
Clinocllore-2M1lb, $\text{Mg}_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$	14.0
Anorthite, sodian, intermediate, $(\text{Ca, Na})(\text{Si, Al})_4\text{O}_8$	13.9
Glagolevite, $\text{NaMg}_6(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{O})_8 \cdot \text{H}_2\text{O}$	4.4
Graphite, syn, C	3.0
Ferrierite, $(\text{Na,K,Mg})_2(\text{Si,Al})_{18}\text{O}_{36} \cdot 9\text{H}_2\text{O}$	2.9
Nepheline, potassian, syn, $(\text{K, Na})\text{AlSiO}_4$	2.4
Illite-2M1 (NR), $(\text{K,H}_3\text{O})\text{Al}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$	2.3
Muscovite-1M, syn, $\text{KAl}_2\text{Si}_3\text{AlO}_{10}(\text{OH})_2$	2.0

X-ray phase analysis showed that the main rock-forming minerals in the ore are quartz, albite, clinocllore, etc. X-ray fluorescence analysis of the original ore was performed on a Venus 200 PANalytical B.V. (PANalytical B.V., Holland). The analysis showed that the main valuable component in the original ore sample is copper, the content of which is 0.462%. The bulk is oxygen - 49.958%, silicon - 23.856%, aluminum - 7.27%, iron - 3.975%, calcium - 2.683%.

A sample of the original ore was analyzed on a JXA-8230 electron probe microanalyzer from JEOL. Polished sections were scanned with fixation of ore and rock-forming minerals with the determination of their composition (Figure 1).

Microscopic examination showed that copper minerals account for about one percent and are represented by chalcopyrite. The sizes of ore minerals range from thousandths to 0.04-0.07 mm in cross-section. They are found in the form of free grains, but more often in the form of inclusions in nonmetallic minerals.

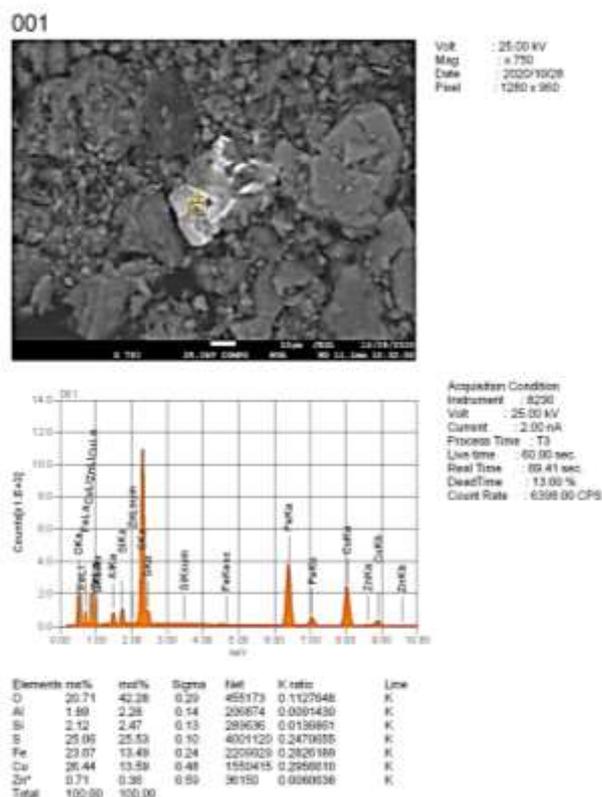


Figure 1 - Dispersions of chalcopyrite in quartz

The granulometric composition of the crushed ore has been determined. The ore was crushed on a laboratory jaw crusher to a size of $-2.5 + 0$ mm. Further, the ore was ground in a ball mill to a size of 95% of the class -0.071 mm. A set of wire sieves with square holes corresponding to the standard scale was used for sieving. The content and distribution of copper and molybdenum were determined in each size class. The data are presented in Table 3. It was shown that most of the copper and molybdenum in this grinding (75-77%) is distributed in the $+50 \mu\text{m}$ and $-20 \mu\text{m}$ classes. The size class of $+50 \mu\text{m}$ contains 29.08 % copper and 37.93 % molybdenum; the $-20 \mu\text{m}$ size class contains 44.9 % copper and 37.7 % molybdenum.

Table 3 - Granulometric composition and distribution of copper and molybdenum by size classes in crushed ore

Size class, microns	Output %	Content, %		Distribution, %	
		Cu	Mo	Cu	Mo
+71	19.0	0.39	0.015	19.5	28.3
-71+50	12.1	0.3	0.008	9.58	9.63
-50+40	11.9	0.37	0.01	11.6	11.8
-40+30	2.93	0.44	0.01	3.40	2.92
-30+20	10.7	0.39	0.009	11.0	9.58
-20+10	23.6	0.41	0.011	25.6	25.9
-10+0	19.7	0.37	0.006	19.3	11.8
Initial ore	100	0.38	0.010	100	100

Dispersion analysis of crushed ore was performed on an FSKh-6K photometric sedimentometer, which is designed to measure the particle size distribution of powders and suspensions with a particle size of fewer than 300 microns.

The results of the dispersion analysis of crushed copper-molybdenum ore are shown in Figure 2.

Ore was crushed to a flotation size of 92% of class -0.074 mm for analysis of variance. The results of the dispersion analysis show that the largest part of the initial sample of crushed ore is the size classes of 15-20 microns and 60-70 microns.

The following parameters of flotation of copper-molybdenum ore were worked out: degree of grinding of ore, consumption of sodium butyl xanthate, consumption of foaming agent T-92.

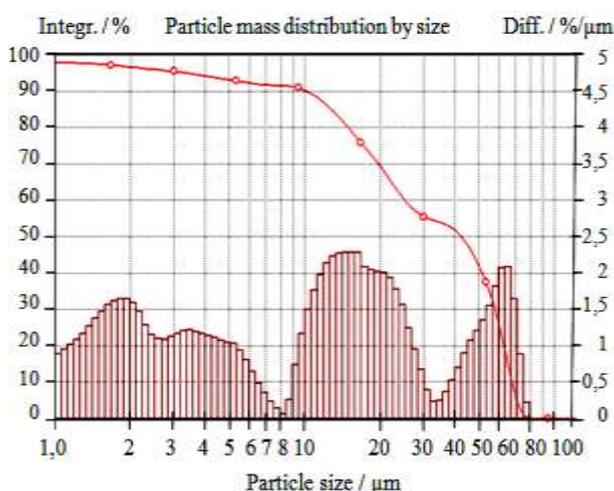


Figure 2 - Dispersion analysis of a sample of crushed copper-molybdenum ore at FSKh-6K

Optimal conditions for flotation are: grinding of 94% ore of class -0.074 mm, Na₂S - 200 g/t; pH 8-9; consumption of butyl xanthate in bulk flotation 160 g/t; T-92 90 g/t; liquid glass in the cleaning of collective copper-molybdenum concentrate 150 g/t. A collective copper-molybdenum concentrate was obtained, in the optimal basic mode, in an open cycle, with a copper content of 16.87% at 76.35% recovery and with a molybdenum content of 0.42% at 78.82% recovery.

The reagent mode of flotation of copper-molybdenum ore with the use of a combined reagent, which is a mixture of sodium butyl xanthate, thionocarbamate, and reafлот in the ratio, in %: 15: 3: 1, has been worked out. Microemulsion of combined flotation agent obtained in JY96-IIN ultrasonic homogenizer allows to improve hydrophobization of slurry particles of copper and

molybdenum minerals. The bubbles of the foaming agent in this case are better fixed on the surface of the floating minerals, which leads to an increase in the technological parameters of flotation.

The optimal dispersion time and particle size of the combined reagent microemulsion were selected using a Winner 2000E laser particle analyzer. Figure 3 shows the results of measuring the emulsion particles of the combined reagent. The optimal dispersion time for the combined reagent solution with a concentration corresponding to the flow rate in flotation is 1 min. At the same time, 99.4% are particles with a particle size of fewer than 3.7 microns.

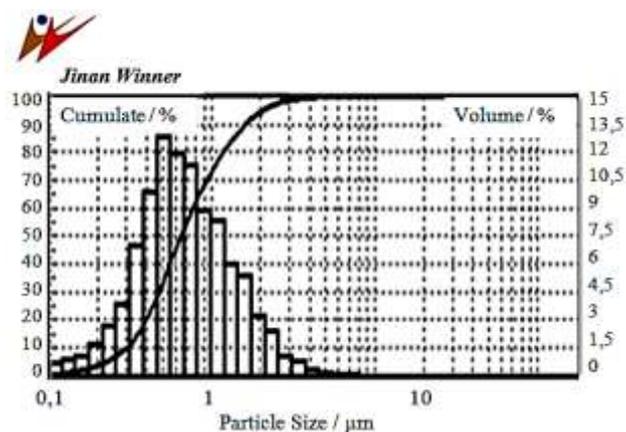


Figure 3 - Particle distribution of the combined reagent obtained on Winner 2000E

Laboratory studies on flotation concentration of ore from a copper-molybdenum deposit in the East Kazakhstan region of Kazakhstan in a closed cycle with the use of a combined flotation reagent in comparison with the basic regime were performed. The results of the flotation of the collective copper-molybdenum cycle are shown in Figure 4.

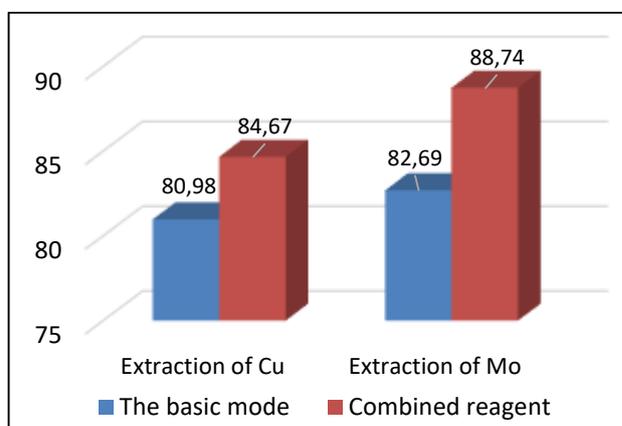


Figure 4 - Results of collective flotation of copper-molybdenum ore in a closed cycle

The presented data show that the use of dispersed microemulsion of combined reagent increases, compared with the basic mode, extraction of copper in the collective copper-molybdenum concentrate by 3.69%, extraction of molybdenum by 6.05%. The copper content in the copper-molybdenum concentrate increases by 1.26%, from 16.8 to 18.06%. The copper content in the flotation tailings decreases from 0.07 to 0.056%. At the same time, the consumption of the combined reagent is 15% less than sodium butyl xanthate.

Thus, the research results show that the use of the combined reagent is promising for the processing of copper-molybdenum ores.

Conclusions

The effect of the combined flotation reagent on the ore flotation of the copper-molybdenum deposit in the East Kazakhstan region of Kazakhstan has been studied. The combined reagent is a mixture of sodium butyl xanthate, thionocarbamate, and reafлот in a ratio, in %: 15: 3: 1. The combined reagent was supplied to the flotation in the form of a microemulsion obtained on an ultrasonic homogenizer JY96-IIN.

The optimal dispersion time of the combined flotation reagent is 60 sec. At the same time, 99.4% are microemulsion particles with a particle size of fewer than 3.7 microns.

Copper-molybdenum concentrate with a copper content of 16.8%, molybdenum 0.40%, and recovery of 80.98% and 82.69%, respectively, was obtained in the optimum basic closed-cycle mode. The use of a microemulsion of a combined reagent increases the extraction of copper into the copper-molybdenum concentrate by 3.69%, the extraction of molybdenum by 6.05%. The copper content in the copper-molybdenum concentrate increases by 1.26%. The copper content in flotation tailings decreases from 0.07 to 0.056%. The consumption of the combined reagent, in comparison with the basic butyl xanthate, is reduced by 15%.

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Құрамдастырылған флотореагентті қолдана отырып мыс-молибден кенін қайта өңдеу мүмкіндігі туралы

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ТҮЙІНДЕМЕ

Мақалада құрамдастырылған реагентті қолдана отырып, Шығыс Қазақстан кенорнының мыс-молибден кенін флотациялау бойынша зертханалық зерттеулердің нәтижелері баяндалған. Ұсақ сеппелі кендерді өңдеу үшін кен минералдарын флотациялаудың тиімділігін арттыруға мүмкіндік беретін байытудың жаңа тәсілдерін және жаңа флотациялық реагенттерді қолдану қажет. Бұл проблеманы әртүрлі жинағыштардың үйлесімді қоспасын қолдану арқылы шешуге болады. Зерттеудің мақсаты - құрамдастырылған реагентті қолдана отырып мыс-молибден кенін флотациялауда мыс пен молибденді бөліп алу дәрежесін арттыру. Зерттелген кен үлгісінде мыстың үлесі 0,42%; молибденнің үлесі 0,009% құрайды. Құрамдастырылған флотореагент ретінде натрий бутил ксантогенатының, ТС-100 тионокарбаматтың және реафлоттың 15: 3: 1 қатынасындағы қоспасы қолданылды. Флотациялаудың алдында реагенттің микроэмульсиясын алу үшін құрамдастырылған реагент JY96-IIN маркалы ультрадыбыстық гомогенизатор арқылы өткізілді. Құрамдастырылған флотациялық реагентті оңтайлы ыдырату (диспергациялау) уақыты

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60 секунд. Бұл жағдайда микроэмульсия бөлшектерінің 99,4%-ның ірілігі 3,7 мкм аспайды. Құрамдастырылған реагенттің микроэмульсиясын қолдану мыс-молибден концентратына мысты бөліп алу дәрежесін 3,69%-ға, молибденді - 6,05%-ға арттырады. Мыс-молибден концентратындағы мыстың үлесі 1,26% -ға артады. Флотациялық қалдықтағы мыстың үлесі 0,07-ден 0,056%-ға дейін төмендейді. Құрамдастырылған реагенттің шығыны базалық бутил ксантогенатымен салыстырғанда 15%-ға төмендейді.

Түйін сөздер: флотация, мыс-молибден кені, флотациялық реагент, ыдырату (диспергациялау), концентрат, бөліп алу.

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О возможности переработки медно-молибденовой руды с применением комбинированного флотореагента

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АННОТАЦИЯ

В статье представлены результаты лабораторных исследований по флотации руды медно-молибденового месторождения Восточно-Казахстанской области Казахстана с применением комбинированного реагента. Для повышения эффективности переработки тонковкрапленных руд необходимо применение новых способов обогащения, флотационных реагентов, позволяющих повысить эффективность флотации рудных минералов. Решение проблемы может быть достигнуто применением сочетания различных собирателей. Целью исследований является повышение извлечения меди и молибдена при флотации медно-молибденовой руды с применением комбинированного реагента. В исследуемой пробе руды содержится 0,42 % меди; 0,009 % молибдена. В качестве комбинированного флотореагента применена комбинация бутилового ксантогената натрия, тионокарбамата ТС-100 и реафлота в соотношении: 15:3:1. Комбинированный флотореагент предварительно перед флотацией для получения микроэмульсии реагента пропускали через ультразвуковой гомогенизатор JY96-IIN. Оптимальное время диспергирования комбинированного флотационного реагента составляет 60 сек. При этом 99,4 % составляют частицы микроэмульсии крупностью менее 3,7 мкм. Применение микроэмульсии комбинированного реагента повышает извлечение меди в медно-молибденовый концентрат на 3,69 %, извлечение молибдена на 6,05 %. Содержание меди в медно-молибденовом концентрате повышается на 1,26 %. Содержание меди в хвостах флотации уменьшается с 0,07 до 0,056 %. Расход комбинированного реагента, по сравнению с базовым бутиловым ксантогенатом уменьшается на 15 %.

Ключевые слова: флотация, медно-молибденовая руда, флотореагент, диспергация, концентрат, извлечение.

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Specific features of uranyl ions extraction by interpolymer system based on polyacrylic acid and polyethyleneimine hydrogels

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ABSTRACT

Uranyl ions sorption of by interpolymer system consisting of polyacrylic acid hydrogel (hPAA) and polyethyleneimine hydrogel (hPEI) has been studied. Rate of uranyl ions extraction by the initial polymers and interpolymer system hPAA-hPEI, polymeric chain binding rate and dynamic exchange capacity of initial polymers and interpolymer system hPAA-hPEI were calculated. Based on obtained outcomes it was found that area of maximum rate of uranyl ions extraction is within the ratios of 67%hPAA:33%hPEI and 33%hPAA:67%hPEI. Maximum uranyl ions extraction rate after 48 hours of hydrogels remote interaction was 90.0 %, when polymeric chain binding rate was 9.1 % and dynamic exchange capacity was 1.14 mmol/g. Rate of uranyl ions extraction by the initial polymer hydrogels 100 % hPAA and 100 % hPEI was 68.0 % and 52.0%. Obtained outcomes showed changes of initial polymeric hydrogels sorption properties in intergel system leading to functional groups obtaining higher reactive ability, which makes it possible to use them for further development of highly efficient uranyl ions extraction sorption technology.

Keywords: hydrogels, interpolymer systems, sorption, polyacrylic acid, polyethylenimine, uranyl ion.

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Introduction

Rare-earth elements are used in multiple areas of contemporary engineering: radio electronics, instrumentation, nuclear science, machinery, chemical industry, metallurgy etc., which is why production and consumption of these elements is continuously growing worldwide. Rare-earth element containing ores extraction is often complicated by their radioactivity which is caused by them containing uranium, thorium and their half-life products. There is development of traditional raw material processing technologies as well as search for new ones in order to make mining of rare-earth elements containing ores

cheaper and produce high-purity individual elements [1-3].

Due to this fact, the issue of rare-earth elements separation from radioactive elements, particularly uranium, is of high importance nowadays [4-6].

Uranium can be removed from solutions by sorption, extraction and other methods. Sorption methods are more preferred nowadays than extraction ones. Sorption methods are more eco-friendly and have fewer technological cycles than extraction technologies [7-9].

Unfortunately, currently developed ion exchange resins cannot be widely applied; also, not all salt and metal ions have complementary

polymeric sorbents. Due to composition diversity of solutions extracted from different deposits it is difficult to study sorption process in model solutions and develop effective sorbents. Use of interpolymer systems allows highly efficient mass extraction of various elements' anions and cations [10-12].

Due to this, the objective of our research was to study depth of uranyl ions sorption during their interaction with interpolymer systems and prospects of using these interpolymer systems for uranium extraction from product solutions.

Experimental part

Equipment. Sorbent mass was determined by weighing at electronic analytical scales MSE125P-100-DO Sartorius Cubis (Germany).

Materials. The research was performed in water environment and in solution of hexaqua uranyl nitrate (UO_2^{2+} concentration = 100 mg/l) as well as polyacrylic acid and polyethylenimine hydrogels. Polyacrylic acid hydrogels were synthesized in presence of linking agent N, N - methylen-bis-acrylamide and red-ox system $\text{K}_2\text{S}_2\text{O}_8 - \text{Na}_2\text{S}_2\text{O}_3$ in water environment. Polyethylenimine hydrogels were synthesized with N, N - dimethylformamide solvent in presence of linking agent epichlorhydrin. Synthesized PAA and PEI hydrogels were crushed into small fractions of $250 < d < 425 \mu\text{m}$. Hydrogel swelling rates were $\alpha_{(\text{hPAA})} = 10,36 \text{ g/g}$, $\alpha_{(\text{hPEI})} = 8,36 \text{ g/g}$.

Intergel couple of polyacrylic acid hydrogel and polyethylenimine hydrogel (hPAA-hPEI) was combined for research purposes.

Experiment. Experiments were done at room temperature. PAA and PEI were taken in dry state. Study of the intergel systems was done as follows: each hydrogel in dry state was placed in separate polypropylene cages. Then polypropylene cages with dry hydrogels were placed in glasses with water and hexaqua uranyl nitrate solutions.

Research of individual polymeric hydrogels sorption properties was done as follows:

1) Estimated amount of each hydrogel in dry state was placed into polypropylene cages.

2) Uranyl ions sorption by individual PAA and PEI hydrogels was done for 48 hours. During this period aliquots were taken for further determination of uranyl ions concentration.

The procedure of studying intergel system sorption abilities is the same as that of studying individual polymer hydrogels.

Uranyl ions determination procedure.

Measurement of uranium mass concentration was done by volumetric titanium-phosphate-vanadate method based on red-ox properties of uranium (IV) and uranium (VI) and its reduction and oxidation reactions.

Uranyl ions extraction (sorption) rate was calculated according to the formula:

$$\eta = \frac{C_{in} - C_{res}}{C_{in}} * 100\%, \quad (1)$$

where C_{in} – uranyl ions initial concentration in solution, mg/l; C_{res} – uranyl ions residual concentration in solution, mg/l.

Total polymer chain binding rate was calculated according to the formula:

$$\theta = \frac{v_{sor}}{v} * 100\%, \quad (2)$$

where v_{sor} – amount of sorbed uranyl ions, mole (calculated as $v_{sor} = m/M$, where m – mass of sorbed uranyl ion, g, M - molecular mass of uranyl ion, g/mole); v – polymer weighed portion (calculated as $v = m/M$, where m – mass of PAA and PEI polymers, g, M - molecular mass of mass of PAA and PEI polymers, g/mole, if two hydrogels are present in the solution, this is calculated as summed amount of each of them), mole.

Dynamic exchange capacity of individual hydrogels and intergel system was calculated according to the formula:

$$Q = \frac{v_{sor}}{m_{sorbent}}, \quad (3)$$

where v_{sor} – amount of sorbed uranyl ions, mole (calculated as $v_{sor} = m/M$, where m – mass of sorbed uranyl ion, g, M - molecular mass of uranyl ion, g/mole); m – polymer weighed portion (if two hydrogels are present in the solution, this is calculated as summed weight of each of them), g.

Results discussion

Previously performed studies [10-12] have shown that almost all interpolymer systems based on acidic (polyacrylic and polymethacrylic acids) and basic (poly-4-vinylpyridine and poly-2-methyl-5-pyridine) lightly cross-linked polymeric hydrogels display higher activity than their initial components. It was also found that polymer ratios which provide higher ions sorption differ significantly depending

on nature of acidic and basic hydrogels and nature of rare-earth metals.

These results were obtained after studying sorption of lanthanum, cerium, dysprosium, neodymium, samarium and erbium by intergel systems. Influence of initial hydrogel state on sorption process was also found. Depending on what gel is used for intergel couple formation (dry, swollen or partially swollen) there can be different hydrogel ratios in intergel systems with high sorption capacity and rare-earth metal ions sorption rate.

However, no work was done to define optimal conditions for maximum sorption and ions selectivity in case of using intergel systems for uranyl ions extraction.

Main feature of intergel systems is absence of direct contact between polymer hydrogels in solution. In other words, this can be called a distant interaction of hydrogels. The general outline of intergel system is given at Figure 1.

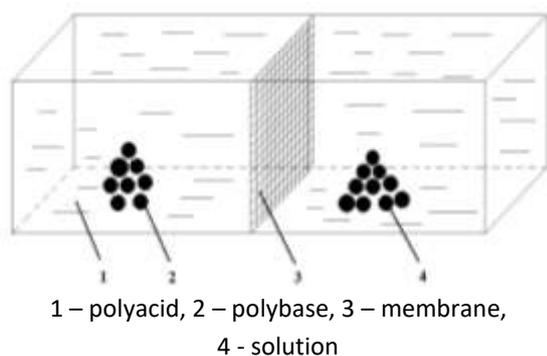
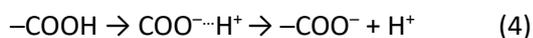


Figure 1 – Intergel system outline

The following chemical reactions occur during distant hydrogel interaction:

1) Dissociation of $-COOH$ – groups of internode links:



It should be considered that first there is ionization with formation of ion couples, which later partially dissociate into separate ions.

2) Atom of nitrogen in pyridine ring is ionized and partially dissociated:



3) Then atom of nitrogen also interacts with proton separated from carboxylic group:



4) H^+ and OH^- ions appearing as a result of functional groups interaction with water molecules form water molecules (true for equimolar concentration of protons and hydroxyl ions):



According to equation 4, carboxylic groups are dissociated into carboxylate anions and protons depends on dissociation rate. As a result of proton adjoining by heteroatoms of nitrogen, total amount of hydrogen atoms in solution decreases, which leads to further dissociation of other (previously non-dissociated) functional carboxylic groups. This happens due to Le Chatelier principle because of equilibrium shift to the right (towards proton formation).

These interactions lead to uncompensated like-charged functional groups formation at internode links of both hydrogels (acidic and basic); these groups bounce off each other according to laws of electrostatics and lead to macromolecular coil expansion. The end result of these electrostatic interactions is significant swelling of polymer macromolecules.

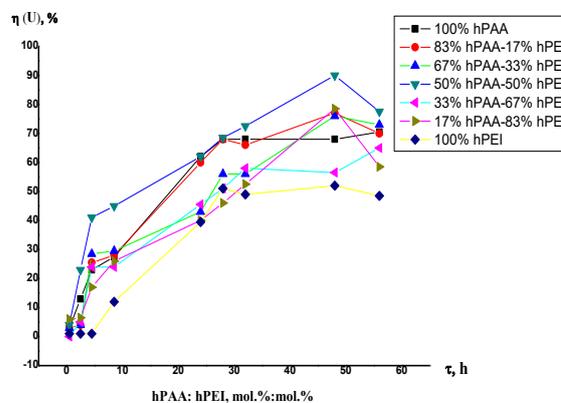


Figure 2 – Dependence of uranyl ions extraction rate by hPAA-hPEI intergel system over time

Figure 2 shows dependence of uranyl ions extraction rate by initial hydrogels and hPAA-hPEI intergel system over time. As the figure suggests, intergel system has increased uranyl ions extraction rate over time. It should be noted that polymeric macromolecules switching to highly ionized state due to hydrogels mutual activation during their remote interaction leads to significantly increased uranyl ions extraction rate with polymeric hydrogels in intergel couples in comparison with initial hydrogels. Most of uranyl ions are sorbed by initial PAA hydrogel and intergel systems through

48-hour interaction with salt solutions. Highest uranyl ions extraction rate is observed in intergel system within 67%hPAA:33%hPEI and 33%hPAA:67%hPEI ratios 48 hours later and is 90,0%. Uranyl ions extraction rate by initial polymer hydrogels - 100%hPAA and 100%hPEI is 68,0% and 52,0%, respectively. Initial PEI hydrogel provides only slight increase of sorption rate over time, however, hPEI (even with low sorption activity towards uranyl ions) actively participates in initial PAA hydrogel activation, which can be seen better within 67%hPAA:33%hPEI and 33%hPAA:67%hPEI ratios.

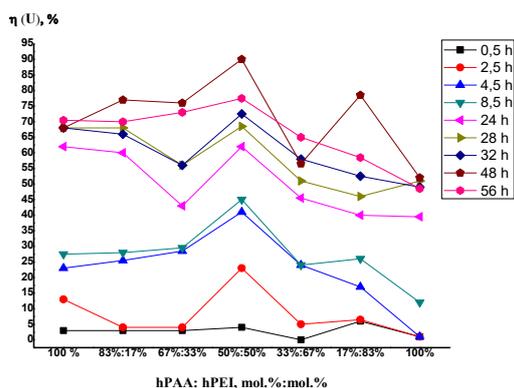


Figure 3 – Dependence of uranyl ions extraction rate by hPAA-hPEI intergel system on hydrogel molar ratio over time

Figure 3 shows dependence of uranyl ions extraction rate by initial hydrogels and hPAA-hPEI intergel system on hydrogel molar ratio over time.

As the figure suggests, the highest uranyl ions sorption occurs within 67%hPAA:33%hPEI and 33%hPAA:67%hPEI ratios. The highest uranyl ions extraction rate after 48 hours of distant hydrogel interaction is 90,0%. Primary reason for such high extraction rate is high polymeric structures ionization due to their mutual activation.

Table 1 shows polymeric chain binding rates (in relation to uranyl ions) by initial polymers and hPAA-hPEI intergel systems over time. The most intensive uranyl ions binding by initial polymers and intergel systems occurs within 48 hours. High degree of polymeric chain binding in relation to uranyl ions is observed at 67%hPAA:33%hPEI and 33%hPAA:67%hPEI components ratios and is 9,1 %. This suggests high macromolecules ionization rate due to mutual activation of PAA and PEI polymers. Individual PAA and PEI polymeric chain binding rate in relation to uranyl ions over 48 hours is 6,8 % and 5,3 %, respectively.

Table 2 shows dynamic exchange capacity (in relation to uranyl ions) by initial hydrogels and hPAA-hPEI intergel systems over time. Obtained data suggest that polymeric hydrogels mutual activation in intergel couples leads to significant increase of exchange capacity values in comparison with initial PEI hydrogel. This is the most distinctive after 48 hours of remote interaction. Intergel system reaches maximum values of dynamic exchange capacity within the ratios of 67%hPAA:33%hPEI and 33%hPAA:67%hPEI after 48 hours of remote interaction and is 1.14 mmol/g.

Table 1 – Polymeric chain binding rates (in relation to uranyl ions) by initial hydrogels and hPAA-hPEI intergel systems over time, %

Polymer chain binding rate (in relation to uranyl ions), %								
τ , h	0,5	2,5	4,5	8,5	24	28	32	48
100%hPAA	0,3	1,3	2,3	2,8	6,3	6,8	6,8	6,8
83% hPAA:17% hPEI	0,3	0,4	2,6	2,8	6,1	6,8	6,7	7,8
67% hPAA:33% hPEI	0,3	0,4	2,8	2,9	4,3	5,7	5,7	7,7
50% hPAA:50% hPEI	0,4	2,3	4,2	4,6	6,3	6,9	7,3	9,1
33% hPAA:67% hPEI	0,0	0,5	2,4	2,4	4,6	5,2	5,8	5,7
17% hPAA:83% hPEI	0,6	0,7	1,7	2,6	4,1	4,7	5,3	8,0
100%hPEI	0,0	0,1	0,1	2,1	4,0	5,2	4,9	5,3

Table 2 – Dynamic exchange capacity (in relation to uranyl ions) by initial hydrogels and hPAA-hPEI intergel systems over time, %

τ , h	0,5	2,5	4,5	8,5	24	28	32	48
100%hPAA	0,04	0,18	0,32	0,38	0,87	0,95	0,95	0,95
83% hPAA:17% hPEI	0,04	0,05	0,35	0,38	0,81	0,92	0,89	1,04
67% hPAA:33% hPEI	0,04	0,05	0,37	0,38	0,56	0,73	0,73	0,99
50% hPAA:50% hPEI	0,05	0,29	0,52	0,57	0,78	0,86	0,92	1,14
33% hPAA:67% hPEI	0,00	0,06	0,29	0,29	0,56	0,62	0,71	0,69
17% hPAA:83% hPEI	0,07	0,08	0,20	0,31	0,47	0,54	0,62	0,93
100%hPEI	0,01	0,01	0,01	0,12	0,45	0,58	0,56	0,60

Conclusion

Based on obtained results it was found that the highest uranyl ions sorption by interpolymer system occurs at 67%hPAA:33%hPEI and 33%hPAA:67%hPEI components ratio. The highest uranyl ions extraction rate after 48 hours of distant hydrogel interaction is 90,0%, where polymeric chain binding rate is 9,1% and dynamic exchange capacity is 1,14 mmole/g. Uranyl ions extraction rate by individual polymer hydrogels - 100%hPAA and 100%hPEI - is 68,0% and 52,0%, respectively. Due to mutual hydrogel activation during their distant interaction polymeric macromolecules

switch to highly ionized state which leads to significant increase of uranyl ions extraction rate in comparison with initial polymers. Obtained outcomes suggest that interpolymer systems can be used for highly efficient sorption technology of extracting uranyl ions and other elements from commercial solutions as well as for concentration, separation of different ions from water solutions for performing technological, environmental and other objectives.

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

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Уранил иондарын полиакрил қышқылы мен полиэтиленимин гидрогельдерінің негізіндегі интерполимерлік жүйемен бөлу ерекшеліктері

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ТҮЙІНДЕМЕ

Полиакрил қышқылы (ПАҚ) және полиэтиленимин (ПЭИ) гидрогелдерінен тұратын интерполимерлік жүйелердің уранил иондарына сорбциясы зерттелді. Бастапқы полимерлер мен ПАҚ-ПЭИг интерполимерлік жүйелерінің уранил иондарын бөлу дәрежесі, полимер тізбегінің байланысу дәрежесі және тиімді динамикалық алмасу сымдылығы есептелді. Алынған нәтижелер негізінде интерполимерлік жүйелердің уранил иондарына максималды сорбциясы

<p>Мақала келді: 14 шілде 2021 Сараптамадан өтті: 07 тамыз 2021 Қабылданды: 15 қазан 2021</p>	<p>67%ПАҚ:33%ПЭИг және 33%ПАҚ:67%ПЭИг қатынастарында болатыны анықталды. Гидрогелдердің қашықтан өзара әрекеттесуінің 48 сағатынан кейін уранил иондарын максималды бөлу дәрежесі 90,0 %, полимерлік тізбектің байланысу дәрежесі 9,1 % және динамикалық алмасу сиымдылығы – 1,14 ммоль/г болды. 100 % ПАҚ және 100 % ПЭИг жеке полимерлік гидрогелдерімен уранил иондарын бөлу дәрежесі сәйкесінше 68,0 % және 52,0 % құрады. Алынған нәтижелер интерполимерлі жүйелердегі бастапқы полимерлік гидрогелдердің сорбциялық қасиеттерінің өзгеретінін, яғни функционалды топтардың реакцияға түсу қабілеті анағұрлым артатынын көрсетті. Бұл оларды уранил иондарын бөлудің жоғары тиімді сорбциялық технологиясын жасау үшін қолдануға мүмкіндік береді.</p> <p>Түйін сөздер: гидрогелдер, интерполимерлі жүйелер, сорбция, полиакрил қышқылы, полиэтиленмин, уранил ионы.</p>
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Особенности извлечения ионов уранила интерполимерной системой на основе гидрогелей полиакриловой кислоты и полиэтиленмина

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<p>Поступила: 14 июля 2021 Рецензирование: 07 августа 2021 Принята в печать: 15 октября 2021</p>	<p>АННОТАЦИЯ Изучена сорбция ионов уранила интерполимерной системой, состоящей из гидрогеля полиакриловой кислоты (гПАК) и гидрогеля полиэтиленмина (гПЭИ). Были рассчитаны степень извлечения ионов уранила исходными полимерами и интерполимерной системой гПАК-гПЭИ, степень связывания полимерной цепи и динамическая обменная емкость исходных полимеров и интерполимерной системы гПАК-гПЭИ. На основе полученных результатов было установлено, что наибольшая степень сорбции ионов уранила интерполимерной системой происходит в пределах соотношений 67%гПАК:33%гПЭИ и 33%гПАК:67%гПЭИ. Максимальная степень извлечения ионов уранила по истечении 48 часов дистанционного взаимодействия гидрогелей составила 90,0 %, при которой степень связывания полимерной цепи составила 9,1 % и динамическая обменная емкость – 1,14 ммоль/г. Степень извлечения ионов уранила индивидуальными полимерными гидрогелями 100%гПАК и 100%гПЭИ составила 68,0 % и 52,0 % соответственно. Полученные результаты показали изменения сорбционных свойств исходных полимерных гидрогелей в интерполимерной системе, приводящие к тому, что функциональные группы преобретают более высокую реакционную способность, что предоставляет возможность их применения для последующей разработки высокоэффективной сорбционной технологии извлечения ионов уранила.</p> <p>Ключевые слова: гидрогели, интерполимерные системы, сорбция, полиакриловая кислота, полиэтиленмин, ион уранила.</p>
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Study of the mechanism of pre-burned ash leaching by hydrochloric acid

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ABSTRACT

The use of hydrochloric acid for processing aluminum-containing raw materials has a number of advantages over other acids, which include: easy decomposition of aluminum compounds with the transfer of aluminum into solution; low solubility of silica in HCl, the possibility of complete separation of the solid residue without significant losses of acid, etc. The paper considers the possibility of using the method for processing ash and slag dumps accumulated in large volumes in the country. Based on the thermodynamic analysis of reactions of interaction between ash components and hydrochloric acid, the behavior of aluminum, iron and nonferrous metal compounds during leaching is studied. It was shown that the preliminary roasting of ash with calcium chloride provides a high extraction of aluminum in the solution from the cinder. Based on experimental studies, the influence of time, temperature and acid consumption on the degree of aluminum extraction into the solution has been established. At optimal conditions of leaching conducted at S:L = 1:3, T = 60 °C, τ = 60 min extraction of aluminum in a solution as chloride amounted to 99.92 %. At the same time the extraction of silica in solid sediment due to the maximum transfer of impurities in the solution was 99.8 %. The mechanism of the leaching process is proposed. The values of activation energy and the order of the reaction, indicating the complex 3-step character of the reactions, have been calculated. It is established that the limiting stage during leaching is the dissolution of anorthite.

Keywords: carbon black, leaching, hydrochloric acid, process mechanism, time, temperature, extraction, activation energy.

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Introduction

Ash is the largest type of waste produced by large thermal power plants and steel mills as a result of coal combustion. More than 100 million tons of ash are produced in the U.S. each year. Annual ash output by developed country is, in million tons: India - 112, China - 100, Germany - 40 and UK - 15 [1, 2, 3].

In the Russian Federation there are more than 170 coal-fired thermal power plants, which burn 650 million tons of coal with the formation of 300 million tons of ash annually. More than 20 thousand km² of land plots are alienated for ash and slag waste storage in Russia, where 1.3-1.5 billion tons of ash are located [4].

In Kazakhstan, the annual output of ash and slag waste is about 19 million tons. To date, more than 300 million tons of waste has been accumulated in ash dumps [5]. In one major megalopolis in Kazakhstan, Almaty, more than 2 million tons of ash and slag waste have been accumulated as a result of three thermal power plants. Only during one heating season about 600 thousand tons of ash waste is added to the accumulated volumes of ash from coal combustion. The generated ash dumps have taken vast areas out of land use and have a negative impact on the environment (pollution of soil, air, groundwater).

The relevance and significance of the issues under consideration are enhanced with the fact that there is

no rational technology for ash processing. Significance of researches in the direction of development of highly efficient technology for ash processing consists in solving two key problems - ecological and technological. Solution of the first problem comes to involving the accumulated and current ash and slag wastes in processing and liberating large territories, and reducing the burden on the environment by reducing the volume of ash and its fine dispersion by the wind (20-40 μ). Solution of the second problem ensures the use of ash as an additional source of raw materials with complex extraction of valuable metals with high added value.

The existing methods of ash processing [6, 7] allow extracting small amounts of valuable components. At the same time, according to the material composition ash can be considered as an independent complex raw material for the extraction of a whole range of metals [8, 9, 10]. Ashes compare favorably with conventional mineral deposits, they are located on the surface and do not require large expenses for extraction.

Positive research results [11, 12] allowed us to formulate a general concept of technology for the processing of ash of different chemical and mineralogical composition. Of particular interest is the application of the technology for the utilization of ash from small boiler plants, located within the boundaries of large cities and megacities.

The proposed technology can become an alternative for the production of alumina, silica and REM in countries where there are no bauxite deposits suitable for the production of alumina by the Bayer method and no natural sources for the production of pure silica and REM.

This paper presents the results of studies of the interaction of cinder components during its leaching with hydrochloric acid together with calcium chloride. Based on thermodynamic analysis of reactions of interaction between the components of the cinder with hydrochloric acid, the behavior of aluminum, iron and nonferrous metal compounds in the leaching process has been studied.

As a result of experimental studies, regularities of aluminum compounds dissolution during hydrochloric acid leaching depending on time, temperature, and hydrochloric acid consumption have been established. Optimal parameters of the leaching process providing maximum aluminum extraction into the solution as its chloride 99.92 % and high silica extraction into solid commercial sediment - 99.8 % have been determined.

Research methods

The main methodological principle for studying the mechanism of ash leaching with hydrochloric

acid is the thermodynamic approach to the description of cinder leaching, which provides reliable determination of qualitative and quantitative characteristics of the formed complex composition solid (cinder) and liquid solutions of hydrochloric acid leaching.

Determination of the influence of hydrochloric acid consumption, temperature and time on the completeness of silica extraction into the commercial product in the form of precipitate and the maximum extraction of aluminum, nonferrous metals, REM and other associated elements in the solution was based on experimental results.

For the experiments a firing result, obtained under optimal burning conditions ($T=1100$ °, CaCl_2 consumption was twice higher than the required from stoichiometry for mullite decomposition, $\tau=60$ min) of non-magnetic ash fraction together with calcium chloride, was used. The non-magnetic fraction of ash was obtained by magnetic separation of ash from a thermal power plant in Almaty [12].

The elemental and phase composition of solid and liquid products of cinder leaching with hydrochloric acid was performed using a D8 Advance analyzer (Bruker), α -Cu, tube voltage 40 kV, current 40 mA. Processing of the obtained data of the diffraction patterns and calculation of the interplanar distances were performed using the EVA software. Sample interpretation and phase search were performed by Search/match using the PDF-2 powder diffractometer database.

In order to clarify and obtain reliable results of the phase composition of the initial cinder and leach products the X-ray diffractometric analysis on diffractometer DRON-3 with CuCa-radiation, β -filter was additionally performed. The diffractogram conditions: $U=35$ kV; $I=20$ mA; $\theta=2\theta$; detector 2 deg/min. X-ray phase analysis on a semi-quantitative basis was performed on powder sample diffractograms using the method of equal weights and artificial mixtures. Quantitative ratios of crystalline phases were determined. Interpretation of the diffractograms was performed using the data from the ICDD: Powder Diffraction File (PDF2) and diffractograms of clean minerals. For the main phases the calculation of the content was carried out.

The total number of experiments ($3k=9$) was determined based on the influence of two parameters on the required parameters, each of which was set in three levels: $S:L = 1:2; 1:3; 1:4$ and temperature - 40, 60, 80 °C. 30 % HCl hydrochloric acid was used in the experiments. Initial weight of cinder in all experiments was 243 g. Time of cinder

leaching was 60 minutes. For each experiment by results of elemental composition of the received products the material balance was calculated, their data were used for a choice and substantiation of optimum parameters of process.

The technique of carrying out of experiments consisted in the following. The 243 g of crushed char was loaded into a glass flask and concentrated hydrochloric acid was added to it in the specified quantity S:L. The beaker with the contents was then placed on a thermostat and leaching was started using an agitator. The stirrer speed was 300 rpm. The thermostat was used to set the desired leaching temperature.

After the required time the suspension was filtered and the solid sediment was separated from the productive solution. The solid sediment (cake) after washing with water (pH=5-7) and drying was sent for chemical and X-ray phase analysis.

Productive solution was analyzed for aluminum, calcium, iron, nonferrous metals and REM. Composition of washing solution was determined by the difference of loaded and received materials based on the material balance of each experiment.

Under the conditions of the established optimum regimes the experience of leaching of slag with hydrochloric acid was carried out on an enlarged laboratory scale. The methodology of the experiment was as follows. Source materials (cinder and HCl) were continuously fed for leaching. HCl-acid consumption was 4 l/h. The consumption of cinder was 0.8 kg/h. The leaching time was 60 minutes. The slurry obtained after the set leaching time was continuously discharged from the reactor through the overflow into a laboratory batch filter. The solid precipitate (cake) after leaching was filtered and after washing with water was sent for drying. The total amount of cinder subjected to leaching - 1091,38 g. The received products of leaching - a solution and cake, were subjected to the elemental and phase analysis.

On the basis of the received results, the material balance of enlarged-balance leaching of cinder under the conditions of an optimum mode of conducting process: S:L=1:3, T=60 °C and τ =60 min was made up.

Results and discussion

The complete elemental composition of the initial cinder obtained under optimal firing conditions is presented in Table 1.

The phase composition of the cinder subjected to leaching is presented in Table 2.

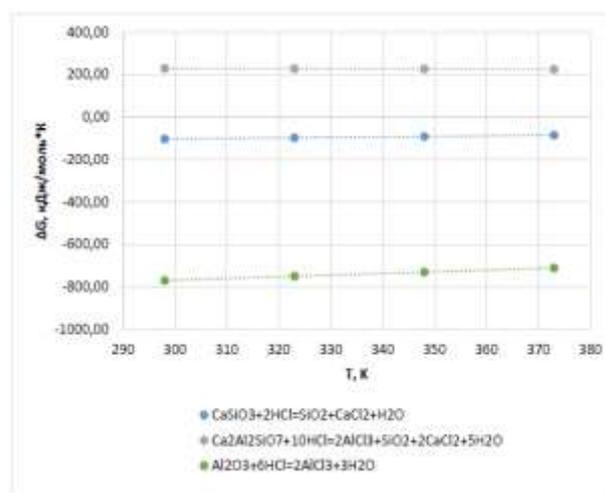
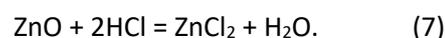
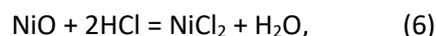
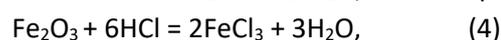
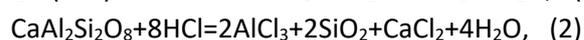
Table 1 - Elemental composition of the cinder

Elements	Content, %
Al	9,87
Si	19,7
Ca	25,7
Fe	0,8
O ₂	22,7
Cl	19,5
(Cu + Zn + Ni), ppm:	298,0
Cu	22,0
Zn	221,0
Ni	55,0
ΣREM, ppm:	74,0
Sc	29,0
Y	45,0

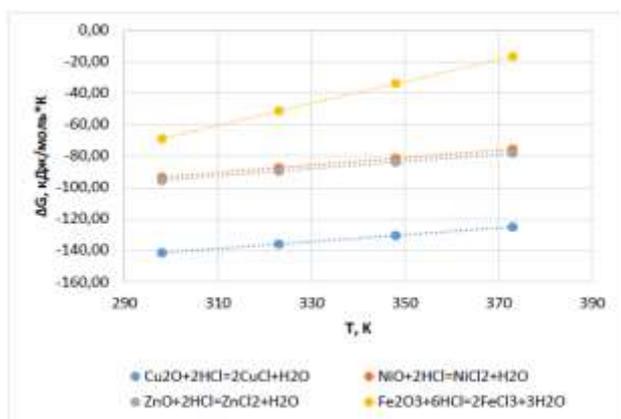
Table 2 - Results of semi-quantitative X-ray phase analysis of the cinder

Name of phase	Formula	Concentration, %
Gehlenite	Ca ₂ Al(SiAl)O ₇	25,68
Anorthite	CaAl ₂ Si ₂ O ₈	5,34
Pseudowollastonite	CaSiO ₃	30,13
Hematite	Fe ₂ O ₃	0,64
Other		38,21

Taking into account the established phase composition of the cinder, the mechanism of its leaching process with hydrochloric acid can be represented by reactions:



A)



B)

Figure 1 - The dependence of the Gibbs free energy on temperature for reactions (1) - (7)

The temperature dependence of the Gibbs free energy loss for reactions (1) - (7) is shown in Fig. 1.

We can see that the probability of reactions of interaction of gehlenite and anorthite with hydrochloric acid in the temperature range 298...373 K, providing the transition of aluminum in the solution as its chloride, is almost impossible because of the positive values of the Gibbs free energy of reactions (1), (2). There is a high probability of wollastonite decomposition by hydrochloric acid in reaction (3) with the formation of calcium chloride and quartz. The formation of a free amount of CaCl₂ seems not crucial, as it is recycled and returns to the head of the technology - to the process of burning ash.

High negative values of the Gibbs free energy of reactions (4) - (7) indicate the possibility of iron and non-ferrous metals transfer in the form of their chlorides into the solution. The established regularities show that according to thermodynamic calculations the transfer of aluminum from its readily soluble compounds (gelenite, anorthite) into the solution by leaching the cinder with hydrochloric acid is not possible. At the same time, the results of experimental studies fully confirm the possibility of high aluminum extraction into solution from the cinder. The observed pattern indicates a complex mechanism of the cinder leaching process with hydrochloric acid and can be interpreted by the results of the experiments.

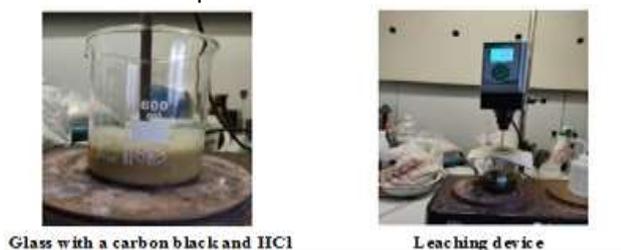


Figure 2 - Laboratory equipment for leaching

The cinder leaching with hydrochloric acid was carried out using laboratory equipment, the general view of which is shown in Fig. 2.

Fig.3 shows products of cinder leaching with hydrochloric acid obtained under optimum conditions of leaching: T:L=1:4; T=60 °C; τ=60 min.



Figure 3 - Products of cinder leaching with hydrochloric acid (S:L=1:4; T=60 °C; τ=60 min)

Dependence of aluminum extraction into solution on leaching time and process temperature is shown in Fig. 4.

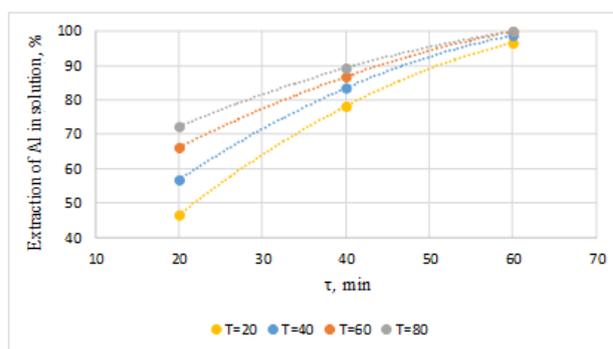


Figure 4 - Dependence of aluminum extraction into solution on leaching time and temperature

It can be seen from fig.4 that aluminium recovery into solution during initial stage of leaching - during leaching time increase from 20 to 40 minutes - significantly increases in temperature change from 20 to 80 °C. A further increase in the leaching time has little effect on the aluminum extraction in solution. The maximum aluminum extraction into solution is reached at 60 minutes.

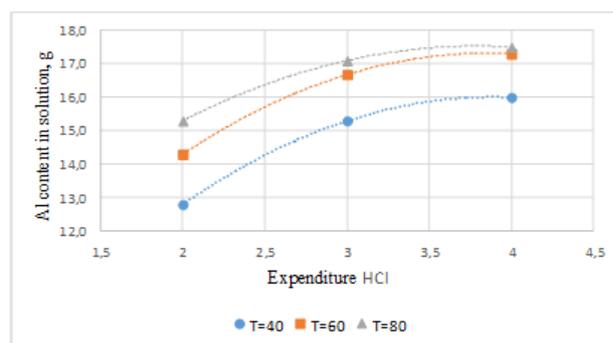


Figure 5 - Dependence of the aluminum content in the solution on the HCl flow rate (S:L) and temperature

An increase in temperature in this area has only an insignificant influence on aluminum extraction into solution.

The dependence of aluminum content in solution on HCl consumption and temperature is shown in Fig. 5.

It is easy to see that the influence of the HCl consumption on the solubility of aluminum from the cinder is more significant than the temperature. If the ratio T:L=1:4, the increase in temperature from 40 to 60°C has no significant effect on the transfer of aluminum into solution. This is also confirmed by the dependence of aluminum recovery into solution, which at T:L=1:4, in the temperature variation interval from 60 to 80 °C does not change, and remains practically on the same level ~99,96 % (Fig.6).

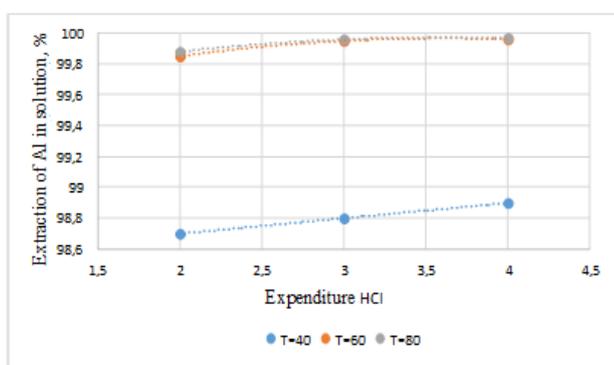


Figure 6 - Dependence of aluminum extraction into solution on the dependence of HCl (S:L) and temperature

SiO₂ content in the sediment at S:L=1:2 and temperature 40 °C, is ~ 98,8 % (Fig.7), which indicates a weak dissolution of silica in HCl and its maximum concentration in the solid sediment. A sharp increase in silica content in the precipitate from 98 to 99.5 % at 40°C is observed when the T:L ratio increases from 2 to 4. At T:L=1:4 the increase in temperature from 60 to 80 °C has only a small effect on the increase in silica content in the sediment, from 99.6% to 99.7%.

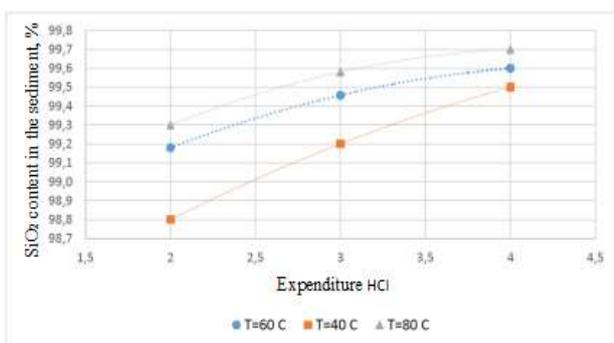


Figure 7 - Dependence of silica content in sediment on the HCl flow rate (S:L) and temperature

The maximum silica extraction into sediment ~99.9 % is reached at S:L=3, and remains constant at this level regardless of further temperature increase, as it can be seen in Fig.8.

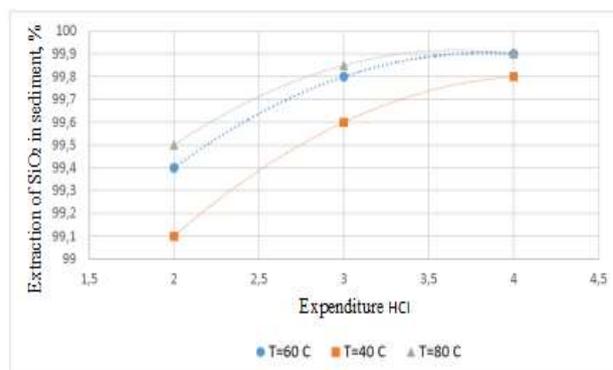


Figure 8 - Dependence of silica extraction on the HCl flow rate (S:L) and temperature

Determination of kinetic parameters of the leaching process

To determine the kinetic parameters of the cinder leaching process with hydrochloric acid, experimental data on the dependence of aluminum extraction degree in the solution on temperature, duration and concentration of hydrochloric acid were used (Fig. 4, 5). Based on these data, using the known kinetic equations and the Arrhenius equation [13], the values of apparent activation energy and the order of reactions were calculated.

$$dC / dt = K(T) \cdot C^n, \quad (8)$$

$$K(T) = A \cdot \exp(-E_a / RT), \quad (9)$$

where: K - reaction rate constant;
C - concentration of the reactant;
n - order of reaction;
A - pre-exponential multiplier or frequency factor of the constant characteristic of this reaction;
E_a - activation energy;
R - universal gas constant, R = 8.31 J/K-mol.

Determination of the activation energy (E_a) was carried out for the standard concentration of the reagent (30 % HCl) for four temperatures (20, 40, 60 and 80 °C).

After transforming equation (9) we can obtain expressions for determining the activation energy:

$$\text{Lg}K = \text{Lg}A + E_a / 2,3 \cdot T, \quad (10)$$

$$E_a = 2,3 \cdot \text{tg}\alpha. \quad (11)$$

The dependence of the logarithm of the reaction rate constant on 1/T is shown in Fig. 9.

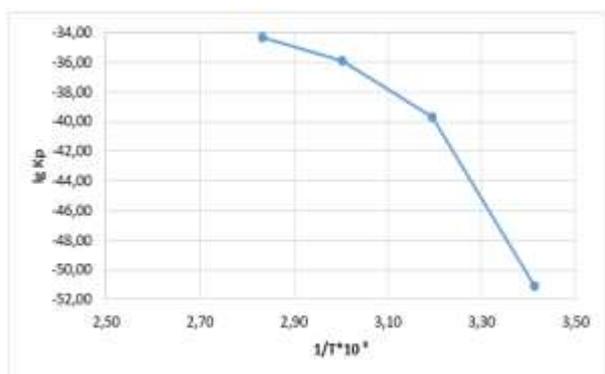


Figure 9 - Dependence of the rate constant of the reaction of dissolution of cinder dissolution by hydrochloric acid from inverse temperature

On fig. 9 it is possible to allocate 3 sites that testifies to change of character of interaction between reacting components. For each area by the slope tangent (11) was determined the value of apparent activation energy: at 20 °C - 83.4 kJ/mol, at 40 °C - 53.12 kJ/mol, at 60 °C - 32.34 kJ/mol.

Bauxite leaching is caused by the step nature of dissolution and strongly depends on the duration of the process. In the initial period, when there is enough reagent, there is a simultaneous dissolution of all the components of bauxite and the speed of the entire process is determined by the rate of the chemical reaction. At 40 °C and leaching duration of 20 minutes the wollastonite (reaction (3)), hematite by reaction (4) and nonferrous oxides by reactions (5) - (7) are dissolved completely. A further increase in time up to 40 min leads to the dissolution of helenite and anorthite by reactions (1) and (2). This begins to form amorphous silicon dioxide, which is present in the form of silicic acid, makes it difficult to supply the reagent (HCl) to the reaction zone. The process moves into the mixed region. A further increase in the leaching time leads to an increase in the amount of amorphous silica, indicating that the process proceeds in the diffusion region. At this stage, the main source of aluminum in the solution is helenite, while anorthite still remains in the solid residue. Consequently, the limiting reaction of the cinder leaching process is the dissolution of anorthite by reaction (2).

Table 3 – Material balance of the process of leaching pellet with hydrochloric acid under optimal conditions. S:L = 1:3; T = 60 °C; τ = 60 min

Name	g	%	Al			SiO ₂			Ca			Fe		
			I	II	III	I	II	III	I	II	III	I	II	III
Uploaded														
Initial deposit	1091.38	22.44	66.98	6.07	100.00	286.24	26.23	100.00	338.07	30.65	100.00	5.40	0.49	100.00
Hydrochloric acid	3771.66	77.56												

To determine the order of reaction for the reagent (HCl), we used experimentally obtained dependences of aluminum content in the solution on the leaching duration at different concentrations of hydrochloric acid and constant temperature (Fig. 5). For two concentrations of reagent under condition of identical technological regimes, equation (8) can be written in the form [14]:

$$d\tau_1 / d\tau_2 = (C_1 / C_2)^n. \quad (12)$$

By logarithmizing equation (8), we can obtain an expression to calculate the order of the reaction:

$$n = \text{Lg}(d\tau_1 / d\tau_2) / \text{Lg}(C_1 / C_2). \quad (13)$$

Using equations (8) and (13), we determined the values of the reaction order. It was found that the kinetics of the process is significantly affected by the consumption of hydrochloric acid. At low values of HCl consumption (S:L=1:2) and temperature 60°C, the index of reaction order is fractional (n = 0.57), which corresponds to the kinetic region. When the HCl flow rate increases to S:L=1:4, the reaction order value, n ≈ 1, which indicates that the reaction (2) proceeds in the diffusion mode.

On the basis of the received results optimum parameters of process of cinder leaching by hydrochloric acid have been determined:

- hydrochloric acid consumption, S:L - 1:3;
- HCl concentration - 30 %;
- Leaching temperature - 60 °C;
- Extraction of aluminum in the solution - more than 99.0%;
- silica yield (precipitate) - more than 25% of the weight of the cinder;
- silica content in the sediment - more than 99.7%;
- extraction of silica in the sediment - more than 99,0%.

Material balance of enlarged-laboratory leaching of sludge (1091.38 g) with hydrochloric acid obtained under conditions of optimal process parameters is shown in Table 3.

Total:	4863.04	100.00	66.98		100.00	286.24		100.00	338.07		100.00	5.40		100.00
Received														
Precipitate	287.23	4.35	0.05	0.02	0.08	285.67	99.46	99.8	0.20	0.07	0.06	0.05	0.02	1.00
Solution	4575.81	95.65	66.93	1.46	99.92	0.57	0.01	0.2	337.87	7.38	99.94	5.34	0.12	99.00
Total:	4863.04	100.00	66.98		100.00	286.24		100.00	338.07		100.00	5.40		100.00

O			HCl			Прочие		
I	II	III	I	II	III	I	II	III
144.99	13.29	100.00				249.70	22.64	8.64
			1131.50	30.00	100.00	2640.16	70.00	91.36
144.99		100.00	1131.50		100.00	2889.86		100.00
						1.25	0.43	0.04
144.99	3.17	100.00	1131.50	24.73	100.00	2888.61	63.13	99.96
373.22		100.00	1131.50		100.00	2889.86		100.00

I – quantity, g; II – content, %; III – distribution, %

The yield of silica in the form of precipitate was ~26% of the weight of the cinder in the charge. The chemical composition of the pure silica obtained was, % (wt.): 99,5 SiO₂; 0,02 Al; 0,07 Ca; 0,02 Fe.

The composition of the obtained mother liquor, g/l: 16.68 Al; 0.14 SiO₂; 84.21 Ca; 1.33 Fe; 281.9 HCl; 0.004 Cu; 0.037 Zn; 0.001 Ni; 0.012 ΣREM; others.

High aluminum extraction into the solution was achieved - 99.92 %.

Extraction of silica into solid commercial product - 99.8 %.

Conclusions

Based on the thermodynamic analysis of the reactions of interaction between the components of the cinder with hydrochloric acid, the behavior of aluminum, iron and non-ferrous metal compounds in the leaching process was studied.

As a result of experimental studies, regularities of aluminum compounds dissolution during hydrochloric acid leaching have been established depending on time, temperature, and hydrochloric acid consumption. Optimal parameters of leaching process providing maximum aluminum recovery into solution in a form of its chloride 99.92 % and high

silica recovery into solid commercial sediment - 99.8 % have been determined.

The mechanism of pre-burned ash leaching in hydrochloric acid has been established. It is shown, that the process speed is limited by anorthite dissolution and leaching of ash by hydrochloric acid proceeds stepwise in 3 stages in the temperature interval: at temperatures 20-40 °C - in the kinetic region (E_a = 83.4 kJ/mol, n = 0.57), at 40-60 °C - in the intermediate region (E_a = 53.12 kJ/mol), at 60-80 °C - in the diffusion region (E_a = 32.34 kJ/mol, n ≈ 1).

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

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Алдын ала күйдірілген күлді тұз қышқылымен шаймалау механизмін зерттеу**Досмухамедов Н.К., Жолдасбай Е.Е., Даруеш Ғ.С., Арғын А.Ә., Құрмансейтов М.Б***Сәтбаев университеті, Алматы, Қазақстан*

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 Қабылданды: 22 қазан 2021

ТҮЙІНДЕМЕ

Құрамында алюминий бар шикізатты өңдеу үшін тұз қышқылын пайдалану басқа қышқылдармен салыстырғанда бірқатар артықшылықтарға ие, ол артықшылықтарға мыналарды жатқызуға болады: алюминий қосылыстарының ерітіндіге ауысып ыдырауының қарапайымдылығы; HCl-да кремнеземнің ерігіштігінің төмен болуы, қышқылды көп шығындамай қатты қалдықты толық бөліп алу мүмкіндігі және т.б. Жұмыста республика аумағында үлкен көлемде жинақталған күл-қож үйінділерін қайта өңдеу тәсілін қолдану мүмкіндігі қарастырылған. Күл компоненттері мен тұз қышқылының өзара әрекеттесу реакцияларын термодинамикалық талдау негізінде шаймалау кезінде алюминий, темір және түсті металдар қосылыстарының әрекеттері (таралуы) зерттелді. Күлді кальций хлоридімен алдын-ала күйдіру арқылы алюминийдің ерітіндіге жоғары дәрежеде бөлінуі қамтамасыз етіледі. Тәжірибелік зерттеулер негізінде ерітіндіге алюминийді бөліп алу дәрежесіне қышқыл шығынының, уақыттың, температураның әсері анықталды. Шаймалауды жүргізудің оңтайлы режимі жағдайында Т:Ж = 1:3, Т = 60 °С, τ = 60 мин. алюминийдің хлорид түрінде ерітіндіге бөлінуі 99,92% құрады. Бұл ретте қоспаларды ерітіндіге барынша максималды ауыстыру нәтижесінде кремнеземді қатты тұнбаға бөліп алу 99,8% болды. Жұмыста шаймалау процесінің механизмі ұсынылды. Белсендіру энергиясының мәндері және реакциялардың күрделі 3 сатылы сипатын көрсететін реакция тәртібі есептелді. Анортит еріген кезде шаймалаудың шекті кезеңі болатындығы анықталды.

Түйін сөздер: күйінді, шаймалау, тұз қышқылы, процестің механизмі, уақыт, температура, бөліп алу, активтендіру энергиясы.

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Исследование механизма выщелачивания предварительно обожженной золы соляной кислотой**Досмухамедов Н.К., Жолдасбай Е.Е., Даруеш Ғ.С., Арғын А.А., Курмансейтов М.Б.***Satbayev University, Almaty, Kazakhstan***АННОТАЦИЯ**

Использование соляной кислоты для переработки алюминий содержащего сырья имеет ряд преимуществ по сравнению с другими кислотами, к которым можно отнести: простоту разложения соединений алюминия с переводом алюминия в раствор; низкую растворимость кремнезема в HCl, возможность полного отделения твердого остатка без существенных потерь кислоты и др. В работе рассмотрена возможность применения способа для переработки золошлаковых отвалов, накопленных в больших объемах на территории республики. На основании термодинамического анализа реакций взаимодействия между компонентами золы с соляной кислотой изучено поведение соединений алюминия, железа и цветных металлов при выщелачивании. Показано, что предварительный обжиг золы с хлоридом кальция обеспечивает высокое извлечение алюминия в раствор из огарка. На основании экспериментальных исследований установлено влияние времени, температуры и расхода кислоты на степень извлечения алюминия в раствор. В условиях оптимального режима ведения выщелачивания Т:Ж = 1:3, Т = 60 °С, τ = 60 мин. извлечение алюминия в раствор в виде хлорида составило 99,92 %. При этом извлечение кремнезема в твердый осадок за

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счет максимального перевода примесей в раствор составило 99,8 %. Предложен механизм процесса выщелачивания. Рассчитаны значения энергии активации и порядок реакции, указывающие на сложный 3-х ступенчатый характер протекания реакций. Установлено, что лимитирующей стадией при выщелачивании является растворение анортита.

Ключевые слова: огарок, выщелачивание, соляная кислота, механизм процесса, время, температура, извлечение, энергия активации.

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Modification of microstructure of LD slag for recovery of hybrid flux material

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ABSTRACT

The Basic Oxygen Furnace steel making process produces BOF slag (LD slag) at a rate of about 125 kg/t. The LD slag contains about 18% Fe in wustite and dicalcium ferrite and about 45% CaO. These minerals are an excellent source of alternative flux material for the steel industry. Through slag modification and in-depth characterization studies, investigations were carried out to develop a material that could be utilized as an alternative flux material. Detailed characterization studies were conducted using SEM-EPMA and XRD to identify the changes in the crystal structure, phase distribution, grain size and liberation size of minerals. The grain size of phases was found to be between 10-150 µm for normally cooled slag and 20-250 µm for slowly cooled slag. It was also shown that slow cooling promotes the formation of an additional phase which is essentially the dicalcium silicate phase (C₂S) with some amounts of FeO and MgO in the crystal lattice. Overall, it was observed that about 50% of the LD slag could be recovered as alternative flux material containing approximately 30% CaO and 30% Fe content. This alternative flux material is an excellent source of material for use in steel industries because of its low melting slag formation.

Keywords: LD slag, characterization, hybrid flux, cooling rate, microstructure.

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Introduction

The ferrous metallurgical slag mostly consists of granulated BF slag and Steel slag cooled in the air, known as Linz Donawitz (LD) or Basic Oxygen Furnace (BOF) Slag. The distribution of BF slag and Steel slag is about 58% and 42% respectively. The specific rate of generation of LD slag from steel making process is about 125 kg/ton [1-4].

The LD slag tapped out of the converter may sometimes contain up to 25% metallic iron, which needs to be recovered to minimize metal losses [5]. The non-magnetic LD slag has useful mineral phases like dicalcium silicate (C₂S), tricalcium silicate (C₃S), dicalcium alumino ferrite, magnesio-wustite and some amount of free lime [5]. It has also been reported that LD slag may contain some amount of periclase, Mn cordierite and glass content [6].

The non-metallic LD slag has a basicity of greater than 3 in view of higher CaO content which goes as high as 50% in some cases. The CaO is present in the form of dicalcium and tricalcium silicate and free lime. Since free lime tends to stabilize in the presence of water, it gets converted to portlandite Ca(OH)₂ which ultimately results in volumetric instability and expansion of the slag or any structure made out of the non-metallic slag [7]. The expansion is associated with the cracking of the structures over some time. The expansion is also caused due to the presence of free MgO (periclase) which is the cause of delayed expansion and cracking [8-9].

Many literatures report that using LD slag as a flux material improves the iron ore sintering efficiency, and this is because of the fast melt formation during the sintering process. In addition, the iron oxide present in non-metallic LD slag also

adds to the iron burden, thereby reducing the specific consumption of iron ore [10-11]. The constraint, however, is because of the high phosphorus content of LD slag which restricts its usage in iron ore sintering [12].

Extensive research has been done over the last 40 years on stabilizing LD slag to make it suitable for civil engineering applications. Research has also been done in recycling and reuses applications within the steel industry [13-16].

It is reported that the use of non-metallic LD slag in Bhilai Steel Plant, India, was discontinued due to the higher content of Phosphor and Sulphur [17]. The phosphorus removal from LD slag is a much-researched topic and, several studies have been carried out on this subject [18-23].

The bulk utilization of LD slag through CO₂ sequestration has also been attempted and it is reported that about 6-11% of the CO₂ generated from LD converter can be sequestered using LD slag [24].

The research work available so far suggests that not much research has been done on the recovery of hybrid flux material, which contains both lime and iron oxide. Therefore, this research work focuses on the objective to develop enablers for synthesizing a material that is a hybrid material containing lime and iron oxide and has excellent slag met properties when used in the iron making process.

The research work presented in this paper is attempts to develop enablers through preliminary modification and characterization studies of modified slag.

The modification of crystal structure promotes grain growth and segregation of elements in various, thereby providing an opportunity to separate iron and calcium ferrite-based phases as hybrid materials. The detailed characterization studies were carried out to reveal the grain size, crystal structure, elemental distribution in various phases and the degree of liberation. The studies were conducted for two different cooling. The standard industrial practice of cooling in 3 hours and an extended period of 6 hours were chosen for revealing the changes in the above characteristics.

Materials and Methods

LD Slag. The LD slag used for various experiments was obtained from Tata Steel Ltd (Jamshedpur, India). As explained in the preceding section, the slag treatment process at Tata Steel Ltd, Jamshedpur, consists of crushing the material up to

6mm, followed by metal recovery. The non-metallic slag generated after the recovery of metallic iron was taken for conducting the experiments since this is a significant area of concern. The non-metallic slag size 0-6mm comprises substantial chunk of the total slag volume generated during steel making in LD converters.

Characterization. The chemistry of LD slag non-metallic rejects taken for research studies was performed Using-Inductively coupled plasma spectroscopy (ICP-MS). Figure 1 presented below shows the total composition of LD slag

The as-received LD slag was subjected to particle size distribution to understand the distribution of various oxide phases in different size classes. Table 1 presents the data obtained on particle size distribution that was carried out using sieve analysis.

The particle size distribution data suggests that the distribution of iron oxide is relatively more in coarser fractions than the finer fractions. This indicates that the relative size of wustite grains is more than the C₂S and C₃S grains. The weight retained on various sieves from coarse to fine size is presented in Table 1. The d₅₀ particle size of the slag is about 1.1mm.

The particle size distribution also suggests that hydrated phases are more in the more acceptable size classes, which is evident from the higher loss on ignition content (LOI). The coarser size classes show relatively lower LOI% while the same is as high as 16% for the finest size class of -0.075mm. Therefore, it can be concluded from this that the free lime and MgO content disintegrate during crushing and reports to the acceptable size class where it hydrated in the presence of water when the slag is cooled.

As discussed earlier, a grade wise distribution of Fe suggests that the particles that the coarser particles are rich in iron content while the finer particles are lower in iron content. The grindability of the iron-rich wustite and ferrite is a possible reason behind the preferential segregation of iron grains. The rationale put here for the difference in the grade of coarse and fine particles also agrees with few research works conducted on studying the of grindability of steel slag. The work done by Wang et al. [25] also found similar results when studying the cementitious property of steel slag powder based on their size. In this study, XRD studies were conducted with fine and coarse fractions of steel slag, and it was observed that coarse particles contained more of RO phase and wustite phase while the finer fractions contained more C₃S and C₂S.

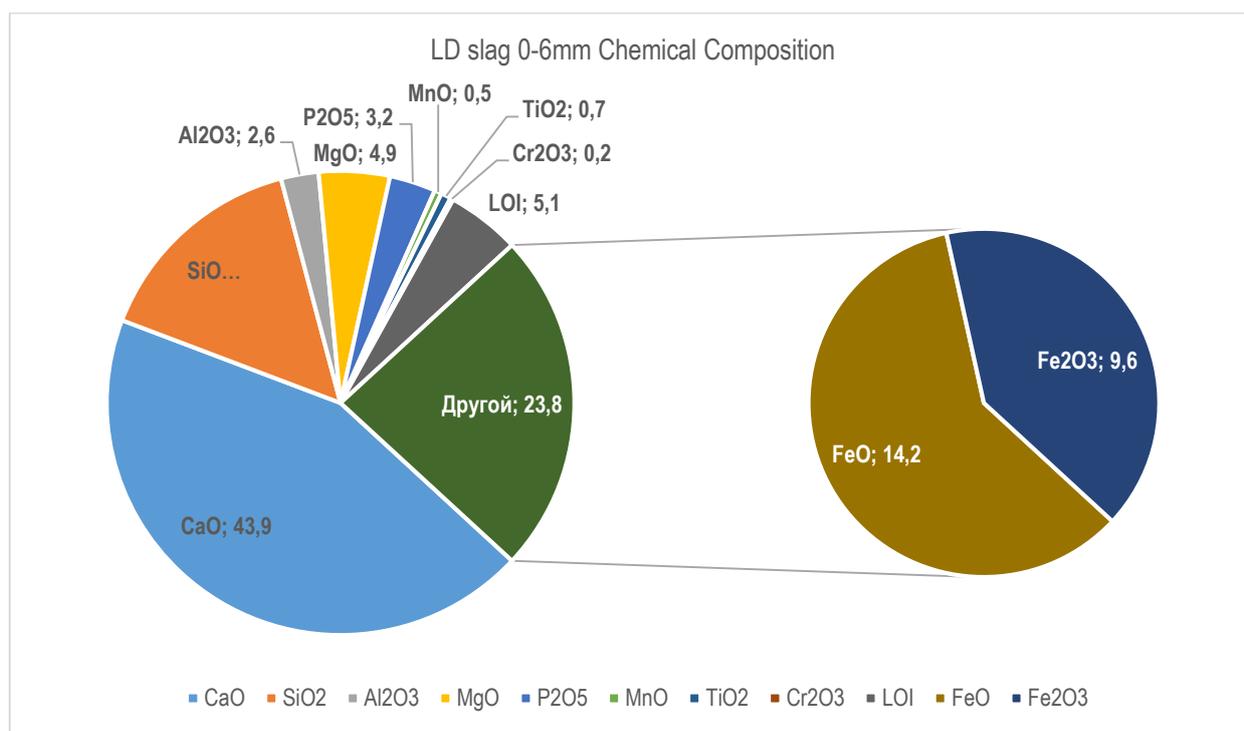


Figure 1 - Chemistry of as-received LD slag

Table 1 - Sieve analysis of as-received LD slag

Size(mm)	Wt%	Fe(T)%	FeO%	SiO ₂ %	CaO%	Al ₂ O ₃ %	MgO%	P%	LOI%
-10+6	13.8	17.88	18.06	14.96	45.45	2.54	4.75	1.34	4.5
-6+3	18.6	20.92	20.64	14.03	44.57	3.38	4.54	1.34	3.8
-3+1	22.2	21.01	20.64	15.3	43.62	2.79	4.06	1.36	4.1
-1+0.5	4.9	20.53	26.49	15.95	40.84	2.73	5.12	1.36	4.3
-0.5+0.25	25.1	16.67	12.77	15.4	43.9	2.48	5.55	1.42	8.9
-0.25+0.15	4.1	14.52	12.9	15.04	43.25	2.11	6.39	1.48	11.1
-015+0.1	3.3	15.43	11.87	14.15	44.15	2.28	5.22	1.6	13.6
-0.1+0.075	3.3	15.44	10.32	13.67	43.2	2.66	5.2	1.62	14.6
-0.075	4.7	11.94	7.22	13.87	43.56	3.38	6.01	1.65	17.4
Total	100	18.38	17.01	14.90	43.96	2.76	4.93	1.40	6.88

Modification of LD slag through controlled cooling rate. The LD slag was modified in two ways:

1. Re-melting and cooling in the crucible for 3 hours followed by cooling in the atmosphere
2. Re-melting and cooling in the crucible for 6 hours followed by cooling in the atmosphere.

The re-melting of the solid slag was carried out in a graphite crucible in a furnace capable of

achieving a temperature of 1800°C. The solid slag sample was melted by heating at a rate of 6-8 °C/minute. The slag sample was melted entirely over 5 hours.

After melting the slag sample, the same was allowed to cool as per the cooling pattern mentioned above. The graph depicting the cooling rate of the melted slag samples is shown in Figure 2.

The slag cooled over 3 hours was named as typically cooled slag and the slag cooled over 6 hours was called as slowly cooled slag.

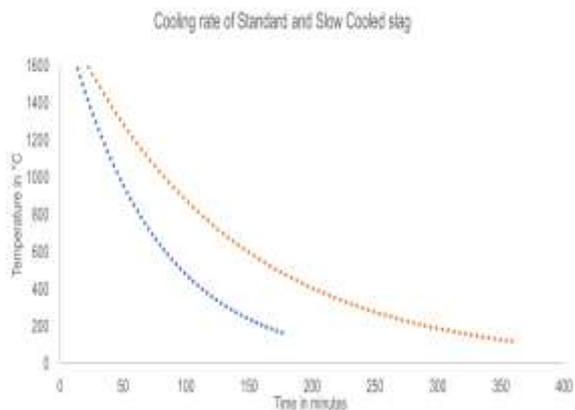


Figure 2 - Cooling rate of LD slag for 3 hours and 6 hours of the cooling period

Results and Discussion

Elemental Mapping of Normal Cooled Slag. The LD slag was characterized using SEM-EDS and the preliminary images and the mapping of various elements as shown in Figure 3. Table 2 presented below gives the pointwise mapping of various elements. The SEM image distinguishes various phases in terms of different shades of black, white and grey colour.

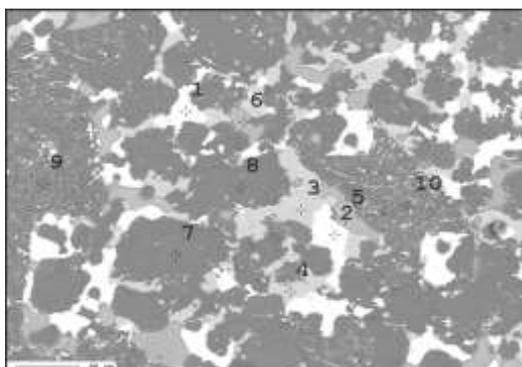


Figure 3 - SEM image of as-received LD slag showing different phases marked with numbers

Odd metal droplets are also seen in the SEM image, which is very fine in size, which suggests that these metal droplets are entrapped in the slag matrix. The EDS elemental mapping shows darker black phases, which are calcium silicate phases having lower atomic mass. The metal oxide phases containing FeOx, MgOx and MnOx are identified as lighter phases. The magnification of the microscope

clearly distinguishes various phases and it can be seen that the size of the crystal of various phases is of the order of only a few μm .

Figure 4 presented below shows the XRD image of the as-received LD slag. The XRD analysis to identify the phases confirmed the findings of SEM analysis. The primary phases present include dicalcium silicate, tricalcium silicate, wustite, calcium ferrite and magnesio ferrite phase. The presence of these phases was also confirmed from the XRD analysis.

The SEM elemental mapping image and the composition suggest that the light phase combines calcium ferrite and the RO phase. The SEM elemental mapping shows the composition of various phases, and it is observed from the data that the dicalcium silicate phase also contains about 4-6% P_2O_5 . Similarly, the tricalcium silicate phase also includes P_2O_5 but is considerably lower than the dicalcium silicate phase. The elemental mapping results suggest about 2% presence of P_2O_5 in the C_3S phase. Further, when looking at the data of light phases such as magnesio ferrite and calcium ferrite, it is observed that the proportion of phosphorus distribution is much lower in these phases and only about 0.3% P_2O_5 maximum is observed in these phases. The elemental mapping data also suggests that the calcium ferrite phase contains a considerable amount of Al_2O_3 , which goes up to 6% in most cases. The C_3S phase containing a higher amount of phosphorus more significant is unstable beyond 2% is P_2O_5 and dissociates into C_2S and CaO . Thus it is seen that C_3S includes only up to 2% P_2O_5 . This theory has also been supported in few published literature works [26].

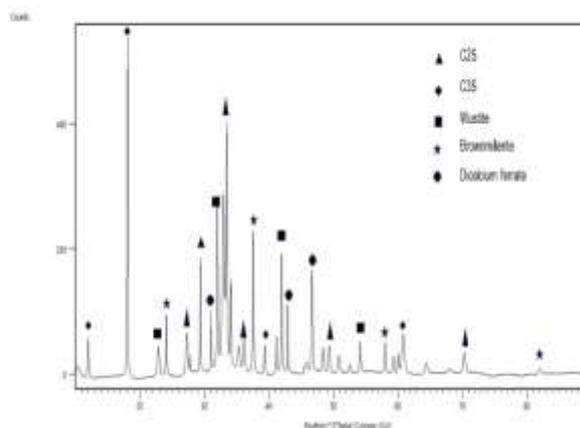


Figure 4 - X-ray diffraction image of as-received LD slag

The phase quantification was done using image scanning software, and the same was corroborated with the results of chemical analysis and XRD

Table 2 - Elemental mapping of various phases corresponding to Figure 3

Mineral	1	2	3	4	5	6	7	8	9	10
SiO ₂	24.78	0.00	0.02	0.55	1.30	0.00	0.00	28.32	27.64	21.70
Al ₂ O ₃	0.98	0.01	0.02	6.25	6.30	0.02	0.01	0.12	1.25	0.70
MgO	0.17	14.29	12.18	0.98	0.83	0.46	0.49	0.00	0.02	0.04
Na ₂ O	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.01	0.00	0.00
TiO ₂	0.82	0.00	0.07	7.90	8.69	0.00	0.01	0.32	0.37	0.29
CaO	63.51	9.24	10.48	48.93	49.18	58.82	58.89	65.81	65.66	72.02
K ₂ O	0.03	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00
FeO	4.20	74.59	75.23	35.11	33.21	39.91	39.78	0.84	0.83	3.21
MnO	0.05	1.86	1.99	0.05	0.19	0.78	0.79	0.00	0.03	0.22
P ₂ O ₅	5.31	0.00	0.01	0.21	0.29	0.01	0.00	4.57	4.18	1.55
Phase	Ca-Si-O	Fe-Mg-O	Fe-Mg-O	Ca-Fe-Al-O	Ca-Fe-Al-O	Fe-Ca-O	Fe-Ca-O	Ca-Si-O	Ca-Si-O	Ca-Si-O

Table 3 - Quantification of various phases in Normal Cooled LD slag

Phase quantification from XRD corroborated from	
Dicalcium Silicate (2CaO.SiO ₂)	35.0%
Tricalcium Silicate (3CaO.SiO ₂)	17.2%
Magnesio Wustite (Fe _{0.7} Mg _{0.3} O)	20.1%
Dicalcium ferrate (Ca ₂ Fe ₂ O ₅)	14.5%
Dicalcium Alumino ferrate (Ca ₂ (Al _{1.3} Fe _{0.7})O ₅)	7.1%
Lime (CaO)	6.1%

studies. Table 3 presented below shows the quantification of various phases that are present in normally cooled LD slag.

The mineral modal analysis was carried out using SEM to understand the grain size of various phases and evaluate a separation size of phases based on their liberation size, which depends on the presence of various phases in different size classes. The images of SEM taken for the steel slag sample subjected to modal analysis is shown in Figure 5, along with the elemental mapping of the sample.

The elemental mapping shows the concentration of the element in different grains present, and it also shows the relative grain size of different phases. Figure 6 shown above was captured for estimating the liberation size of various

phases. The grains were compared on a relative scale of 200 μm, as shown in Figure 6. Based on the available results, it is seen that the grain size of iron-bearing crystals range from 25-150 μm, with most of the crystals being in the coarser range. Similarly, the image taken for mapping of calcium phase shows a crystal size of such phases in the range of 50-300 μm.

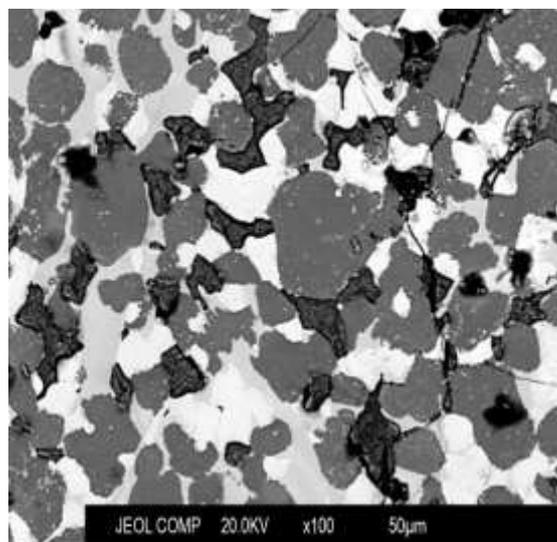


Figure 5 - SEM image of as-received LD slag for modal analysis

Comparative results on grain size, crystal structure and phases of Slow and Normal Cooled Slag. Figure 7, shown below, is the SEM image of the LD slag cooled under a slow cooling rate in the furnace.

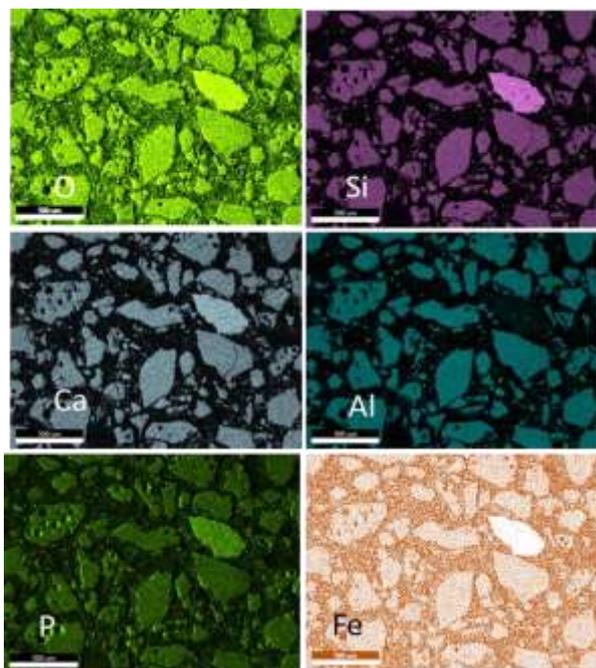


Figure 6 - Elemental mapping and liberation size analysis of as-received LD slag

It is seen from the image and Table 4 that the point 1 and 2 which was determined to contain 100% metallic Fe is much larger compared to the metallic Fe that was present in the LD slag that was cooled under standard cooling rate. It is also seen that the phases dicalcium ferrite and the calcium aluminoferrite are much larger compared to the same under standard cooling rates. Similarly, the grain size of the dicalcium silicate phase is large. The significant difference, however, was the presence of two more phases which were identified through elemental mapping. These phases are primarily the dicalcium silicate phases which have formed a solid solution with iron and magnesium. This data suggests that the slower cooling rates promote the

crystallization of new phases, and, the grain growth of the phases is also seen under slower cooling rates.

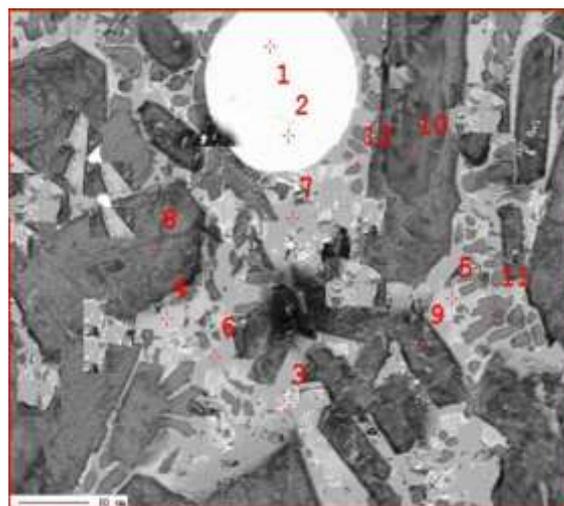


Figure 7 - SEM image of slowly cooled slag

The additional phase of Ca-Si-Fe-Mg-O contains almost the same distribution of iron as seen in the calcium ferrite phase. The composition of this new phase shows about 35% FeO. The slowly cooled slag shows a higher distribution of iron content in this phase and is about 41% compared to 35% in standard cooled slag. The formation of this new phase opens the possibility of recovering iron values simultaneously with calcium minerals as a hybrid flux material.

The SEM image of the two types of slags was taken for capturing the data on liberation size and the grain size of individual phases. The images as shown below in Figures 8 and 9 indicate that the grain size of separate phases under a slow cooling rate is relatively more than that under standard cooling conditions.

Table 4 - Elemental mapping corresponding to Figure 7

Mineral	1	2	3	5	6	7	8	9	11	12
SiO ₂	0.03	0.06	18.19	8.56	1.77	2.00	21.01	24.35	21.36	19.16
Al ₂ O ₃	0.00	0.03	0.91	0.02	4.50	4.24	0.7	1.95	1.06	0.51
MgO	0.01	0.00	3.96	0.32	0.48	0.44	0.08	0.15	0.15	3.07
Na ₂ O	0.02	0.00	0	0.03	0.00	0.00	0.00	0.00	0.00	0
TiO ₂	0.01	0.03	0.39	0.09	9.47	8.37	0.35	0.45	1.94	0.42
CaO	0.00	0.00	40.08	21.46	41.49	43.11	71.21	65.97	64.38	43.65
K ₂ O	0.00	0.00	0.03	0.00	0.01	0.00	0.01	0.04	0.06	0.02
FeO	99.89	99.88	34.50	68.24	41.57	41.35	2.43	2.07	3.07	32.12
MnO	0.02	0.00	0.31	1.26	0.08	0.10	0.26	0.05	0.03	0.16
P ₂ O ₅	0.01	0.00	0.76	0.04	0.63	0.49	1.98	4.97	7.92	0.88
Name	Fe	Fe	Ca-Si-Mg-Fe-O	Ca-Fe-Si-O	Ca-Fe-Al-O	Ca-Fe-Al-O	Ca-Si-O	Ca-Si-O	Ca-Si-O	Fe-Mg-Ca-Si-O

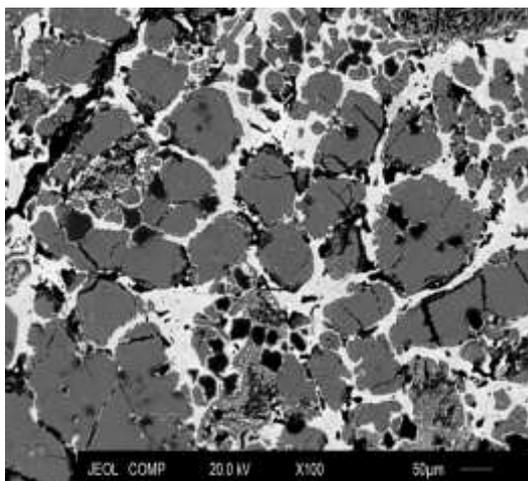


Figure 8 - SEM image of slowly cooled slag

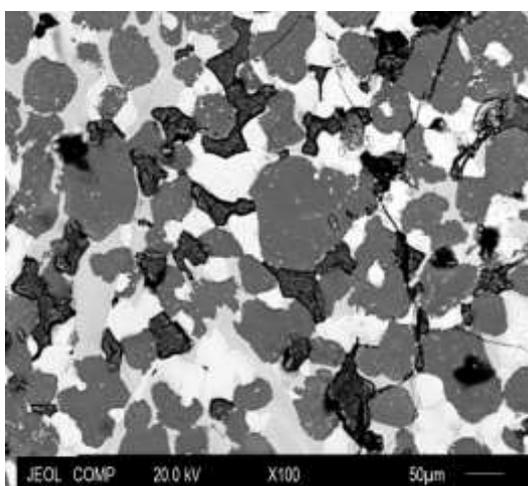


Figure 9 - SEM image of normally cooled slag

The Table 5 shows the data pertaining to the grain sizes of various phases for slags cooled under normal and slow cooling rates.

Table 5 - Grain size of crystals in slow and normal cooled slag

Phase	Standard cooling rate (3 hours)	Slow cooling rate (6 hours)
	Grain Size (µm)	
Dark-coloured C ₂ S and C ₃ S phase	10-150	50-150
Light-coloured Iron bearing phase	10-100	20-150

Table 5 shows the data obtained with SEM-EDS and corroborated with XRD studies. The results suggest that the slowly cooled slag contains an additional phase of dicalcium silicate with a high amount of Fe and Mg content, and the total content of this phase is about 6.2%.

The XRD image presented in Figure 10 below suggests that a new phase containing dicalcium silicate primarily with iron and magnesium oxide emerges when the slag is cooled slowly. It is also seen that the C₃S phase in slowly cooled slag is comparatively lower than standard cooled slag.

Further, the peak intensity in the case of slowly cooled slag also indicates the changes in concentration of individual phases. Higher peak intensity for many phases in slowly cooled slag implies that the mineral phases become richer in grade with the significant mineral. Further, the XRD results of a new phase are also corroborated by the SEM elemental mapping, which shows a new phase containing Fe-Mg-Ca-Si-O elements.

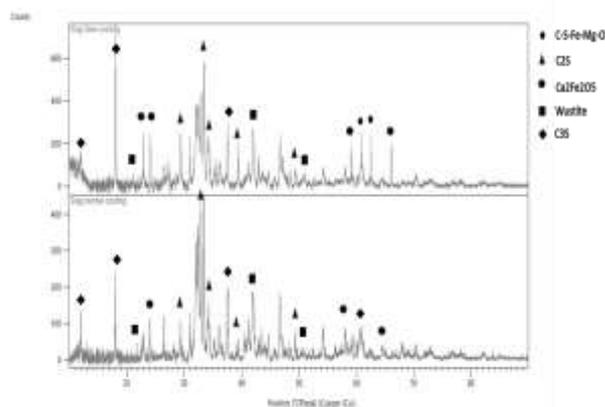


Figure 10 - XRD image of slowly cooled slag showing a new phase

The phase-wise distribution of various phases as calculated from SEM and XRD data is presented in Table 6 below.

It is seen from the results that the individual phases like dicalcium ferrite, tricalcium ferrite and calcium ferrite have all reduced by a smaller proportion and a new phase composed of Fe-Mg-Ca-Si-O has emerged, which is about 6.1% in total.

Therefore, as confirmed by the characterization studies, the basis for separating iron-rich minerals from the slag should be to slowly cool the slag slowly, thereby allowing maximum time for crystallization and growth of phases. The cooling rate is an essential parameter in grain size control [27-28]. A slower cooling rate helps migrate more calcium minerals to the iron-bearing phase of

calcium ferrite and more iron in the calcium bearing phase Ca-Si-Fe-Mg-O.

Tables 7 and 8 presented below show various phases' distribution in LD slag cooled under standard and slow cooling rates.

The mineral liberation analysis of normal and slow cooled slag is shown in Figures 11 and 12.

The graph indicates that the liberation of the C_2S and C_3S phase from iron-bearing phase is much better in the case of slowly cooled slag especially at the coarser size (0.25-0.5mm). The degree of liberation at this size for standard cooled slag is about 50%, while the same value for slowly cooled slag is about 75%. The liberation of these phases at other size classes is marginally better for slowly cooled slag. The degree of liberation is defined as the number of particles in a size class that is at least 80% liberated from each other.

By the above explanation, it can be inferred that in size range of >0.05 mm, the grains with at least 80% degree of liberation are presently more than 90% in standard cooled slag. Similarly, for the case of 0.25-0.50mm size range in standard cooled slag, the

grains with a degree of liberation greater than 80% are present only 50%. This means that the grain size in this size range has 50% non-liberated grains, which have a degree of liberation of less than 80%.

Figures 13 and 14 below show the cumulative weighted average liberation of 0-0.5mm LD slag for normal cooled and slow cooling conditions.

The significant difference between the two cases can be seen in the weighted average liberation of 0.5-0.25mm size class. The standard cooled slag shows only about 18% liberation, while the slowly cooled slag indicates approximately 27% liberation. The cumulative liberation of slowly cooled slag, 80.9%, is mostly the result of higher liberation in 0.5-0.25mm fraction, and almost 80% of this difference is coming from this size class. The size class 0.25-0.10mm contributes about 1% to the difference in cumulative liberation. The data indicates that the slowly cooled slag can be efficiently separated at the same grind size compared to standard cooled slag. The difference in liberation by 10% will improve the yield and the grade of concentrate.

Table 6 - Phase quantification of Slow Cooled and Standard Cooled slag

Phase quantification from XRD corroborated from Chemical analysis	Wt%	
	Normal Cooled	Slow Cooled
Dicalcium Silicate ($2CaO.SiO_2$) with Phosphate phase	35.0	32.7
Tricalcium Silicate ($3CaO.SiO_2$) with Phosphate phase	17.2	16.5
Magnesio Wustite ($Fe_{0.7}Mg_{0.3}O$)	20.1	18.5
Dicalcium ferrate ($Ca_2Fe_2O_5$)	14.5	13.4
Dicalcium Alumino ferrate($Ca_2(Al_{1.3}Fe_{0.7})O_5$)	7.1	6.6
Lime (CaO)	6.1	6.1
Dicalcium silicate with Fe-Mg	Nil	6.2

Table 7 - Distribution of various phases as a function of size class in normally cooled slag

Size fraction(mm)	Wt%			
	C_2S & C_3S	Mg-Fe-O	Ca-Fe-O	Ca-Fe-Al-O
0.25-0.5	58	24	10	8
0.10-0.25	62	21	11	6
0.05-0.10	65	15	14	6
-0.05	67	14	12	7

Table 8 - Distribution of various phases as a function of size class in slowly cooled slag

Size fraction (mm)	Wt%				
	C ₂ S & C ₃ S	Mg-Fe-O	Ca-Fe-O	Ca-Fe-Al-O	Ca-Si-Fe-Mg-O
0.25-0.5	58	20	10	6	6
0.10-0.25	59	19	11	5	6
0.05-0.10	61	18	11	4	6
-0.05	62	17	12	4	5

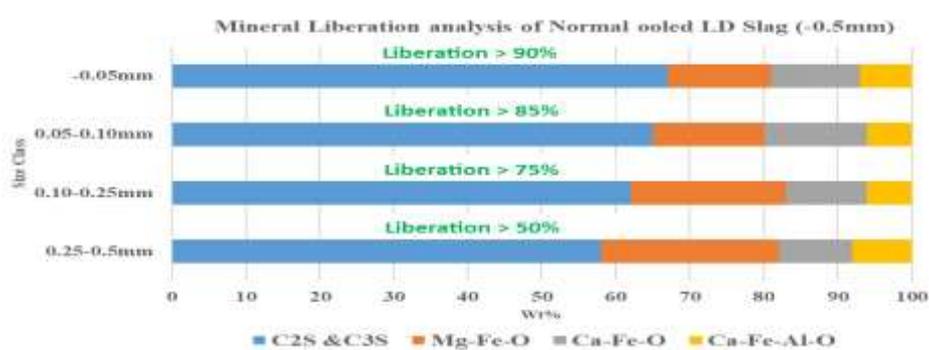


Figure 11 - Mineral liberation analysis of normally cooled slag at 0.5mm grind size

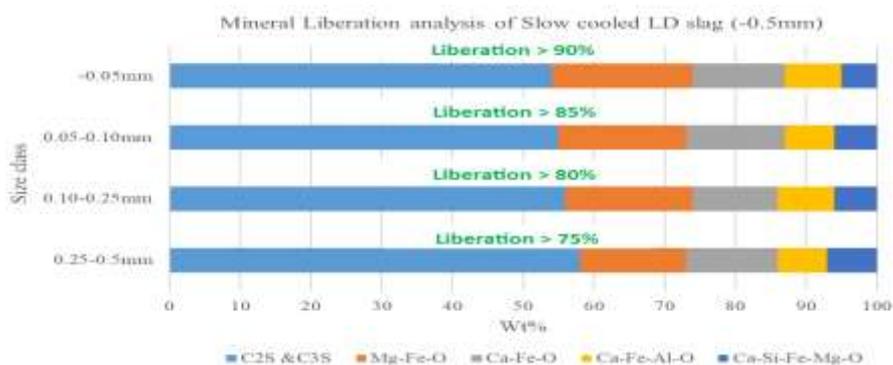


Figure 12 - Degree of liberation of slowly cooled slag at 0.5mm



Figure 13 - Cumulative degree of liberation of normally cooled slag at 0.5mm size

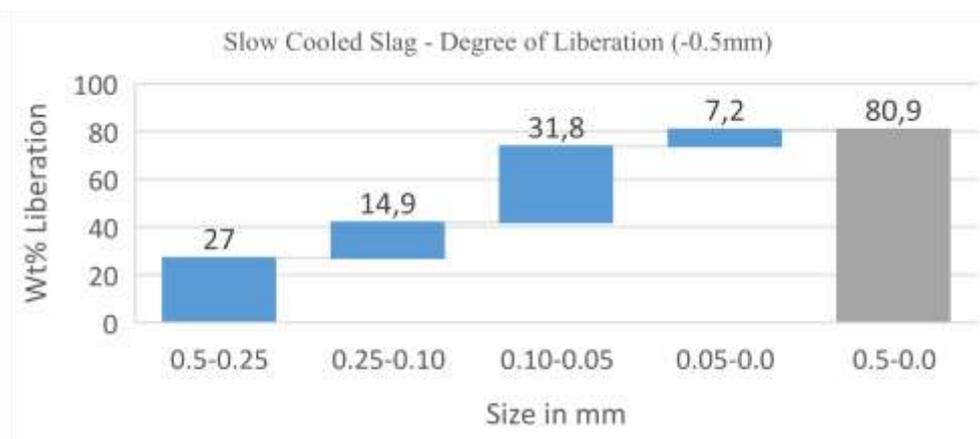


Figure 14 - Cumulative degree of liberation of slowly cooled slag at 0.5mm size

Conclusions

The present research work focused on developing enablers and characterization of material to develop a hybrid material containing both lime and iron oxide. The hybrid material is an excellent source of material for the iron and steel industry since it helps in easy melt formation during the process.

A research gap exists in the area of slag modification through control on cooling rate. In this process, any segregation in the elemental distribution of phases would result in the concentration of elements. Based on the characterization and detailed experimental studies and analysis of results, the following conclusions are drawn.

1. The as-received LD slag (also referred to as Normally cooled slag), which is cooled in 3 hours in industrial practice is different from the slowly cooled slag in respect to its crystal size and mineral liberation. The grain size of various grains in normally cooled slag was between 10-150 μm while the same for slowly cooled slag was 20-250 μm indicating that the slow cooling has resulted in grain growth and better liberation.

2. The liberation analysis indicated that at 0.5mm grind size the cumulative liberation of normally cooled slag was 69.2%, while 80.9%, for slowly cooled slag.

3. It was also shown that slow cooling promotes the formation of an additional phase which is essentially the dicalcium silicate phase (C_2S), with some amounts of FeO and MgO in the crystal lattice. This additional phase constituted about 6.2% in slowly cooled slag.

4. The results also confirm that with slow cooling, there is an increased concentration of phosphorus phase in calcium silicate phase C_2S and C_3S . The phosphorus concentration was up to 8% in slowly cooled slag against 5% in normally cooled slag.

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

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Гибридті қождамалық материалды алу үшін ЛД-қождың микроқұрылымын модификациялау

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ТҮЙІНДЕМЕ

Болат өндіру процесінде оттегі пешінде шығымы шамамен 125 кг / т болатын конвертерлік қож (ЛД- қож) түзіледі. ЛД-қож құрамындағы вюстит пен екі кальцийлі ферритте шамамен 18% Fe және шамамен 45% CaO бар. Бұл минералдар болат өнеркәсібі үшін балама қождамалардың (флюстердің) тамаша көзі болып табылады. Қожды модификациялау және терең зерттеулер арқылы балама қождамалық материал ретінде қолдануға болатын материалды әзірлеу бойынша зерттеулер жүргізілді. Кристалл құрылымының, фазалық таралудың, түйіршіктердің мөлшерінің өзгеруін анықтау үшін SEM-EPMA және XRD көмегімен сипаттамаларға егжей-тегжейлі зерттеу жүргізілді. Фазалардағы түйіршіктердің мөлшері қалыпты салқындатылған қож үшін 10 -нан 150 мкм -ге дейін және баяу салқындатылатын қож үшін 20 -дан 250 мкм -ге дейін болатындығы анықталды. Баяу салқындату кристалдық торда FeO мен MgO-ның белгілі мөлшерлері бар екі кальцийлі силикат фазасы болып табылатын қосымша фазаның пайда болуына ықпал ететіні де көрсетілді. Жалпы алғанда, ЛД-қожының шамамен 50% -ы шамамен 30% CaO және 30% Fe бар балама қождамалық материал ретінде алынуы мүмкін екендігі айтылады. Бұл балама қождама балқу температурасы төмен қож түзуіне байланысты болат өнеркәсібінде қолдануға арналған тамаша материал көзі болып табылады.

Түйін сөздер: ЛД-қож, сипаттама, гибридті қождама (флюс), салқындату жылдамдығы, микроқұрылым.

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Модификация микроструктуры ЛД-шлака для получения гибридного флюсового материала

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АННОТАЦИЯ

В процессе производства стали в кислородной печи образуется конвертерный шлак (ЛД-шлак) с расходом около 125 кг/т. ЛД-шлак содержит около 18% Fe в вюстите и двухкальциевом феррите и около 45% CaO. Эти минералы являются отличным источником альтернативных флюсов для сталелитейной промышленности. Посредством модификации шлака и углубленных исследований, были проведены обследования для разработки материала, который можно было бы использовать в качестве альтернативного флюсового материала. Подробные исследования характеристик были проведены с использованием SEM-EPMA и XRD для выявления изменений в кристаллической структуре, фазовом распределении, размере зерен. Было обнаружено, что размер зерна фаз составляет от 10 до 150 мкм для нормально охлаждаемого шлака и от 20 до 250 мкм для медленно

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охлаждаемого шлака. Также показано, что медленное охлаждение способствует образованию дополнительной фазы, которая по существу представляет собой фазу двухкальциевого силиката с некоторыми количествами FeO и MgO в кристаллической решетке. В целом отмечено, что около 50% ЛД-шлака может быть извлечено в качестве альтернативного флюсового материала, содержащего примерно 30% CaO и 30% Fe. Этот альтернативный флюс из-за образования шлаков с низкой температурой плавления является отличным источником материала для использования в сталелитейной промышленности.

Ключевые слова: ЛД-шлак, характеристика, гибридный флюс, скорость охлаждения, микроструктура.

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