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Engineering and Technology

Removal of Impurities from Refractory Gold Ore using Bio-reduction and Bio-oxidation processes

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ABSTRACT

Gold in refractory gold ore is difficult to be extracted by conventional metallurgical methods due to the presence of sulfide minerals with elevated levels of iron (Fe), sulfur (S), and arsenic (As) as impurities, resulting in low gold (Au) recovery. Conventional methods such as cyanide leaching has been proven ineffective for gold extraction from refractory ore due to gold being intricately bound within the sulfide minerals. Consequently, this study explores the application of bioleaching as an alternative to conventional cyanide leaching. Shewanella oneidensis (S. oneidensis) and Acidithiobacillus ferroxidans (A. ferroxidans) serve as bio-reduction and bio-oxidation agents, respectively in the bioleaching process. The composition of minerals in the ore was determined through XRD analysis (Model: Rigaku's Miniflex 600) and EDX analysis (Model EDX 3). Meanwhile, SEM analysis (Zeiss EVO LS15 SEM) was utilized to examine the morphology structure. The concentrations of impurities (Fe, S, and As) were assessed using a spectrophotometer (Model: DR3900 Hach) meanwhile the Au concentration was determined through ICP-OES (Model: G8015A5110 ICP-OES). Sieved refractory gold ore samples with less than 32 um and varying in weight (0.5 g, 1.0 g, 1.5 g, 2.0 g), underwent bio-reduction and bio-oxidation processes. The results indicated a rougher surface morphology of the raw sample as observed through SEM analysis. Furthermore, XRD and EDX results demonstrated a decrease in impurity concentrations, suggesting a potential increase in gold purity. Notably, the bio-reduction process exhibited a superior enhancement in Au concentration with the value of 138.89% compared to biooxidation with the value of 122.22%. Thus, the bio-reduction process proved more effective in increasing Au concentration compared to bio-oxidation.

Keywords: Bioleaching, *S. oneidensis*, *A. Ferroxidans*, gold, ICP-OES.

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Introduction

Metallurgists commonly divide gold ores into two primary categories: free milling ores and refractory ores. Refractory gold ore, recognized as a preg-robbing mineral, contains gold intricately intertwined with sulphide minerals like pyrite, pyrrhotite, arsenian pyrite, stibnite and arsenopyrite [1]. This complex composition poses challenges in extracting gold [2].

Refractory gold ore, a valuable material primarily composed of sulphide minerals like arsenian pyrite and arsenopyrite (ultrafine gold), poses a challenge for gold recovery through conventional cyanide leaching methods, which can typically retrieve over 90% of gold from free-milling ore [3]. However, refractory gold ore often exhibits traits that hinder gold separation from sulphides, resulting in a lower gold recovery rate (less than 20%) using the same conventional method [4]. As an alternative, bioleaching is a method employing microorganisms has gained significant attention from gold miners and researchers worldwide. This approach aims to break down preg-robbing minerals by eliminating metal impurities, leading to an increased concentration of gold [5].

Bioleaching methods are increasingly being utilized for Au recovery from refractory ore that cannot be processed effectively by conventional methods [5]. It proposed a greener method by using microorganisms to dissolve the impurities from the refractory gold ore to ensure higher Au concentration recovery achieved. This process implied the conversion of an insoluble element to soluble compound followed by the selected metal recovery via either the metabolic activities or microbe's products [6].

In addition, bioleaching has been widely adopted in industry for gold recovery [7], primarily because its effectiveness hinges on the efficient ability of microorganisms to extract gold from ores. Therefore, microorganisms like *A. ferrooxidans* and *S. oneidensis* have been utilized to enhance the purity of gold compared to traditional methods like cyanidation or carbon-in-pulp (CIP), which rely on optimized chemical processes for achieving high gold recovery rates [8]. Bioleaching methods offer cost-effectiveness in terms of operational expenses due to reduced chemical usage and lower energy consumption when contrasted with conventional techniques [9]. From an environmental perspective, bioleaching is often favored as it minimizes the use of toxic substances such as cyanide, thereby mitigating risks associated with acid mine drainage and related environmental hazards in sulfide-containing ores [10]. Furthermore, ongoing research in bioleaching focuses on improving efficiency, optimizing microbial strains, and developing innovative bioreactor designs, indicating the continual advancement of these methods [11].

In the course of this research, *S. oneidensis* and *A. ferroxidans* were employed respectively as bio-reduction and bio-oxidation agents in the bioleaching process. The aim was to break down preg-robbing minerals by extracting Fe, sulfur, and arsenic [12] which are the predominant elements in the sample leading to a heightened concentration of Au. Furthermore, bioleaching is recognized as an environmentally sustainable and cost-effective method in gold production [13]. Conversely, bioleaching is perceived as a rapid and efficient means of eliminating [14].

The primary objectives of this research are to identify and characterize the mineral composition of refractory gold ore, specifically focusing on elements such as arsenopyrite, hematite, magnetite and quartz. Meanwhile, the Scanning Electron Microscopy (SEM) used to examine the morphology structure of the refractory gold ore. Furthermore, the effectiveness of bio-reduction and bio-oxidation processes in enhancing gold concentration of the refractory gold ore was assessed by examining the removal efficiency of metal impurities.

Experimental part

Sample Preparation

The refractory gold ore was obtained from Benua Sunda Cari Gali. The samples were broken down into small particles using a geological hammer and sieved using a RETSCH Sieve Shaker AS 200 (China) until size <32 *u*m.

Characterization of refractory gold ore

The sieve samples were sent to XRD and EDX to determine the percentage composition of the mineral. Meanwhile, the samples were sent to SEM to analyze the morphology structure of the mineral.

Preparation of inoculum using S. oneidensis MR-1 strain

S. oneidensis MR-1 strain was cultured in Luria–Bertani broth. A single colony of bacteria from the LB agar plate was inoculated into 5 mL of LB media and shaken overnight at 30°C and 150 rpm [15]. Subsequently, the microbial culture was transferred to the autoclaved conical flask containing 50 mL of LB media and cultivated aerobically for 5 hours at 30 °C and 150 rpm. The optical density of the seed culture was 5 which was measured by using Genesys 20 Spectrophotometer at the wavelength of 600 nm.

Preparation of inoculum using A. Ferroxidans strain

A. ferrooxidans strain was cultured in Leptospirillum (hh) media [16]. 1 ml of pure strain bacteria was added into 50 mL of Leptospirillum (hh) media and shaken in an incubator shaker for 14 days at 30°C and 170 rpm. After 14 days, the colour of the medium was changed to reddish brown with 5 OD measurements and 600nm of wavelength.

Incubation of sample for bio-reduction process using S. oneidensis

The sterilized refractory gold samples with different weights consist of (5 g,1.0 g, 1.5 g, and 2.0 g) were placed into 50 ml of LB media in serum bottles. Subsequently, 0.5 ml of inoculum was added and incubated for 19 days of bio-reduction process at 30°C with 170 rpm. The incubation period was 19 days which microbial growth had reached its stationary phase. The concentration of Fe (II) and sulphate were measured every 3 to 4 days using the ferrozine assay and sulfatVer 4 reagent.

Incubation of sample for bio-oxidation process using A. ferroxidans

The sterilized refractory gold samples with different concentrations (5g, 1.0 g, 1.5g, 2.0g) were placed into 50 ml of Leptospirillum (hh) media. After that, 10 ml of inoculum was added and incubated for 19 days of bio-oxidation at 30°C with 170 rpm. The concentration of Fe (II) and sulphate were measured every 3 to 4 days for 19 days using the ferrozine assay and sulfatVer 4 reagent.

Determination of Fe (II) using Ferrozine assay

The ferric iron reduction is represented by production of ferrous iron by ferrozine assay. 200 µl of bioleached sample from serum bottles were transferred into 2 ml of microcentrifuge tube and added with 1000 µl of 0.5 M of hydrochloric acid. During the assay, 0.5 M hydrochloric acid is applied to keep the pH low to prevent oxidation of Fe (II) and to dissolve Fe (III) particles so that Fe (II) that is absorbed in Fe (III) particles were released. The microcentrifuge was placed in the dark places for 30 minutes and then 50 µl sample from the microcentrifuge was transferred into a cuvette containing 950 µl of ferrozine assay. Subsequently, A spectrophotometer (DR3900, HACH) was then d using equation 3.1 used to take the reading using 562nm of wavelength. The final absorbance reading of the sample obtained [17].

Fe (II) concentration (mM):

$$\frac{(final\ absorbance\ reading - 0.016)}{0.1999} \qquad (1)$$

Determination of iron (Fe), arsenic (As), gold (Au) via ICP-OES

After characterization, the treated and untreated samples were proceeded with total digestion technique by microwave digester. The process of digestion was followed [18], in which the samples have been weighed about 0.5 g and placed into the white flask. Subsequently, added 68% of nitric acid HNO3, 48% of hydrofluoric acid (HF), and 50% of hydrogen peroxide (H_2O_2) were with the ratio of 4:3:2. Later, the digested samples were sent to ICP-OES to analyse the concentration of total Fe, As, and Au.

Analyzation using ICP-OES

The determination of the gold, total iron and arsenic were measured by taken 5-10 mL of the digested samples and then measured using ICP-OES from Agilent Technologies 5110 (California, U.S). The calibration curve of Au was recorded in the range of 1 mg/L to 5 mg/L using 242.794 nm of Au wavelengths. The data obtained indicated the value of the composition mineral left in the refractory gold ore.

Removal Percentage

The analysed results were recorded to determine the removal percentage (R%) of the impurities by applying the formula as shown in the equation 3.2 [19].

$$R\% = \frac{C_0 - C_e}{C_0} \times 100\% \qquad (2)$$

Where C_o is the initial impurity concentration, C_e is the impurity final concentration.

Results and Discussion

Characterization of ore using XRD

Refractory gold ore was analysed using XRD and DIFFRAC EVA software. The aim of this characterization was to identify the S-Q value's percentage of minerals presented in the refractory gold samples. As shown in Figure 1, the percentages in the S-Q value of impurities i.e., arsenopyrite, magnetite, and hematite in the raw sample were 14.2%, 12.1%, and 13.4%, respectively, followed by 60.3% of quartz as the remaining mineral in the samples. Hematite and magnetite were considered as the principle's ore of iron. In addition, magnetite is a primary component of an iron oxide that contains equal amounts of Fe (II) and Fe (III) [20]. On the other hand, the detection of arsenopyrite by XRD indicates Au was present in the sample [21]

. Meanwhile, the presence of quartz in the samples denotes low Au content, defining them as refractory gold ore [22].

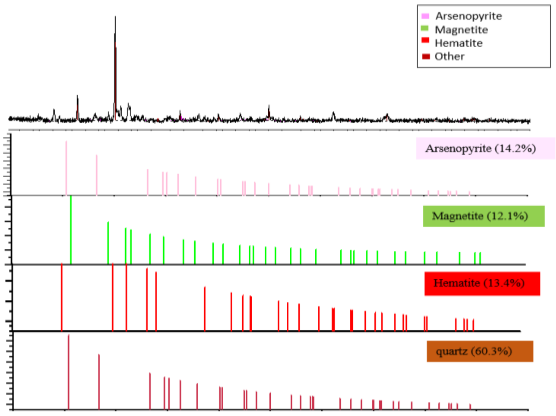

Figure 1 - The percentage in the S-Q value of mineral composition in the raw sample

Characterization of ore by Energy Dispersive X-ray analysis (EDX)

The characterization using EDX was performed to determine elemental composition of refractory gold ore. Figure 2 illustrates the percentage of iron (Fe) and sulphur were 37.7% and 12.4%, respectively. The presence of iron (Fe) and sulfur (S) in the refractory gold ore was regarded as impurities that required removal to enhance the concentration of Au.

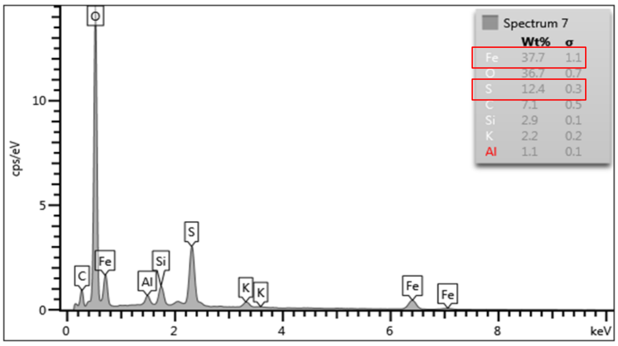

Figure 2 - The elemental composition of solid surfaces for the raw sample

Characterization of ore by scanning electron microscope (SEM).

The morphology structure of the samples was analyzed by SEM analysis. The surface morphology of the raw sample is shown in Figure 3 which the pyrite surface was relatively smooth without treatment.

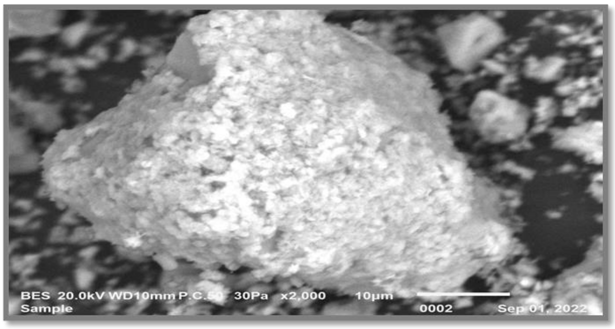

Figure 3 - SEM photograph of raw sample

Removal of metal impurities (Fe, S, As) from refractory gold ore

(a) Iron removal through reduction of Fe (III) to Fe (II) from refractory gold ore

In this study, the removal of Fe applied the usage of *S. oneidensis MR-1* and *A. Ferroxidans* as the bacteria that undergo bio-reduction and bio-oxidation processes, respectively. Bio-reduction process for Fe removal involved the reduction of insoluble Fe (III) to soluble Fe (II). Meanwhile, bio-oxidation implies the oxidation of Fe (II) to Fe (III). The produced Fe (III) acts as an oxidant to oxidize the metal sulphide forming the sulphur metal and soluble Fe (II) ion.

Figure 4 and 5 showed a Ferrozine assay reading at 562 nm to determine the concentration of Fe (II) ion for bio-reduction and bio-oxidation processes, respectively. The weight samples in both processes are 0.5 g, 1.0 g, 1.5 g, and 2.0 g, with abiotic serving as the control in the absence of bacteria strains. The concentration of Fe (II) was increased by days for both processes. The result for the Abiotic sample showed a constant reading, indicating that Fe reduction did not occur without bacteria strains. Based on observation for both processes, the incubation of 2.0 g of weight sample has a higher Fe (II) concentration reading as compared to other samples.

In the bio-reduction process, Fe (III) was reduced to Fe (II) by *S. oneidensis* which used organic carbon or hydrogen as an electron donor [23]. The transfer of electrons from the cell to the iron minerals is performed through direct contact between the cell and the mineral surface [24]. It means the Fe (III) ion gained an electron forming the soluble Fe (II) ion to be discarded from the refractory gold ore.

On the other hand, the concentration of Fe (II) in the bio-oxidation process using *A. ferrooxidans* also showed an increased value as days increased. The Fe (II) was removed by oxidation of *A. ferrooxidans* which these bacteria take up O_2 and CO_2 and oxidize Fe (II) (energy source) to Fe (III), which dissolve metal ions. Fe (III) was reacted with Sulphide mineral and metal, and reduced to Fe (II). The purple color was produced when the ferrozine reagent reacted with the Fe (II) in the solution. The darker purple in the solution corresponds to a higher concentration of ferrous iron (Fe II). Fe (II) concentration was chosen as a crucial parameter to regulate the procedure for both bio-reduction and bio-oxidation.

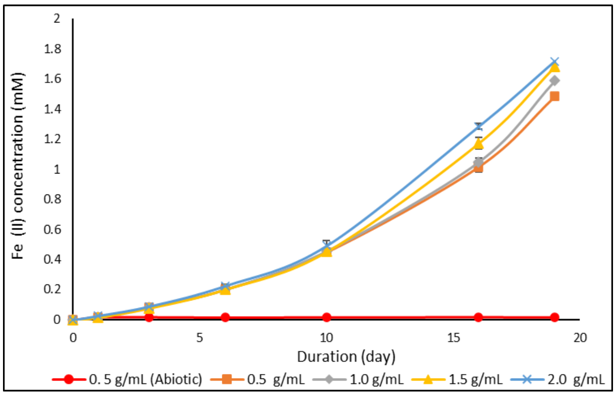

Figure 4 - Fe (II) concentration obtained during bio-reduction process within 19 days

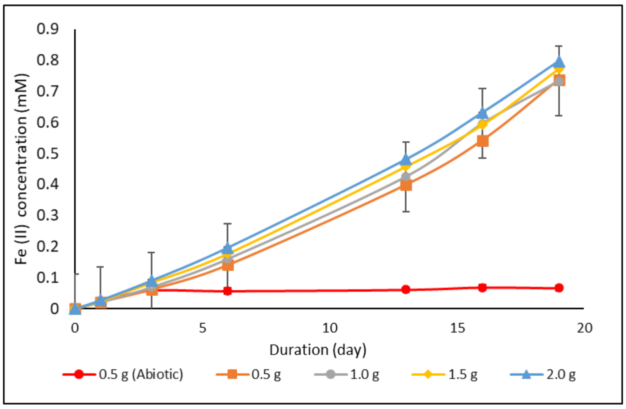

Figure 5 – Fe (II) concentration obtained during bio-oxidation process within 19 days

In addition, the remaining Fe in the refractory gold ore after bioleaching was measured and the result presented in Figure 6. Obviously, the concentration of Fe in the refractory gold ore was decreased for both bio-reduction and bio-oxidation processes compared to the raw sample. The lowest value of Fe concentration was shown by the weight sample of 2.0 g indicating high removal of Fe had been achieved compared to 0.5 g, 1.0 g and 1.5 g. This was due to the high amount of weight sample consisting of a large value of Fe resulting in the increment of Fe dissolution in the ore. Moreover, the remaining Fe in the ore after the bio-reduction process for 2.0 g of weight sample exhibited lower value than the bio-oxidation process. It means that bio-reduction proposed a better process in Fe removal compared to the bio-oxidation as Fe (III) was well-dissolved in bio-reduction causing the low value of Fe left in the ore.

Therefore, Figure 7 and Figure 8 revealed the increment of Au concentration from refractory gold ore when the removal percentage of Fe increased via bio-reduction and bio-oxidation, respectively. In detail, bio-reduction with 70.12% of Fe removal shows higher Au concentration can be achieved with 0.23 ppm rather than bio-oxidation with 0.21 ppm with 61.81% of Fe removed.

(b) Sulphur removal from refractory gold ore through formation of sulphate.

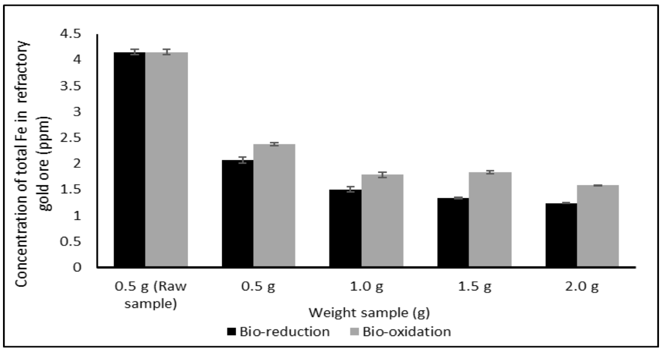

Figure 6 - The concentration of total Fe in refractory gold ore after 19 days of bioleaching process

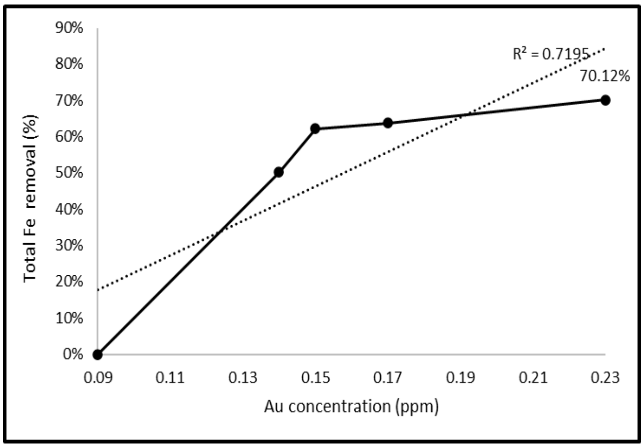

Figure 7 - Correlation between Au concentration and Fe removal for bio-reduction process

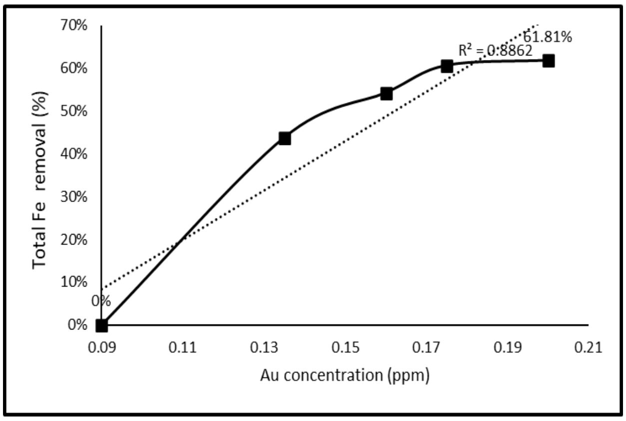

Figure 8 - Correlation between Au concentration and Fe removal for bio-oxidation process

Bio-reduction and bio-oxidation were able to dissolve sulphur from ore samples and formed sulphate (soluble) by following sulphur cycle and direct contact mechanism. The concentration of sulphate was checked by a spectrophotometer using SulfatVer 4 sulphate reagent. From the observation, when the sample becomes cloudy, it possibility determined that sulphate was present. Figures 9 and Figure 10 illustrated the concentrations of sulphate for bio-reduction and bio-oxidation, respectively. From the analysis results of both processes, the biotic samples had higher sulphate concentrations compared to the abiotic sample.

Sulfate ion is primarily produced when metal sulphide dissolves. *S. oneidensis* was used in the bio-reduction experiment to produce ion sulphate from the mineral sulphide (insoluble). Previous studies revealed that specific *Shewanella* species link the oxidation of organic substances (or hydrogen) to the dissimilatory reduction of S_0, a reaction that doesn't require the cell and S_0 particle to come into direct contact with each other [25]. There are two mechanisms for microbial respiration of oxidizing bacteria based on an interspecies sulphur cycle and extracellular cell. In this study, extracellular cell was interacted with S0 and SO_3^{2-} to generate thiosulphate ($S_2O_3^{2-}$) [26].

Meanwhile, the bio-oxidation process involved oxidation of element S from refractory gold ore. This process required the presence of both water and oxygen [27]. Sulphur oxidation (S, S_2^-, $S_2O_3^2$) can generate energy for bacterial growth. Sulphur is a better energy substrate than Fe (II) because it produces more ATP at the same molar level [28]. The CO_2 fixation process of *A. ferrooxidans* requires both sulphur oxidation and high redox potential electron transfer. Bacteria can adsorb sulphur intocell surface and transport it to the periplasmic space via bacterial outer membrane protein [29]. After a series of biological oxidation pathways, it is finally oxidised to sulphate ions and released on the cell's surface. Besides that, sulphur also can be oxidized to sulfuric acid. Sulphur oxidation mechanisms are classified into two types. The first one is when sulphur is the only substrate under aerobic conditions and is oxidised to sulfuric acid by sulphur dioxygenase. The second one occurs when both Fe (II) and Sulphur are used as substrates in anaerobic conditions and Sulphur is converted to sulfuric acid by the combined action of hydrogen sulphide Fe (III) oxidoreductase, sulfuric acid Fe (III) oxidoreductase, and Fe (II) oxidoreductase [30].

Moreover, the increment of sulphur removal via bio-reduction by *S. oneidensis* and bio-oxidation by *A. ferroxidans* resulting to the enhancement of Au concentration left in refractory gold ore as shown in Figure 11 and Figure 12, respectively. The bio-reduction and bio-oxidation had removed 97.21% and 97.70% of sulphur from the refractory gold ore with 0.23ppm and 0.21ppm of Au concentration obtained, accordingly. The results of removal of sulphur only show a slight difference for both processes. However, bio-oxidation by *A. ferroxidans* was more effective as it was sulphur-oxidizing bacteria that productively for removing sulphur where the strain cell interacted directly with the sulphur surface affecting to the enhancement of sulphur dissolution from refractory gold ore [31].

(*C) Arsenic removal from refractory gold ore*

The reduction of arsenic was measured by ICP-OES after 19 days of bioleaching. Figure 13 results showed the removal of arsenic for each weight sample was increased after bioleaching process with the percentage removal from 82.01% (0. 5 g of weight sample) to 84.93% (2.0 g of weight sample) for the bio-reduction process and 91.65% (0.5 g of weight sample) to 93.87% (2.0 g of weight sample) for the bio-oxidation process.

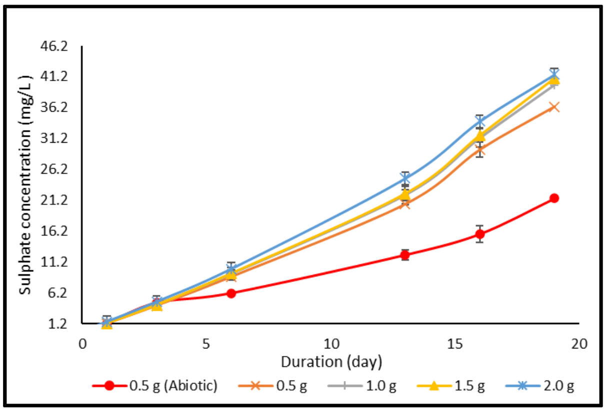

Figure 9 - Sulphate concentration obtained during the bio-reduction process within 19 days

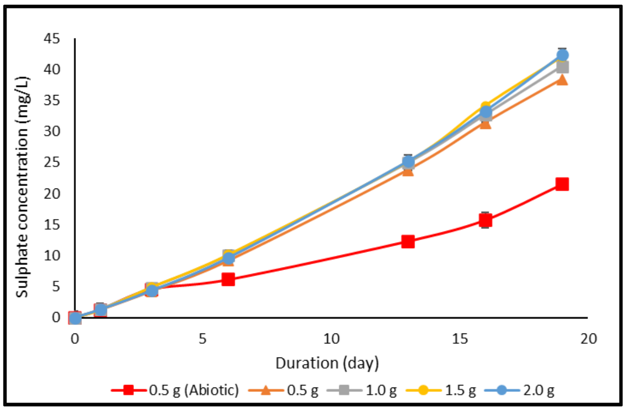

Figure 10 - Sulphate concentration obtained during the bio-oxidation process within 19 days

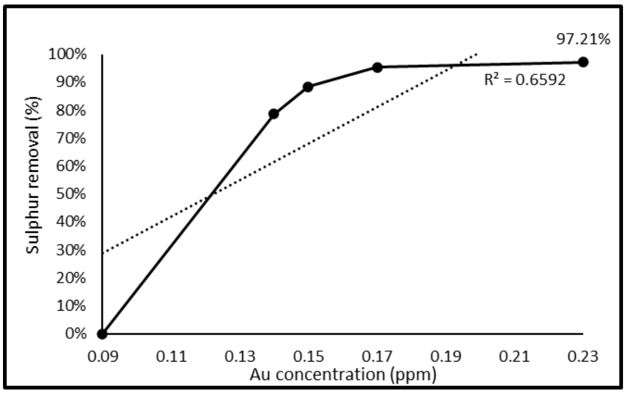

Figure 11 - Correlation between Au concentration and S removal for bio-reduction process

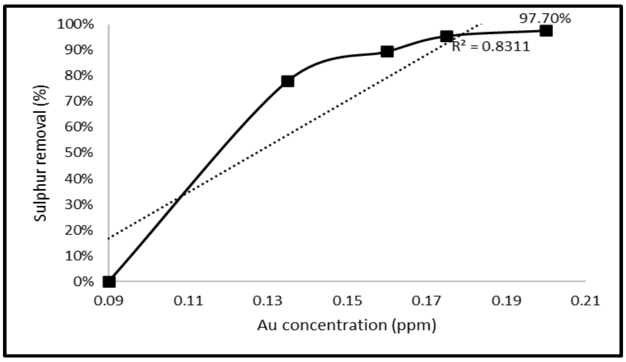

Figure 12 - Correlation between Au concentration and S removal for bio-oxidation process

The breakdown of Fe and S from arsenopyrite (FeAsS) via bio-reduction and bio-oxidation processes released free arsenic such as As (III) and As (V). In bio-reduction, As (V) undergoes a reduction process by gaining electrons from the *S. oneidensis* and producing soluble As (IIII) [32]. In this case, the removal of arsenic higher by bio-reduction compared to bio-oxidation process because the rate of As (V) reduction was more rapid than other electron acceptors such as nitrate, thiosulfate, manganese (IV) oxide, and iron resulting to the increment of the arsenic removal [33]. Meanwhile, the removal of arsenic from the bio-oxidation process was not efficient compared to bio-reduction due to the removal of As (III) is more difficult than the removal of As (V) [34]. This reaction occurred through the oxidation of Fe (II) to Fe (III) ions and simultaneously oxidation of As (III) to As (V) producing some ferric arsenate [35]. Subsequently, the removal of arsenic from refractory gold ore affected the enhancement of Au concentration with the value obtained 0.23 ppm and 0.22 ppm via bio-reduction and bio-oxidation processes as shown in Figure 14 and Figure 15, respectively.

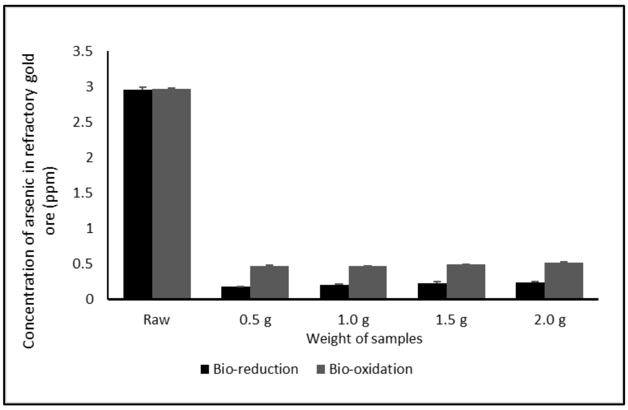

Figure 13 - The concentration of arsenic in refractory gold ore after 19 days of bioleaching

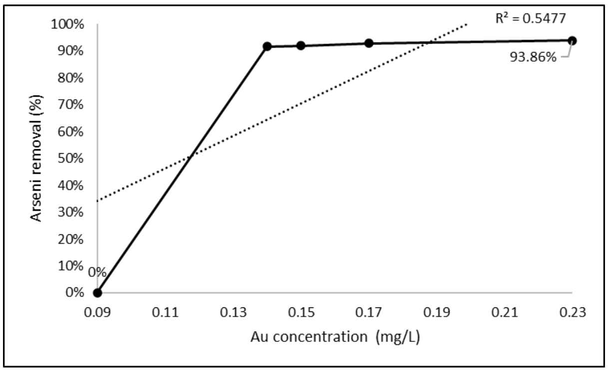

Figure 14 - Correlation between Au concentration and arsenic removal for bio-reduction process

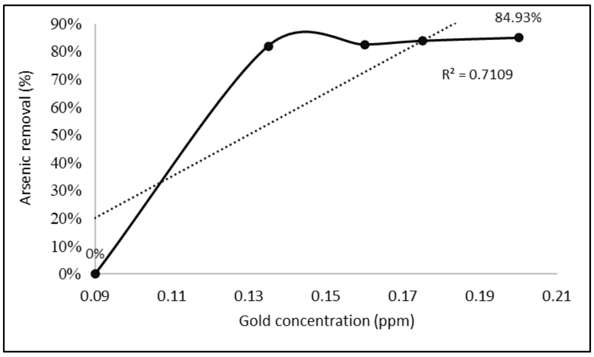

Figure 15 - Correlation between Au concentration and arsenic removal for bio-oxidation process

Conclusions

As a conclusion, the impurities of refractory gold ore namely Fe, S, As were successfully reduced by bioleaching technique using *S. oneidensis* and *A. ferroxidans* as a bio-reduction and bio-oxidation agents, respectively. The results from XRD and EDX show As, Fe, S exist in the refractory gold ore. In addition, the SEM analysis has shown a rough morphological structure that indicates the presence of pyrites.

The Au concentration was enhanced by the bioleaching process, yielding values of 138.89% for bio-reduction and 122.22% for bio-oxidation, respectively. The bio-reduction has been proven more effective, primarily due to its enhanced removal of impurities in comparison to bio-oxidation. This was supported by significant correlation values between Au concentration and the percentage removal of impurities (Fe, S, and As) with respective R^2 values of 0.7109, 0.6261, and 0.953.

CRediT author statement: **Nazirah Awang Husain**: Conceptualization, Methodology, Software. **Abdul Hafidz Yusoff** and **Muhammad Noorazlan**: Data curation, Writing draft preparation, Supervision. **Wee Seng Kew** and **Noorfazliani Shoparwe**: Visualization, Investigation. **Chang Shen Chang** and **Nur Nabihah Yusof**: Software, Validation. **Mohammad M. Fares:** Reviewing and Editing.

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Қиын өңделетін алтын кенінен қоспаларды биототықсыздану әдістерімен жою және биототығу процестері

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Қабылданды*: 2 мамыр 2024*

ТҮЙІНДЕМЕ

Қиын өңделетін алтын кеніндегі алтынды кәдімгі металлургиялық әдіспен алу қиын, себебі қоспалар ретінде құрамында темір (Fe), күкірт (S) және мышьяк (As) болатын жоғары сульфидті минералдар бар, нәтижесінде алтын (Au) аз бөлінеді. Цианидті шаймалау сияқты дәстүрлі әдістер алтынның сульфидті минералдармен күрделі байланысқандығына байланысты қиын өңделетін кеннен алтын алу үшін тиімсіз екендігі дәлелденді. Бұл зерттеуде әдеттегі цианидті шаймалауға балама ретінде биошаймалауды қолдану зерттеледі. Shewanella oneidensis (S. oneidensis) және Acidithiobacillus ferroxidans (A. ferroxidans) биошаймалау процесінде сәйкесінше биототықсыздану және биототығу агенттері ретінде қызмет етеді. Кендегі минералдардың құрамы XRD талдауы (Модель: Rigaku's Miniflex 600) және EDX талдауы (EDX 3 үлгісі) арқылы анықталды. Сонымен қатар, SEM талдауы (Zeiss EVO LS15 SEM) морфологиялық құрылымды зерттеу үшін пайдаланылды. Қоспалардың концентрациясы (Fe, S және As) спектрофотометрдің (үлгі: DR3900 Hach) көмегімен бағаланды, ал Au концентрациясы ICP-OES (үлгі: G8015A5110 ICP-OES) арқылы анықталды. Ірілігі 32 мм-ден аз және салмағы әртүрлі (0,5 г, 1,0 г, 1,5 г, 2,0 г) електен өткізілген қиын өңделетін алтын кенінің үлгілері биототықсыздану және биототығу процестерінен өтті. Нәтижелер SEM талдауы арқылы байқалған өңделмеген үлгінің бетінің кедір-бұдырлы морфологиясын көрсетті. Сонымен қатар, XRD және EDX нәтижелері қоспа концентрациясының төмендегенін анықтады, бұл алтын тазалығының ықтимал жоғарылауын байқатады. Атап айтқанда, биототықсыздану процесі 122,22% мәні бар биототығумен салыстырғанда 138,89% мәндерімен Au концентрациясының жоғары деңгейін көрсетті. Осылайша, биототықсыздану процесі биототығумен салыстырғанда Au концентрациясын арттыруда тиімдірек болды.

Түйін сөздер: Биосілтілеу, S. oneidensis, A. Ferroxidans, алтын, ICP-OES.

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Удаление примесей из упорной золоторудной руды методами биовосстановления и процессы биоокисления

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АННОТАЦИЯ

Золото из упорной золотой руды трудно извлечь традиционным металлургическим методом из-за присутствия сульфидных минералов с повышенным содержанием железа (Fe), серы (S) и мышьяка (As) в качестве примесей, что приводит к низкому содержанию золота (Au). восстановление. Традиционные методы, такие как цианидное выщелачивание, оказались неэффективными для извлечения золота из упорной руды из-за того, что золото сложно связано с сульфидными минералами. Следовательно, в этом исследовании рассматривается применение биовыщелачивания в качестве альтернативы традиционному цианидному выщелачиванию. Shewanella oneidensis (S. oneidensis) и Acidithiobacillus FerrOXIDANS (A. FerrOXIDANS) служат агентами биовосстановления и биоокисления соответственно в процессе биовыщелачивания. Состав минералов в руде определялся с помощью рентгеноструктурного анализа (модель: Miniflex 600 компании Rigaku) и анализа EDX (модель EDX 3). Тем временем для изучения морфологической структуры использовался анализ СЭМ (Zeiss EVO LS15 SEM). Концентрации примесей (Fe, S и As) оценивали с помощью спектрофотометра (модель: DR3900 Hach), а концентрацию Au определяли с помощью ICP-OES (модель: G8015A5110 ICP-OES). Просеянные образцы упорной золоторудной руды с крупностью менее 32 мкм и различной массой (0,5 г, 1,0 г, 1,5 г, 2,0 г) подверглись процессам биовосстановления и биоокисления. Результаты показали более шероховатую морфологию поверхности необработанного образца, наблюдаемую с помощью SEM-анализа. Кроме того, результаты XRD и EDX продемонстрировали снижение концентрации примесей, что указывает на потенциальное увеличение чистоты золота. Примечательно, что процесс биовосстановления продемонстрировал превосходное увеличение концентрации Au со значением 138,89% по сравнению с процессом биоокисления со значением 122,22%. Таким образом, процесс биовосстановления оказался более эффективным в увеличении концентрации Au по сравнению с биоокислением.

	Ключевые слова: Биологическое выщелачивание, S. oneidensis, A. Ferroxydans, золото, ICP-OES.
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Mini review polyurethane hybrids: preparation, characterization and applications

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ABSTRACT

Polyurethane hybrids (PUHs) are a type of versatile materials with a broad variety of possible applications. Considering the connections between their structure and characteristics, this is especially true. Because of its special mechanical stability, toughness, stickiness, sustainability of the finished product, biological properties, and chemical properties, PUHs are the subject of extensive research and development for use in a wide range of applications. Polyurethane /acrylic hybrids are important type of binders in coating industries due to their exceptional properties. This mini review aims to provide an overview of different types of polyurethane/acrylic hybrids, including waterborne, blending, and UV curable hybrids. The synthesis of these hybrids through addition and emulsion polymerization techniques is discussed, emphasizing the importance of achieving intimately homogenous latex. The hybrids (PUHs) enhanced the physical, chemical, and mechanical properties of the final products including coatings, paints, adhesives, and performance of other products. In addition, the anticorrosion coatings based on PUHs exhibits the properties of polyurethane and acrylic to reduce or prevent the corrosion.

Keywords: Polyurethane hybrids, Acrylic, Water borne, UV curable, Blending, Emulsion

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Introduction

Acrylic-polyurethane hybrids are binders based on combining polyurethane and acrylic and become important type of binders in coating industries because of their high-performance properties, good dispersion to the pigments and lower cost, as well as the highest performance of polyurethane such as excellent chemical resistance, adhesion, sustainability of the final products, toughness, and mechanical stability [[1], [2], [3], [4], [5], [6], [7], [8], [9], [10]]. The properties of hybrids depend on the types, concentrations, ratios, and molecular weight of raw materials of polyurethane and acrylic. To achieve the highest properties of polyurethane and acrylic polymer is to synthesise polyurethane/acrylic hybrids using addition and emulsion polymerization, resulting in intimately homogenous latex [[10], [11], [12], [13], [14]].

There are different kinds of polyurethane/acrylic hybrids: 1) emulsion waterborne polyurethane/acrylic hybrids which produce water-base hybrids based on different kinds of surfactants including anionic, cationic and nonionic surfactants as well as acrylic monomers with hydroxyl groups. 2) blending polyurethane prepolymer with polyacrylic through cross-linking between functional groups of both polymers to produce a blending copolymer with the highest physical and chemical properties. 3) UV-curable waterborne polyurethane/acrylic to produce eco-friendly polymer using UV-radiation for polymerization of polyurethane-acrylic with a network structure to improve mechanical properties as well as chemical and corrosion resistance. Therefore, waterborne UV-curable coating exhibited excellent hardness, scratch-resistance, impact-resistance as well as chemical and corrosion resistance. 4) polyurethane/acrylic solution type: polymerization of hybrids was prepared by solution technique in presence of solvents including toluene, acetone and characterized different standard methods [[15], [16], [17], [18]].

Emulsion waterborne polyurethane/ acrylic hybrids

Stable emulsions of waterborne poly(urethane-urea) and hybrid materials including n-butyl acrylate (BA), glycidyl methacrylate (GMA), and perfluoro decyl acrylate with varying acrylate contents were effectively synthesized by Lee *et al.*2013 [19]. The emulsify of the waterborne emulsion was restricted at 40 wt. % acrylic monomer content. With the highest acrylate content prompted expanded molecule size, hardness, thermostability, and water/methylene iodide-contact points, while diminishing consistency, lengthening at break, water enlarging and surface energy.

While Sukhawipat *et al.* 2020 [20] combined a mixture of waterborne polyurethane by emulsion technique process utilizing a mix of hydroxyl telechelic and hydroxylated oil as the polyol. The waterborne polyurethane showed good dependability with 16% complete solids content and shaped excellent coatings. Further improved mechanical properties were accomplished by emulsified butyl acrylate (BA) and methyl methacrylate (MMA) co-monomers onto the waterborne. The extent of BA/MMA was found to impact the morphology, mechanical properties, surface wetting, and cement strength of the films. Waterborne hydroxyl-practical polyurethane/acrylic emulsions for two-part coatings were created by Ma *et al.* 2015 [21] through the copolymerization of hydroxyethyl acrylate (HEA)/BA with methyl methacrylate and acrylic-ended polyurethane scattering. The results showed that expanding the HEA/BA weight proportion diminished molecule sizes, limited size circulation, and expanded emulsion consistency. Films showed upgraded warm obstruction, substrate bond, rigidity, and hardness, however, decreased water opposition and expanded wettability with higher HEA/BA proportions. Application in two-part coatings further developed water obstruction, decreased wettability, and further expanded glass change temperature, warm steadiness, attachment, rigidity, and hardness. The review recommends that hydroxyl bunches in polyurethane add to hydrogen holding and covalently crosslinked networks with polyisocyanate in the coatings. Liu *et al.* 2020 [22] incorporated semi-gleam waterborne polyurethane-polyacrylate half and half scatterings with shifting styrene/butyl acrylate monomer proportions utilizing arrangement polymerization and stage reversal. The PUA films displayed superb bond qualities and great hardness.

Qu *et al.* 2014 [23] synthesized semi-batch acrylic-polyurethane emulsions by emulsion copolymerization, using a combination of acrylic monomers and an isocyanate-ended polyurethane. The authors examined the effect of polyurethane content on the emulsion morphology and film properties. Expanding polyurethane content stimulated harsher film surfaces. Ultra violet conveyance spectra diminished with higher polyurethane content, lining up with changes in film surface unpleasantness. Electrophoresis on an aluminum composite surface and ensuing drying at 120°C brought about films with phenomenal mechanical execution because of a restoring response among polyurethane and the air conditioner copolymer. The film gleam dropped to 4.0 after electrophoresis testing, showing possible use in elimination electrophoresis applications.

Alvarez *et al.* 2018 [24] studied the combination of waterborne polyurethane/acrylate scatterings by joining with bisphenol-A-glycidyl dimethacrylate. Using a prepolymer self-emulsifying approach, waterborne polyurethane/acrylate were organized with styrene and n-butyl acrylate in the polyacrylate segment and isochrone diisocyanate, poly (tetramethylene ether) lycol, dimethylolpropionic corrosive, and ethylenediamine in the polyurethane section. As the polymerization initiator, a redox pair configuration of hydrogen peroxide and ascorbic corrosive was added. Expanding the bisphenol-A-glycidyl dimethacrylate/1,4 butanediol proportion expanded molecule size, yielding stable scatterings with adversely charged particles and low thickness regardless of high solids content (27 wt. %). The expansion of 35 wt.% bisphenol-A-glycidyl dimethacrylate fundamentally expanded cross-cut attachment of polyurethane/acrylate coatings to treated steel.

Pardini *et al.* 2018 [25] synthesized PU/DEA hybrid films with pH-responsive characteristics by preparing films with different concentrations of 2-(diethylamino)ethyl methacrylate (DEA) and a polyurethane based on isophorone diisocyanate (PU). In instance, in the DEA-rich hybrid system (50 wt. %), batch investigations analyzing Cu^{2+} and Zn^{2+} sorption on the polymer films show best removal at pH 4.0 with an initial concentration of 250 mg/L for each ion. Zn^{2+} is more favored by the polymer systems than Cu^{2+} is, and the equilibrium sorption data closely match the Langmuir sorption isotherm model.

Deng *et al.* 2018 [26] conducted a study, where hybrid emulsions of waterborne polyurethanes-acrylate were synthesized using isophorone diisocyanate, polytetramethylene glycol, and an acrylate monomer. The study concentrated on how different characteristics of the hybrid emulsions and films were impacted by the NCO/OH ratio and the polyurethane/polyacrylic ratio. The findings demonstrated that the hybrids latex particles exhibited regular spherical shapes and excellent stability. Particularly at a polyurethane/polyacrylic ratio of 30/70, the hybrids films displayed a significant loss factor (tanδ) of ≥0.3 across a temperature range of 75℃, making them suitable for damping applications.

Degrandi-Contraires *et al.* 2013 [27] demonstrated the production of urethane/acrylic hybrid latexes for pressure-sensitive adhesive applications by miniemulsion polymerization. The technique provided addition polymerization of an isocyanate-terminated polyurethane with hydroxyl groups of one acrylic component (HEMA) and simultaneous free-radical polymerization of acrylic monomers. The concentration of HEMA significantly influenced the polymer microstructure, impacting the gel content, crosslinking density, and the formation of smaller loops in the network. Computer simulations using a Monte Carlo method provided insights into the polymer microstructure, revealing the potential for developing a new generation of urethane/acrylic with enhanced shear resistance. While Lopez *et al.* 2011 [28] conducted one-step miniemulsion polymerization to prepare waterborne polyurethane-acrylic hybrid nanoparticles for use in pressure-sensitive adhesives. The addition of polyurethane significantly increased cohesive strength, resulting in a much higher shear holding time, making it desirable for pressure-sensitive adhesives. Nevertheless, phase separation was caused by the addition of a tiny amount of methyl methacrylate to the acrylic copolymer, leading to a hemispherical morphology and reduced tack energy. The study underscores the sensitivity of viscoelastic and adhesive properties to polymer network architecture, emphasizing the importance of precise composition and synthesis conditions. In order to investigate the effects of colloidal structure, grafting between the two polymers, and the makeup of the polymer phases on the mechanical properties of cast films, Mehravar *et al.* 2019 [29] created a number of polyurethane/acrylic dispersions using a solvent-free approach. The dispersions exhibited a polyurethane shell/acrylic core structure, translating into a morphology that acted as a filler material, allowing the use of high T_g copolymers, and resulting in films with exceptional mechanical strength. Grafting between polyurethane and acrylic phases enhanced compatibility but had a minimal impact on mechanical characteristics. The study provides design principles for synthesizing polyurethane/acrylic hybrids with controlled mechanical properties. Poly(siloxane–ether–urethane)-acrylic (PU-AC) hybrid emulsions were created by adding different amounts of hydroxyethoxypropyl-terminated polydimethylsiloxane (PDMS) to the acrylic-terminated poly(ether–urethane) backbone in a study by Yi *et al.* 2017 [30]. Larger particle sizes and reduced viscosity in the hybrid emulsions were observed upon the introduction of PDMS, according to in situ copolymerization with methyl methacrylate and butyl acrylate via an emulsion technique. The resulting films exhibited improved flexibility, water resistance, and surface hydrophobicity with increasing PDMS content, making them potentially valuable for applications such as fouling-release coatings, biomaterials, and surface finishing.

Waterborne polyurethane/acrylic hybrid emulsions were prepared by Ma *et al.* 2015 [31] using a hybrid synthesis technology. The content of 2-ethylhexyl acrylate and N-acryloylmorpholine affected the hybrid emulsions and films that resulted from the polymerization of methyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate, and N-acryloylmorpholine in the presence of acrylic-terminated polyurethane dispersion, as the study examined. This study demonstrated that the addition of ethylhexyl acrylate enhanced film elasticity, while N-acryloylmorpholine contributed to high gloss, substrate adhesion, toughness, and hardness. The combination of both monomers produced hybrid materials with moderate properties, and an increase in the N-acryloylmorpholine/ethylhexyl acrylate weight ratio resulted in changes in emulsion properties and film characteristics, including a synergistic effect on film gloss and increased hydrogen bond interaction with higher N-acryloylmorpholine content.

A study on the production of hydroxyl-functional polyurethane-acrylate (PUA) emulsions for two-component coatings was carried out by Ma *et al.* 2015 [21]. The effects of changing the hydroxyethyl acrylate/BA ratio on PUA emulsions, films, and two-component coatings were observed through copolymerization of varying weight ratios of hydroxyethyl acrylate (HEA) and BA with a constant amount of methyl methacrylate (MMA) and acrylate-terminatedpolyurethane (PU). Increasing the HEA/BA weight ratio led to smaller particle sizes, a narrower particle size distribution, increased special surface area, and higher viscosity in the emulsions. The resultant PUA films showed improved hardness, tensile strength, adhesion on surfaces, and thermal resistance, but also increased wettability and decreased water resistance. Furthermore, in two-component coatings, the reaction between polyisocyanate (PIH) and the hydroxyl group of PUA resulted in covalent crosslinking, leading to increased glass transition temperature, improved water resistance, and enhanced adhesion, tensile strength, and hardness in the cured films.

The fabrication of stable emulsions of crosslinkable waterborne polyurethanes (CWPU) and waterborne polyurethane-acrylic (CWPU/AC) hybrids using variable amounts of trimethylolpropane (TMP) and acrylic monomers was studied by HyeLin *et al.* 2016 [32]. The investigation focused on the effects of these components on emulsion stability, particle size, viscosity, as well as the mechanical, thermal, and surface properties of resulting film materials. The study found that specific content limits of TMP and acrylic monomer were critical for emulsion stability. The film samples, enriched with silicone and fluorine according to XPS analysis, exhibited improved tensile strength, modulus, and hardness with increasing crosslinkable TMP/acrylic monomer content, demonstrating potential for high-performance antifouling coating materials at an optimum composition of approximately 0.04 mol/50 wt%. Zhang *et al*. 2014 [33] successfully prepared a waterborne polyurethane–polyacrylic ester hybrid emulsion (PUPA) by physically blending polyacrylic ester emulsion (PA) and waterborne polyurethane emulsion (PU). The hybrid nanoparticles were characterized for structure and chemical components, revealing promising properties. While PUPA-C, a humidity-sensitive coating, showed noteworthy humidity sensitivity and retention qualities, films made from PUPA revealed good hardness, gloss, water resistance, and water absorption. In their comprehensive investigation of PU/acrylic hybrid dispersions, Mehravar *et al.* 2019 [34] highlight the importance of seeded emulsion polymerization in the large-scale synthesis of surfactant-free waterborne PU/acrylic hybrids. PU's dominance in film formation allows the incorporation of acrylic compositions with higher T_g values without major effects on the film formation process. The study underscores the need for ongoing research, particularly considering environmental concerns and evolving regulations impacting PU/acrylic hybrid synthesis. Yi *et al.* 2017 [35] created robust waterborne polyurethane-acrylic (PU-AC) hybrid emulsions with different AC/PU weight ratios (45/55 to 70/30) by using allyl polyoxyethylene ether (APEE) as a coupling agent. The resulting emulsions exhibited a core-shell structure without cross-linking of copolymers. Increasing the AC/PU weight ratio led to larger particle sizes and broader size distributions, accompanied by reduced emulsion viscosity. The films that were produced using these emulsions showed enhanced mechanical characteristics, including higher water resistance, water contact angle, glass transition temperature, shore A hardness, tensile stress, and storage modulus. The choice of acrylate type (MMA, BA, or their mixture) influenced emulsion properties for specific applications. The study underscores APEE's role in establishing chemical bonds between PU and AC, promoting self-emulsification during polymerization, and facilitating the synthesis of high AC/PU ratio PU-AC hybrid emulsions. Water-borne polyurethanes (WPU) ended with vinyl groups and various concentrations of dimethylolpropionic acid (DMPA) were produced by Wu *et al.* 2019 [36].These WPU emulsions were utilized as surfactants in the soap-free emulsion copolymerization to produce core-shell polyurethane/polyacrylate (PUA) composite emulsions. The incorporation of WPU in copolymerization resulted in low surface tension (38.8 mN m^-1), and the reactive seed with WPU achieved a high final conversion of acrylic monomer (98%). The core-shell structure of PUA was confirmed by FTIR-ATR, and the compatibility between WPU and PUA improved with increased grafting efficiency, as observed in TEM results. PUA composite particle morphology changed from scattered to multi-core, core-shell, and core-shell architectures with different DMPA contents. Tensile testing revealed reinforcing and toughening effects in PUA films with increased DMPA content. In order to overcome the inadequate water resistance of conventional waterborne polyurethane (WPU), Xu *et al.* 2021 [37] created CO_2-triggered hydrophobic/hydrophilic switchable waterborne polyurethane–acrylate (WPUA) containing methyl methacrylate (MMA) units. The resultant WPUA, especially with 10 weight percent MMA, showed excellent mechanical qualities, such as high tensile strength (16.7 MPa) and modulus (85.9 MPa), as well as outstanding water resistance (low water uptake of 2.15 weight percent and linear swelling ratio of 0.17 L%). The study highlighted the stable dispersion of CO_2-triggered WPUA latex particles in water and their excellent properties post-film formation. Ma *et al.* 2017 [38] created a composite emulsion, waterborne polyurethane-acrylate (WPUA), by polymerizing waterborne polyurethane (WPU) as a seed emulsion dispersion, followed by methyl methacrylate (MMA) and BA. To examine their impact on performance qualities, the researchers altered the mass ratio of MMA to BA and the concentration of polyacrylate (PA) in WPU, using poly(propylene carbonate) (PPC) diol as a soft segment. The resulting WPUA films showed improved adhesion, pencil hardness, water resistance, and hydrophilicity, indicating good compatibility and a synergistic effect between PPC-based WPU and PA, leading to enhanced thermal properties and coating characteristics. Maurya *et al.* 2018 [39] present a comprehensive review on polyurethane-acrylate (PUA) oligomers, a novel class of polyurethanes produced by capping polyols with diisocyanate and acrylate. The review covers topics such as structure, modification, reactive diluents, curing, and the mechanical, optical, and thermal behavior of PUA, providing insights into the chemistry and mechanisms underlying these oligomers. The authors highlight the growing demand for modifying PUA to enhance its properties and note that the understanding of PUA chemistry has advanced to a level where tailor-made formulations for specific applications can be developed. Waterborne polyurethane modified by acrylate/nano-ZnO (PUA/ZnO) was manufactured and employed by Jiang *et al*. 2018 [40] to improve the wet rubbing fastness of cotton fabric dyed reactively. The treated fabrics showed a notable improvement of about 0.5-1 rate in wet rubbing fastness, achieving a rating of 3-4. Moreover, the treated fabrics exhibited enhanced ultraviolet protection with a UPF level of 50+, and SEM analysis revealed a smooth and reticular coating on the fabric surface, contributing to improved rubbing fastness by reducing mechanical friction forces. Using a solvent-free technique, Shi *et al.* 2013 [41] created a TDI-polyurethane/polyacrylate (TDI-PU/PA) composite emulsion by substituting methyl methacrylate (MMA) and butyl acrylate (BA) for acetone as a diluent. TDI, polypropylene glycol (PPG), 1,6-hexanediol (HDO), and dimethylol propionic acid (DMPA) were used in the emulsion synthesis, with the resulting latex film exhibiting increased tensile strength and pendulum hardness. The addition of MMA improved water resistance, and compared to IPDI-PU/PA, TDI-PU/PA offered cost efficiency and increased pigment loading, enhancing film hardness, and covering power.

Blending polyurethane/acrylic hybrids

Mehravar *et al.* 2019 [42] zeroed in on study of blending synthetically united polyurethane/(meth)acrylic half and half scatterings for wood floor coatings. Utilitarian monomers with hydroxyl gatherings and different vinyl functionalities (acrylic, allylic, methacrylic) were utilized for joining polyurethane and acrylic polymer stages. The polymerization method of (meth)acrylic monomers (bunch and semibatch) and the reactivity of monomers during acrylic polymerization were examined. The utilization of less responsive monomers brought about restricted gel portion arrangement, while additional receptive twofold bonds prompted higher gel content and molar mass. TEM examination showed that united mixtures displayed more homogeneous molecule and film morphologies. Comparing the connected and non-united polymer films, the former showed a greater Young's modulus and strain solidifying, with a more articulated impact for crossovers with higher gel content. Wood floor coatings arranged with these scatterings showed last properties practically identical to an industrially accessible reference covering. Kozakiewicz *et al. 2016* [43] in the second part of the survey centers around the blend and portrayal of watery polyurethane-acrylic scatterings (APUAD) with cross breed molecule structures. These scatterings yield coatings that show better properties analyzed than those created from mixes of watery polyurethane scatterings (APUD) and acrylic polymer scatterings. The paper talks about the potential outcomes of crosslinking coatings from APUD and APUAD, as well as the development of filled composites, including nanocomposites, from these scatterings. Also, the survey momentarily sums up current uses of APUD and APUAD. The paper features huge turns of events and distinguishes regions where further examination is required, zeroing in on the blend, portrayal of APUAD, and investigating crosslinked and filled frameworks including APUD or APUAD. Peruzzo *et al.* 2011 [44] blended polyurethane/acrylate cross breed composites with changing acrylic content (10-90 wt.%) through emulsion polymerization of acrylic monomers within the sight of preformed polyurethane chains. Mixes with identical acrylic content were likewise ready by blending polyurethane and acrylic scatterings. FTIR, UV, SEC, TEM, AFM, DLS, SAXS/WAXS, and gel division examination were among the methods used to portrayal. Mechanical characteristics, surface roughness, pencil and Buccholz hardness, and partially settled water contact point. The half breeds displayed crosslinked structures with changing molecule and film morphologies in view of acrylic content, showing non-straight conduct in film properties. Actual mixes exhibited a steady change from polyurethane to acrylic. FTIR showed preferred similarity in mixture frameworks over in actual mixes. By SAXS, crossover composites containing up to 70% acrylic were homogenous, while AFM uncovered ease isolation in mixes at all piece levels. Mehravar *et al.* 2017 [45] investigate the glue properties of strain delicate cements (public service announcements) got by mixing latexes with various qualities. Generally, public service announcement execution is surveyed in view of the sub-atomic load of the solvent polymer division and gel content. In any case, the examination recommends that depending entirely on gel portion and sol atomic weight distorts the portrayal. All things considered, the review stresses the requirement for an extensive comprehension of the whole sub-atomic weight dissemination, decided utilizing Lopsided Stream Field-Stream Fractionation (AsFlFFF), for a more significant connection between polymer microstructure and glue properties. Saeed *et al.* 2013 [46], conducted a study where emulsion-synthesized polyurethanes/polyurethane blend resins offer an environmentally conscious solution by minimizing solvent usage during leather resin application, thereby addressing pollution concerns. The resulting films exhibit desired properties such as high flexibility, gloss, fast-dry, and non-flammability, coupled with high thermal stability and cost-effectiveness. PU/PA-1, PU/PA-2, and PU/PA-3 blend resins exhibit notably varied drying times (4.0 to 7.0 min), with the faster curing reaction in PU/PA-1 attributed to a higher hexamethylene diisocyanate (HDI) content, leading to enhanced crosslinking. By adding polyacrylate resin emulsions, the films become impermeable in organic solvents and water, extending the polyurethanes' application endurance.

Mohamed *et al.* 2020 [47], conducted research focused on developing an eco-friendly water-based protective coating for steel pipelines, aiming to replace coatings containing hazardous materials to eco-friendly ones. The coating, formed by blending acrylic emulsion (AC) with varying proportions of polyurethane (PU) polymer, underwent comprehensive characterization to assess chemical structure and morphology. Additionally, the innovative mixed metal pigment that was generated from bauxite ore was added to the modified acrylic emulsion (AC-PU). The formulated coatings, particularly those with AC mixed with 15% polyurethane and the prepared pigment, demonstrated superior corrosion protection in 3.5% NaCl and 10% HCl solutions compared to other formulations and individual polymers. Negim et al. 2023 [48] prepared polyurethane hybrids based on different kinds of polyurethane and 2-hydroxyethyl methacrylate to modifiy unsaturated polyester resins. The results showed that the polyurethane hybrids improved physical and mechanical properties of polyester due to the crosslinking between hybrids and polyester.

UV curable waterborne polyurethane/acrylic

The raw ingredient for UV-curing coatings is waterborne polyurethane that is UV-curable. Environmentally friendly and safer than solvent-based paints are waterborne UV curing coatings. Since UV-curing technology is environmentally friendly and has superior qualities including high hardness, gloss, scratch resistance, and chemical resistance because of the high crosslink density from the acrylate group, it has therefore been proposed as a solvent-borne coating replacement. When creating products with unique waterborne qualities like low skin irritation and no flash point, UV polyurethane might be a useful tool. UV-curable waterborne polyurethane dispersions made by addition of copolymers of polycarbonate diols with various end-capping groups. According to the molecular weight (800, 1000, or 2000 g/mol) of polycarbonate diols, the physical properties were analyzed, and the authors [49] investigated the impacts of the polyol molecular weight on the UV-curing behavior. Similar research was conducted to determine how the end-capping group's functionality affected the physical characteristics and behavior of UV curing. To give the end-capping group functionality, 2-hydroxyethylmethacrylate, 2-hydroxyethylacrylate, and pentaerythritol tri-acrylate were utilized, in that order. The findings demonstrated that when the molecular weight of the polycarbonate diols decreased, so did the pendulum hardness, curing rate, and conversion. Compared to the other dispersions with mono-methacrylate or mono-acrylate functionality, the dispersion with tri-acrylate functionality on end-capping groups exhibited significantly higher pendulum hardness, curing rate, and conversion. UV-curable polyurethane dispersions were created by Kim *et. al.* (2006) [50] using varying prepolymer chain lengths and capping agents, such as 2,3-epoxy-1-propanol (glycidol) and 2-hydroxyethyl acrylate. Because the terminal isocyanate groups were capped with glycidol, the resulting films based on polyurethane dispersion had exceptional hardness, maximum elongation at break above 200%, and were tack-free before curing.

Conclusion

Polyurethane hybrids (PUHs) are versatile materials with a wide range of potential applications. The combination of polyurethane and acrylic in hybrid binders has gained significant attention in the coating industry due to their exceptional properties. Polyurethanes hybrids, particularly those incorporating acrylic components offer a wide range of properties and applications. The synthesis and characterization of polyurethane/acrylic hybrids through various techniques, including emulsion and addition polymerization, have been discussed. The resulting polyurethanes hybrids exhibit improved mechanical stability, adhesion, toughness, and chemical resistance. These materials have shown great potential in coating industries, two-part coatings, damping applications, and pressure-sensitive adhesives. Further research and development in this field can lead to the exploration of new hybrid combinations and the enhancement of their properties for various applications.

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Полиуретан гибридтеріне кішігірім шолу: дайындалуы, техникалық сипаттамасы, және қолданылуы

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ТҮЙІНДЕМЕ

Полиуретанды будандар (гибридтер) (ПУГ) алуан түрлі қолданылу аясы бар, әмбебап материал. Олардың құрылысы мен сипаттамаларының арасындағы байланысты есепке алғанда бұл ең өзекті мәселе. Арнайы механикалық тұрақтылығына, беріктігіне, жабысқақтығына, дайын өнімнің тұрақтылығына, биологиялық және химиялық қасиеттеріне байланысты полиуретанды будандар ПУГ қолданбалардың кең ауқымында пайдалану үшін ауқымды зерттеулер мен әзірлемелердің нысаны болып табылады. Өзінің өзіндік қасиеттеріне орай полиуретанды гибридтер мен акрил бояу өнеркәсібіндегі байланыстырғыштардың маңызды түрі болып саналады. Бұл қысқаша шолудың мақсаты полиуретанды/акрилді гибридтердің әртүрлі түрлеріне шолу жасау, соның ішінде су негізіндегі, қоспа және ультракүлгін сәулесімен қатырылатын гибридтерді таныстыру. Барынша біртекті латекске қол жеткізудің маңыздылығын көрсете отырып, қоспалы және эмульсиялы полимерлеу әдістерінің көмегімен осы будандардың синтезі талқыланады.

Түйін сөздер: полиуретанды будан (гибрид), акрил, су негізінде, ультракүлгін сәулелерімен қатыру, қоспа, эмульсия.

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Мини-обзор полиуретановых гибридов: получение, характеристика и применение

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АННОТАЦИЯ

Полиуретановые гибриды (ПУГ) представляют собой тип универсальных материалов с широким спектром возможных применений. Учитывая связь между их строением и характеристиками, это особенно актуально. Благодаря своей особой механической стабильности, прочности, липкости, устойчивости готового продукта, биологическим и химическим свойствам ПУГ являются предметом обширных исследований и разработок для использования в широком спектре применений. Гибриды полиуретана и акрила являются важным типом связующих в лакокрасочной промышленности благодаря своим исключительным свойствам. Целью этого мини-обзора является предоставление обзора различных типов гибридов полиуретана и акрила, включая гибриды на водной основе, смеси и гибриды, отверждаемые УФ-излучением. Обсуждается синтез этих гибридов с помощью методов аддитивной и эмульсионной полимеризации, подчеркивая важность достижения максимально гомогенного латекса.

Ключевые слова: полиуретановые гибриды, акрил, на водной основе, отверждаемые УФ-излучением, смешивание, эмульсия.

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Engineering and Technology

Research on the production of sorbent based on bentonite clay for wastewater treatment from chemical industries

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ABSTRACT
In our country, the problem of water purification remains urgent, with the growth of external factors contributing to this, which can include an increase in the number of industrial enterprises, the development of agriculture, urban growth and others. To solve the problem of water purification it is economically advantageous to create new sorbents, with the available resources in our country.For the processing of of bentonite clay under experimental conditions, instrumental test methods were chosen using a scanning electron microscope (SEM) of the Jeol JSM-6490l V brand, a multi-parameter portable cyberscanner (PCD 650 Eutech) and a Q-1500 Derivatograph. In this article, we studied the bentonite of the Darbaza deposit. For physico-chemical analysis of clay from the Darbaza deposit, a specially selected sample was crushed, and sieved and its chemical composition was determined. *Results.* Based on the results of instrumental studies, the elemental and mineralogical composition of bentonite clay from the Darbazinsky deposit was determined using a scanning electron microscope JSM-6490l V (Jeol, Japan) using the energy-dispersive method. The resulting sorbent based on bentonite clay has a high sorption capacity and is recommended for use in the treatment of wastewater from chemical industries. The resulting sorbent based on bentonite clay from the Darbaza deposit makes it possible to purify wastewater from phosphate production from phosphate and other ions up to 60%. The developed sorbent based on bentonite clay has environmental and economic efficiency and connections with the use of local natural resources. Thus, it should be noted that for adsorption treatment of wastewater from chemical industries with a high degree, it is possible to use effective sorbents based on bentonine clays from the Darbaza deposit. It should also be noted that the use of bentonite clays for water purification by the sorption process is an effective and affordable alternative to adsorbents that show high adsorption capacity for various compounds.

Keywords: bentonite, Darbaza deposit, water treatment, montmorillonite, adsorption, heavy metals.

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Introduction

The problem of wastewater treatment, since the second half of the 20th century, is relevant for all countries of the world. From the colloid-chemical point of view, wastewater is a heterogeneous mixture of dissolved, colloidal and suspended-in-water impurities of organic and inorganic nature. One of the main pollutants of natural waters is heavy metal ions coming with the wastewater from galvanic shops, mining, ferrous and non-ferrous metallurgy, and machine-building plants.

There are quite a lot of purification methods, but the simplest and most effective methods of water purification are adsorption methods [[1], [2], [3], [4]]. The advantages of these methods are high efficiency, possibility to treat wastewater containing several substances, as well as recovery of these substances. The efficiency of adsorption purification reaches 80-95 % and depends on the chemical nature of the adsorbent, the size of the adsorption surface and its availability, the chemical structure of the substance and the chemical form of its presence in the medium. Kazakhstan is famous for its rich deposits of various minerals, as well as natural clay - bentonite, the properties of which will be investigated in this article. The diverse application of bentonite is conditioned by its physical and chemical abilities. The greatest use of bentonite clay is in medicine, drilling, metallurgy, foundry, construction, agriculture, environmental programs, adsorbents, fillers, etc [[5], [6], [7], [8], [9]].

The world bentonite reserve is 5.5 billion tons, 45% of which is accounted for by China, and 15% by the United States, the remaining reserve is accounted for by Russia, Turkey, Greece, India, etc. Kazakhstan has large reserves of bentonite clay, only in South Kazakhstan there are more than 6 deposits of bentonite, Keles, Darbaza, Lenger, Andreevs, Dzerzhin, Ildersay, etc., in East Kazakhstan there are known such deposits as Tagans, Dinosaur, Manraksk, etc. The total reserve of bentonite clay is more than 150 million tons [10].

Since the problem of water purification from various pollutants remains urgent, and our country is rich in the presence of many deposits of bentonite clay, which in composition is not inferior to Wyoming bentonite (USA), it is economically advantageous to use it for water purification. Of the many known methods of purification, sorption methods of purification are economically advantageous and effective, as the efficiency of sorption can reach 80-90% depending on the nature of the adsorbent used [11].

Natural clay minerals are widely used as sorbents. They have good physical and chemical characteristics as well as high absorption capacity. Adsorption properties of bentonites can be regulated both by methods of physical action and by chemical activation.

From a practical point of view, bentonite occupies a special place among clay minerals. One of the areas of bentonite use is wastewater treatment from chemical contaminants, where it is used as a sorbent.

Experimental part

The initial sample of clay with sorbing properties was selected in the South Kazakhstan region, Saryagash district, Darbaza deposit.

The following methods of physical and chemical analysis were used to study the structure and structure of clay: scanning electron microscope, FTIR spectrometer and X-ray phase analysis. The chemical composition of bentonite was determined using a JSM6490LV scanning electron microscope. The IR absorption spectra were taken on a ShimadzuIRPrestige-21 FT-IR spectrometer with a Miracle total internal reflection (TIR) attachment by PikeTechnologies.X-ray phase analysis was carried out on a Bruker D8ENDEAVOR diffractometer (Germany).

Differential-thermal analysis of the initial sample of bentonite clay of Darbazin deposit, selected on the floodplain of the Keles River was performed on a Q-1500 derivatograph in the laboratory "Sapa" of M. Auezov SKU. For physico-chemical analysis of clay from Darbaza deposit, a specially selected sample was crushed, and sieved and its chemical composition was determined. Figure 1 shows bentonite samples in the original and pulverized form.

Bentonite clay is a complex rock, the base of which is montmorillonite, which has the formula $Si_8Al_4O_{20}(OH)_4 \times nH_2O$, where silicon can be replaced by various cations (aluminum, iron, zinc, magnesium, calcium, sodium, potassium, etc.). Montmorillonite has a three-layer crystalline structure, the outer layers are silicon-oxygen tetrahedrons, with silicon in the middle and associated hydroxyl groups or oxygen at equal distances from it. The middle layer is represented as octahedrons with oxygen atoms or hydroxyl groups in the tops and aluminum, iron or magnesium atoms between them [[12], [13]].

Figure 1 - Bentonite samples in initial and crushed form of Darbaza deposit

In order to study the composition of bentonite clay, the result of a scanning electron microscope (SEM) was obtained (Figure 2), and the elemental composition of the initial clay sample of the Darbaza deposit was determined (Table 1).

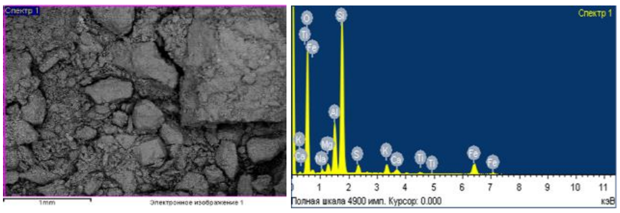


Figure 2 – Microstructure and elemental analysis of bentonite clay of Darbaza deposit

Table 1 - Elemental composition of bentonite clay of Darbaza deposit

Elemental composition of clay Weight %							
Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
1.48	2.61	14.87	51.4	2.66	1.29	0.80	9.98

The elemental composition of the sample shows that the bentonite of the Darbaza deposit contains large amounts of silicon, aluminum and iron compounds, which explains the adsorption capacity of the studied object, it should also be noted the content of associated metal compounds in the form of oxides, hydroxides, carbonate and sulfate salts, which reduce the adsorption capacity of the object. In practice, to improve adsorption properties bentonite is subjected to activation, which in turn is divided into chemical and acidic [14].

To determine the mineral composition of the clay of the Darbaza deposit, IR spectroscopy and X-ray phase analysis were performed (Figure 3,4).

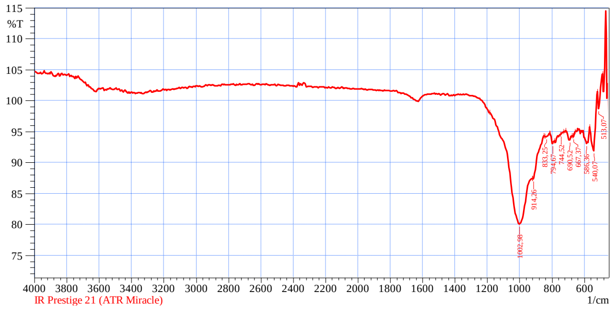


Figure 3 - IR spectrum of bentonite from Darbaza deposit

Decoding of spectra shows that in bentonite of Darbaza deposit small peaks in the region of 1600-1700cm^{-1} and 3600-3700cm^{-1} are observed, which are characteristic for Na-O and O-H groups. The presence of peaks in the region of 950-1050 cm^{-1} confirms the presence of the main group Si-O, which is one of the main constituents of bentonite. Peaks in the region of 740-800 cm^{-1} which are characteristic of Al-O are observed.

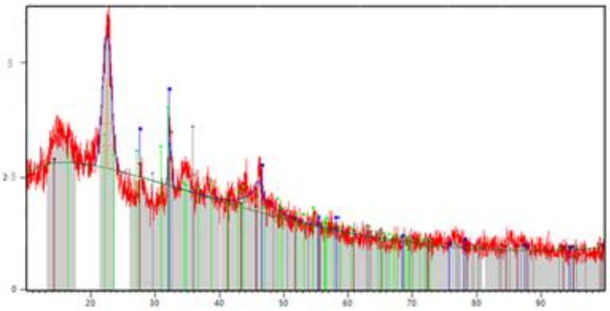


Figure 4 - XRF of Darbaza bentonite

Analysis of the data obtained by XRF showed that the bentonite clay sample from Darbaza deposit has three intense and several non-intense diffraction maxima: - d equal to 5.02; 3.342; 1.55 are characteristic of the phases of muscovite, which has the formula $K_2O·3Al_2O_3·6SiO_2·2H_2O$;

- d equal to 3.21; 2.77; 2.227; 1.995; 1.560; 1.49; 1.292 are characteristic phases of potassium feldspar, which has the formula $Na_2O·Al_2O_3·6SiO_2$;

- d equal to 4.47; 3.42; 3.06; 2.60 are characteristic of phases of montmorillonite, which has the formula $Si_8Al_4O_{20}(OH)_4 \times nH_2O$;

- d equal to 3.85; 2.291; characteristic of kaolinite phases, $Al_2O_3·2SiO_2*2H_2O$.

The presence of minerals, bentonite muscovite explains the sorption properties of the studied bentonite sample. Graphical dependences of DTG and DTA curves on temperature are shown in Figure 5.

Figure 5 - DTA of Darbaza bentonite

Analysis of the obtained graphical data showed that the studied sample is characterized by two pronounced and one insignificant endo-effects and four exo-effects. Endoeffect at T=180°C indicates the removal of surface moisture and at 550 °C partial desulfatization of iron-containing impurities. The exoeffect at 870°C is characteristic of decarbonization of magnesium and calcium carbonates. Insignificant exo-effects at 280-450°C are characteristic of burnout of organic impurity components. Exoeffects at 525-530 °C indicate the burnout of sulfur impurities of bentonite clay.

Activation [15] of bentonite clay is carried out as follows: A certain mass of bentonite clay is suspended in a water-sprite solution (ratio 1:1.5 cm^3, temperature 80-100 ^{0}C) for 60 minutes and at the same time a modifier solution is prepared by dissolving octadecylamine in aqueous-alcohol a solution containing an equimolar amount of hydrochloric acid (up to pH = 7.0) at the same temperature. A solution of octadecylammonium chloride salt is added in portions to the bentonite clay suspension with continuous stirring throughout the entire period of the activation process. After dosing of the modifier solution is completed, the suspension is stirred for an additional 30 minutes and cooled to room temperature.

To separate unbound activated bentonite clay, it is centrifuged repeatedly, washed with a hot aqueous-alcohol solution, and then with distilled water [16]. The completeness of washing is assessed by the residual content of chlorine ions by adding a few drops of a 5% silver nitrate solution to the mother solution. The resulting product is dried at a temperature of 80^{0}C in a vacuum to constant weight. The cation exchange capacity of bentonoite clay is 90 mEq/100 g with an average silicate platelet diameter of ~75 nm. To determine the functional groups of the resulting activated bentonite clay, spectral analysis was carried out with an IR Fourier spectrometer (Zhimadzu IR Prestige-21). The result of IR spectroscopy after the activation process is shown in Figure 6.

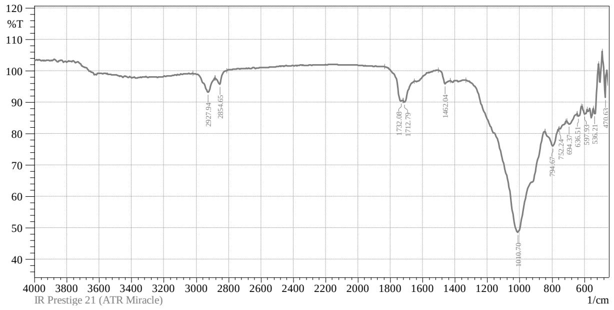


Figure 6 – IR absorption spectra of Darbaza bentonite clay after activation

According to the results of the IR spectra it was revealed that Darbaza activated bentonite clay appears absorption bands in the region of 2924 and 2854cm^{-1} related to stretching vibrations of the methylene group and also corresponds to the asymmetric bending vibration of methyl groups in the region of 1458cm^{-1}. The absorption bands at 1712-1735 cm^{-1} are characteristic of stretching vibrations of acrylate groups. Pendulum vibrations of methylene groups in the region of 798 cm^{-1} are also observed. There is a slight increase in the absorption band with a peak at 1010 cm^{-1} (1100-837 cm^{-1}) corresponding to the stretching vibrations of the Si-O-Si group.

Table 2 – Physico-chemical and mechanical properties of sorbents based on bentonite clay

Name	Density, g/cm^3	Specific surface area, cm^2/g
Bentonite clay from the Darbaza deposit	2.07	1380
	Average granule, mm	Strength, MPa
	10-13	4.4
Activated bentonite clay from the Darbaza deposit	Density, g/cm^3	Specific surface area, cm^2/g
	2.30	1445
	Average granule, mm	Strength, MPa
	10-13	5.25

From Table 2 it follows that the physico-chemical and physico-mechanical parameters of acid-activated bentonite clay are higher than those of a conventional bentonite clay sample and can increase the mechanical strength of sorbents to 5.25 MPa, which facilitates repeated use for wastewater treatment.

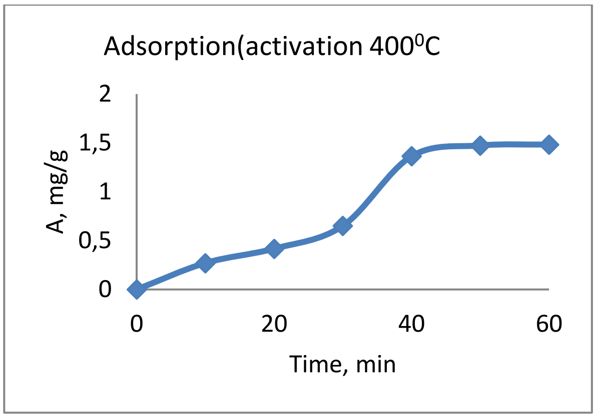
Determination of the physicochemical and mechanical parameters of the sorbent based on bentonite clay before and after activation was carried out by GOST 28177-89 [[17], [18]].

The discussion of the results

The obtained results of elemental analysis in Table-1 confirm that the bentonite clay of the Darbaza deposit belongs to the alkaline earth group. Since its complex consists of calcium and magnesium cations. Bentonite has a porous structure, due to porosity - high swelling, which determines their optimal sorption characteristics. The mechanism of sorption of bentonite clays is that sorbates are introduced between planes, while the structure the layers themselves remain unchanged. It should be noted that scientists [19] have concluded that the sorption process on bentonite clay is predominantly a physical process, includes ion exchange and is controlled by diffusion in the solution film.

The resulting sorbent based on bentonite clay has a high sorption capacity and is recommended for use in the treatment of wastewater from chemical industries.

The sorption capacity and the dependence of the process on the time and temperature of the resulting sorbent are shown in Figure 7.



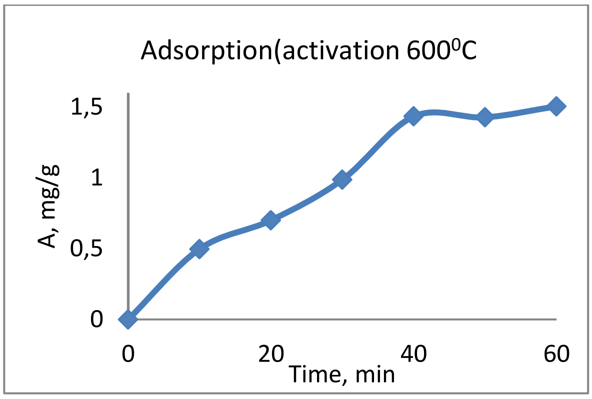


Figure 7 - Dependence of adsorption on process time.

From Figure 7 it follows that the adsorption capacity of the resulting sorbent increases by 10-15% after activation. The studies were carried out on a laboratory installation with software control of a liquid flow rate of 3.5-4.0l/min, in the temperature range of 20-40^{0}C. In laboratory studies, we used wastewater from the mineral fertilizer plant (MFP) of LLP «Kazphosphate», characterized by the presence of the following chemical compounds, %: P_2O_5-2,0-2,1, SO_3-0,6-0,8, CaO-2,8-3,1, K_2O-0,6-0,8, MgO -0,8-1,1, $A1_2O_3$-0,8-0,9, Fe_2O_3-0,3-0,4.

After using the sorbent, the chemical composition of the wastewater has the following composition, %: P_2O_5-1,1,0-1,2, SO_3-0,3-0,33 CaO-1,5-1,7, K_2O-0,2-0,2,5 MgO -0,3-0,4, $A1_2O_3$-0,3-0,4, Fe_2O_3-0,1-0,15.

The composition of wastewater before and after the sorption process was determined according to GOST 26449.1 [20].

Based on the results of the experimental studies, it can be concluded that the resulting sorbent based on bentonite clay from the Darbaza deposit makes it possible to purify wastewater from phosphate production from phosphate and other ions up to 60%.

Conclusions

Based on the results of instrumental studies, the elemental and mineralogical composition of bentonite clay from the Darbazinsky deposit was determined using a scanning electron microscope JSM-6490l V (Jeol, Japan) using the energy-dispersive method. Differential thermal analysis was used on a bentonite clay sample to monitor changes in the raw material that occur as a result of heat treatment. Based on X-ray phase analysis, the phase composition of bentonite clay was determined. IR spectroscopic analysis was also carried out to determine the structural features of the starting raw materials and the finished product.

The developed sorbent based on bentonite clay has environmental and economic efficiency and connections with the use of local natural resources. Thus, it should be noted that for the adsorption treatment of wastewater from chemical industries, it is possible to use effective sorbents based on bentonine clays from the Darbaza deposit to a high degree. It should also be noted that the use of bentonite clays for water purification by the sorption process is an effective and affordable alternative to adsorbents that show high adsorption capacity for various compounds.

***CRediT author statement*:** **Ishanova M.N:** Conceptualization, Data curation, Writing- Original draft preparation. **Kadirbayeva A.A:** Visualization, Methodology, Software, Investigation, Supervision. **Sarypbekova N.K:** Writing- Reviewing and Editing, Software, Visualization.

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Химия өндірісінің ағынды суларын тазалау үшін бентонит сазы негізінде сорбент алу әдісін зерттеу

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ТҮЙІНДЕМЕ

Біздің елімізде суды тазарту мәселесі өзекті болып қала береді. Бұған өнеркәсіптік кәсіпорындар санының көбеюі, ауыл шаруашылығының дамуы, қалалардың өсуі және т.б. сыртқы факторлардың өсуі ықпал етеді. Суды тазарту мәселесін шешу үшін біздің елімізде бар ресурстардан жаңа сорбенттер алу экономикалық тұрғыдан тиімді болып табылады. Эксперименттік жағдайларда бентонит сазын өңдеу үшін Jeol JSM-6490l V сканерлеуші электронды микроскоп (SEM), көп параметрлі портативті кибер сканер (PCD 650 Eutech) және Q-1500 дериватографы арқылы аспаптық сынақ әдістері таңдалды. Зерттеулердің нәтижелері бойынша энергия-дисперсиялық әдіспен JSM-6490l V (Джеол, Жапония) сканерлеуші электронды микроскоптың көмегімен Дарбаза кен орнындағы бентонит сазының элементтік және минералогиялық құрамы анықталды. Алынған бентонит балшық негізіндегі сорбент жоғары сорбциялық қабілетке ие және химия өнеркәсібінің ағынды суларын тазартуда қолдануға ұсынылады. Дарбаза кен орнынан алынған бентонит сазының негізінде алынған сорбент фосфат өндірісінің ағынды суларын фосфаттан және басқа иондардан 60%-ға дейін тазартуға мүмкіндік береді. Бентонит сазы негізінде жасалған сорбент жергілікті табиғи ресурстарды пайдаланылғандықтан экологиялық және экономикалық тиімді болып келеді. Сонымен, химия өнеркәсібінің ағынды суларын адсорбциялық тазарту үшін Дарбаза кен орнының бентонитті саз негізіндегі тиімді сорбенттерді жоғары дәрежеде қолдануға болатындығы анықталды. Сондай-ақ, сорбциялық процесс арқылы суды тазарту үшін бентонит саздарын пайдалану әртүрлі қосылыстар үшін жоғары адсорбциялық қабілетін көрсететін адсорбенттерге тиімді және қолжетімді балама болып табылатынын атап өткен жөн.

Түйін сөздер: бентонит, Дарбаза кен орны, суды тазарту, монтмориллонит, адсорбция, ауыр металдар.

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Исследование получения сорбента на основе бентонитовой глины для очистки сточных вод химических производств

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АННОТАЦИЯ

В нашей стране проблема очистки воды остается актуальной, причем этому способствует рост внешних факторов, к которым можно отнести увеличение количества промышленных предприятий, развитие сельского хозяйства, рост городов и другие. Для решения проблемы очистки воды экономически выгодно создание новых сорбентов, из имеющихся в нашей стране ресурсов. Для обработки бентонитовой глины в экспериментальных условиях были выбраны инструментальные методы испытаний с использованием сканирующего электронного микроскопа (СЭМ) марки Jeol JSM-6490l V, многопараметрического портативного киберсканера (PCD 650 Eutech) и дериватографа Q-1500. По результатам инструментальных исследований определен элементный и минералогический состав бентонитовой глины из Дарбазинского месторождения с использованием сканирующего растрового электронного микроскопа JSM-6490l V (Jeol, Япония) энерго-дисперсионным методом. Полученный сорбент на основе бентонитовой глины имеет высокую сорбционную способность и рекомендуется применять при очистке сточных вод химических производств. Полученный сорбент на основе бентонитовой глины из Дарбазинского месторождения позволяет очистить сточные воды фосфатного производства от фосфатных и других ионов до 60%. Разработанный сорбент на основе бентонитовой глины имеет экологическую и экономическую эффективность, связи с использованием местных природных ресурсов. Таким образом, следует отметить, что для адсорбционной очистки сточных вод химических производств с высокой степенью возможно использование эффективных сорбентов на основе бентониновых глин из Дарбазинского месторождения. Также следует отметить, что использование бентонитовых глин для очистки воды процессом сорбции является эффективной и доступной альтернативой адсорбентов, которые показывают высокую адсорбционную емкость по отношению к различным соединениям.

Ключевые слова: бентонит, месторождение Дарбаза, очистка воды, монтмориллонит, адсорбция, тяжелые металлы.

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Engineering and Technology

Experimental studies for the Development of special equipment for cleaning cedar nuts from the shell

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ABSTRACT

The research is aimed at studying Cedar nut seeds and the use of special pneumatic reactive and centrifugal equipment for their processing. The main purpose of the work is to develop equipment for cleaning cedar grain. The article describes the features of Cedar nut seeds, which are widely distributed in the east of the Republic of Kazakhstan, and also presents a technological scheme for extracting Cedar nut kernels. The main attention is paid to the results of the development of special equipment that allows you to separate the kernels of cedar grain from the shell without damaging them. Experiments were carried out on this equipment, the results of which were presented in the form of graphs. Studies have shown what air velocities and torques are used to eject grains of various sizes when exposed to a target. In the first experiment, it is shown at what air velocity the grains are peeled from the shell, depending on their diameter, that is, cedar grains are peeled from the shell when hitting a target with an air velocity of 5 mm-41 m/s, 6 mm – 39 m/s, 7 mm – 38 m/s, 8 mm-35 m/s, 9 mm-31 m/s. In the second experiment, it is shown at which torque of the disc, depending on the diameter of the grains, that is, cedar grains are peeled from the shell when hitting a target with a torque of 5 mm – 15 N* m, 7 mm –13 N*m, 8 mm-10 N* m, 9 mm - 8 N* m.

Keywords: cedar nut, pneumatic jet, centrifugal, equipment, complex processing.

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Introduction

Research and review articles on the Cedar nut (Pinus sibirica du Tour) have so far been devoted mainly to the biochemical characteristics of its grains, and the prospects for the use of grains for medical, food and technical purposes [[1], [2]]. At the same time, the scientific literature does not sufficiently cover the technological aspects of the production of such products. Studies have shown that the average weight of a cedar grain is 0.23-0.25 grams. Grains are 9 mm, medium — 7-9 mm, small — 7 mm and less. In particular, when cedar nuts are processed into kernels or cedar oil, a shell is formed, which accounts for an average of 51-59% of the weight of the original raw material, and 5-10% of the same residue contains grains with a disturbed structure [[3], [4]]. Currently, in the Russian Federation and European countries, a large number of medicines, medicinal oils and pine nuts from pine nuts are widely used as a food additive. And in the Russian Federation, plants for the production of pine nuts as finished products are developing.

The analysis of technical means and technical literature on the separation of pine nuts from the shell showed that they are designed for large-scale production, have high energy consumption, complex technologies, and the need to use a large amount of equipment. Since the pine nut grows only in the east of Kazakhstan, only farms are cultivated around it, so small multifunctional equipment is required. The use of such equipment makes it possible to reduce transportation costs and increase the profitability of production.

That means that it is relevant to design small equipment designed to accurately separate the cedar texture from the bark without disturbing its structure. Therefore, careful processing from cedar nuts without disturbing the structure of the grain is an urgent problem. And to solve this problem, the following tasks were set:

- Study of the technical and physical characteristics of cedar nuts growing in the eastern region of the Republic of Kazakhstan;
- analysis of the scheme of installations for separating cedar nuts from the Shell to determine the promising direction of research;
- development of a project for carefully separating the Cedar grain from the bark without destroying its structure;

This article is devoted to the consideration of the main technological aspects of complex processing without disturbing the structure of the Cedar nut grain.

Experimental part

For processing Cedar nut grain, which comes in large batches, the design of the equipment changes significantly, depending on the mechanical properties, regional and climatic characteristics of the region of its growth, as well as the technology of preparation and primary processing. The large distribution of physical characteristics makes us pay more attention to the first stage of the technological process [[5], [6], [7]]. Primary sorting and calibration will allow you to highlight the nut with underdeveloped kernels and residues. The amount of primary waste can be from 3 to 15% of the total weight of raw materials. The moisture content of the seeds that come for processing is very important, they can vary from 10 to 30%. High humidity of the nuclei leads to their destruction and loss. The low moisture content of the shell increases its hardness and relative size of the nuclei, which prevents the separation of the nuclei from the Shell and beyond [[8], [9], [10]].

Therefore, when working out the industrial process of peeling cedar nuts, a sequence of operations was found that included convective drying of nuts with warm air to ~10% humidity and short-term humidification of them for 2-8 hours [[11], [12], [13]]. Thus, at a relatively low humidity of the nuclei, it is possible to achieve a high humidity of the Shell, which ensures a decrease in its strength and an increase in its relative size. As a result, the distribution indicators of finished products are significantly improved [[14], [15], [16]].

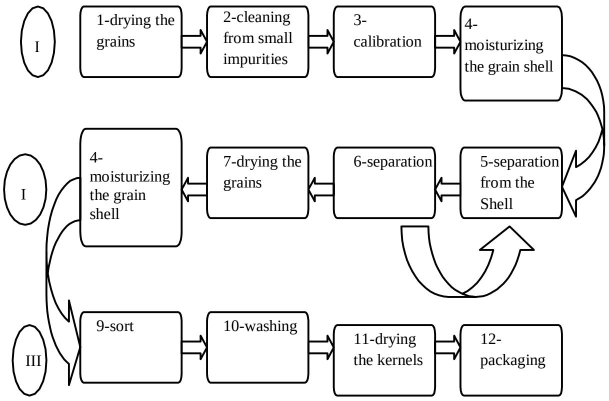

Figure 1 - Technological scheme for obtaining Cedar nut kernels

Figure 1 shows the scheme of complex processing of cedar nuts. The Cedar grain preparation stage (I) consists of four stages: (1) drying the grains, (2) cleaning them from fine impurities by airing, (3) calibration, (4) moistening the grain shells. At the stage of peeling (II), in pneumatic or centrifugal peeling equipment, the grain is separated from the shell (5), in the drum separator (6) there is a destruction of the grain shell, that is, the separation of the shell from cedar nuts and unprocessed grains, then the peeled grains are pre-dried in a convection drying cabinet (7), and then the cleaning of the protective film (8) is performed. At Stage III, grain sorting (9), washing (10), drying (11) and packaging (12) are carried out [[17], [18]].

Since the kernels of nuts on the market must meet the requirements for environmentally friendly food products, we know that during their processing it is not necessary to use any chemical reagents, high temperatures and other effects that can lead to partial destruction of the protein - vitamin complex of the seeds. For this reason, of all the possibilities, the mechanical method of separating the grain from the Shell was chosen. Traditional mechanical methods of processing grains are relatively simple and usually involve separation from the Shell between rotating cylinders or millstones [[19], [20]].

In semi-industrial conditions, reactive stripping equipment has been tested, which works as follows. Cedar nut seeds through the ejector node (figure 2) the accelerator enters the tube, where it gains a speed of ~ 40 m/s with an air flow, and then, when hitting the target, they are reflected. The impact Force acquires efficiency with a change in the speed of the air flow due to the strength and elasticity of the shell. This makes it possible to reduce the destruction of the nuclei during impact to a minimum. The disadvantages of this method should include relatively low performance and low efficiency, since the efficiency of air compression is low. In addition, it is necessary to purify the compressed air from compressor oil vapors, otherwise the chemical composition of the grain may change.

Therefore, for an industrial installation, a device without the above disadvantages is a multi – channel centrifugal stripping equipment (figure 3) applied. It works as follows. From the hopper, cedar nuts are fed by the dispenser to a disk of radius R, which rotates at an adjustable angular velocity, where, under the influence of centrifugal force, N is distributed along radial channels. By friction against the walls of the channels, the grains acquire a linear velocity close to r at the exit, and then reflect when hitting the target.

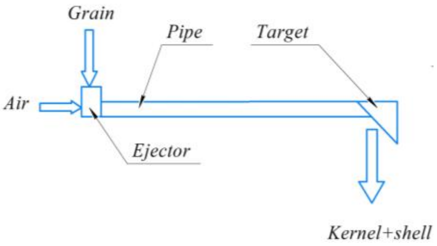

Figure 2 - Pneumatic jet stripping equipment

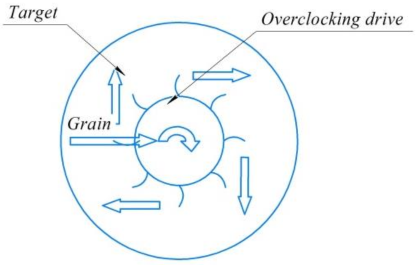

Figure 3 - Multi-channel centrifugal stripping equipment

The resulting grain is sucked into a tube through the ejector assembly, where it is accelerated by airflow. At the moment of hitting the target, its reflection occurs. The nuclei and shells are discharged into the receiver by air. The resulting grain is fed to the centre of the rotating accelerator disk, where it is distributed through radial channels and, having a linear speed close to r in them, hits and reflects the annular target.

This force is determined by the time the grain pulse collides with the normal target. In turn, the collision time depends on the elasticity of the grain shell, that is, its moisture and direction at the time of collision.

To assess the effect of air velocity on the separation of the shell from the grain, a number of experiments were conducted, where sensors were installed at various points to measure air velocity in different parts of the target and due to centrifugal force. In the first type of experiment, cedar grains with different diameters were used as a control group to determine how the diameter affects the air velocity required to peel them from the shell. In the second case, by setting different speeds of rotation of the disk, the centralizing force was calculated and the efficiency of separating the shell from the grain at each speed was measured.

An analysis of the data was carried out in order to determine the relationship between the grain diameter, the air velocity and the disk required for their purification. Due to this, a dependence graph was constructed and statistical methods were used to assess the significance of the results obtained.

The study was carried out on special equipment that allows you to separate the kernels of cedar grain from the shell without damaging them. The data was processed using Statistica 10 statistical analysis software. A one-factor analysis of variance was performed for different grain diameters.

The results of the experiment showed that grain diameters require higher air velocities for successful shell cleaning and this is useful for optimizing the cleaning process. This process made it possible to quantify the effect of grain diameter on the air velocity required to peel them from the shell.

Discussion of results

The above dimensions of the booster channel made it possible to reduce the distribution of impact force, thereby reducing costs and increasing productivity. When using dried healthy grains, the yield of the finished product was increased to 30-33%, and the yield of the decomposer increased to 150-200 kg of processed raw materials per hour.

A mixture of cores, unbreakable cores and shells from centrifugal stripping equipment enters the drum separators, where they are separated from each other. The seeds are wrapped in a loop, and the kernels come to pre-dry. As practice shows, such nuclei are harvested from 5 to 20-25% depending on the conditions of seed collection, processing, storage. After that, the commercial nuclei reach a humidity of less than 3% for washing and final drying. Dry kernels can be stored for a long time in the open air, without losing their marketable properties.

Experiments on the cleaning from the shell of Cedar grain on pneumatic jet stripping equipment were carried out and filled in Table 1. As a result of the experiment, it was observed that between an air speed of 42 m/s and 30 m/s, Cedar grains were peeled from their shells without disturbing the grain structure.

Table 1 – Experiment results on pneumatic jet stripping equipment

		Cedar grain sizes				
Experiment №		5mm	6mm	7mm	8mm	9mm
1	Air velocity, m/s	42 m/s	38 m/s	37 m/s	36 m/s	33 m/s
2		40 m/s	40 m/s	39 m/s	34 m/s	31 m/s
3		41 m/s	38 m/s	36 m/s	36 m/s	32 m/s
4		41 m/s	41 m/s	39 m/s	35 m/s	32 m/s
5		42 m/s	39 m/s	38 m/s	35 m/s	30 m/s

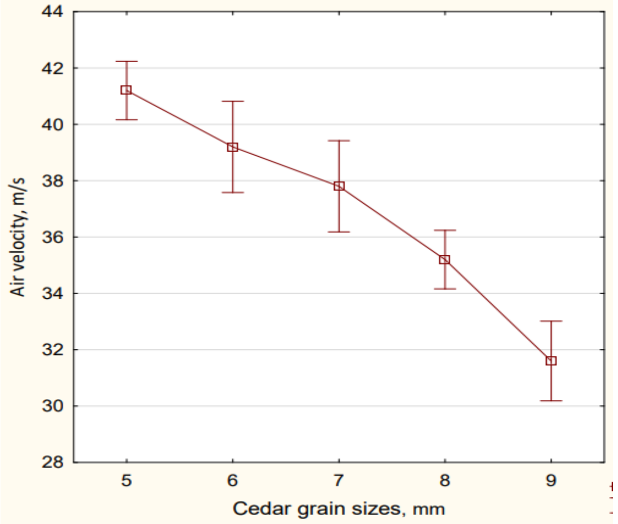

Figure 4 - The ratio of air velocity to grain diameter in pneumatic jet stripping equipment

Figure 4 shows the experiment results for the ratio of air velocity to grain diameter in pneumatic jet stripping equipment. The experiment shows at what air speed the grains peel, depending on their diameter , that is, 5 mm Cedar grains are reflected when struck at an air speed of 41 m/s, 6 mm – 39 m/s, 7 mm – 38 m/s, 8 mm-35 m/s, 9 mm-31 m/s.

In the first case, the results of the experiment showed that for successful cleaning of grain from the shell, a high air supply rate is required, but not more than 45 m/s and not less than 25 m/s, which is useful for optimizing the cleaning process.

Experiments were carried out on the equipment of centrifugal stripping of Cedar grain and filled in Table 2. As a result of the experiment, it was observed that between 18 N*m and 7 N*m of torque, Cedar grains are peeled from their shells without disturbing the grain structure.

Table 2 - Experiment results on centrifugal stripping equipment

		Cedar grain sizes				
Experiment №		5mm	6mm	7mm	8mm	9mm
1	Torque, N*m	16 N*m	14 N*m	12 N*m	11 N*m	9 N*m
2		14 N*m	15 N*m	11 N*m	9 N*m	7 N*m
3		18 N*m	16 N*m	13 N*m	10 N*m	8 N*m
4		15 N*m	16 N*m	14 N*m	9 N*m	7 N*m
5		17 N*m	15 N*m	14 N*m	9 N*m	8 N*m

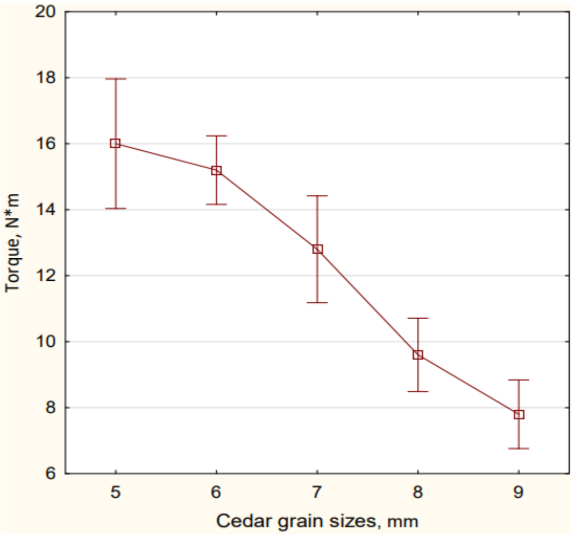

Figure 5 - The ratio of torque to grain diameter in centrifugal stripping equipment

Figure 5 shows the experiment results for the ratio of torque to grain diameter in Centrifugal stripping equipment. The experiment shows at what torque the disc peels, depending on the diameter of the grains, that is, 5 mm Cedar grains separate from the shell when hitting the target with a torque of 16 N*m, 6 mm – 15 N*m, 7 mm – 13 N*m, 8 mm-10 N*m, 9 mm - 8 N*m.

Numerous experiments have shown that the disadvantage of this method is the low yield of the finished product and the destruction of the grain structure. With an average grain weight without a shell of 43%, the yield was less than half of the specified number. We were able to eliminate losses using the shock method, which occurs when the detachment of the grain shell hits the target.

Conclusion

A technological scheme for the complex processing of cedar nuts has been developed, which includes the production of refined grains of Cedar nuts. It has been shown that optimal peeling conditions are achieved after drying and short-term moistening of nuts. As a result of the experiments performed, it was shown at what airspeed and with what torque grains of different sizes are peeled when hitting the target. In the course of semi-industrial experiments, it was found that among the tested types of Walnut peeling equipment, good results are achieved through the use of multi-channel centrifugal peeling equipment.

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

CRediT author statement

A.H. Hamitbek: Reviewing and editing, software, **A.E. Kairbaeva:** Analysis of scientific research results, interpretation of results, **M.V. Kopylov:** Research, methodology, data processing

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Балқарағай жаңғағын қабығынан тазартуға арналған арнайы жабдықты әзірлеу бойынша эксперименттік зерттеулер

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ТҮЙІНДЕМЕ

Зерттеу балқарағай жаңғағының дәнін зерттеуге және оларды өңдеу үшін арнайы пневматикалық реактивті және орталықтан тепкіш жабдықты қолдануға бағытталған. Жұмыстың негізгі мақсаты – балқарағай жаңғағын тазартуға арналған арнайы жабдықты әзірлеу. Мақалада Қазақстан Республикасының шығысында кең таралған балқарағай жаңғағы тұқымдарының ерекшеліктері сипатталған, сондай-ақ қарағай жаңғағы дәндерін алудың технологиялық схемасы ұсынылған. Балқарағай дәнінің ядроларын қабықтан зақымдамай бөлуге мүмкіндік беретін арнайы жабдықты әзірлеу нәтижелеріне назар аударылады. Осы жабдықтарда эксперименттер жүргізілді, олардың нәтижелері график түрінде ұсынылды. Зерттеулер нысанаға қарай бағытталған әртүрлі өлшемдегі дәндерді қабығынан тазарту үшін қандай ауа жылдамдығы мен айналу моменттері қолданылатынын көрсетті. Бірінші сынақта дәндер диаметріне қарай қабықтан қандай ауа жылдамдығымен тазартылатыны көрсетілген, яғни 5 мм-41 м/с, 6 мм – 39 м/с, 7 мм – 38 м/с, 8 мм -35 м/с, 9 мм-31 м/с ауа жылдамдығымен нысанаға соғылған кезде балқарағай дәндері қабықтан тазартылатыны көрсетілген. Екінші сынақта дәндердің диаметріне байланысты дискінің қандай айналу моментімен айналу керегі көрсетілген, яғни 5 мм-15 н * м, 7 мм-13 н * м, 8 мм-10 Н* м, 9 мм-8 Н*м айналу моментімен нысанаға соғылған кезде қабықтан тазартылаңы көрсетілген.

Түйін сөздер: балқарағай жаңғағы, тазалау жабдығы, пневматикалық жабдық, орталықтан тепкіш жабдық, технологиялық схема

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Экспериментальные исследования по разработке специального оборудования для очистки кедровых орехов от скорлупы

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АННОТАЦИЯ
Исследование направлено на изучение семян кедрового ореха и применение специального пневматического реактивного и центробежного оборудования для их обработки. Основная цель работы заключается в разработке специального оборудования для очистки кедрового ореха. В статье описываются особенности семян кедрового ореха, которые широко распространены на востоке Республики Казахстан, а также представлена технологическая схема извлечения ядер кедрового ореха. Основное внимание уделено результатам разработки специального оборудования, которое позволяет отделить ядра кедрового зерна от оболочки без их повреждения. Проведены эксперименты на данном оборудовании, результаты которых были представлены в виде графиков. Исследования показали, какие скорости воздуха и крутящие моменты используются для выбрасывания зерен различного размера при воздействии на цель. В первом испытаниии показано, при какой скорости воздуха зерна очищаются от скорлупы в зависимости от их диаметра , то есть кедровые зерна очищаются от скорлупы при ударе по мишени со скоростью воздуха 5 мм-41 м/с, 6 мм – 39 м/с, 7 мм – 38 м/с, 8 мм-35 м/с, 9 мм-31 м/с. Во втором испытании показано, при каком крутящем моменте диска , в зависимости от диаметра зерен, то есть 5 мм – 15 Н*м, 7 мм – 13 н*м, 8 мм-10 Н*м, 9 мм - 8 Н*м при ударе по мишени с крутящим моментом очищаются от скорлупы.

Ключевые слова: *кедровый орех, оборудование для очистки, пневматическое оборудование, центробежное оборудование, технологическая схема*

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Engineering and Technology

Study of tribological characteristics of micro-arc calcium phosphate coatings on titanium

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ABSTRACT
Tribological characteristics of implants, such as wear resistance and friction coefficient, play a critical role in ensuring their durability and functionality when interacting with surrounding tissues. These parameters influence the implant's ability to withstand mechanical loads and minimize wear throughout its service life. Minimizing friction between the implant and biological tissues not only helps prevent mechanical damage but also reduces the risk of inflammatory reactions, ensuring better biological compatibility. In this study, calcium phosphate coatings were obtained using the micro-arc oxidation method with different duty cycle of current to investigate their tribological characteristics. The coatings deposited on titanium had a structure with volcano-like formations with pores ranging from 66 to 98 micrometers. The thickness of the coatings varied from 74.3 to 100 micrometers depending on the conditions during microarc oxidation. Tribological tests were conducted using a ball-on-flat setup with reciprocating motion. The coatings were subjected to tribological tests against SHX15 steel under normal loads of 5 and 20 N. Depending on the applied load, the friction coefficients of the coatings ranged from 0.029 to 0.034 at 5 N and from 0.9 to 1.26 at 20 N. Analysis of wear parameters and micrographs of worn surfaces indicate that the mode with a pulse current duty cycle of 17.3% during micro-arc oxidation allows for the production of titanium surface coatings with high wear resistance.

Keywords: calcium phosphate coating, micro-arc oxidation, duty cycle, friction coefficient, wear.

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Introduction

Titanium and its alloys are widely used in various industries due to their unique combined properties [[1], [2], [3]]. This versatility is attributed to both mechanical (low elastic modulus, low density, corrosion resistance) and biological characteristics (high bioinertness, bioactivity, and biocompatibility) [[4], [5], [6]], making titanium and its alloys a preferred choice, especially in medical applications as implants. However, despite their valuable properties, there are some clinical issues with titanium implants regarding their interaction with the human body and their long-term usage [[7], [8]]. To address such issues, it is necessary to create biocompatible materials or calcium phosphate coatings that promote the formation of a transitional zone between bone and the implant. This area should have a strong connection to the implant material without the risk of rejection, as well as a macro- and microstructure compatible with the organism [[9], [10]].

Currently, there is a wide range of developed methods for depositing calcium phosphate (CaP) coatings on metallic implants, such as plasma spraying [11], micro-arc oxidation [12], detonation gas spraying [13], magnetron sputtering [14], electrochemical deposition [15], sol-gel, and others.

Considering all the advantages and disadvantages of these methods, the micro-arc oxidation (MAO) method has gained widespread popularity in the last decade as a method for applying bioactive CaP coatings to titanium surfaces. Literature [[16], [17]] notes that the MAO method allows for the production of CaP coatings providing high adhesion strength between the substrate and the coating.

Traditionally, CaP coatings have been used to enhance the osseointegration of metallic implants. However, during the implantation procedure, the coatings are usually subjected to significant shear stresses, which can lead to their delamination and wear from the metal surface, deteriorating their functionality [17]. Therefore, studying the tribological and adhesion properties of MAO coatings requires additional attention and evidence. Analysis of tribological characteristics can help better understand the behavior of biomaterials [5]. Furthermore, titanium alloys limit their further application in medicine due to low wear resistance [[18], [19]].

Recently, there has been growing interest in the scientific community in the tribology of CaP coatings, and several studies have been conducted in this direction. For example, Santos A. and colleagues [5] conducted tribocorrosion research on a titanium oxide and calcium phosphate coating. The Ti/TiO_2/CaP coating provided 99.93% protection in static experiments and significantly reduced corrosion during tribocorrosion tests in simulated body fluid. The application of TiO_2/CaP resulted in reduced tribological parameters: friction coefficient (CoF) to 0.25 and wear rate (WR) to 578.45 μm^3/J. The work [20] showed that the presence of rutile titanium in the composition of CaP coatings obtained by the MAO method is a key factor in improving the tribocorrosion properties of coating surfaces. The authors explain this by the impact softening properties of the nanocomposite gradient structure of the CaP coating. Marques I.D. and colleagues [21] investigated the influence of the Ca/P ratio in the electrolyte on the tribocorrosion properties of biofunctional coatings obtained by the MAO method on a titanium alloy. The study by [22] examined the phase structure, morphology, chemical composition, corrosion mechanism, and tribocorrosion behavior of CaP coatings obtained at different voltages (380, 400, 420 V). The sample processed at 420 V showed the highest wear volume after tribocorrosion. The mechanism of tribocorrosion of samples at 380 and 420 V was mainly determined as the wear effect.

The results of the aforementioned studies are of high quality and provide valuable information in the field of tribology of CaP coatings, bringing us closer to understanding the real wear of implants in the human body. However, to date, there have been no studies on the influence of current parameters in the micro-arc oxidation method on the tribological characteristics of CaP coatings.

The aim of the study was to investigate the morphology, microstructure, and tribological characteristics of calcium-phosphate coatings depending on the pulse current duty cycle during micro-arc oxidation of titanium.

Experimental part

Materials

Plates measuring 10 mm x 5 mm x 1 mm made of VT1-0 grade titanium (equivalent to titanium GRADE 2) were used as substrates. Prior to oxidation, the substrates underwent mechanical processing. The preparation of the titanium surface for coating included cutting, grinding, degreasing with hexane, and rinsing in distilled water. The electrolyte was prepared with the following composition: a 30% aqueous solution of orthophosphoric acid (H_3PO_4, thermal grade A) + hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$ - 60 g/L) + calcium carbonate ($CaCO_3$ - 100 g/L). The hydroxyapatite (HA) was sourced from Sigma Aldrich with a dispersity of <5 µm. The electrolyte was poured into an ultrasonic bath, where it was further mixed with an electric stirrer. To ensure chemical reactions were complete, the electrolyte was allowed to stand in the bath for two days.

Micro-Arc Oxidation (MAO) process

A micro-arc oxidation setup was assembled for this work, in which a 150 W stainless steel ultrasonic bath was used as the electrolysis bath. A custom-built pulse power source was employed, capable of varying the voltage from 0 to 700 V with a constant pulse duration of 300 µs, allowing for different duty cycles of 0.0102 (35%), 0.0049 (17,3%), and 0.0022 (8,3%) seconds. MAO was conducted in anodic mode at 300 V with a processing duration of 10 minutes. Three series of experiments were conducted in the electrolyte to perform MAO on the surface of titanium samples with varying pulse current duty cycles (modes A, B, C), as schematically shown in Figure 1. The treated samples were labeled according to modes A, B, and C.

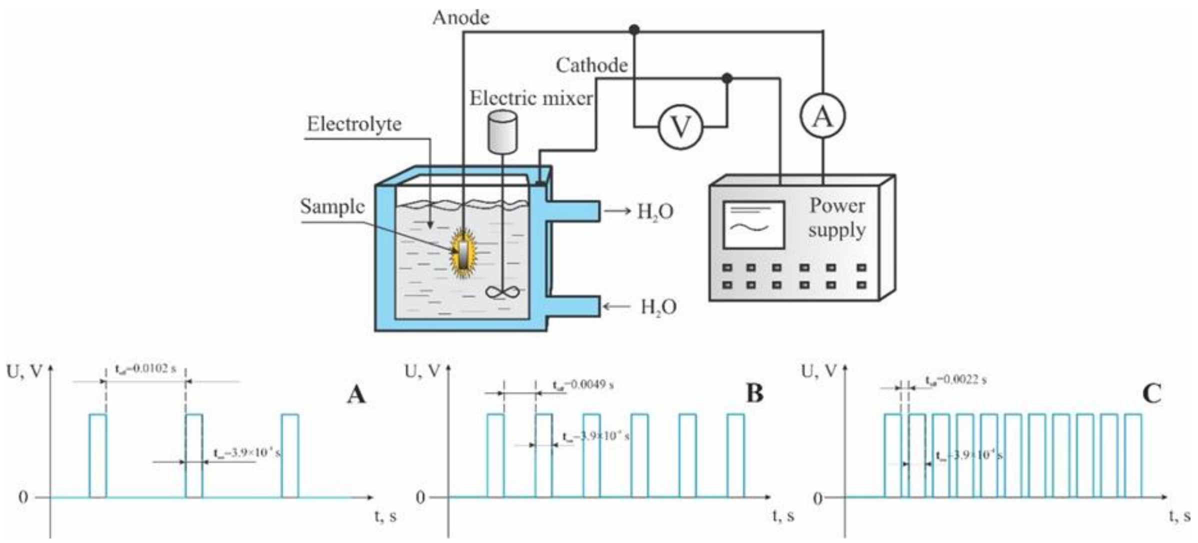

Figure 1 - Schematic diagram of MAO and characteristics of the electric pulse current applied in different coating synthesis modes

Methods for Studying CaP Coatings

Titanium samples after MAO were examined using scanning electron microscopy (SEM) and profilometry, and they were subjected to tribological testing under dry friction conditions at room temperature. Surface morphology and elemental composition analysis, as well as thickness measurements, were carried out using a scanning electron microscope model Phenom ProX with EDS (Phenom, Netherlands) at various magnifications. Surface roughness was measured with a profilometer, the Diavite DH-5 (DIAVITE AG, Switzerland). Each sample was measured 5 times, with the average roughness result from the five measurements reported. The measurement length was 4 mm.

Tribological tests were conducted on a custom-designed setup to determine the friction coefficient (CoF) of samples through reciprocating motion. The tribological test conditions were close to the DIN 51834-1:2010 standard. The setup consisted of a holder for the counter-body with a load, a sample displacement mechanism, an electronic control unit, and a laptop. A 4 mm diameter steel ball made of SHX15 steel was used as the counter-body. Test parameters included: ball displacement speed of 26 mm/sec, friction track length of 5 mm, total friction path length of 5 m, 500 cycles, and loads of 5 and 20 N.

Results and Discussion

Morphology, thickness, composition, and roughness of the coating

CaP coatings exhibit different surface morphologies depending on the duty cycle of the MAO pulse current. Figure 2 shows SEM images of the surface morphology and thickness of the CaP coating obtained at 300 V across all pulse current modes: A, B, and C. In modes A and B, the coating forms a porous structure with spherical aggregates and volcano-like structures with pores. The sizes of spherical aggregates in mode A are 98 ± 7.8 µm, while in mode B they are 66 ± 5.5 µm. Changing the duty cycle to mode C results in not only spherical structures but also walls and fragments thereof. The average size of these structures is 66.5 ± 5.1 µm. Notably, the porous structures (with pore sizes ranging from 15 to 50 µm) promote nutrient circulation in biomedical implant materials [23]. The thickness of the coatings increases from 74.3 µm to 100 µm as the pulse duty cycle decreases, likely due to a greater number of pulses (from A to C), leading to thicker CaP coatings in MAO.

The elemental composition of the CaP coating shows the presence of Ca, P, O, and Ti, as shown in Table 1. All samples exhibit a significant increase in oxygen content, which is a characteristic of the MAO method. The Ca/P ratio is a key indicator of bioactivity. Given this parameter, the coatings produced are likely related to bioresorbable phases. These could include CaP coatings with a lower Ca/P ratio (Ca/P = 1.67) compared to HA [24]. As the duty cycle decreases (from A to C), the Ca/P ratio increases from 0.3 to 0.4. This might be due to intensified deposition of Ca2+ ions from the electrolyte. Additionally, as the coating thickness increases, the titanium content decreases while the calcium content increases in elemental analysis with changes in the MAO pulse current duty cycle.

The surface roughness of an implant is one of the critical characteristics during osteointegration. According to the literature [[25], [26]], the roughness parameter Ra in the range of 4 < Ra < 7 µm is considered optimal, as it promotes enhanced osteogenic differentiation on such rough titanium surfaces. The obtained CaP coatings had roughness within this range, indicating that depending on the application mode, the roughness parameter Ra was recorded within the range of 5.7 to 6.11 µm. The other roughness parameters are shown in Table 2.

Tribological study of CaP coatings

During tribological testing, the surface of the CaP coating in contact with the SHX15 steel counter-body underwent degradation, leading to the formation of wear tracks. Figure 3 shows typical morphologies of worn coating surfaces after tribological tests at a load of 20 N against a steel ball for different MAO application modes. At a 5 N load, wear tracks were barely noticeable, so to study the wear characteristics in greater detail, tracks formed at a 20 N load were selected. As a result, extensive wear tracks were observed on the worn surfaces.

The wear tracks for the sample processed in mode A exhibited two distinct zones: the first was a wear track with surface layer removal, and the second had pits corresponding to locations where the coating delaminated due to intense wear. The width of the wear track in the first zone was 488 ± 65 µm, while in the second zone, it was 234 ± 66 µm. Among the three coatings studied, the sample processed in mode A showed the lowest wear resistance, as indicated by the greater depth of the wear track. One reason for this low resistance could be the higher surface roughness [[27], [28]]. In contrast, the tribological behavior of the other coatings showed a different wear pattern. As shown in Figure 3, the coatings obtained in modes B and C exhibited surface wear without noticeable exposed substrate. The width of the wear tracks for these coatings was 538 ± 138 µm for mode B and 745 ± 191 µm for mode C.

Roughness measurements using SEM within the wear tracks were 3.63 µm for the mode A coating, 585 nm for the mode B coating, and 947 nm for the mode C coating. This data helps characterize the extent of wear-related roughness. A visual comparison of surface degradation, wear pattern, and wear volume after tribological testing suggests that the coating produced in mode B has the highest wear resistance among those studied, supported by the absence of delamination and a narrower wear track.

Table 1 - Elemental composition of calcium phosphate coatings on titanium and the Ca/P ratio

Coating	Elemental composition (ат. %)				Ca/P
	Ca	P	O	Ti	
A-300 V	3.26	10.52	77.33	8.89	0.3
B-300 V	3.50	10.38	77.43	8.69	0.34
C-300 V	4.60	11.37	78.13	5.90	0.4

Table 2 - Parameters for measuring the surface roughness of CaP coatings deposited with different duty cycles in MAO

Coating	Surface roughness measurement parameters					
	Mean arithmetic deviation of profile, Ra (µm)	Profile roughness height across ten points, Rz (µm)	Maximum profile height, Rmax (µm)	R3z, (µm)	Rt, (µm)	Rq, (µm)
A	6.11	35.5	43.5	25.6	43.5	7.75
B	5.70	30.7	40.6	26.5	40.6	7.11
C	5.76	20.0	20.0	20.0	20.0	6.62

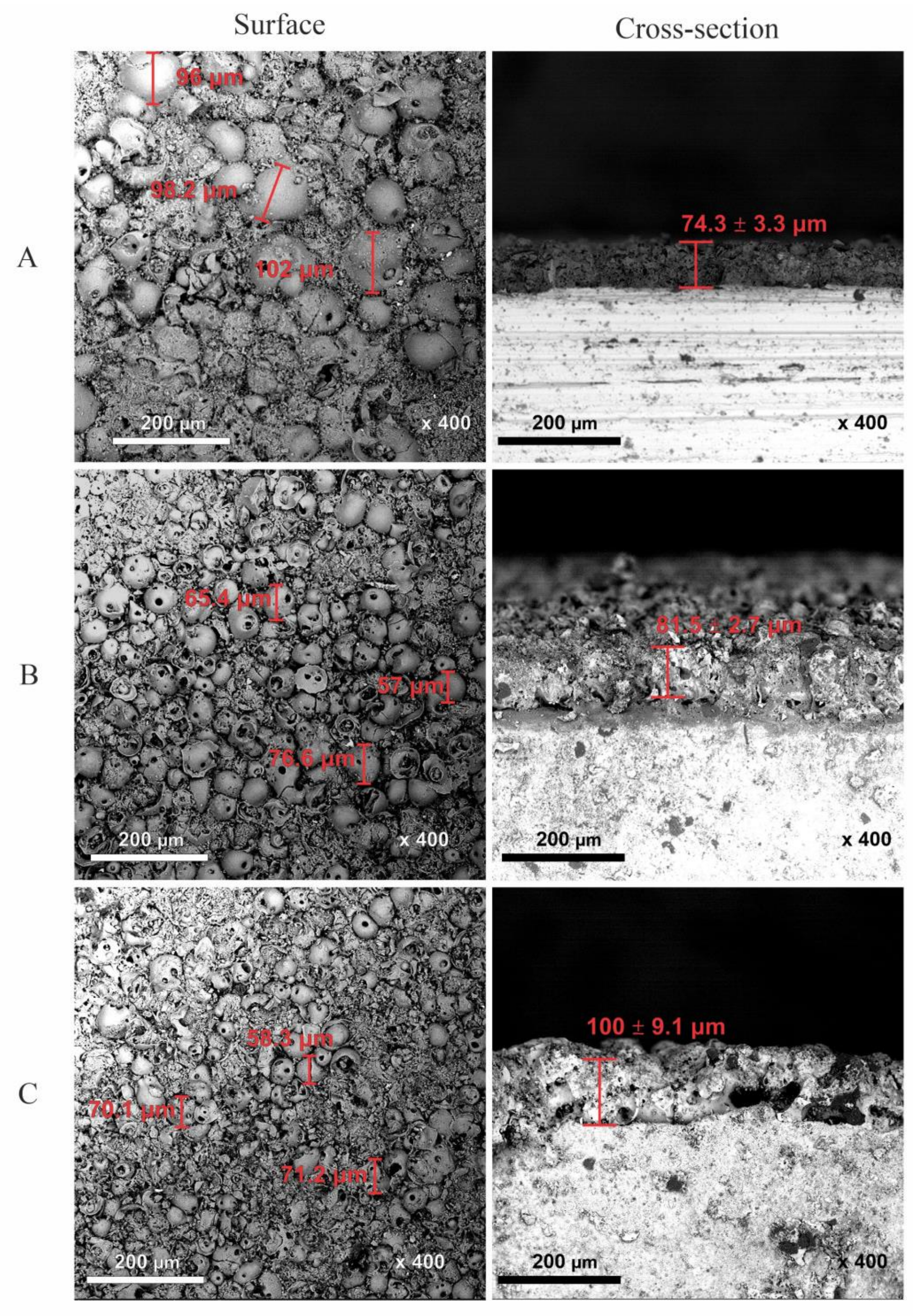

Figure 2 - Surface morphology and thickness of CaP coatings obtained in duty cycle modes: A, B, and C

According to the friction test results (Figure 4), the coefficient of friction (CoF) in all studied coatings showed stable behavior, except for minor spikes or changes. During tests with a 5 N load (depicted by the black line in Figure 5), there were initial minor spikes in the CoF graphs, indicating a break-in period for the surface. The break-in period could be due to the smoothing of surface roughness peaks on the coatings [29]. Increasing the normal load from 5 to 20 N led to a higher CoF. These results indicate a significant influence of load on the wear response of the materials studied. As for the CoF graphs at a 20 N load (depicted by the red line in Figure 5), after 50 cycles of friction, if a decrease in CoF is observed for coatings deposited in modes B and C, there is an increase in CoF for mode A, which continues up to 200 cycles. A possible reason for this might be the delamination of ceramic material particles during tribological testing, which increases the surface roughness and consequently leads to higher CoF values [17].

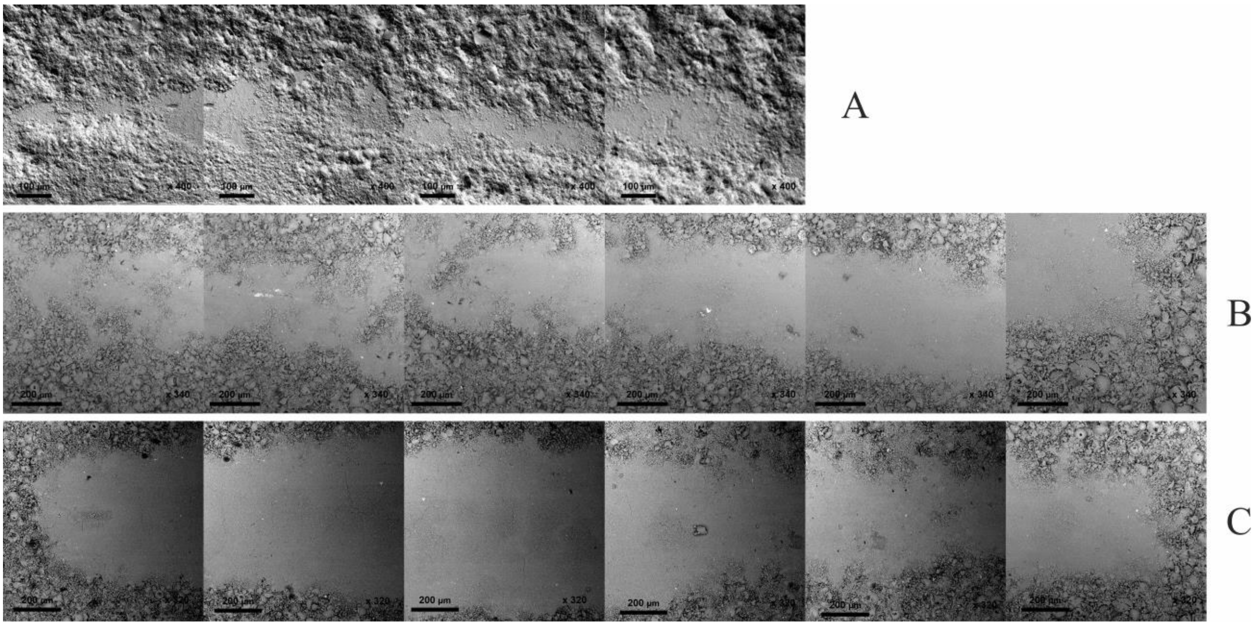

Figure 3 - SEM Images of wear tracks after tribological testing of CaP coatings deposited in duty cycle modes: A, B, and C

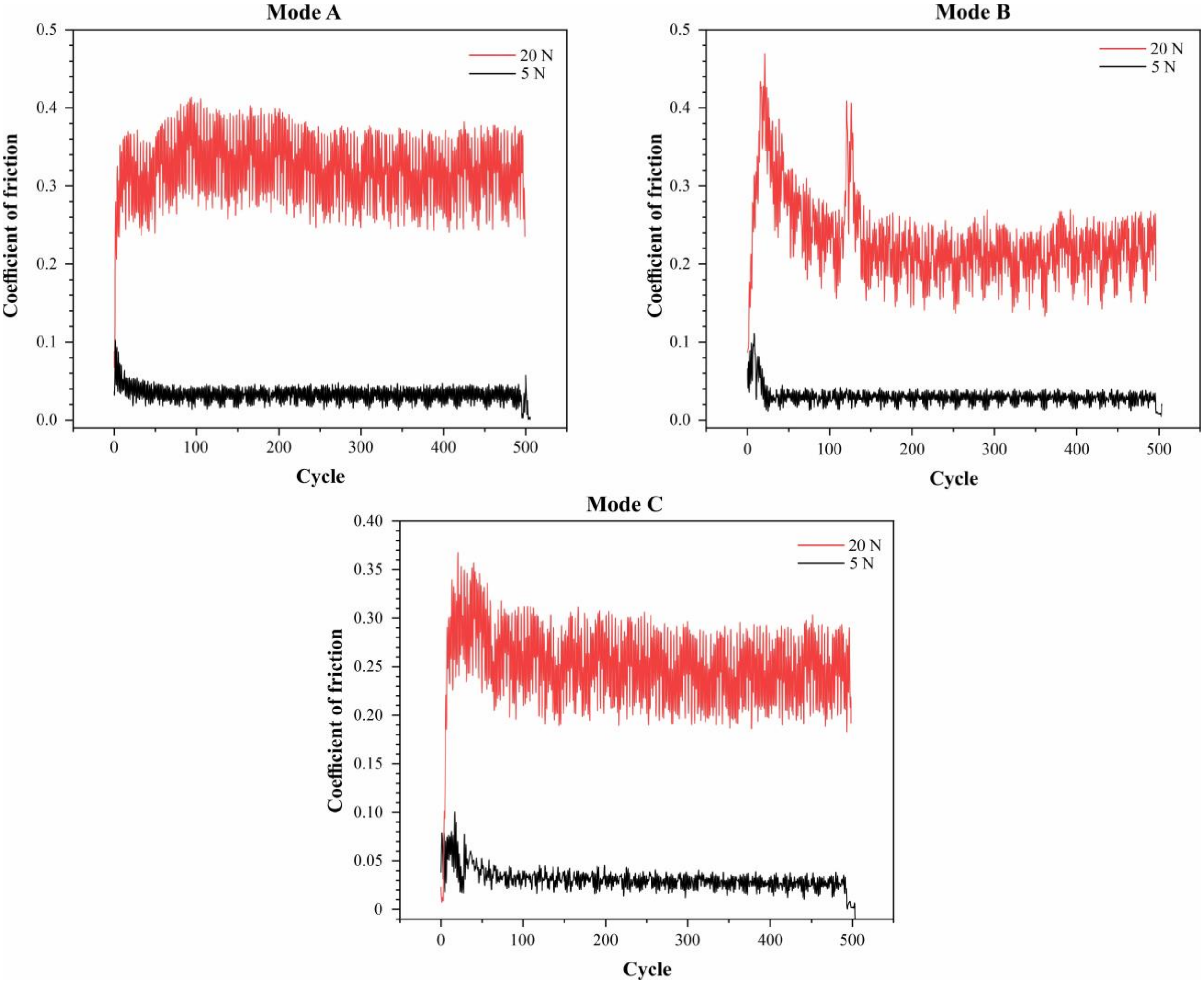

Figure 4 - CoF graph for CaP coatings deposited in duty cycle modes: A, B, and C

Figure 5 shows the averaged values of the CoF at 5 N and 20 N loads and the wear track width for the CaP coatings. The lowest average CoF is observed for the CaP coating obtained in Mode B of the MAO process, with a CoF of 0.029 at 5 N and 0.909 at 20 N. The highest CoF, 0.034, is noted for the coating in Mode A. The median CoF values for all coatings were as follows: A 5N – 0.034, A 20N – 1.396, B 5N – 0.026, B 20N – 0.89, C 5N – 0.024, C 20N – 1.058. When comparing wear track width, the coating in Mode B demonstrates the highest wear resistance due to its narrower width at 5 N. For 20 N, the narrowest wear track is recorded for the coating in Mode A at 488 µm. However, it's important to note that this coating also exhibits deeper wear grooves. Consequently, when considering wear volume, the coating in Mode B displays lower wear than other coatings. In summary, the tribological data suggest that Mode B of the MAO process allows for the deposition coataing with high wear resistance on titanium surfaces.

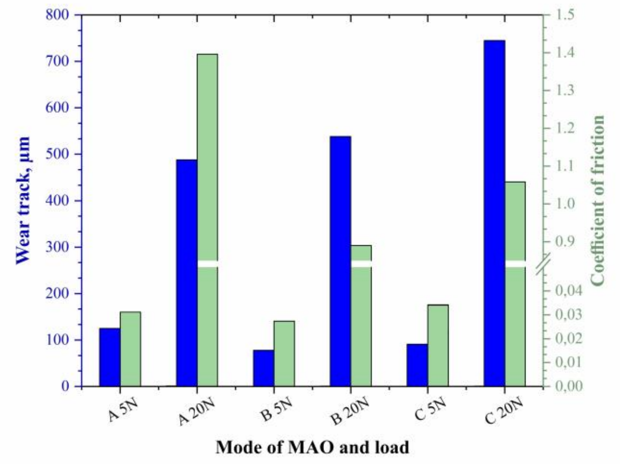

Figure 5 - The wear track and the averaged CoF values for loads of 5 N and 20 N

Coatings applied in mode B exhibit less wear and better integrity retention under load compared to other modes, which can be explained by several reasons outlined below. Mode B results in the formation of smaller spherical aggregates (66 ± 5.5 µm) compared to mode A and, unlike mode C, prevents the formation of fragmented structures. The consistency and uniformity of these smaller spherical aggregates may contribute to the creation of a more compact and homogeneous coating, thereby enhancing its wear resistance. Transitioning from mode A to B increases the calcium content, which contributes to structural integrity through a denser phosphate matrix. Consequently, mode B likely induces beneficial structural changes, such as a more uniform and compact microstructure, optimal roughness, and improved chemical composition, enhancing its wear resistance.

Conclusions

The micro-arc oxidation method successfully applied calcium-phosphate coatings to the VT1-0 titanium surface with varying pulse duty cycles in an electrolyte containing a 30% aqueous solution of orthophosphoric acid, hydroxyapatite, and calcium carbonate. The coatings underwent tribological testing against SHX15 steel under normal loads of 5 N and 20 N. From the study, the following conclusions can be drawn:

1. Investigation into the morphology of coatings resulting from MAO with various pulse duty cycles on the titanium surface showed a common structure featuring volcano-like formations with pores. The average size of these structures ranged from 66 to 98 micrometers. Decreasing the pulse duty cycle (from 35% to 8,3%) caused the coating thickness to increase from 74.3 micrometers to 100 micrometers due to the higher number of pulses.
2. The surface roughness of the coatings fell within the optimal range of 5.7 to 6.11 micrometers, conducive to enhanced osteogenic differentiation. Following tribological testing, the roughness within the wear track decreased by 6 to 10 times compared to the initial condition.
3. The Ca/P ratio, a critical bioactivity indicator, varies with changes in the MAO pulse current duty cycle. A decrease in this ratio is observed as the duty cycle increases, suggesting an enhancement in the bioactive potential of the coatings. The presence of bioresorbable phases in the coatings indicates their suitability for biomedical implant applications, particularly where nutrient circulation within the implant material is crucial.
4. Wear resistance studies showed that the coating produced in duty cycle 17.3% had the highest wear resistance among the coatings tested. The absence of delamination, the narrow wear track width, and a favorable coefficient of friction indicated the high wear resistance of the coatings obtained in this mode. This is attributed to the smaller, more uniform spherical aggregates formed, which result in a more compact and homogenous layer, offering better protection against wear. The wear patterns and friction coefficient data corroborate the superior performance of MAO mode (voltage 300 V, duty cycle 17.3%), where the coatings exhibit minimal delamination and maintain structural integrity even under higher loads.

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

CRediT author statement

A. Mamaeva: Conceptualization, Validation, Investigation, Project administration. **A. Kenzhegulov**: Methodology, Software, Validation, Investigation, Data curation, Writing - Original Draft, Visualization. **A. Panichkin**: Conceptualization, Validation, Visualization, Investigation. **M. Panigrahi**: Writing - Review & Editing. **D. Fischer**: Software, Resources, Funding acquisition.

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Титандағы микродоғалы кальций-фосфат жабындарының трибологиялық сипаттамаларын зерттеу

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ТҮЙІНДЕМЕ

Импланттардың трибологиялық сипаттамалары, мысалы, тозуға төзімділігі және үйкеліс коэффициенті, олардың қоршаған тіндермен өзара әрекеттесу кезінде төзімділігі мен функционалдылығын қамтамасыз етуде маңызды рөл атқарады. Бұл параметрлер имплантаттың механикалық жүктемелерге төтеп беру қабілетіне және оның қызмет ету мерзімін ұлғайтуға, тозуды минималдауға ықпал етеді. Имплантат пен биологиялық тіндер арасындағы үйкелісті минималдау механикалық зақымданудың алдын алуға ғана емес, сонымен бірге қабыну реакцияларының қаупін төмендетуге көмектеседі, бұл жақсы биологиялық үйлесімділікті қамтамасыз етеді. Бұл жұмыста олардың трибологиялық сипаттамаларын зерттеу үшін импульстік токтың әртүрлі жұмыс циклдерінде микродоғалық тотығу арқылы кальций фосфатты жабындары алынды. Титанға отырғызылған жабындар 66-дан 98 микрометрге дейінгі вулкан тәрізді тесіктері бар құрылымдармен болды. Жабындардың қалыңдығы микродоғалық тотығу кезінде алынған жағдайға байланысты 74,3-тен 100 микрометрге дейін өзгерді. Трибологиялық сынақтар шар-жазықтық схемасы бойынша қайтымды ілгерілеме қозғалыс арқылы жүргізілді. Жабындар 5 және 20 Н қалыпты жүктемелерде ShKh15 маркалы болатқа қарсы трибологиялық сынақтардан өтті. Түсірілген күшке байланысты жабындардың үйкеліс коэффициенттері 5 Н кезінде 0,029-дан 0,034-ке дейін және 20 Н кезінде 0,9-дан 1,26-ға дейін болды. Тозу көрсеткіштерін талдау және тозған беттердің микрокескіндері микродоғалық тотығу кезінде импульстік токтың импульсті жұмыс циклі 17,3% болатын режимінің титан беттерінде тозуға төзімділігі жоғары жабындарды алуға мүмкіндік беретінін көрсетті.

Түйін сөздер: кальций-фосфат жабыны, микродоғалық тотығу, ток қуыстылығы, үйкеліс коэффициенті, тозу.

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Исследование трибологических характеристик микродуговых кальций-фосфатных покрытий на титана

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АННОТАЦИЯ

Трибологические характеристики имплантатов, такие как сопротивление износу и коэффициент трения, играют критическую роль в обеспечении их долговечности и функциональности при взаимодействии с окружающими тканями. Эти параметры влияют на способность имплантата выдерживать механические нагрузки и минимизировать износ в течение всего срока его службы. Минимизация трения между имплантатом и биологическими тканями не только помогает предотвратить механические повреждения, но и снижает риск воспалительных реакций, обеспечивая лучшую биологическую совместимость. В данной работе были получены кальций-фосфатные покрытия методом микродугового оксидирования при разной скважности импульсного тока для исследования их трибологических характеристик. Осажденные покрытия на титане имели структуру с вулканоподобными образованиями с порами от 66 до 98 микрометров. Толщина покрытий варьировалась от 74,3 до 100 микрометров в зависимости от условия получения при микродуговом оксидировании. Трибологические испытания проводились по схеме шар-плоскость с помощью возвратно-поступательного движения. Покрытия были подвергнуты трибологическим испытаниям против стали ШХ15 при нормальных нагрузках 5 и 20 Н. В зависимости от приложенной нагрузки коэффициенты трения покрытий составляли от 0,029 до 0,034 при 5 Н и от 0,9 до 1,26 при 20 Н. Анализ показателей износа и микрофотографии изношенных поверхностей свидетельствуют о том, что режим со скважностью импульсного тока 17,3 % при микродуговом оксидировании позволяет получать на поверхностях титана покрытия с высокой износостойкостью.

Ключевые слова: кальций-фосфатное покрытие, микродуговое оксидирование, скважность тока, коэффициент трения, износ.

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Metallurgy

Study of the influence of temperature and duration of chlorinating roasting on the extraction of gold from E-waste

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ABSTRACT

In this work, based on experimental studies, the effect of roasting temperature and duration on the chlorination of gold from E-waste under low-temperature conditions was studied. It has been established that in the low-temperature range of 150-300 °C, the gold content in the residue shows a sharp decrease, reaching its minimum of 8 ppm at 250 °C. A further increase in temperature does not affect the gold content in the cinder. It has been shown that during chlorinating roasting above a temperature of 250 °C, side reactions should be expected to occur with the formation of additional phases representing chlorides of copper, iron and other elements. The results of SEM and XRD analyzes of the solid phase obtained after chlorinating roasting at a temperature of 250 °C and a roasting duration of 20 minutes showed the presence of copper and iron chlorides in them. Optimal technological parameters and modes of the process of chlorinating roasting of E-waste with gaseous chlorine have been established: temperature – 250 °C; roasting duration – 20 minutes; chlorine consumption is 1.5 times more than the stoichiometrically required amount (SRA) for gold chlorination. Under optimal roasting conditions, a high, up to ~97.6%, recovery of gold in the form of gold chloride ($AuCl_3$) was achieved. The results of the experiments can be a basic basis and make it possible to conduct more representative experiments (scaling) in the future, taking into account the established optimal technological parameters. This will provide a chance to evaluate the possibility of extracting gold from E-waste of different types and compositions and to conduct further research on obtaining pure gold from the collected representative amount of gold sublimate $AuCl_3$ by smelting.

Keywords: E-waste, gold, roasting, $AuCl_3$ sublimate, temperature, recovery.

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Introduction

Increasing environmental requirements necessitate the introduction of new accessible technologies with the transition to a circular economy. The issues of resource-saving of primary raw materials and reducing the costs of metal production are the main tasks nowadays, the solution of which requires finding new types of sources of raw materials for the production of metals. One of the promising areas is the involvement of secondary raw materials in the processing, which is becoming widespread in European countries where there is a clear shortage of high-quality primary raw materials. In recent years, the recycling of waste electronic and electrical equipment, combined into a separate category, and referred to in the scientific literature as electronic waste (E-waste) [[1], [2], [3], [4], [5], [6], [7]], has received high interest and development.

Known technologies for processing E-waste, including pyro-, hydro- and biometallurgical technologies, require serious modernization, both in terms of technology and environmental requirements [[8], [9], [10], [11], [12], [13]]. The lack of rational technology for processing E-waste has led to its growth in terms of volume. According to experts [[14], [15], [16]], up to 343 thousand tons of electronic waste are accumulated in Kazakhstan per year, which could be used as an additional source of raw materials for the production of valuable metals.

The use of chlorinating technologies for processing E-waste, which is currently widely used for the extraction of valuable metals from various types of primary raw materials and technogenic waste [[17], [18], [19], [20]], has a high theoretical and practical interest. The results of systematic studies carried out in [19] showed the possibility of selective extraction of gold from various types and compositions of primary gold-bearing raw materials at a relatively low temperature. The positive results obtained by the authors indicate the prospects of using chlorine gas as a chlorinating reagent for the sublimation of gold in the form of its sublimate ($AuCl_3$) from E-waste. However, for a more detailed assessment, data on the completeness and rate of interaction of gold with chlorine is important. Knowledge of these factors is necessary to study the mechanism of the process of chlorination of E-waste with chlorine gas.

This research [20] on the interaction of E-waste components with gaseous chlorine shows the fundamental thermodynamic possibility of selective gold extraction from E-waste. Significant factors affecting gold recovery during low-temperature chlorinating roasting of E-waste with chlorine gas are chlorine consumption, temperature, process duration and impurity content. At low temperatures (100-250 ^{0}C), only $AuCl_3$ has high vapor pressure. Therefore, it can be argued that the main factors influencing the completeness of gold extraction from E-waste will be the temperature and duration of the process. In this case, the consumption of chlorine should be optimal, and it should be spent on the chlorination of gold, the content of which, as the literature data show, in E-waste can vary from 50 to 350 ppm, depending on the type and composition of electronic scrap.

To obtain quantitative data on the recovery and rate of gold chlorination, this article contains studies on the chlorination of gold from E-waste in a stream of chlorine gas. The effect of roasting temperature and time on the chlorination of gold and its extraction from E-waste in the form of a volatile sublimate $AuCl_3$ was studied.

Materials and research methods

Computer boards were used as the initial object. -35 mesh PC board materials were prepared in advance using an SM 300 cutting mill from Retsch GmbH. The gold content in the source material is 310 ppm.

Roasting was carried out in a temperature-controlled laboratory electric furnace Nabertherm HTC-03/15/B170 at a temperature of 250 ^{0}C in an atmosphere of excess chlorine gas. The heating rate of the furnace was constant and amounted to 12 ^{0}C/min.

In all experiments, the gas flow (chlorine), to optimize it, was constant and amounted to 150 ml/min. The consumption of chlorine was 1.5 times higher than the stoichiometrically required amount (SRA) for the chlorination of gold according to the reaction: $2Au + 3Cl_2 = 2AuCl_3$.

Experiments were carried out at temperatures of 150, 200, 250 and 300 ^{0}C. The experimental time varied from 10 to 20 minutes in 5-minute increments. The experimental methodology is based on the experimental planning theory method, which makes it possible to determine the influence of temperature and process duration on the extraction of gold from E-waste under conditions of chlorination with chlorine.

The total number of experiments was 16 experiments. Each experiment was repeated three times for reproducibility to obtain accurate results. At the end of each experiment, the weight of the residue was monitored. The presence of gold in the residues obtained after roasting was determined based on the results of elemental, SEM and XRD analyses. The gold content in the residue was additionally determined by the traditional method of chemical analysis.

Based on the results of experimental data, the values of gold recovery from E-waste at different temperatures and roasting times were calculated.

Diagram of the laboratory setup and experimental methodology

The general diagram of the laboratory installation for gold extraction is shown in Fig. 1.

The experimental procedure was as follows. The initial sample was loaded into boat crucible 4 and placed in a quartz reactor 2 installed in the zone of a uniform temperature field of electric furnace 1. The working area of the furnace allows for placing four boat crucibles at the same time, which can increase the amount of raw material being roasted. In our case, we used one boat crucible with a minimum weight of 15 g.

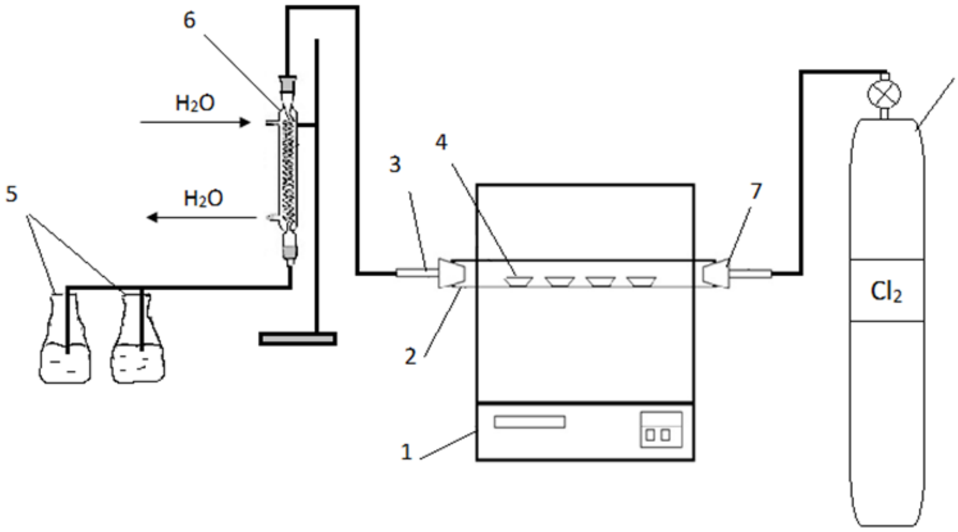


Figure 1 – General diagram of the laboratory installation to extract gold from E-waste:
1 – Nabertherm HTC-03/15/B170 electric furnace; 2 – quartz reactor;
3 – gases containing AuCl3 sublimate; 4 – boats crucible for samples;
5 – exhaust gas absorbers; 6 – AuCl3 sublimate trapping device;
7 – plug with a hole for supplying chlorine to the reactor;
8 – cylinder with chlorine (gas). *The picture was illustrated by the authors.*

The quartz reactor is plugged on opposite sides with a plug, which has holes for the input and output of gases. The roasting was carried out in a stream of chlorine gas, which was supplied from cylinder 8 through a plug with a hole 7 into a quartz reactor 2.

Sublimate ($AuCl_3$) formed during roasting was removed from the reactor through pipeline 3 and captured in a specially designed device 6. Continuous removal of the sublimate from the reaction zone ensured that the gold chlorination reaction proceeded practically in the absence of its chlorides in the reaction zone.

Exhaust gases containing chlorine were captured in absorption flasks containing lime milk. At the end of the experiment, the furnace was turned off. The solid residue obtained after the experiment was removed from the furnace, weighed and subjected to chemical and phase analysis. The degree of gold chlorination under various experimental conditions was determined by the difference, taking into account the amount of the initial sample and the resulting residue and the gold content in them.

Results and discussion

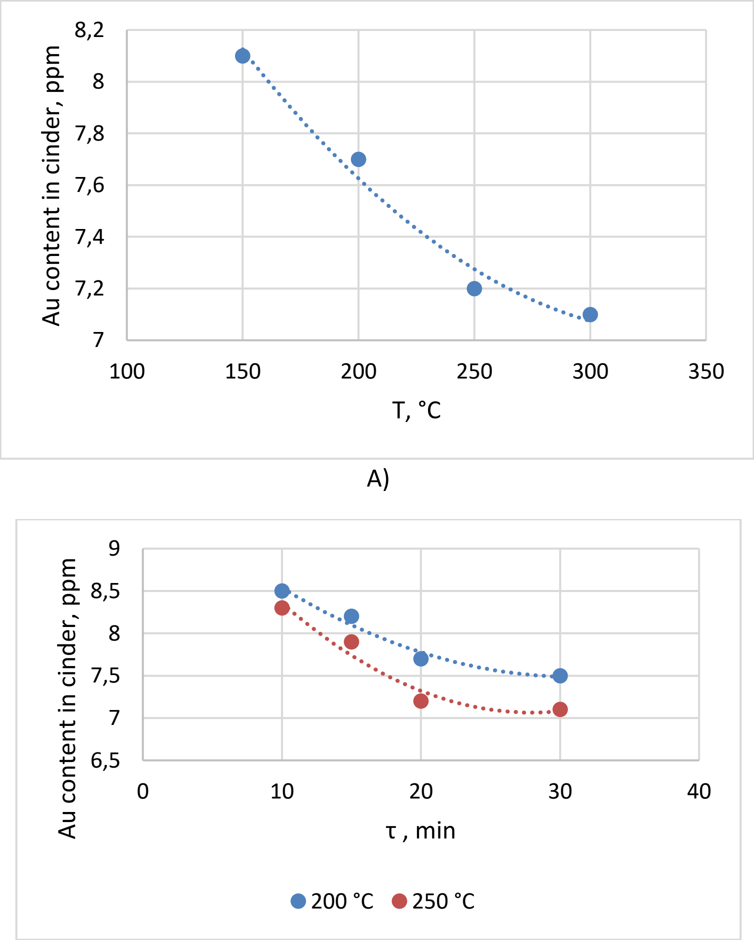
The results of experiments on low-temperature chlorination of E-waste with gaseous chlorine are given in Table 1.

Figure 2 shows the dynamics of changes in the gold content in the source material depending on the temperature and duration of roasting.

It is easy to notice that in the low-temperature range of 150-300 °C, the nature of the curve of the dependence of the gold content in the residue on temperature shows a sharp decrease in the gold content, reaching its minimum of 8 ppm at 250 °C (Fig. 2 (A)). A further increase in temperature does not affect the gold content in the cinder. This indicates that during chlorinating roasting above a temperature of 250 °C, side reactions should be expected to occur with the formation of additional phases representing chlorides of copper, iron and other elements. In particular, as shown by the results of SEM and XRD analyses, copper and iron chlorides were found in the residues obtained after chlorinating roasting at a temperature of 250 °C and a roasting time of 20 minutes. The obtained results are in good agreement with the results of thermodynamic analysis of the reactions of interaction of E-waste components with gaseous chlorine, where during chlorinating roasting of E-waste at low temperatures (below 400 °C), a high thermodynamic probability of interaction of non-ferrous metals (Cu, Pb, Zn) was established with chlorine gas to form solid chlorides.

Table 1 - Results of experiments on chlorination of E-waste with chlorine

#	Initial weight, g.	Temperature, ºC	Time, min	Quantity of residue, g.	Content of Au in the residue, ppm
1	200	150	10	73	8.8
2	200	150	15	65	8.4
3	200	150	20	54	8.1
4	200	150	30	49	7.9
5	200	200	10	71	8.5
6	200	200	15	67	8.2
7	200	200	20	57	7.7
8	200	200	30	50	7.5
9	200	250	10	70	8.3
10	200	250	15	64	7.9
11	200	250	20	99	7.2
12	200	250	30	52	7.1
13	200	300	10	68	8.4
14	200	300	15	54	7.8
15	200	300	20	49	7.1
16	200	300	thirty	46	7



A)

B)

Figure 2 – Dependence of gold content in the residue on temperature (A) at τ = 20 min., and roasting duration (B)

From Fig. 2 (B) it is clear that the duration of roasting is an equally important parameter affecting the chlorination of gold: an increase in the roasting time also leads to a decrease in the gold content in the residue obtained after roasting. At T = 200 °C and roasting time τ = 20 minutes, the gold content in the residue is reduced from 310 ppm to 9.5 ppm. The greatest effect of reducing gold in the residue is achieved at T = 250 ^{0}C and roasting time τ = 20 minutes: the gold content in the residue is 8 ppm.

The most significant technological indicator of the chlorination roasting process is the extraction of gold from E-waste under experimental conditions. Based on the task set, using the results of experiments, the values of gold extraction into sublimates in the form of AuCl3 sublimate were calculated.

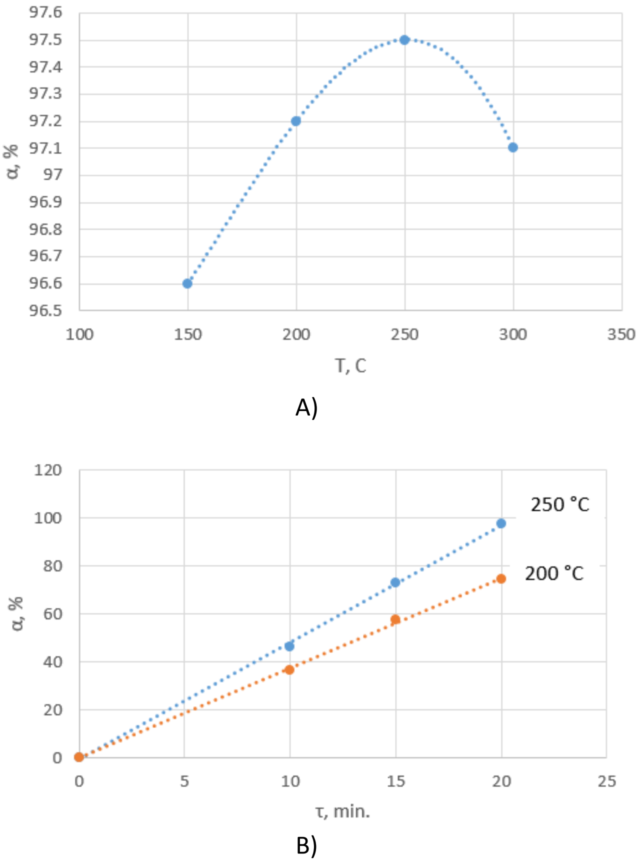
Gold recovery was calculated using the formula:

$$\alpha = 100 - (\frac{Me_{cinder}}{Me_{scrap}} * 100),$$

where: Me $_{cinder}$ – metal content in the cinder, %;
Me $_{scrap}$ – metal content in the original scrap, %.

Figure 3 shows the graphical dependences of gold extraction (α) on temperature and roasting duration, developed from the results of experimental data.

The recovery of gold from E-waste increases with increasing temperature. Moreover, its sharp increase, at a constant roasting time, is observed in the temperature range of 100-250 ^{0}C, reaching its maximum at 235 ^{0}C (τ = 20 min.) equal to ~97.6% (Fig. 3 (A)). A further increase in temperature does not affect gold extraction; on the contrary, a slight decrease is observed, which is associated with a change in the phase composition of the starting material during the roasting process. At high roasting temperatures (more than 250 ^{0}C), sintering of the material occurs with the formation of additional phases: $CuCl_2$; FeClO and $Cu_2Cl(OH)_3$, which inhibit the interaction of gold with chlorine and reduce the reaction rate. However, as experimental results show, the greatest reduction of gold with chlorine is achieved up to a temperature of 250 ^{0}C. Further chlorination of gold can be achieved by increasing the temperature, however, the resulting gold sublimate will decompose into metallic gold and chlorine to the point of capture. In addition, at elevated temperatures, we should expect changes in the composition of the gas phase due to the volatilization of undesirable accompanying metals (As, Cd, etc.), as well as organics due to the thermal destruction of plastics, etc.



A)

B)

Figure 3 – Dependence of gold recovery (α) on temperature (A) at τ = 20 min., and duration (B)

Increasing the experiment time, at a constant temperature, has a significant effect on gold recovery in the time range from 10 to 20 minutes, sharply increasing gold recovery during roasting to a maximum of 20 minutes (Fig. 3 (B)). Increasing the temperature reduces the roasting time and increases the gold recovery, indicating that the roasting time has a negligible effect on gold recovery from E-waste.

The obtained positive experimental results provide a chance to select the optimal technological parameters and modes of the process of chlorinating roasting of E-waste with gaseous chlorine: temperature – 250 ^{0}C; roasting duration – 20 minutes; chlorine consumption is 1.5 times higher than its stoichiometric required amount for chlorination of gold. The established parameters provide high gold recovery up to ~97.5% from E-waste in the form of $AuCl_3$ sublimate.

The results of the experiments can serve as a basic basis to conduct more representative experiments (scaling) in the future, taking into account the established optimal technological parameters. This will allow us to evaluate the possibility of extracting gold from E-waste of different types and compositions and to conduct further research on obtaining pure gold from the collected representative amount of gold sublimated $AuCl_3$ by smelting.

Conclusions

Based on experimental studies, the influence of roasting temperature and time on the chlorination of gold from E-waste has been established. Extraction from E-waste, at a constant roasting time, increases with increasing temperature and reaches its maximum equal to ~97.6% at 235 ^{0}C (τ = 20 min.). A further increase in temperature does not affect gold extraction; on the contrary, a slight decrease is observed.

At a constant temperature, increasing the duration of the experiment from 10 to 20 minutes linearly increases the extraction of gold during roasting. Increasing the temperature reduces the roasting time and shifts gold recovery towards higher levels.

Optimal technological parameters and modes of the process of chlorinating roasting of E-waste with gaseous chlorine have been established: temperature – 250 ^{0}C; roasting duration – 20 minutes; chlorine consumption is 1.5 times more than SRA for gold chlorination. Under optimal roasting conditions, a high, up to ~97.6%, recovery of gold in the form of gold chloride ($AuCl_3$) was achieved.

The obtained data will be used for further research on the extraction of gold from E-waste of various types and compositions in the form of $AuCl_3$ sublimate and the isolation of pure gold from it.

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

CRediT author statemen: **E.Zoldasbay:** Supervision, Conceptualization, Methodology. **A. Argyn:** Data curation, Writing- Original draft preparation. **M.Kurmanseitov:** Investigation. **K.Dosmukhamedova:** Investigation, Software, Validation: **G.Daruesh:** Writing-Reviewing.

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Хлорлап күйдіру кезінде Е-қалдықтарынан алтынды бөліп алуға температура мен процес ұзақтығының әсерін зерттеу

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ТҮЙІНДЕМЕ

Бұл жұмыста эксперименталды зерттеулер негізінде төмен температура жағдайында күйдіру температурасы мен уақытының Е-қалдықтардан алтынның хлорлануына әсері зерттелді. 150-300 °С аралығындағы төмен температурада қалдықтағы алтынның мөлшері 250 °С температурада 8 ppm-ге тең минимумға жете отырып, күрт төмендейтіні анықталды. Температураның одан әрі өсуі өртенді құрамындағы алтынға әсер етпейді. 250 °С-тан жоғары температурада хлорлап күйдіру кезінде жанама реакциялардың жүруі нәтижесінде қосымша фазалар мыс, темір және басқа элементтердің хлоридтерінің түзілетіні анықталды. 250 °С температурада және 20 минут хлорлап күйдіру уақытынан кейін алынған қатты фазаны SEM және XRD талдауларының нәтижелері оларда мыс және темір хлоридтерінің барын көрсетті. Е-қалдықтарды хлор газымен хлорлау процесінің оңтайлы технологиялық параметрлері мен режимдері белгіленді: температура - 250 °C; күйдіру ұзақтығы – 20 мин.; хлор шығыны алтынды хлорлау үшін СҚМ-нен 1,5 есе көп. Оңтайлы күйдіру жағдайында жоғары ~97,6% дейін алтын хлорид ($AuCl_3$) түрінде бөліп алынды. Жүргізілген тәжірибелердің нәтижелері базалық негіз бола алады және белгіленген оңтайлы технологиялық параметрлерді ескере отырып, одан әрі өкілетті эксперименттерді (масштабтау) жүргізуге мүмкіндік береді. Бұл әртүрлі типтегі және құрамдағы Е-қалдықтардан алтынды бөліп алу мүмкіндігін бағалауға және жиналған алтын сублиматының $AuCl_3$ өкілетті мөлшерінен балқыту арқылы таза алтын алу бойынша одан әрі зерттеулер жүргізуге мүмкіндік береді.

Түйін сөздер: Е-қалдықтар, алтын, күйдіру, $AuCl_3$ сублиматы, температура, бөліп алу.

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Исследование влияния температуры и продолжительности хлорирующего обжига на извлечение золота из Е-отходов

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АННОТАЦИЯ

В работе на основании экспериментальных исследований изучено влияние температуры и времени обжига на хлорирование золота из Е-отходов в условиях низких температур. Установлено, что в интервале низких температур 150-300 °C содержание золота в остатке показывает резкое снижение с достижением своего минимума, равного 8 ppm, при 250 °C. Дальнейший рост температуры на содержание золота в огарке не влияет. Показано, что в процессе хлорирующего обжига выше температуры 250 °C следует ожидать протекания побочных реакций с образованием дополнительных фаз, представляющих хлориды меди, железа и других элементов. Результаты SEM и XRD-анализов твердой фазы, полученной после хлорирующего обжига при температуре 250 °C и времени обжига 20 минут, показали наличие в них хлоридов меди и железа. Установлены оптимальные технологические параметры и режимы процесса хлорирующего обжига Е-отходов газообразным хлором: температура – 250 °C; продолжительность обжига – 20 мин.; расход хлора в 1,5 раза больше СНК для хлорирования золота. В оптимальных условиях ведения обжига достигнуто высокое, до ~97,6 %, извлечение золота в виде ее хлорида ($AuCl_3$). Результаты проведенных опытов могут служить базовой основой и позволяют в дальнейшем провести более представительные эксперименты (масштабирование) с учетом установленных оптимальных технологических параметров. Это позволит оценить возможность извлечения золота из различного по типу и составу Е-отходов, и провести дальнейшие исследования по получению чистого золота из собранного представительного количества сублимата золота $AuCl_3$ путем плавки.

Ключевые слова: Е-отходы, золото, обжиг, сублимат $AuCl_3$, температура, извлечение.

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Metallurgy

An annealing-free method for processing high-moisture iron-containing sludge of metallurgical production

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ABSTRACT
The purpose of this study was to study the possibility of producing high-strength briquettes from high-moisture iron-containing slimes by hydration with quicklime (chemical dehydration) in combination with dolomite dust from a degusting system and carbon-containing pulverized materials and developing a drainless technology for the production of complex self-healing briquettes. The physicochemical conditions of the hydration process, temperature and time parameters of the process were studied, and the choice of active dehydrating materials significantly increased the degree of hydration of the composite system and their optimal ratios, and the period of the beginning and end of self-hardening were determined. The conditions of combining the processes of dehydration, and self-hardening with the processes of melding, when applying external pressure to a hardening mixture in a meld to obtain a coated material in the form of a briquette in one technological cycle are considered, which is one of the main provisions of the scientific novelty of the proposed method. Optimal conditions for the production of high-strength briquettes suitable for metallurgical production technologies, excluding the stages of thermal drying and firing, have been established, and a set of strength properties occurs in the air. The method allows obtaining a self-healing dipped material by introducing a carbon-containing reducing agent into a slurry-lime self-hardening mixture. Cheap waste pulverized limestone and dolomite roasting wastes are used as a dehydrating material, and pulverized carbonaceous materials (coke and coal screenings) are used as a reducing agent. Unlike well-known technical solutions, the proposed technology and the method incorporated in it eliminates the storage of iron-containing sludge in a sludge storage facility and allows you to organize a drainless scheme of non-annealing and the production of complex self-healing iron-containing material for the production of steel and rolled products. The technology will make it possible to organize production for the processing of high-moisture iron-containing sludge, pulverized calcium- and magnesium-containing and carbon-containing pulverized waste and also solves the problems of environmental pollution and land allocation for the storage of industrial waste.

Keywords: sludge, dust, processing, dehydration, pelletizing, briquetting.

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Introduction

The "Green Industry" is becoming a new trend that ensures the implementation of the concept of sustainable development [[1], [2]]. Despite the popular opinion that metallurgy is a "dirty" industry, large companies, over the past decades, have been implementing and developing new environmentally friendly solutions, improving production processes. Today, two main directions can be identified in which metallurgy is moving towards increasing the environmental friendliness of production:

- development of technologies aimed at reducing harmful emissions and cleaning production processes;
- closure of the production cycle, when various materials and resources are used several times or sold for further processing.

Creation of a closed cycle, in terms of emissions into the atmosphere and wastewater or secondary raw materials. The transition to low-waste technologies within the framework of the closed-loop concept is the most difficult and most important part of the "green industry" [[1], [2], [3],

[4]]. The metallurgical industry is one of the largest sources of formation of significant volumes of large-tonnage mineral waste with various compositions and is accompanied by the formation of a significant amount of various wastes, reaching 30% of steel production. It consists of about 80% slag and about 20% dust and other waste. At the same time, waste is often technologically superior to iron ore materials extracted from the subsurface. However, despite its high resource potential, waste from the mining and metallurgical industries in Kazakhstan is mainly used as raw materials for the construction industry, but even here the volume of recycled material does not reach 10% of the annual volume of education. The utilization of man-made waste can not only contribute to saving resources, i.e. obtaining an alternative source of raw materials, but also reduce environmental pollution. In addition, the integrated use of man-made waste can potentially reduce production costs and increase economic benefits.

One of the most problematic areas is the technology of storing high-moisture waste from metallurgical production in tailings dumps. For example, iron-containing sludge is sent through multi-kilometre sludge pipelines to a tailings dump in the form of pulp with a solid: liquid 1 mass ratio: 2. The technology requires significant costs for transporting the pulp to the tailings pond and returning the clarified water after settling into the technological cycle [[5], [6], [7], [8]]. Due to the lack of effective dewatering and fumigation technologies, these materials are usually stored in tailings dumps, where they are mixed with other slurries and dust and their metallurgical value is lost. On the other hand, at full-cycle metallurgical enterprises, when calcining limestone and raw dolomite, a large amount of finely dispersed calcium and magnesium-containing waste is formed in the form of lime and dolomite dust, which are excellent dehydrating and binding materials and, as a rule, these materials are not in demand and are stored in ash and sludge storages. Taking into account the emerging trend of reducing the total iron content in natural iron ore concentrates (45-50%), an alternative secondary raw material can be an iron-containing oxidized material obtained from high-moisture iron-containing sludge and pulverized waste from lime production and firing of crude dolomite to partially replace iron ore concentrate. This approach will reduce the need for natural iron ore and flux materials. This is possible if there is a technology for preparing sludge for metallurgical processing. In Kazakhstan, millions of tons of ash and sludge waste from various industries are deposited in sludge storages, forming man-made deposits of iron-containing and fluxing materials that can serve as secondary metallurgical raw materials and a partial substitute for natural iron ore raw materials. In addition, they are usually located near metallurgical enterprises.

Literature review

Until now, tailings disposal has remained the only common treatment option for this sludge other than recycling, but if recycled, these iron oxides have the potential to provide significant economic benefits. The technology under consideration for storing “liquid” waste from metallurgical production has several disadvantages: high one-time capital costs for the construction and operation of slurry pipelines and tailings dumps; there is a high probability of migration of harmful chemicals into groundwater if the protective screens of the base and sides of the tailings dump are damaged.

The known technology for storing ore enrichment waste in underground workings and tailings with the use of a hardening agent additive allows the use of underground workings of the enterprise with production capacity for storage [[5], [6]].

Reducing the risk to the environment by storing high-moisture metallurgical waste in underground goaves and tailings with the addition of a hardener solves important scientific, practical and social problems. This is achieved by hardening hazardous ingredients, selecting the compositions of hardening mixtures and converting them into a solid state [[6], [7], [8]].

In world practice, technologies for agglomerating mineral sludge by cold briquetting under pressure are known, based on the use of binders made of powdered materials [[9], [10], [11], [12], [13], [14], [15], [16]]. The wet sludge is mixed with suitable binding materials to obtain a homogenized mixture. The finished mixture is fed into a briquette press and after applying pressure to the mold, a briquette is obtained, which is subjected to heat treatment and firing.

Briquetting provides wide opportunities for recycling fine waste; it is also promising from the point of view of obtaining a metallized product since reducing agents can be introduced into the briquetted charge [[19], [20], [21], [22], [23], [24], [25], [26], [27]].

The advantages of briquetting are that this method makes it possible to obtain standard products with adjustable sizes and technological properties from the waste of various chemical compositions and properties, increase the density of bulk materials, prevent freezing and caking of finely dispersed waste in bins and dosing equipment, and reduce dust during transportation and use. The efficiency of using useful components in briquettes is significantly higher than in any other state (in a fine or polydisperse fraction, in sorted form). Compared to agglomeration and pelletizing, briquetting of iron-containing waste has several advantages:

- briquettes have the same shape and weight, are characterized by a high iron content, density and strength, and better transportability;
- all the oxygen in the briquette remains active, while in the agglomerate it is in a bound state (in the form of silicates), which is especially important for blast furnace production;
- environmental safety of briquetting: waste-free, no high temperatures during production;
- the possibility of using carbon-containing filler in a briquette in any ratio to activate processes in a metallurgical furnace (carburizing, reducing agent, energy carrier);
- the possibility of recycling all types of fine waste from metallurgical production.

To reduce moisture when processing sludge, thermal drying is traditionally used, which quickly reduces the moisture content in the sludge [[10], [15], [21], [27]]. Sludge dewatering by hydration of calcium and magnesium-containing materials (chemical dewatering), as a new processing technology, has the advantage of energy saving and environmental protection and its ability to reduce the volume and quantity of sludge. This method makes it possible to obtain hardened material without thermal firing [[28], [30], [31], [32]].

There are known studies on the hardening of sludge from wastewater treatment plants by hydration using cement and lime [[28], [29], [30], [31], [32]]. Cement and lime are mixed with the sludge in certain proportions to dewater the sludge and harden it. It was established that the rate of sedimentation and dewatering of the hardened sediment depended on the ratio of hardener to sludge. The higher the ratio, the more obvious the dehydration effect, and the maximum dehydration reduction value is 13%.

Currently, chemical curing is a more advanced sludge treatment method. The method eliminates the problems of low efficiency and severe pollution of traditional methods of storing sludge in a sludge reservoir or sludge fields [[28], [29], [30], [31]]. The principle of hydration of wet tailings with cement was incorporated in the above-mentioned technology of storage in abandoned mines [[5], [6], [7], [8]].

When disposing of man-made waste from metallurgical production, non-firing methods of agglomeration are increasingly effective, which have fundamental advantages in comparison with high-temperature methods of thermal drying. This is expressed in high technical and economic indicators (cost, capital and current costs, energy consumption, etc.) and environmental indicators (3-5 times reduction in the degree of environmental pollution) [[17], [18], [19], [21], [26]].

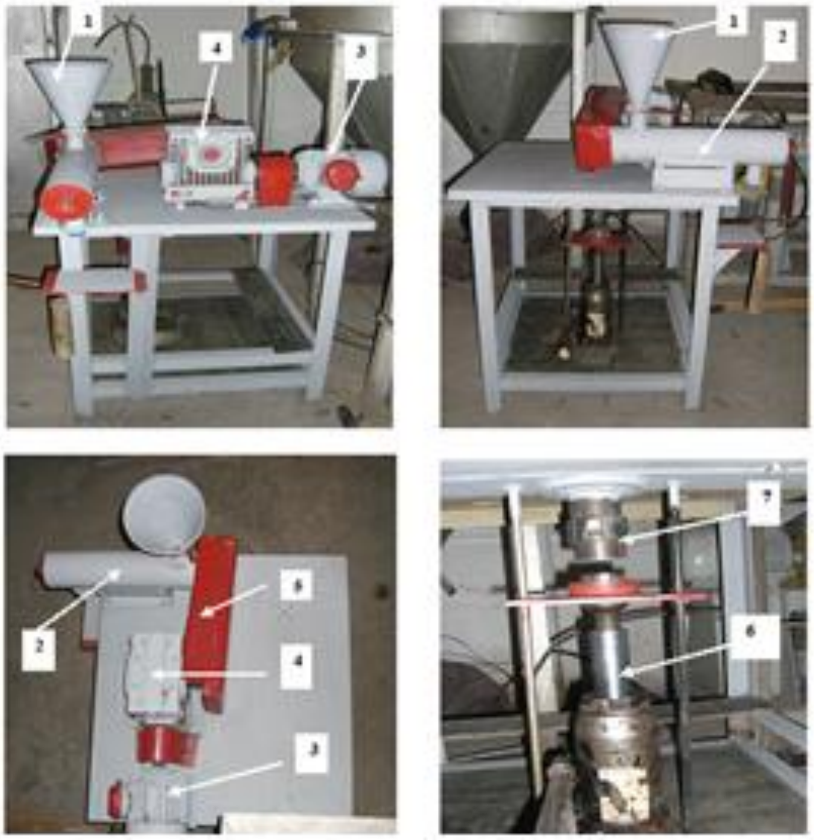
Once cured, the product must have mechanical resistance to allow some basic work such as transport and oven loading and the type of binder plays an important role. Regardless of the chosen binder, a reliable briquette should retain all of the above-mentioned properties as much as possible.

The purpose of this study was to study the possibility of producing high-strength briquettes from high-moisture iron-containing slurries by hydration with quicklime powder (chemical dehydration) in combination with dolomite dust from the dust removal system and carbon-containing dust materials and developing a drainless technology for the production of complex self-healing briquettes.

Research Methodology

When carrying out this work, we proceeded from the condition of developing a technology for the chemical dehydration of iron-containing sludge with a moisture content of 60-90%, obtaining sludge-lime mixtures without the use of complex equipment and the use of lime and dolomite dust, which are secondary material resources.

To study the processes of combining the operations of dewatering, self-hardening and agglomeration of iron-containing sludge, a laboratory installation was developed (Fig. 1) and experiments were carried out to study the conditions that ensure the production of iron-containing briquettes suitable for use in steel production.



1-receiving hopper (funnel); 2 - screw mixer (activator); 3 – electric drive; 4 - reducer;
5 - belt drive; 6 - hydraulic press; 7 - cylindrical mold

Fig. 1 - Scheme of a laboratory plant for cleaning converter gas-rich, briquetting iron-containing sludge

Table 1 - Fractional composition of components

Component	Content, % by fraction, mm							
	>2.5	1.6-2.5	1.0-1.6	0.63-1.0	0.1-0.63	0.063-0.1	0.05-0.063	<0.05
Converter sludge	-	-	-	7,8	27,2	2,8	1,2	61,0
Lime dust	15.8	11.9	10.7	7.9	23.7	11.9	13.8	4.3
Dolomite dust	-	2.0	3.3	4.0	16.0	34.0	13.3	27.4

Mixing was done manually, and the volume of materials used was measured using measuring containers. During the mixing and holding process, the temperature was measured, the time was recorded and the rate of dehydration of the mass was calculated. The mixing process lasted 5-10 minutes until a homogeneous mass was obtained.

Molding was carried out on a laboratory hydraulic press with a force of 125, 180 and 280 kN.

As source material for the preparation of slurry-lime mixtures and briquettes, converter sludge with a moisture content of 60-90% was used, taken from the slurry pipeline at the time of its pumping from radial settling tanks to the ash and sludge storage tank.

For chemical dehydration of the initial sludge, lime dust from gas purification of the KS-1000 furnace and dolomite dust from a rotary kiln were used. In the process of research in laboratory conditions, the physicochemical properties of converter sludge taken from the slurry pipeline at the time of pumping, lime and dolomite dust, and lime-slurry mixtures were studied (Table 1, 2).

When preparing experimental mixtures, the volumetric ratio of converter sludge, lime and dolomite dust varied from 0.5 to 2.0 parts by volume (Table 3).

Table 2 - Average chemical composition of components, %

Component	$C_{общ}$	$Fe_{общ}$	CaO	$CaO_{акт}$	SiO_2	MgO	MnO	AL_2O_3	P	S	п.п.п	Прочие
Converter sludge	2.60	55.60	16.40	-	2.10	2.05	1.27	1.87	0.60	0.25	10.50	7.79
Lime dust	-	-	84.90	68.0	-	0.77	-	-	-	0.02	11.0	3.31
Dolomite dust	-	5-6	44.50	-	3.71	26.52	-	1.74	-	-	15.00	7.77

Table 3 - Composition of sludge-lime mixtures

Mixture number	Content, volume fractions		
	Converter sludge	Lime dust	Dolomite dust
1	1.0	1.0	-
2	0.5	1.5	-
3	0.5	-	1.5
4	1.0	1.0	0.5
5	1.0	1.5	0.5
6	1.0	2.0	0.5
7	0.5	1.0	-
8	0.5	1.5	-
9	0.5	2.0	-

After mixing these components, various technological parameters of the resulting mixtures were determined: humidity, temperature, dehydration rate, and hardening time.

Briquettes with a diameter of 50 mm and a height of 60 mm were prepared from slurry-lime mixtures using a mechanical press at loads of 125, 180 and 280 kN/briquette. After keeping the briquettes in natural conditions for 1.5 and 15 days, their strength was assessed by crushing in a press.

Research results

The process of chemical dehydration (hydration) of converter sludge with lime and dolomite dust is characterized by an exothermic reaction between active CaO and excess moisture in the sludge. The process was accompanied by an increase in system temperature. As the research results have shown, the change in the rate of dehydration is directly proportional to the change in temperature during the process of mixing sludge pulp with dewatering components and holding, which made it possible to develop a new method for assessing the degree of chemical dehydration. The technique makes it possible to study the mechanism and kinetics of the chemical dehydration process based on the nature of changes in the temperature of the mixture.

According to the colloid-chemical theory of hardening, the chemical transformations that occur when mixing lime with sludge of high humidity are described by the following reaction:

$$3CaO \cdot SiO_2 + 4{,}5\ H_2O = CaO \cdot SiO_2 \cdot 2{,}5H_2O + 2Ca(OH)_2 \quad (1)$$

The curing process of the system is purely physical and mechanical. Calcium hydrosilicate is very slightly soluble in water, and remains in a colloidal state for a long time, gradually recrystallizing, and then compacting and strengthening. The cement paste acquires cohesion and strength and turns into a solid monolithic body. Chemical processes are completed sometime after the interaction of the binder, in our case pulverized lime, with sludge water to form a fragile loose mass.

Its transformation into a stone-like body occurs due to the formation of a crystalline intergrowth of calcium hydroxide and hydrosilicates. The hardening period is the longest and is characterized by a slight release of heat.

When the binder, in our case pulverized lime, comes into contact with excess moisture from the sludge, there is a so-called preparatory period, during which a saturated solution is formed. The heating of the mixture at this moment is insignificant, since the dissolution process is endothermic. Upon reaching saturation, the cement paste quickly heats up due to the hydration reaction.

It has been established that chemical dehydration of sludge pulp occurs through a two-stage mechanism. The first stage the process is characterized by an exothermic reaction of interaction of the dehydrating component with water with the formation of calcium hydroxide with water according to reaction (2) and occurs in the kinetic region, accompanied by an increase in temperature and rate of dehydration.

$$CaO + H_2O = CaO(OH)_2 \qquad (2)$$

It has been established that the first stage of chemical dehydration, i.e. chemical binding of moisture ends with a maximum increase in temperature (Fig. 2).

Depending on the mineralogical and dispersed composition, the initial moisture content of the sludge and the mixing speed, the intensity and speed of hydration changes.

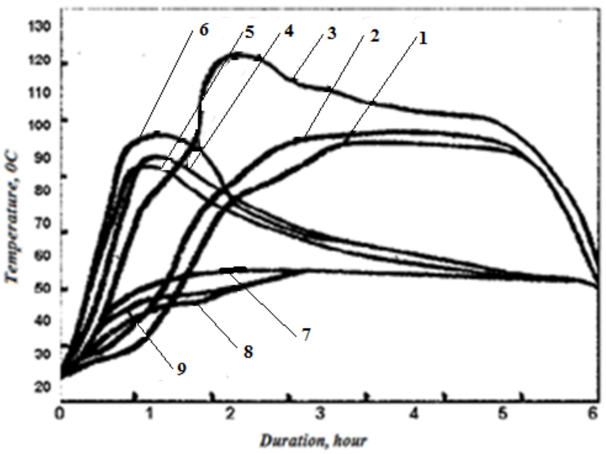


Fig. 2 - The nature of the temperature change during solidification of the slurry-lime mixture

The heat released as a result of the exothermic reaction goes to evaporate moisture. As the research results have shown, at this stage the bulk of the moisture is removed and an increase in the rate of dehydration is observed, which ends when the maximum temperature of the mixture is reached (Fig. 2). The intensity of this chemical interaction depends on the degree of mixing and the maximum area of contact of the reacting substances and the activity of CaO. In this case, the surface of the adsorbed layer of lime particles is deformed, and a more durable crystalline structure of Ca(OH)2 is formed, which cements the resulting sludge-lime mass, and also makes it possible to obtain strong briquettes from this mass. At this point, the moisture content of the mixture is 15-25% and a further decrease in the moisture content of the mixture occurs according to the law of molecular diffusion with a falling rate of dehydration and temperature of the mixture.

Further binding of residual moisture is controlled by the diffusion transport of water molecules through a thin diffusion boundary layer that forms on the surface of the dehydrating material particles. The surface, boundary layer consists of crystallized calcium hydroxide and carbonate, formed as a result of the reaction of calcium hydroxide absorbing carbon dioxide from the surrounding atmosphere according to reaction (3)

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \qquad (3)$$

At the second stage of dehydration, hardening of the mixture begins, caused by supersaturation of the wet mixture with calcium hydroxide. Crystallization centers are metal particles of sludge (iron oxides). Crystals of calcium hydroxide and calcium carbonate coalesce with other oxides present in the sludge into a relatively strong and hard mass.

Thus, the second stage of chemical dehydration generally determines the total duration of obtaining a semi-dry solid mass of sludge-lime mixture suitable for transportation and further disposal in the charge of the sintering or converter process. It has been established that the intensity of chemical dehydration, i.e. the duration of the first and second stages depends on the type of dehydrating materials, the activity of CaO, MgO in it, its fractional composition, as well as the degree of mixing of the main components.

The use of pure pulverized lime as a dehydrating component with a CaO content of at least 60% (compositions No. 7-9) is characterized by a low dehydration rate (Fig. 2). The residual moisture after the first stage is (35-40%), and hardening of this mixture continues for more than 12 hours.

The use of one pulverized lime with active CaO (75-80%) is characterized by a higher rate of dehydration (compositions No. 1-2) and a residual moisture content of 20-30%. The total time for dehydration and hardening of the mixture is 6 hours, obtaining a residual moisture content of 18-20%.

Treatment of slurry pulp with pure dolomite dust, although it reduces the duration of the first stage of dehydration to 2 hours and the residual moisture before the hardening process to 15-17%, but the sludge-lime mixture turns out to be selfdisintegrating. After 24 hours it crumbles with subsequent dusting and cannot be used in metallurgical production technology.

The best results were obtained when treating slurry pulp with a moisture content of 60-90% with a mixture of pulverized lime and dolomite (compositions No. 4-6). This reduces the duration of the main stage of dehydration until the beginning of the hardening period of the mixture. The total duration of dehydration and hardening is 3 hours. получением влажности твердой массы 10-15 %.

Treatment of sludge with lime and dolomite dust intensifies the process of chemical dehydration, which is confirmed by a higher level of temperature rise and rapid hardening of the sludge-lime mixture. This is explained by the presence of dolomite dust, in addition to CaO (45%) and the presence of MgO in it up to 27%. In addition, in dolomite dust, in addition to CaO and MgO, there are clay components - AL_2O_3, SiO_2, and Fe_2O_3, which form silicates with CaO and MgO, aluminates and ferrites of calcium and magnesium, which have high astringent properties. These compounds, when in contact with water, quickly harden in air and contribute to the formation of a fast-hardening slurry-lime mixture.

Since after the completion of the first stage of dehydration a paste-like mass with a residual moisture content of 16-30% is obtained, the possibility of combining the stages of dehydration, self-hardening and agglomeration in one technological cycle was studied

The compressive strength of briquettes produced by pressing with a force of 125, 180 and 280 kN had 94, 265 and 505 kN/cm2, respectively, and density, respectively, 2.7 kg/cm3. The number of fines less than 5 mm falling onto a steel plate from a height of 2 m was 0.6%.

Moreover, those made using dolomite dust (compositions No. 4 and No. 5) were distinguished by increased strength compared to briquettes using pure lime dust.

The humidity of the briquettes after 24 hours was 9%, and after 15 days it was in the range of 0.3-0.5% and did not lose their shape. Moreover, the strength of the briquettes practically did not change during their ageing process, and they turned out to be quite suitable for transportation via conveyor systems and transfers of charge supply paths.

If we consider the economic aspect of the proposed technology, then the most acceptable for production are compositions No. 4 and No. 5, which do not require large amounts of lime and dolomite dust.

Discussion of the research results

As shown by the results of experiments on combined chemical dehydration, self-hardening and molding processes, the strength of the resulting briquettes is affected by the heat release process in the first stage of hydration. It has been established that the maximum strength of briquettes is obtained by pressing the sludge-lime dough at the moment the mixture reaches its maximum temperature. Briquettes made earlier than this moment had low strength, which, apparently, is explained by their destruction under the influence of thermal stresses and steam release during the period of intense heating. An even greater decrease in the strength of briquettes is observed during pressing much later than the maximum heat release, probably due to the loss of thixotropic properties by the hydration products.

Research results have shown that the optimal moisture content of the charge required for the production of high-quality briquettes from iron-containing sludge should not exceed 15-20%.

A distinctive feature of the proposed method of agglomeration from all known ones is the use of the synergistic effect of moisture hydration by active calcium and magnesium oxides, accompanying self-hardening of lime paste sludge and combination with the briquetting process. New patterns have been established that have made it possible to develop a non-firing method for obtaining agglomerated material in the form of self-healing briquettes from iron-containing sludge and waste dusty materials (lime and dolomite dust and carbon-containing dust).

The proposed technology does not require drying or firing, and strength properties are gained when the material is cooled in air for 24 hours.

The established patterns of chemical dewatering of iron-containing sludge with dust-like waste from the production of lime and dolomite made it possible to develop a drainless technological scheme for the production of iron-containing briquettes (Fig. 3).

A closed sludge recycling cycle is envisaged, in which the water will be drained for reuse, and the condensed sludge will be used in full to prepare a sludge-lime mixture.

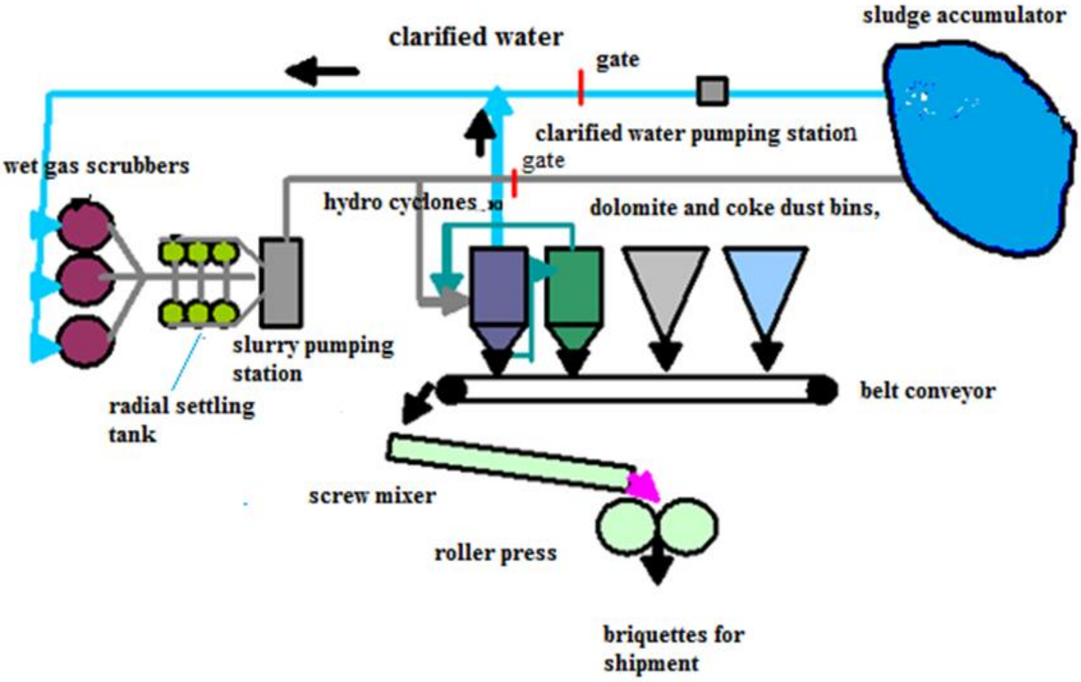


Fig. 3 - Technological scheme for the production of sludge-lime briquettes for converter production
Note: The drawing was created by the author

Currently, pumps pump converter sludge from radial settling tanks to the ash and sludge storage tank three times a day, 650 m3 each, which is about 2000 m3 per day. The interval between pumping sludge is 5-7 hours. The main technological operations will take place in this interval.

The positive side of this method is that there is no need to wait for the sedimentation of solid particles of sludge, as is used in settling tanks; the entire technological process of preparing for sludge disposal occurs while pumping the sludge through the sludge pipeline. The estimated moisture content of sludge after hydrocyclones is about 50%.

Drainless technology is carried out as follows. Slurry from wet gas cleaning technology or systems is pumped directly to the proposed installation (Fig. 2), to a dewatering unit, where the slurry is dewatered in pressure hydroclones GNS-500 and GNS-250, to a moisture content of 40-50%. The condensed sludge is sent to a conveyor, where pulverized lime and/or pulverized dolomite, as well as screening of coke breeze or pulverized coal, are dosed. Materials from the conveyor are fed into a two-roll screw mixer-activator, where the processes of mixing and chemical dehydration are carried out. From the mixer, the dehydrated heated sludge-lime mixture enters a press (roller or vibropress), where the processes of final hardening and molding occur and at the output we obtain agglomerated material in the form of a briquette with a moisture content of 5-9%. Briquettes are stored on pallets for cooling at ambient temperature. Clarified water from the hydrocyclone is pumped out and returned to the technology.

The performed technical and economic calculations showed that the construction of the site and the use of the slurry-lime mixture in the sinter production charge according to the proposed method of chemical dehydration of waste from the production of lime and dolomite, with the disposal of 70 thousand tons of converter sludge, will save 52.5 thousand tons of iron ore annually, 2. 8 thousand tons of manganese ore, 7.0 thousand tons of fuel equivalent and 21.0 thousand tons of limestone. The effect is achieved by saving iron ore materials and replacing them partially with iron contained in sludge and lime, as well as by reducing budget payments for environmental pollution.

The proposed technology makes it possible to create a closed water supply system not through a purification pond (sludge reservoir), but through the proposed installation, which significantly reduces water consumption, labor and energy costs for transporting the pulp through many kilometres of slurry pipelines to the sludge reservoir and returning clarified water to the technology, as well as the costs of maintaining slurry pumps, slurry pipelines and sludge accumulators.

Thus, iron ore slurry in the form of agglomerated composite material can be used as a substitute iron ore concentrate in end-to-end technology for smelting steel and cast iron. There is no need to allocate land for sludge storage and achieve more complete recycling of industrial waste.

The proposed project is the basis for the creation of closed metallurgical environmentally friendly resource-saving processes that solve not only the problems of raw materials and maximum involvement of waste in economic circulation but also environmental problems of production.

The competitiveness of the proposed technology compared to other analogues is as follows:

- transportation and storage of sediments in a sludge storage tank is eliminated;
- labour and energy costs for transportation and storage of sludge, maintenance of slurry pumps, slurry pipelines and sludge accumulators are reduced;
- there is no need to dry the sludge before agglomerating and firing iron ore briquettes;
- organizing a one-stage process of dehydration, self-hardening and molding to produce complex iron-carbon-containing agglomerated material in one production cycle;
- dispose of waste dusty waste from burning lime and dolomite, as well as screenings of coke or coal.

This version of the technology was introduced at ArcelorMittal Temirtau JSC in the water supply shop for the dewatering of oil-containing and iron-containing waste from rolling production (oily scale) using powdered lime and dolomite dust to produce lime scale for sintering production [33].

Conclusion

The study of the physicochemical conditions of hydration processes, temperature and time parameters of the process made it possible to select active dehydrating materials and their optimal ratios, which significantly increase the degree of hydration of the composite system and the period of the beginning and end of self-hardening. The conditions for combining the processes of dehydration, and self-hardening with molding processes when applying external pressure to the hardening mixture in a mold with the production of agglomerated material in the form of a briquette in one technological cycle are considered, which is one of the main provisions of the scientific novelty of the proposed method. Optimal conditions have been established for the production of high-strength briquettes suitable for metallurgical production technologies, excluding the stages of thermal drying and firing, and the development of strength properties occurring in air.

The method makes it possible to obtain self-healing agglomerated material by introducing a carbon-containing reducing agent into a self-hardening slurry-lime mixture. Cheap waste materials are used as dewatering material dusty waste from burning limestone and dolomite, and dusty carbon-containing materials (coke and coal screenings) as a reducing agent.

In contrast to known technical solutions, the proposed technology and the method incorporated in it eliminates the storage of iron-containing sludge in a sludge storage facility and makes it possible to organize a drainless scheme of non-firing agglomeration and the production of complex self-healing iron-containing material for the production of steel and rolled products. The technology will make it possible to organize production for the processing of high-moisture iron-containing sludge, dusty calcium- and magnesium-containing and carbon-containing dusty waste and also solve the problems of environmental pollution and land acquisition for storage of production waste.

The proposed technology solves not only technological, but also environmental problems: reducing environmental pollution and land allocation for storage of industrial waste, reducing environmental charges for waste storage, as well as pollution of off-balance and groundwater.

The self-hardening properties of sludge when treated with dewatering materials based on industrial waste can also be implemented for the disposal of hazardous sludge waste, for example in abandoned mines. This will prevent contaminated water from entering water bodies while eliminating the need for the construction and maintenance of ash and sludge storage tanks without the danger of breaking dams and flooding adjacent arable lands.

Ash and sludge waste dewatered using the proposed method can be used for landscape work, as well as in the industry for the production of various building materials.

Conflict of interest. The authors declare that they have no conflict of interest about this research, whether financial, personal, authorship, or otherwise, that could affect the research and its results presented in this paper.

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Металлургиялық өндірістегі ылғалдылығы жоғары темірі бар шламды күйдірмей өңдейтін әдіс

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ТҮЙІНДЕМЕ

Бұл зерттеудің мақсаты шаңды кетіру жүйесіндегі доломит шаңымен және құрамында көміртегі бар шаң материалдарымен үйлесімде сөндірілмеген әк ұнтағымен гидратация (химиялық сусыздандыру) арқылы ылғалдылығы жоғары темірі бар шламдардан беріктігі жоғары брикеттерді алу мүмкіндігін зерттеу және осы негізде өздігінен қалпына келетін кешенді брикеттерді өндірудің ағынсыз технологиясын жасау болды. Гидратация процесінің физика-химиялық жағдайлары, процестің температуралық-уақыттық параметрлері зерттелді, композиттік жүйенің гидратация дәрежесін айтарлықтай арттыратын белсенді сусыздандыру материалдарын таңдау және олардың оптималды арақатынастары, басталу мен аяқталу кезеңі және өздігінен қатаюы анықталды. Бір технологиялық циклде брикет түріндегі агломерацияланған материалды өндірумен қалыптағы қатайтатын қоспаға сыртқы қысым түсіру кезінде сусыздандыру, өздігінен қатаю процестерін қалыптау процестерімен біріктіру шарттары қарастырылады, бұл ұсынылған әдістеменің ғылыми жаңалығының негізгі ережелерін құрайды. Термиялық кептіру және күйдіру кезеңдерін қоспағанда, металлургиялық өндіріс технологияларына жарамды беріктігі жоғары брикеттерді өндіру үшін оңтайлы жағдайлар белгіленді және беріктік қасиеттерінің жиынтығы ауада қалыптасады. Әдіс құрамында көміртегі бар тотықсыздандырғышты өздігінен қататын суспензия – әк қоспасына қосу арқылы өздігінен түзілетін агломерацияланған материалды алуға мүмкіндік береді. Құрғататын материал ретінде әктас пен доломитті күйдіргеннен қалған ұнтақталған арзан қалдықтар, ал тотықсыздандырғыш ретінде құрамында көміртегі бар материалдар (кокс және көмір скринингтері) пайдаланылады. Белгілі техникалық шешімдерден айырмашылығы, ұсынылған технология мен оған енгізілген әдісте шлам қоймасында темірі бар шлам сақталмайды және күйдірмейтін агломерацияның ағынсыз схемасын ұйымдастыруға және болат пен прокат өндіруге арналған құрамында темірі бар өздігінен қалпына келетін материалды өндіруге мүмкіндік береді. Технология ылғалдылығы жоғары темірі бар шламды, құрамында кальций мен магнийі және көміртегі бар шаңды қалдықтарды өңдеу бойынша өндірісті ұйымдастыруға мүмкіндік береді, сонымен қатар қоршаған ортаны ластамау және өндірістік қалдықтарды сақтау үшін қажетті жерді алу мәселелерін шешеді.

Түйін сөздер: шлам, шаң, өңдеу, сусыздандыру, агломерация, брикеттеу.

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Безобжиговый способ переработки высоковлажных железосодержащих шламов металлургического производства

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АННОТАЦИЯ

Целью данного исследования было изучить возможность производства высокопрочных брикетов из высоковлажных железо-содержащих шламов гидратацией негашеной пылевидной известью (химическое обезвоживание) в комбинации с доломитовой пылью из системы обеспыливания и углеродсодержащих пылевидных материалов и разработки на этой основе бессточной технологии производства комплексных самовосстанавливающих брикетов. Исследованы физико-химические условия процесса гидратации, температурно-временные параметры процесса, определен выбор активных обезвоживающих материалов значительно повышающих степень гидратации композитной системы и их оптимальных соотношений, период начало и конца самоотвердения. Рассмотрены условия совмещения процессов обезвоживания, самоотвердения с процессами формования при приложении внешнего давления к твердеющей смеси в пресс-форме с получением окускованного материала в форме брикета в одном технологическом цикле, что составляет одно из основных положений научной новизны предложенного способа. Установлены оптимальные условия получения высокопрочных брикетов пригодных для технологий металлургического производства, исключающих стадии термической сушки и обжига, а набор прочностных свойств происходит на воздухе. Способ позволяет получать самовосстанавливающий окускованный материал введением в шламоизвестковую самотвердеющую смесь углеродсодержащего восстановителя. В качестве обезвоживающего материала используются дешевые бросовые пылевидные отходы обжига известняка и доломита, а в качестве восстановителя пылевидные углеродсодержащие материалы (отсевы коксика и угля). В отличие известных технических решений предлагаемая технология и способ заложенной в ней исключает складирование железосодержащих шламов в шламохранилище и позволяет организовать бессточную схему безобжигового окускования и производство комплексного самовосстанавливающего железосодержащего материала для производства стали и проката. Технология позволят организовать производство по переработке высоковлажных железосодержащих шламов, пылевидных кальций- и магнийсодержащих и углеродсодержащих пылевидных отходов и решает также проблемы загрязнения окружающей среды и отвода земель для хранения отходов производства.

Ключевые слова: шлам, пыль, переработка, обезвоживание, окускование, брикетирование.

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Metallurgy

Influence of silica on the crystallization of sodium hydroaluminate

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ABSTRACT

To extract aluminium from highly concentrated aluminate solutions of alumina-containing raw materials, decomposition is performed through the crystallization of sodium hydroaluminate. This paper presents the results of a study on the stability of aluminate solutions. To calculate the probable yield of Al_2O_3 in the solid phase, it is necessary to determine the crystallization rate of sodium hydroaluminate according to the composition of the initial solutions and the conditions of the process. The influences of SiO_2 content on the decomposition of aluminate solutions with Na_2O_k concentrations of 540 g/dm^3 and 590 g/dm^3 with and without inoculum were studied. In addition, the influence of silica on the appearance of precipitating crystals of sodium hydroaluminate was considered. A sharp increase in the stability of the aluminate solutions at rest in the presence of silica was observed. Different crystallization conditions for sodium hydroaluminate have been investigated. Silica slows the crystallization process of sodium hydroaluminate, affecting both the nucleation and crystal growth rates. The effect of SiO_2 on the rate of decomposition is similar to the reduction in the degree of supersaturation.

Keywords: Alumina solution, silica, sodium hydroaluminate.

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Introduction

The sintering and Bayer methods are used to process alumina-containing raw materials used in industry [[1], [2], [3], [4], [5]]. Processing by the hydrochemical alkaline method results in high-modulus aluminate solutions with caustic modulus ($α_k$) values of 6–12. The properties of aluminate solutions significantly depend on the technological process [[6], [7], [8], [9][10]]. Two methods are used for aluminium extraction from the obtained aluminate solutions: decomposition and carbonization [[11], [12], [13], [14]].

Aluminium hydroxide precipitation is performed by the spontaneous decomposition of supersaturated solutions.

When $Al(OH)_3$ is separated by carbonization, the solution is treated with CO_2-containing gases.

When opening high-siliceous aluminosilicate rocks with hydroalkali technology, high-modulus aluminate solutions are obtained. In addition, spontaneous decomposition of these solutions with aluminium hydroxide extraction is impossible, and carbonization is economically unfeasible due to the transfer of expensive caustic alkali into carbonate products. Therefore, for aluminium extraction from highly concentrated aluminate solutions, a decomposition method based on the crystallization of sodium hydroaluminate is used. Then, the obtained product is dissolved in industrial water to obtain aluminium hydroxide by decomposition.

The crystallization process is a bottleneck of the hydrochemical method. The obtained solid phases are finely dispersed, contain a large amount of entrained mother liquor and are poorly filtered; additionally, the resulting solution has a high caustic modulus (1.8-2), which adversely affects the subsequent conversion–decomposition process [11].

To calculate the probable yield of Al_2O_3 in the solid phase, it is necessary to determine the crystallization rate of sodium hydroaluminate according to the composition of the initial solutions and the conditions of the process. Of great importance for the crystallization of sodium aluminate is the presence of silica in the solution.

Silicon is the main impurity in bauxite, and is also one of the most harmful impurities in the process of the alumina production using alkaline method such as the conventional Bayer process [15]. The presence of even small amounts of silica in Oaluminate solutions sharply inhibits the crystallization of sodium hydroaluminate. To realize its recycling, the alkali-silicate solution needs to be desiliconized [16]. After leaching by a hydrochemical method, the solutions contain a maximum of 10 g/dm^3 SiO_2, from which only a small part of the Al_2O_3 can be separated into a solid phase. Moreover, the crystallization process proceeds at a very low rate. Therefore, it is necessary to purify the solution from silica.

There is a known method [17] in which some silica is removed from high-modulus aluminate solutions by decreasing the solubility of sodium aluminosilicate in relatively low-concentration Na_2O_c solutions. For this purpose, the solutions are diluted to 300 g/dm^3 Na_2O and stirred at 90 °C for 2–3 h. The silica in this case precipitates in the form of sodium aluminosilicate. Therefore, the silicon modulus of the μ_{Si} solution (mass ratio of Al_2O_3/SiO_2) increases from 7–10 to 50–100. A similar method combining desiliconization with sludge separation was recommended in the literature [18]. In the process of bauxite sintering, CaO is added to bind SiO_2 and obtain $2CaO\text{-}SiO_2$ [[19], [20]]. CaO is not used during the hydrochemical processing of high-modulus bauxite with a silicon modulus exceeding 7, since the SiO_2 content is low enough, and the losses are insignificant [21].

The deep desiliconization of aluminate solutions with silicon moduli (μ_{Si}) of 8–12 can be performed by binding silica to hydrogenates in the polythermal regime. Studies on the conditions allowing the decomposition of unsilicified aluminate solutions have not been carried out.

The distribution of Na, Al, and Si between the solid and liquid phases depends on the chemical compositions of the silicate and aluminate solutions [22].

The influence of SiO_2 on the rate of decomposition of aluminate solutions and the formation of hydroaluminate crystals under different conditions has not been sufficiently clarified, and the mechanism of silica action in this process remains unclear. This work aims at studying the influence of silica on the production of sodium hydroaluminate.

Materials and methods

The kaolin sample from Alexeevskoe deposit was used in this study. The sample was determined to contain Al_2O_3 35.6%; SiO_2 43.2% and other components 21.2%, the silicon modulus was 0.6. The kaolin sample was submitted to autoclave leaching using 240 g/ dm^3 Na_2O for 90 min at 240°C. Obtained solution was evaporated to a concentration of 540 g/dm^3 of Na_2O in total; 115.5 g/dm^3 of Al_2O_3; and 0.609 g/dm^3 of SiO_2 with a μ_{Si} of 7.5–8.5. Silica was added as an alkaline sodium silicate solution containing 550 g/dm^3 of Na_2O_{cu} and 200 g/dm^3 of SiO_2. The solution with added silicate solution was heated until it boiled and then cooled to the experimental temperature.

Leaching was carried out in a thermostat with a stirrer.

The resulting precipitates were X-ray amorphous, and the phase composition could not be identified by X-ray diffraction (XRD) analysis. Consequently, we indirectly determined their compositions from the values of μ_{Si} and α_k (caustic modulus).

Experimental part

The decomposition kinetics of solutions with a Na_2O content of 540 g/dm^3 (α_k=8) in the presence of different amounts of silica are shown in Figure 1. These experiments were carried out without inoculum since it was possible to trace the influence of silica on nucleation in this case. Stirring was performed at a speed of 15 rpm.

The obtained data show that small amounts of silica (from 0.3 to 0.6 g/dm^3) affect the initial period of crystallization. In this case, the average rate of the process decreases sharply, especially at the maximum point, but the content of SiO_2 in solution practically does not change. The effect of 0.8 g/dm^3 of SiO_2 (μ_{Si} = 136) is more noticeable than that of a smaller amount. At a SiO_2 content of 1.7 g/dm^3 (μ_{Si} = 64, curve 4), the rate decreases throughout the process. After 5 h of stirring, the Al_2O_3 content in the solution is 21.4 g/dm^3 instead of 14.5 g/dm^3 at an SiO_2 content of 0.3 g/dm^3. However, this amount of SiO_2 has a negligible effect on the alumina yield (80–86%). With the addition of 2.6 g/dm^3 of SiO_2 (μ_{Si} = 40), an induction period appears, and the maximum rate of the is approximately halved; however, after 3 h, approximately 70% of the Al_2O_3 is released into the solid phase. Thus, even without inoculum, sodium hydroaluminate can be isolated from solutions containing 540 g/dm^3 of Na_2O with a silicon modulus of 40 at a satisfactory rate. It is known [23] that for solutions containing 500 g/dm^3 of Na_2O_k (α_k=7) at μ_{Si} = 50 in the presence of an inoculum for 7 h equivalent to either 2.5% of the solution weight or 33% of the solution Al_2O_3 content precipitates only 50% of the Al_2O_3, and only at μ_{Si} = 100 is the yield 73%.

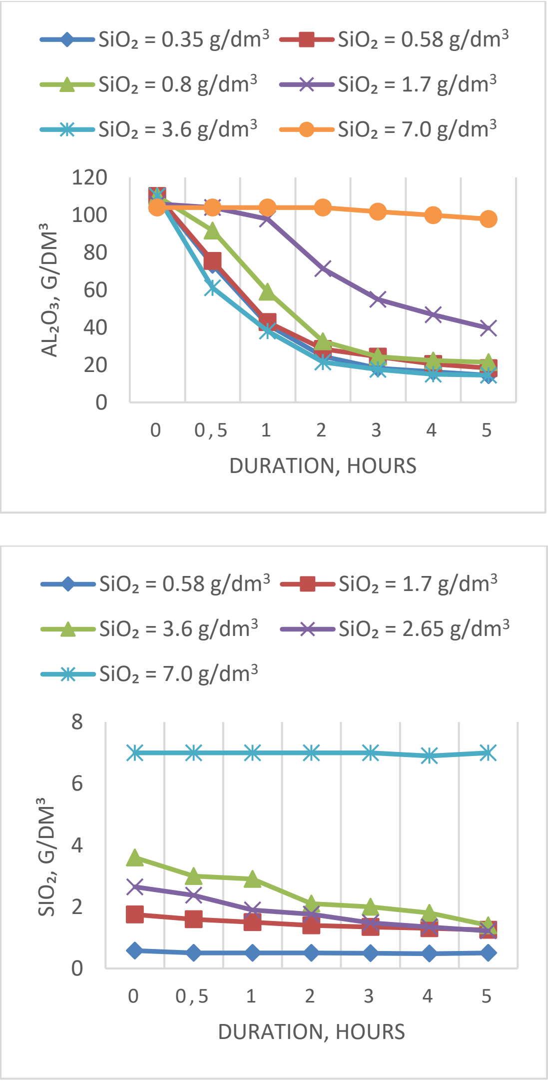

Figure 1 - Kinetic curves of the decomposition of aluminate solutions with a Na_2O_k concentration of 540 g/dm^3 depending on the SiO_2 content

A higher Al_2O_3 content (μ_{Si} = 30) in the solution with a Na_2O_k concentration of 540 g/dm^3 considerably slows the process. Even with stirring for 3 d (10 g/dm^3 of SiO_2), the concentration of Al_2O_3 in the solution is 48 g/dm^3. The SiO_2 content in the solution first gradually and then sharply decreases in the first hour of stirring. The silicon modulus of the solutions with low SiO_2 contents (0.3–0.9 g/dm^3) gradually decreases, and at 2.6–3.6 g/dm^3, the silicon modulus peaks, which agrees with the data in the present work. The final μ_{Si} at an SiO_2 content of 0.6 g/dm^3 in the initial solution is low and equals approximately 17 at 1.7 g/dm^3. The silicon modulus of the mother solution is low because silica is practically not removed from it, and a small amount of aluminium oxide is present. For the silica-rich solutions, the μSi after 5 h of stirring is 25–27.

The effect of silica on the average rate of decomposition of the solutions is similar to the decrease in the degree of supersaturation [24]. The solubility of aluminosilicate in aluminate solutions increases with increasing Na_2O_k concentration, while the solubility of sodium hydroaluminate decreases. Under these conditions, we attempt to isolate aluminate from high-silica aluminate solutions.

While decomposing aluminate solutions with a Na_2O_k content of 590 g/dm^3 at α_k = 8 and a temperature of 45 °C (Figure 2), the presence of 2.3 g/dm^3 of SiO2 (μ_{Si} = 47) does not substantially affect the crystallization rate of sodium hydroaluminate. At a SiO_2 content of 4.6 g/dm^3 (μ_{Si} = 27), decomposition proceeds at a noticeably reduced rate, but after 5 h of stirring, 77% of the Al_2O_3 is released into the solid phase. In the presence of 6.5 g/dm^3 of SiO_2 in the solution, 70% of the Al_2O_3 precipitates during this time interval. Thus, the decomposition process proceeds at a satisfactory rate, even when the silicon modulus of the solution is 20.

The SiO_2 content decreases during the first 2 h of stirring and remains almost unchanged afterward. The silica modulus of the solution gradually decreases by a factor of 2 after 5 h.

Most of the silica (>50%) remains in the solution, and its amount does not decrease when stirred with sodium hydroaluminate precipitate; this result is in good agreement with previously obtained data [3].

Precipitation from solutions with 540 g/dm^3 of Na_2O_k (stirring at 15 rpm) has a caustic modulus in the range of 1.8–2.0. For solutions with a Na_2O_k content of 590 g/dm^3, the caustic modulus is 1.7–1.9. In the latter case, after stirring at 80–90 °C for 2 h and cooling to 45 °C, precipitates with a low alkali content (α_k = 1.5–1.6) are obtained.

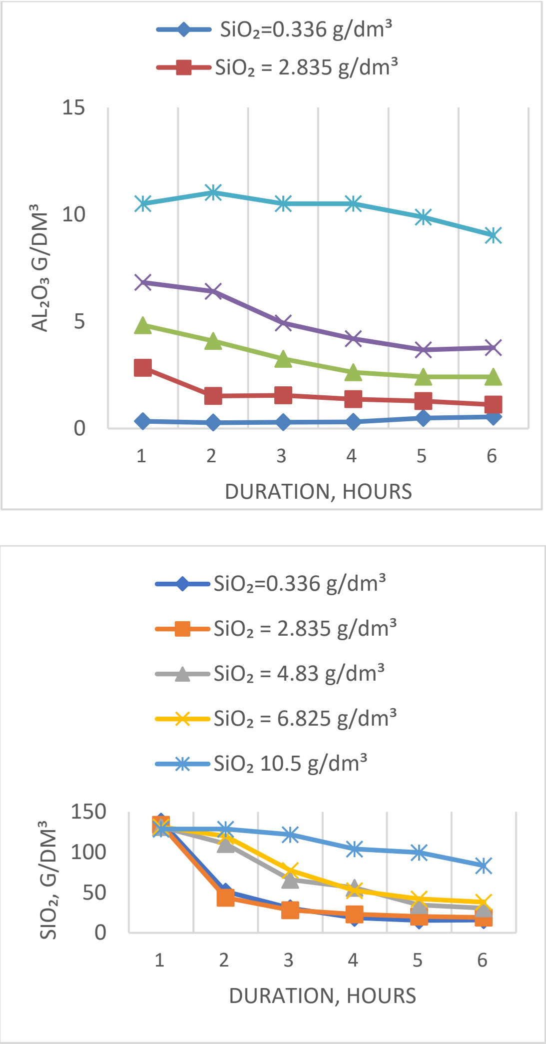

Figure 2 - Kinetic curves of decomposition of aluminate solutions with Na_2O = 590 g/dm³ in the presence of different amounts of silica

Microscopic examination of the solid phases shows that sodium hydroaluminate is represented by large crystals (200–1000 microns), and the crystals are not faceted. This morphology complicates the filtration process (Figures 3 and 4).

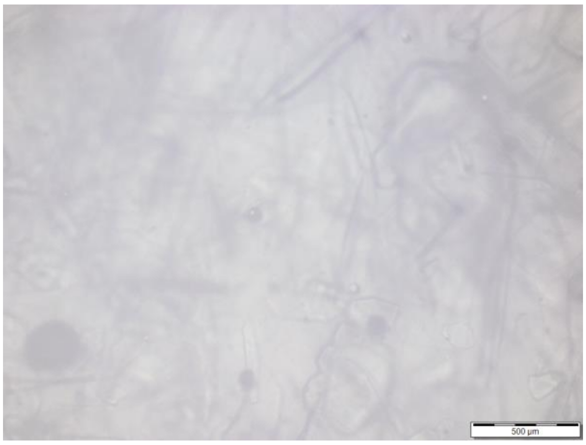

Figure 3 - Sodium hydroaluminate precipitate, 40×

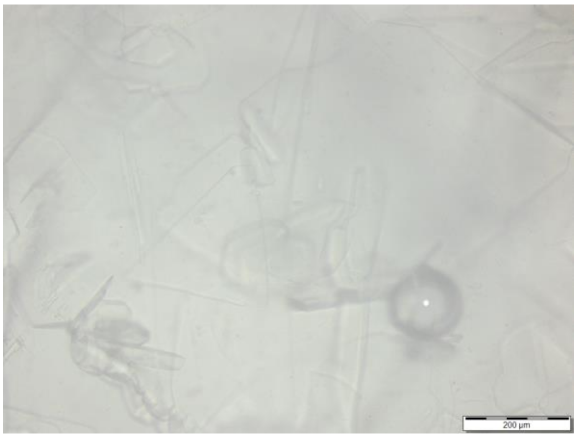

Figure 4 - Precipitate of sodium hydroaluminate, 100×

If the influence of silica on the crystallization of sodium hydroaluminate is reduced to adsorption, it is likely that introducing additional inoculum into the solution can remove SiO_2, thus accelerating the crystallization process [24].

According to the literature [25], when using a dispersed inoculum, the degree of maximum decomposition is 73.9% after 7 h.

The results of studying the decomposition of aluminate solutions containing silica in the presence of inoculum are given below. The size of the initial aggregates ranges from 200 to 1000 microns.

The solutions are stirred with the inoculum at a speed of 85 rpm. The obtained data are shown in Figure 5. In the presence of inoculum equivalent to 16% of the Al_2O_3 content in an aluminate solution containing 10 g/L of SiO_2 (μ_{Si} = 10), no induction period is observed on the kinetic curves. After 1 h, approximately 15% of the Al_2O_3 is released, after which the crystallization is very slow (3% Al_2O_3 in 4 h). When 16% of the inoculum is added to the solution after stirring for 1–2 h, the curve again shows a jump. After 4 h, 35% of the Al_2O_3 is released. Thus, each new portion of inoculum (16%) contributes to the crystallization of 18% Al_2O_3; specifically, to isolate 70% of sodium hydroaluminate, approximately 70% of the inoculum is needed.

A similar pattern is observed in the presence of 5.0 and 3.3 g/L of SiO_2 (μ_{Si} = 20 and 32). The alumina yields after are 60 and 75% in the presence of 5.0 and 3.3 g/L of SiO_2, respectively, which are significantly greater than those previously obtained in the presence of 37.5% inoculum (probably coarse crystalline). These data show the principal possibility of sodium hydroaluminate extraction from nondispersed solutions. However, the precipitates formed in this case are finely dispersed and contain a large amount of alkali (α_k = 2–3).

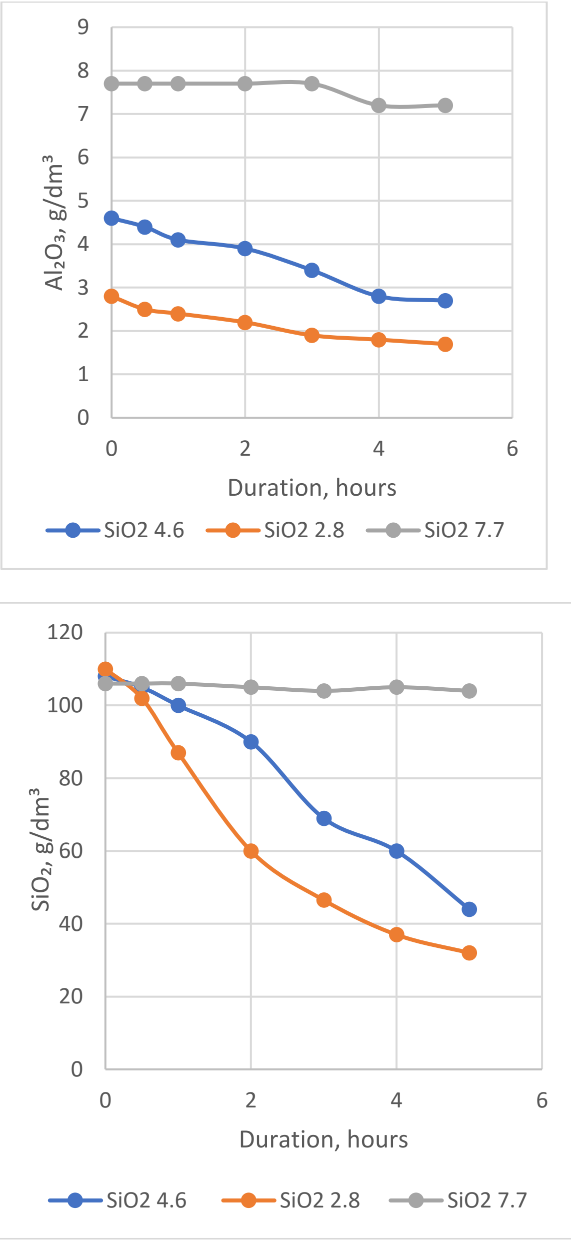

Figure 5 - Kinetic curves of aluminate solution decomposition in the presence of inoculum

Microscopic examination of many precipitates shows that in the presence of 2–3 g/L of SiO_2, monosodium hydroaluminate crystals grow in the form of thin plates with pelletized tops. The dispersibility of the precipitates is related to the conditions of production, depending on the concentrations of Na_2O and Al_2O_3, the temperature, and the method and speed of mixing, which should be the same as those in pure solutions to ensure that the difference in α_k is nonsignificant. Sometimes, without inoculum, relatively large crystals grow with increasing SiO_2 content in solution. Small crystalline precipitates (1–3 µm) are difficult to study by the crystal–optical method. Therefore, for this purpose, large crystals of sodium hydroaluminate (reaching 200 µ) are obtained by stirring the solutions in rotating nickel autoclaves at temperatures of 45 and 85°. The Na_2O_k contents of the solutions are 532 and 620 g/L, and the caustic moduli are 4, 8 and 12. Silica is added at a concentration of 10 g/L. The appearance of hydroaluminate crystals obtained in the presence of silica is very different from that of crystals precipitated from pure solutions. Thus, thin, rounded flakes form from solutions with α_k =8–12 (532 and 620 g/L of Na_2O) at 45° (Figure 6). The cross sections are shaped like elongated lenticels with high interference colours. From solutions with α_k =4 and Na_2O concentrations of 532 and 620 g/L (45 and 85 °C), various oval and rounded aggregates are formed (Figure 6 (c)). At α_k =12 (620 g/L) and α_k =8 (530 g/L), round lamellar crystals grow, with similar small formations appearing on the surface (Figure 6 (2)). Without silica, 8-cornered laminae form under these conditions. From a solution with α_k =8 (620 g/L) at 85 °C, crystals (Figure 6 (e)) precipitate (Figure 6 (2)), which have a pronounced stepped surface, sometimes in the form of typical helical dislocations. From pure solutions, well-bounded 12-angular plates are formed in this process. When aluminate solutions with α_k =8 and a Na_2O concentration of 620 g/L (45 °C) decompose, clear crystals precipitate instead of forming plates, as shown in Figure 6 (e). No sodium aluminosilicate crystals are observed in the precipitate. There is a tendency for the light refractive indices of sodium hydroaluminate to decrease. For precipitates obtained at 45°, mainly the ray of ordinary light (No; 0.005–0.007 decreases). Crystals formed in the presence of silica at 85° have a ray of extraordinary light (Ne) with a lower value than that of pure precipitates.

In the presence of 7.8 g/L of SiO_2 during 5 h of contact, the content of Al_2O_3 in the solution almost does not change, and despite the high silica content, the latter is not deposited on the surface of the seed in appreciable amounts.

At a SiO_2 content of 4.6–2.8 g/L in the initial solutions, the crystallization process proceeds at a relatively high rate. The amount of silica in the solution gradually decreases.

If sodium hydroaluminate does not crystallize, the silica is not deposited on the inoculum in appreciable quantities. In general, hydroaluminate and silica are deposited together, which indicates is a relationship between Al_2O_3 and SiO_2 in the solution.

Results and discussion

The effect of silica on the stability of aluminate solutions and the appearance of precipitating sodium hydroaluminate crystals is noted. The stability of aluminate solutions at rest in the presence of silica increases dramatically.

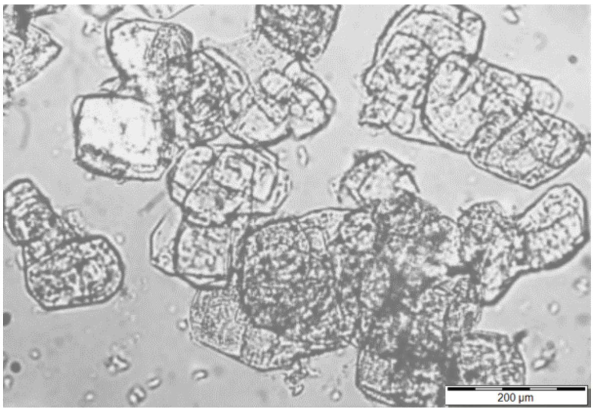

Figure 6 - Sodium hydroaluminate precipitate in the presence of SiO_2, 100×

When standing solutions with a Na_2O content of 500–520 g/L (α_k =8) in the presence of 0.2 g/L of SiO_2, sodium hydroaluminate precipitates after 1–2 d. At SiO_2 =3 g/L, the solution does not decompose within 7 d, and at 7–10 g/L, the solution is stable for approximately one month. With the mechanical stirring of these solutions, an induction period occurs, and the amount of SiO_2 in the solution increases. During the crystallization of sodium aluminate in the presence of a large amount of inoculum with different dispersity degrees, no preferential deposition of silica can be observed. In general, the sodium aluminate is released into the solid phase only during the simultaneous crystallization of sodium hydroaluminate. With the introduction of the active inoculum, a new portion of the hydroaluminate crystallizes with the silica. These phenomena lead to the concept that the effect of SiO_2 is a consequence of the poisoning of active centres on the seed crystals and acts on the state of sodium hydroaluminate in solution. However, the effect of silica is not limited to the formation of sodium aluminosilicate because it binds a relatively small part of dissolved aluminium, thus slightly decreasing the degree of supersaturation of solutions by 0.2–0.5 at C_p–S_n/S_n = 5.5–7.

The increase in the degree of saturation at an unchanged SiO_2 content in solution is similar to the decrease in silica concentration. In solutions with concentrations of Na_2O (590 g/L), the solubility of aluminosilicate increases, and as a result, its influence on the crystallization rate of sodium hydroaluminate decreases. The interaction of sodium silicate with surface molecules of aluminate and the adsorption of aluminosilicate from the solution, occurs at the sites with the highest surface energy, which include the tops of crystals.

Further deposition of hydroaluminate molecules occurs mainly on the faces; thus, the crystals have a rounded shape. The formed crystals have a mosaic structure, and the entrained aluminosilicate is distributed in the form of single molecules or small groupings on the surface of the cells since X-ray analysis does not reveal any change in the interplanar distances. Moreover, free aluminosilicate is not detected in the sediments.

The stability of aluminate solutions at rest in the presence of silica increases dramatically. For standing solutions with a Na_2O content of 500–520 g/L (α_k =8) in the presence of 0.2 g/L of SiO_2, sodium hydroaluminate precipitates in 1–2 d. At SiO_2 =3 g/L, the solution does not decompose within 7 d, and at 7–10 g/L, the solution is stable for approximately one month.

Conclusions

Different crystallization conditions for sodium hydroaluminate have been investigated. Silica slows the crystallization process of sodium hydroaluminate, affecting both the nucleation and crystal growth rates. The effect of SiO_2 on the rate of decomposition is similar to the reduction in the degree of supersaturation.

At a Na_2O concentration = 540 g/L (α_k =8), the crystallization of sodium hydroaluminate even without inoculum proceeds at a satisfactory rate (70% Al_2O_3 in 5 h) at μ_{Si} = 40. When the Na_2O content increases to 590 g/L, the solutions with μ_{Si} =19 decompose quickly. Moreover, approximately half of the SiO_2 remains in the liquid phase.

The possibility of crystallization of sodium hydroaluminate from nonsilica aluminate solutions (SiO_2 content reaching 10 g/L, Na_2O content of 500–530 g/L, and α_k =8) by introducing a large amount of inoculum has been established.

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

Author Contributions CRediT: **R. Abdulvaliyev**: Conceptualization, writing original draft preparation **S. Gladyshev**: Methodology, writing – review and editing **N. Akhmadiyeva**: Data curation, writing – review and editing. **G. Ruzakhunova:** formal analysis**, S. Tugambay:** formal analysis.

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Кремнийдің натрий гидроалюминатының кристалдануына әсері

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ТҮЙІНДЕМЕ

Жоғары концентрлі алюминат ерітінділерінен алюминий алу үшін құрамында алюминий оксиді бар шикізатты өңдеу кезінде натрий гидроалюминатының кристалдануымен ыдырау әдісі қолданылады. Al_2O_3-тің қатты фазаға ықтимал шығымдылығын есептеу үшін бастапқы ерітінділердің құрамына және процестің шарттарына байланысты натрий гидроалюминатының кристалдану жылдамдығын білу қажет. Ерітіндіде кремнеземнің болуы натрий алюминатының кристалдану процесі үшін үлкен маңызға ие. Мақалада алюминат ерітінділерінің тұрақтылығын зерттеу нәтижелері берілген. SiO_2 мөлшерінің Na_2O_k концентрациясы 540 г/дм^3 және 590 г/дм^3 болатын алюминат ерітінділерінің бұрын дайындалған натрий гидроалюминат түріндегі (затравканы) қосып және қоспай алюминат ерітінділерінің ыдырауына әсері зерттелді. Кремнеземнің түзілетін натрий гидроалюминатының кристалдарының сыртқы түріне әсері қарастырылды. Алюминат ерітінділерінің кремнеземнің қатысында тыныштықтағы тұрақтылығының күрт жоғарылауы анықталды. Натрий гидроалюминатының кристалдануының әртүрлі шарттары зерттелді. Кремний диоксиді натрий гидроалюминатының кристалдану процесін бәсеңдететіні, эмбрион түзілуіне де, кристалдардың өсу жылдамдығына да әсер ететіні көрсетілген. SiO_2-нің ыдырау жылдамдығына әсері қанығу дәрежесінің төмендеуіне ұқсас. Кремнийсізделмеген алюминат ерітінділерінен натрий гидроалюминатының кристалдануының негізгі мүмкіндігі көбірек (затравка) енгізу арқылы анықталды.

Түйін сөздер: алюминат ерітіндісі, кремний диоксиді, натрий гидроалюминаты.

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Влияние кремния на кристаллизацию гидроалюмината натрия

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АННОТАЦИЯ

При переработке глиноземсодержащего сырья для извлечения алюминия из высококонцентрированных алюминатных растворов применяется метод разложения с кристаллизацией гидроалюмината натрия. Чтобы рассчитать вероятный выход Al_2O_3 в твердую фазу, необходимо знать скорость кристаллизации гидроалюмината натрия в зависимости от состава исходных растворов и условий проведения процесса. Большое значение для процесса кристаллизации алюмината натрия имеет наличие в растворе кремнезема. В статье представлены результаты исследования устойчивости алюминатных растворов. Было изучено влияние содержания SiO_2 на разложение алюминатных растворов с концентрацией Na_2Oк 540 г/дм^3 и 590 г/дм^3 с добавлением затравки в виде предварительно полученного гидроалюмината натрия и без него. Было рассмотрено влияние кремнезема на облик выпадающих кристаллов гидроалюмината натрия. Установлено резкое повышение устойчивости алюминатных растворов в покое в присутствии кремнезема. Были исследованы различные условия кристаллизации гидроалюмината натрия. Показано, что кремнезем замедляет процесс кристаллизации гидроалюмината натрия, действуя и на зародышеобразование и скорость роста кристаллов. Действие SiO_2 на скорость разложения аналогично снижению степени пересыщения. Установлена принципиальная возможность кристаллизации гидроалюмината натрия из необескремненных алюминатных растворов путем введения большего количества затравки.

Ключевые слова: алюминатный раствор, кремнезем, гидроалюминат натрия.

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Metallurgy

Investigation of the possibility of using depleted bauxite in alumina production at the Pavlodar aluminum plant

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ABSTRACT

The topic of processing low-grade or low-quality bauxite is highly relevant in modern conditions due to the gradual depletion of high-quality bauxite reserves. Consequently, there is an increasing need to explore alternative sources of raw materials for aluminum production and its derivatives. Processing low-quality bauxite ores can become an effective solution, reducing dependence on limited high-quality resources and ensuring production stability in the long term. Such research has significant potential for developing technologies capable of optimizing aluminum production processes and enhancing its competitiveness in the global market. Bauxites from the Krasnooktyabrsky bauxite ore management with low aluminum oxide content (37 – 40% by mass) and a silicon module up to 2.0 are considered as potential blending materials for sintering bauxite in alumina production due to the depletion of high-quality bauxite reserves. This article presents the results of research on their processing into alumina at the Pavlodar Aluminum Plant. Laboratory and pilot-scale studies were conducted to assess the feasibility of using low-quality bauxite in alumina production and to determine the techno-economic indicators of processing. The research results confirmed the technological feasibility of processing depleted bauxites with a silicon module of 1.95 - 2.0 in the sintering section while maintaining the quality of sinter and extracting useful components. The maximum proportion of blending of depleted bauxites with the main bauxite was determined not to exceed 50%.

Keywords: depleted bauxite, alumina production, sintering process.

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Introduction

The impending shortage of natural raw materials with acceptable quality for processing, such as bauxite, is a prerequisite for the involvement of depleted or substandard bauxite of the lowest quality in the production of alumina, which will compensate for the technological shortcomings of the raw materials.

At ore deposits, rich and easily accessible areas have always been developed first, leading to a sharp decrease in metal content in recoverable reserves in recent years, while extraction costs have increased [1].

In these conditions, the relevance of issues related to the extraction and processing of unbalanced ores increases, with reserves on certain deposits reaching tens of millions of tons [1].

The criterion for the feasibility of including unbalanced ores in processing is the metal grade. Its determination is influenced by technical, technological, and economic factors. The effectiveness of combined extraction and processing of balanced and unbalanced ores depends on specific indicators unique to each deposit [1].

Bauxite ores show various forms under geological and physical-chemical effects [2]. While various bauxite classifications had been proposed in the past, the current consensus tends to divide bauxite into karstic and lateritic bauxite [3]. Kazakhstan's bauxites are characterized by an unstable lithological and phase composition, elevated content of ferruginous minerals, carbonates, and organic impurities. Additionally, Kazakhstan possesses other types of alumina-bearing raw materials, such as nepheline syenites, clays, kaolins, and coal ash, which are potential sources for alumina production [[4], [5], [6], [7]].

Most of Kazakhstan's bauxite deposits are complex. Alongside high-grade bauxites, bauxite-bearing formations include alites, which contain a large amount of gibbsite, high-alumina, and basic refractory clays [8].

Reserves of off-balance sheet ores have been formed in metal deposits, the content of which is close to the balance value, but does not ensure profitability with gross mining. At metallic deposits, reserves of unbalanced ores have formed, the content of which is close to the balanced value, but gross extraction does not ensure profitability. Unbalanced reserves include mineral resources that, due to their quantity, quality, complex extraction or processing conditions, are not utilized, but may become the subject of development in the future [1].

Depleted or off–balance bauxite is a low-quality bauxite-like ore with a silicon module ($M_{Si}=Al_2O_3/SiO_2$) below 2.0. Such substandard ores make up the main part of the contact zone of the bauxite deposit, which is formed during mining during the stripping of the ore body, they enter the dumps together with the overburden and are not listed as ore raw materials. A fairly large amount of substandard bauxite is formed; therefore, studies have been conducted on the possibility of involving these bauxites in processing using the Pavlodar aluminum plant sintering method.

Figure 1 – The charging yard on the PAP

Bauxites from Kazakh deposits themselves are low-grade raw materials and abroad are classified as bauxite-like clays, unsuitable for processing into alumina [9].

At one time, thanks to the improvement and development of technologies, as well as the modernization and improvement of the basics of alumina production, it became possible to process low-quality bauxite [10]. It was for the processing of such bauxites that the Pavlodar Aluminum Plant was designed.

The Pavlodar aluminum plant occupies a special place in the global hierarchy of alumina producers and has positive experience in processing low-quality bauxite raw materials into alumina using the world's only technological scheme, the 'Sequential-Parallel Bayer-Sintering' method, achieving satisfactory economic indicators [11].

The Bayer process, currently dominant in alumina production, is suitable only for low-silica bauxites [12]. However, through the sintering process, not only various bauxites but also clays, kaolins, sericites, and other aluminosilicate rocks, whose reserves are inexhaustible, can be processed into alumina [13].

According to the existing technological scheme of the plant, bauxite is processed using the parallel–sequential Bayer-Sintering method. The distribution of bauxite by branches is ~ 91% (Bayer) and 9% (Sintering).

The alkaline sintering method is used for processing bauxites with high silica content, whose silica modulus typically does not exceed 5. This method involves sintering bauxite with soda and limestone. During sintering, the interaction between the alumina of the bauxite and the soda forms sodium aluminate, while the silica is bound by calcium oxide into insoluble dicalcium silicate. Sodium aluminate is leached from the resulting sinter with water [14].

At the Pavlodar Aluminum Plant, an important technological problem was solved for the first time in global practice, involving the large-scale industrial production of high-silica and high-iron bauxites from Kazakhstan [15].

However, according to the mining plan for the Krasnooktyabrsky bauxite ore management from 2020 to 2030, a deterioration in the quality of the ore base is expected in terms of a decrease in the quality of bauxite and an increase in the stripping coefficient, which creates significant risks of an increase in the cost of both bauxite and alumina. Therefore, the topic of involving depleted or substandard bauxite raw materials in the production of alumina has now become relevant.

Partial replacement of bauxite from the Pavlodar aluminum plant Sintering branch with bauxite-like bauxites from the Krasnooktyabrsky bauxite ore will reduce the production of "basic" bauxite by ~ 111 thousand tons per year.

Previously, the Pavlodar aluminum plant Sintering branch had already processed lignite bauxites with a silicon module of ~ 2.0 with optimal technological performance. However, currently, due to the depletion of these bauxite reserves, the Krasnogorsk Ore Management bauxite with M_{Si} 3.5, which is suitable for use in the Bayer branch, serves as a "sintering" one. Therefore, the search for alternative raw materials as "sintering" bauxite was continued.

This paper presents the results of testing an alternative type of bauxite raw materials from the Sintering branch of the Pavlodar aluminum plant – dining bauxite to reduce the cost of alumina production.

Table 1 presents a comparative analysis of bauxite from Kazakhstani deposits with various qualitative indicators:

Table 1 - Chemical composition of Kazakhstani bauxite

Deposits	Al_2O_3	SiO_2	CO_2	M_{Si}
	%			
Krasnooktyabrskoye	42.0	10.9	3.70	3.85
Ayatskoye	44.6	10.7	1.26	4.17
Belinskoe	41.4	10.3	1.79	4.02
Depleted A	37.3	18.9	3.51	1.97
Depleted Б	40.3	20.7	0.31	1.95

Kazakhstan's bauxite deposits, such as Belinskiy, Ayatskiy, and Krasnooktyabrskiy, have Al_2O_3/SiO_2 ratios ranging from 3.0 to 8.0 [16]. Depleted bauxites are characterized by a low content of alumina and an increased content of silicon oxide, and, accordingly, a low silicon modulus of up to 2.0.

Depending on the content of aluminum oxide and silicon modules, bauxites are divided into grades and grades. There is a certain standard corresponding to GOST – 972-74. According to the qualitative characteristics, depleted bauxite does not comply with this GOST.

As a rule, schemes (methods) with its preliminary enrichment are used for low-quality raw materials.

For instance, the method of processing poor and low-grade bauxites with Al_2O_3 content less than 37%, SiO_2 content over 5.5%, and silicon modulus of 2.1 - 3.5, as well as the processing of old tailings of unbalanced ores, which includes ore transportation, their express analysis by radiometric methods, ore quality averaging, nuclear-physical sorting, and lump separation using relay separator, heap bacterial-chemical leaching of SiO_2 with silicate bacteria (Silucius) [17].

In work, it is mentioned about the radiometric enrichment of various types of bauxites from the Middle Timan region, namely unbalanced bauxite, calcining, and Bayer [18]. Radiometric separation from unbalanced bauxite allows the extraction of 36.3% of enriched product with a silicon modulus of 4.2, which is suitable for further calcining.

The article describes the thermochemistry – Bayer method, which allows the processing of various substandard bauxite raw materials, this method may well "compete" with the Sintering method [19].

These methods ensure efficient separation of harmful gangue minerals from bauxite during the raw ore preparation stage. However, despite the promising nature of these methods, the capital and operational costs for bauxite beneficiation are quite high, and in some cases, it is still not possible to obtain concentrates of the desired quality [20].

A method is known for the hydrochemical processing of low-quality aluminosilicate raw materials in the Bayer branch with the addition of lime [21].

The work describes the results of studies of the decomposition of aluminium-containing ores: mudstones and kaolin clays of the Ziddy and Chashma-Sang deposits of the Republic of Tajikistan by mineral acids and chlorine methods [22].

The proposed method allows the processing of substandard bauxite-like raw materials according to the existing Pavlodar aluminum plant scheme without changing and using additional resources while maintaining output. Such a scheme has no analogues in the world practice of producing alumina.

There are relatively few theoretical and technological data in the literature on the processing of bauxite-like raw materials used according to a similar scheme for the production of alumina Pavlodar aluminum plant.

However, a similar technology for processing nephelines with additions of bauxite using the Sintering method is known at the Achinsk Alumina Plant. The depletion of the raw material base of the

Kiya-Shaltyr mine served as a prerequisite for involving non-conforming and unbalanced ores in the processing of nephelines. This allows for reducing capital costs and maintaining quality indicators for extracting useful components without changing the technological scheme of the Achinsk Alumina Plant [23].

Off-balance bauxites (allites) are intended for use as a correlating additive in the processing of nepheline concentrates [8].

The extraction of valuable components from aluminosilicate natural and man-made materials by sintering on Achinsk Alumina Combine was described in one of the articles [24].

Experimental part

Chemical and X-ray fluorescence analysis methods were used in the research.

Chemical analysis of technological samples was carried out by the complexometric method for determining the mass concentrations of aluminum oxide in solutions ranging from 1.0 g/dm^3 to 300 g/dm^3 and sodium oxide in solutions ranging from 1.0 g/dm^3 to 500 g/dm^3.

X-ray fluorescence analysis of the samples was carried out on a wave-dispersive X-ray fluorescence spectrometer Simultix 14 («Rigaku Corporation», Japan).

Figure 2 - Simultix X-ray fluorescence spectrometer

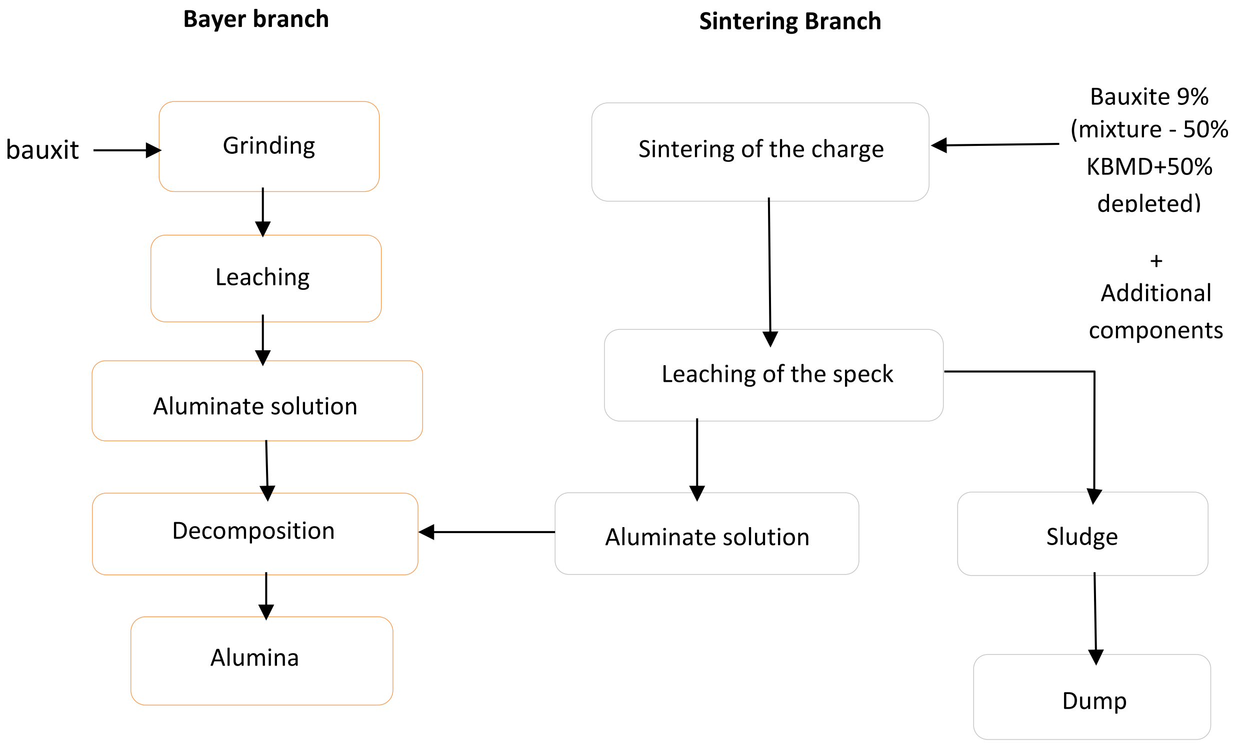

Figure 3 - Block diagram of Bayer-Sintering

Results and Discussion

As mentioned earlier, the Pavlodar aluminum plant works according to a parallel–sequential Bayer–Sintering scheme.

Figure 3 shows the existing block diagram of Bayer Sintering using depleted bauxite in the charge.

Depleted bauxites from the Krasnogorsky bauxite mine (A) and the Vostochno – Ayatskoye (B) deposit were selected for research. In the process of mining ordinary bauxite ore, point (selective) excavation of these bauxites with a silicon module of 1.6 – 2.0 was carried out.

The research methods included pilot industrial tests and standard leaching of industrial sinter in the laboratory.

Laboratory leaching of the sinter was carried out under strictly defined conditions regulated by the standard of the PAP enterprise.

The amount of extraction during laboratory leaching shows how completely Al_2O_3 and Na_2O are converted into soluble compounds during sintering [25].

Preparation for laboratory work.

The leaching of the sinter was carried out in 100 ml of sodium hydroxide solution with a concentration equivalent to 0.5 mol/dm^3 at (L:S) = 10:1 for 15 minutes at a temperature of 75 ˚C under isothermal conditions. After leaching, the chemical composition of the solid precipitate was determined.

The chemical reactions occurring during the leaching of the sinter are presented below:

$$Na_2O \cdot Fe_2O_3 + 2H_2O = 2NaOH + Fe_2O_3 \cdot H_2O \quad (1)$$

$$2Na_2O \cdot nAl_2O_3 \cdot (1-n)Fe_2O_3 + 3H_2O = \\ = 2NaOH + Na_2O \cdot nAl_2O_3 + (1-n)Fe_2O_3 \cdot H_2O + H_2O \quad (2)$$

$$2CaO \cdot SiO_2 + 2NaOH + H_2O = Na_2SiO_3 + 2Ca(OH)_2 \quad (3)$$

$$2CaO \cdot SiO_2 + 2Na_2CO_3 + H_2O = 2CaCO_3 + Na_2SiO_3 + 2NaOH \quad (4)$$

The extraction of aluminum oxide from the sinter into the solution proceeds by reaction 2 in an alkaline (caustic) medium with a pH of 10 to 12. The increase in pH is mainly due to the extraction of caustic alkali from the sinter into a solution by reaction 1 and partially by reaction 4.

Pilot tests on the use of depleted bauxite were carried out in the raw material preparation shop and the PAP sintering shop.

During the testing period, the sinter was selected from all operating furnaces, and the sieve composition and extraction of useful components were determined based on the results of laboratory leaching.

Depleted bauxites were delivered to the Pavlodar aluminum plant with the following qualitative characteristics, presented in Table 2:

Table 2 – Chemical composition of bauxite

Name	Al_2O_3	SiO_2	Fe_2O_3	M_{Si}
	%			
Current sintering bauxite	43.3	10.9	18.8	**3.98**
Depleted bauxite A	37.3	18.9	19.3	**1.97**
Depleted bauxite B	40.3	20.6	17.2	**1.95**

As can be seen from Table 2, depleted bauxites are characterized by a low silicon modulus and a reduced content of Al_2O_3.

Depleted bauxite A was tested first. At the initial stage, this bauxite was supplied with the lowest proportion of charge, which amounted to 18.4 %. Further, its share in the mixture with the current bauxite was gradually increased to 47.1 %. Depleted bauxite B was supplied immediately with the maximum fraction in the composition of the charge - 48.2 %.

As a result of the polythermal high-temperature treatment of the wet initial charge in rotating furnaces, a poly mineral sinter was obtained from newly synthesized solid phases.

The finished product was evaluated according to the quality categories of the sinter: by chemical composition, by the content of fractions -1.0 mm not more than 30 % and by the level of extraction of Al_2O_3 and Na_2O into solution during hydrochemical leaching of the sinter according to [9].

The chemical composition of the charge and sinter is usually determined mainly by the molar ratios of the main oxides – this is an alkaline (alumina) module $(M_{al}) = [Na_2O] + [K_2O \cdot 0{,}66]/[Al_2O_3]$ и limestone module $(M_{limestone}) = [CaO]/[SiO_2]$ [25]. It is important to withstand such physico–chemical conditions so that other compounds are not formed during sintering, which reduces the extraction of useful components during the leaching of sinters.

Figure 4 below shows the alumina and lime sintering modules during the EIT period:

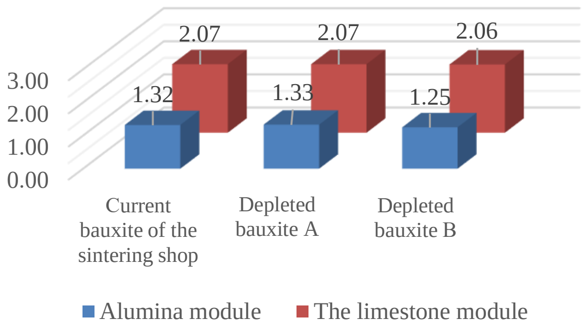

Figure 4 – Alumina and limestone sintering modules

When testing depleted bauxite B, the alumina sinter modulus decreased to 1.25. This was due to a technological violation unrelated to the pilot testing, which led to some deterioration in the quality of the spec (Fig. 4).

During the period of supply of depleted bauxite A to the sintering charge, the sintering quality was maintained in the regulatory values and remained at the level of the control period.

The process of transferring useful components from the sinter to the solution during leaching depends on the size of the sinter crushing and subsequent grinding of the sinter sludge.

Table 3 shows the main indicators for the chemical composition of the solid phase of the dump sludge during the period of the pilot testing.

Table 3 - The main indicators for the chemical composition of the dump sludge during the EIT period

Name	Na_2O	Al_2O_3
	%	
Current sintering bauxite	1.11	4.58
Depleted bauxite A	1.14	4.58
Depleted bauxite B	1.19	5.81

Exceeding the regulated value for the content of Al_2O_3 in the dumped sludge (< 5.0) during the charge period of depleted bauxite B is associated, as shown above, with a decrease in the alumina sintering modulus during the test period.

As follows from the production practice of sintering alumina charges, when the stoichiometry of the preparation of the charge is violated, namely, with a decrease in the alumina module or a lack of alkalis, the content of Al_2O_3 in the dump sludge increases [[4], [26]].

The indicators for the content of useful components in the dumped sludge during the period of charging depleted bauxite A were without deviations.

Further, Table 4 shows the results of the extraction of useful components Al_2O_3 and Na_2O during the pilot testing period.

Table 4 - Indicators for the extraction of Na_2O and Al_2O_3 during the pilot testing period

Name	Na_2O	Al_2O_3
	%	
Current sintering bauxite	95.2	84.6
Depleted bauxite A	95.2	84.9
Depleted bauxite B	95.0	82.2

As we can see, the fact associated with a decrease in the alumina sintering modulus (from 1.32 to 1.25) also affected the recovery of useful components during the charging period of depleted bauxite B, thereby reducing the extraction of Al_2O_3 to 82.2%.

At the stage of mixing depleted bauxite A, there were no deviations in the extraction of useful components.

Also, during the pilot testing period, in comparison with the current sintering bauxite, data on laboratory (standard) leaching of sinter during the charging of depleted bauxite A were analyzed.

Table 5 shows the chemical composition of the sinter/sludge after laboratory leaching during the supply of depleted bauxite A.

Laboratory tests showed that the results of the standard leaching of the sinter of the experimental period were on the same level as the control one, both in terms of the chemical composition of the dumped sludge and in the extraction of useful components (Al_2O_3 and Na_2O).

Based on the results of the pilot testing, the possibility of processing depleted bauxite according to the existing technological scheme was determined. During the mixing of depleted bauxite A, equivalent technological indicators were noted for the quality of sintering and the extraction of useful components (Al_2O_3 and Na_2O) in comparison with the control period – on the current bauxite of the sintering branch.

During the charge period of depleted bauxite B, a violation was noted that was not related to the extraction of bauxite, and with failures within the technological cycle - a decrease in the alumina module ($M_{silicon}$) in the sinter, as a result of which there was a slight decrease in the extraction of alumina from the sinter, amounting to 82.2%.

Table 5 - chemical composition of the sinter/sludge after laboratory leaching

Stage	Name	Chemical composition of the sinter/sludge, %		$M_{alkaline}$	$M_{silicon}$	Extraction of useful components, %	
		Na_2O	Al_2O_3			Na_2O	Al_2O_3
Current bauxite of the sintering shop (control)	Speck	15.18	19.74	1.27	2.07	-	-
	Sludge	0.92	3.58	-	-	95.83	87.67
Depleted bauxite A	Speck	14.85	18.77	1.30	2.09	-	-
	Sludge	0.86	3.41	-	-	96.04	87.48

Conclusions

According to the results of the conducted research, it was determined that, depleted bauxite A and B are characterized by a low flint modulus of 1.97 and 1.95, respectively, in comparison with the current sintering bauxite, the flint modulus of which is 3.98. Such bauxites can only be processed in Sintering branches, chemical analysis of sinters and slurries after laboratory leaching showed a complete correlation in the content of the components. However, there was a slight decrease in Al_2O_3 and Na_2O.

The content of useful components Al2O3 and Na2O during the processing of depleted bauxite remained at the level of the current basic bauxite.

Based on the conducted pilot testing, the technological possibility of processing depleted bauxite A and B with an optimal proportion of charge to the current bauxite was confirmed - no more than 40-50 %.

The involvement of depleted bauxite with such a proportion of charge maintains optimal technical and economic indicators of Sintering conversion, as well as such a balance amount is recommended for continuous use on the Pavlodar aluminum plant.

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

***Author Contributions CRediT*: G. Abikenova:** Management, conceptualization, data curation. **D.Dauletov:** Author's supervision, reviewing and editing. **S. Tverdokhlebov:** Methodology, research, supervision, reviewing. **I. Danchenko:** Research, writing - original draft preparation.

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Павлодар алюминий зауытында алюминий өндірісінде жұтаңдаған бокситтерді пайдалану мүмкіндігін зерттеу

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ТҮЙІНДЕМЕ

Жоғары сапалы боксит қорының бірте-бірте таусылуына байланысты қазіргі жағдайда төмен сортты немесе сапасыз бокситті өңдеу тақырыбы өте өзекті болып табылады. Демек, алюминий және оның басқа өнімдерін өндіру үшін шикізаттың баламалы көздерін іздеу қажеттілігі артып отыр. Төмен сортты боксит кендерін қайта өңдеу шектеулі жоғары сапалы ресурстарға тәуелділікті азайту және өндірістің ұзақ мерзімді тұрақтылығын қамтамасыз ету үшін тиімді шешім бола алады. Мұндай зерттеулер алюминий өндірісінің процестерін оңтайландыруға және оның әлемдік нарықтағы бәсекеге қабілеттілігін арттыруға қабілетті технологияларды әзірлеу үшін маңызды әлеуетке ие. Алюминий оксиді төмен (масса бойынша 37 – 40%) және кремний модулі 2,0-ге дейінгі Краснооктябрь боксит кен басқармасының бокситтері жоғары сапалы боксит қорының таусылуына байланысты алюминий оксиді өндірісінде бокситті күйежентектеу үшін әлеуетті араластырғыш материалдар ретінде қарастырылады. Бұл мақалада Павлодар алюминий зауытында оларды алюминий оксидіне өңдеу бойынша жүргізілген зерттеулердің нәтижелері берілген. Глинозем өндірісінде сапасы төмен бокситті пайдаланудың орындылығын бағалау және өңдеудің техно-экономикалық көрсеткіштерін анықтау үшін зертханалық және тәжірибелік-зерттеу жұмыстары жүргізілді. Зерттеу нәтижелері 1,95 - 2,0 кремний модулі бар жұтаңдаған бокситтерді агломераттың сапасын сақтай отырып және пайдалы компоненттерді бөліп алу кезінде өңдеудің технологиялық мүмкіндігін растады. Жұтаңдаған бокситтерді негізгі бокситпен араластырудың максималды үлесі 50%-дан аспайтыны анықталды.

Түйін сөздер: жұтаңдаған боксит, алюминий оксидін өндіру, күйежентектеу процесі.

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Исследование возможности использования обедненных бокситов в глиноземном производстве на Павлодарском алюминиевом заводе

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АННОТАЦИЯ

Тема переработки низкосортных или низкокачественных бокситов весьма актуальна в современных условиях в связи с постепенным истощением запасов высококачественных бокситов. Следовательно, растет потребность в поиске альтернативных источников сырья для производства алюминия и его производных. Переработка низкокачественных бокситовых руд может стать эффективным решением, снижающим зависимость от ограниченных высококачественных ресурсов и обеспечивающим стабильность производства в долгосрочной перспективе. Подобные исследования имеют значительный потенциал для разработки технологий, способных оптимизировать процессы производства алюминия и повысить его конкурентоспособность на мировом рынке. Бокситы Краснооктябрьского бокситового рудоуправления с низким содержанием оксида алюминия (37–40 % по массе) и кремниевым модулем до 2,0 рассматриваются в качестве потенциальных шихтовых материалов для спекания бокситов в глиноземном производстве в связи с истощением запасов высококачественных бокситов. В данной статье представлены результаты исследований по их переработке в глинозем на Павлодарском алюминиевом заводе. Проведены лабораторные и опытно-промышленные исследования с целью оценки возможности использования низкокачественных бокситов в глиноземном производстве и определения технико-экономических показателей переработки. Результаты исследований подтвердили технологическую целесообразность переработки обедненных бокситов с кремниевым модулем 1,95-2,0 в отделении агломерации с сохранением качества агломерата и извлечением полезных компонентов. Установлено, что максимальная доля смешения обедненных бокситов с основным бокситом не превышает 50%.

Keywords: обеднённый боксит, производство глинозема, процесс спекания.

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Earth sciences

Improvement of the technological scheme for processing zinc concentrates by hydrometallurgical method at JSC Almalyk MMC

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ABSTRACT

The extraction of zinc from concentrates is carried out in pyrometallurgical and hydrometallurgical ways. Obtaining pure zinc of the highest grades is possible using the hydrometallurgical method, in which the calcined sulfide concentrate is subjected to sulfuric acid leaching, a solution of zinc sulfate and a recycled product is formed - a solid residue of the cake leaching process. After purification, the zinc sulfate solution is subjected to electrolytic refining, and the cake is processed pyroly or hydrometallurgically. At JSC "Almalyk MMC" in the process of hydrometallurgical processing of zinc concentrates, the resulting zinc cake is processed by the pyrometallurgical method - rolling. The rolling process takes place in two tubular furnaces (rolling furnaces) 50 meters long and 3.5 meters in diameter at a temperature of 1100–1200^{0}C, in the presence of a reducing agent, coke breeze and petroleum coke. As a result of the rolling process of zinc cakes, sublimates and a solid technogenic residue, clinker, containing copper, gold, and silver are formed. Clinker is processed at the plant in smelting furnaces to extract precious metals, but it is accumulating more than 450 thousand tons. In connection with this, scientific research is currently underway on the processing of zinc cakes using a hydrometallurgical method to eliminate the expensive rolling process of processing zinc cakes; high-temperature (90^0 C**)** sulfuric acid leaching of cakes with a size of 0.074 mm has been developed during leaching for 4-4.5 hours, the extraction of zinc into the solution is 98.5%; copper 92.8%; iron 75.2; cadmium 79.2.

Keywords: zinc, cake, process, leaching, concentrate, cinder, extraction, solution, clinker, coke.

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Introduction

Zinc can be extracted from concentrates in two ways: pyrometallurgical (distillation) and hydrometallurgical (electrolytic). Historically, the first method was pyrometallurgical; two thousand years BC in India they knew a method for obtaining zinc from ore; in Europe only at the end of the 18th century.

Zinc sulfide raw materials can be directly reduced to produce zinc metal:

$$ZnS + H_2 = Zn + H_2S$$

The equilibrium constant of the given reaction at a temperature of 1000 ° C is insignificant; even at a the high value *of* P_{H2}, the yield of reduction products is low [1].

In this connection, it is more rational to carry out separately the oxidation of Zn S (roasting) and the reduction of oxidized zinc to metal. The technology of the method and the hardware design of the process are associated with the peculiarities of the reduction of zinc from oxide, to the metal with carbon and CO occurs at a temperature of 1,000–1,100 ° C, and the boiling point of the resulting zinc is 907 ° C. Advantages The pyrometallurgical scheme is its few stages, high direct extraction of zinc into metal, high productivity of continuous equipment and the ability to process low-quality raw materials. Flaws This scheme means a high consumption of coke, a low complexity of the use of raw materials and the production of zinc of lower grades, and currently in world practice no more than 15% of zinc is obtained using the pyrometallurgical method. This technology is usually used to process poor zinc concentrates with high impurity content [[1], [2]].

Much attention is paid to more complete extraction of the components of zinc-containing raw materials, obtaining pure zinc of the highest grade, and therefore in the production of zinc, the hydrometallurgical method of processing zinc concentrates is currently used, it is also used at Almalyk MMC JSC. In this method (zinc cinder leaching process), maximum extraction of zinc into the zinc sulfate solution occurs and the solid tail of the leaching process is the recycled product zinc cake. The solution after cleaning is transferred to Electra of zinc precipitation, and zinc cake containing 20-23% Zinc is processed using the pyrometallurgical method - the Waelz process.

The Waelz process gives high zinc yields of more than 90-93%, but it is quite expensive due to the high consumption of coke, about 50% of the weight of the zinc cake. As a result of the Waelz process, zinc sublimations are obtained, as well as man-made waste from zinc production, difficult to recycle clinker with a high content of non-ferrous and precious metals, carbon and iron [2].

Clinker from zinc production is mainly processed by smelting in shaft furnaces, the negative side of smelting is the expense of an expensive reducing agent - coke, as well as briquetting or pelletizing of clinker for processing in shaft furnaces [[3], [4], [5], [6]].

Clinker is also processed in a reverberatory furnace, mixing it with concentrate and fluxes, it is loaded into the furnace to extract only noble (gold, silver) metals, and during the smelting process, the elements contained in the clinker carbon are burned aimlessly, and the iron goes into waste slag [[7], [8], [9]].

Scientific research is being conducted around the world on the processing of zinc cakes using the hydrometallurgical method, in order to eliminate the use of expensive coke in the Waelz process. The hydrometallurgical method mainly uses technology that includes: two-stage leaching, the first stage is neutral leaching of Waelz oxides, and the second is acid leaching of the solid residue after neutral leaching [[10], [11], [12], [13], [14], [15], [16]].

The authors of used a promising method - cation exchange leaching of metals from zinc cinder and zinc cake (obtained at the stage of acid leaching), in which the KU-2–8 ion exchanger in the H-form can be used as a reagent, allowing the extraction of 98% of zinc of the total [17].

The authors of developed a technology for processing clinker, waste from zinc production, to produce ferroalloy and sublimates of non-ferrous metals [18]. Clinker from zinc production was used as a raw material to obtain commercial products in the form of ferrosilicon and collective sublimates of non-ferrous metals. The degree of extraction of silicon into the ferroalloy was up to 96%, Fe up to 97%, and in sublimation Zn 99.6%, Pb – 99%.

In work, the Institute of JSC "Uralmekhanobr" developed a technology for enriching clinker of JSC "Electrozinc" by gravity-magnetic-flotation processing to produce carbon-containing concentrate, iron concentrate with a high copper content [19].

The work presents the results of studies on the use of flotation for the enrichment of zinc cakes [20]. The concentrate of the second cleaning contained, %: 44 Zn; 9.3 Fe; 1.5 Cu; 1.1 Pb; 0.88 Ag; 0.009 Au; 2.1 SiO_2 and 27.3 S.

The authors of claim that sodium sulfide used in flotation does not always ensure complete sulfidization of the surface of minerals [21]. Studies of the flotation process on the original product and after preliminary sulfidization by a pyrometallurgical method have found that in the preliminary sulfidation of the product, the extraction of zinc will increase by 17.23%, and lead by 10.07%, compared to the original product without pretreatment.

Authors a method has been developed for processing technogenic waste, which reduces specific fuel consumption by 1.5-1.7 times and increases specific productivity by 1.4-1.5 times. The industrial implementation of the “phase inversion reactor-tubular furnace” unit would make it possible to cost-effectively process slag dumps from the Shymkent lead plant, Waelz clinker , “poor” zinc ores from the Achpolimetal plant, tailings from the Tekeli Mining and Metallurgical Plant and other non-ferrous metallurgical facilities [[22], [23], [24], [25], [26]].

The results of a study of the process of sulfatizing roasting of zinc cakes of PJSC Chelyabinsk Zinc Plant using iron sulfates $FeSO_4$ and $Fe_2(SO_4)_3$ are presented. In laboratory experiments, it was found that from fired samples, no less than 98% of zinc and no less than 88% of copper goes into solution during water washing, while the degree of iron transfer into solution does not exceed 3% [[27], [28], [29]].

An analysis of the processing of zinc production cakes showed that the technological schemes are quite complex, expensive and complete extraction of

Table 1 - Mineralogical composition of zinc cake, %

Product name	Connections, %					
	Zntot	$ZnSO_4$	ZnO	ZnO SiO_2	ZnS	$ZnFe_2O_4$
Zinc cake	21.42	7.97	3.05	3.44	1.07	6.11
	$CuFe_2O_4$	$CuSO_4 \cdot 5H_2O$	Cu_2S	CuO	CdO	$CaSO_4 \cdot 2H_2O$
	5.25	1.45	0.16	0.03	0.02	7.16
	$PbSO_4$	FeS	Fe_2O_3	$CaCO_3$	MnS	MgO
	6.05	1.27	0.56	1.45	1.28	0.45

Table 2 - Chemical composition of zinc cake by fractions

Class, mm	Class yield, %	Content, %							
		Zn	Cu	Pb	Cd	Fe	Al_2O_3	SiO_2	S
+40	1.925	21.89	3.27	6.48	0.22	17.23	4.11	9.23	7.77
-40+20	11.35	21.60	3.38	6.57	0.22	17.34	4.13	9.18	7.75
-20+10	30.35	21.08	2.35	6.52	0.20	16.48	4.08	9.14	7.66
-10+5	32.25	21.62	2.34	6.49	0.21	16.50	4.15	9.36	7.69
-5+2	20.8	21.66	2.23	6.37	0.20	16.66	4.12	9.29	7.71
-2+1	0.7	21.63	3.33	6.25	0.29	14.60	4.07	9.17	7.74
-1+0.315	0.75	21.95	3.37	6.32	0.29	13.75	4.08	9.19	7.65
-0.315+0.140	0.5	22.45	2.29	6.32	0.28	12.09	4.17	9.14	7.68
-0.140	1.375	21.66	2.08	6.39	0.28	12.07	4.18	9.16	7.73

metals is not achieved. In this connection, there is a need to develop a more efficient technology for processing zinc production cakes, one of which is high-temperature leaching.

Objects and methods of research

Cake was taken from the Zinc Plant of Almalyk MMC JSC, %: Zn_{total} -21.42, Zn_{aq} -5.59, Zn_{acid} -13.26, C -0.14, S_{vol} -7, 69, S_{SO4} -6.86, Pb-6.48, Fe-15.21, SiO_2 -9.39, Al_2O_3 -1.42, Cu-2.32, Cd-0.21, CaO-2.67, MnO-0.85, As-0.35. The main chemical compounds of zinc cake are sphalerite, zinc ferrite, copper ferrite, metal silicates, copper sulfate, zinc sulfate, gypsum and sphalerite, and lead sulfate. The mineralogical and fractional composition of zinc cake using spectral, chemical and mineralogical methods of analysis are given in Table. 1-2.

Methodology for high-temperature leaching of zinc cake

To study the process of agitated high-temperature leaching of both preparative reagents and bulk products, a special LR 1000 basic unit was used.

The experiments were carried out as follows: the zinc product was crushed to a fraction of <0.1 mm. A crushed sample of zinc cake was placed in a leaching unit, and a solution of sulfuric acid was added, heated and held for a certain time. The temperature was regulated through a microprocessor automatic controller. Pulp samples for analysis were filtered through a paper filter with a blue ribbon, and the filtrate was analyzed for iron, zinc, copper and other components. After completion of the experiment, the phases were separated by filtration, the cake was washed three times by decantation with hot water (50^{0}C), dried to constant mass and subjected to atomic absorption and X-ray analysis for the content and form of metals.

LR 1000 basic laboratory reactor designed to optimize the reproduction and optimization of chemical reaction processes, as well as for mixing at different temperatures, dispersion, homogenization on a laboratory scale. The temperature of the processed material can reach 120ºC. The temperature of the heating source located under the vessel is adjusted by the set temperature inside the medium. Digital display allows you to clearly monitor speed and temperature.

Discussion of the research results

A study of the influence of the dependence of zinc extraction into solution on temperature at various concentrations of sulfuric acid, the duration of the process on the leaching of zinc from cake with a sulfuric acid solution with a concentration of 120-210 g/l, at various temperatures shows that at the beginning of the process 1 - 1.5 hours, zinc extraction in the solution flows efficiently, and after 4–5 hours the equilibrium of the leaching process is established (Fig. 1-2).

An increase in the duration of the process leads to a decrease in the concentration of sulfuric acid, while the iron content in the solution increases (Fig. 3).

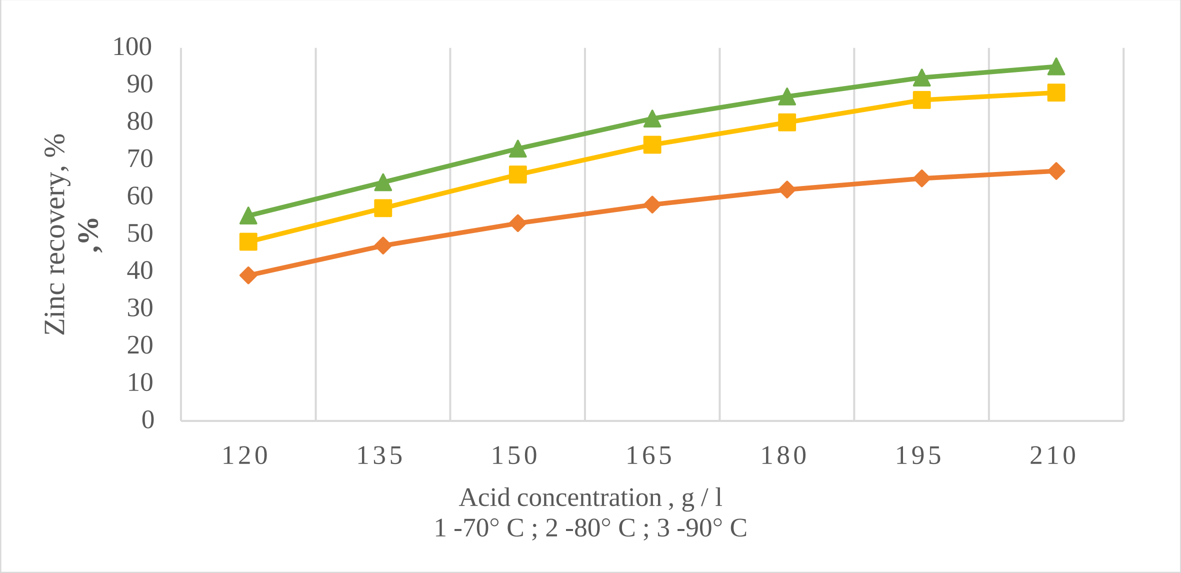

Fig.1 - Extraction of zinc from cake during zinc cake leaching process which depends on temperature.

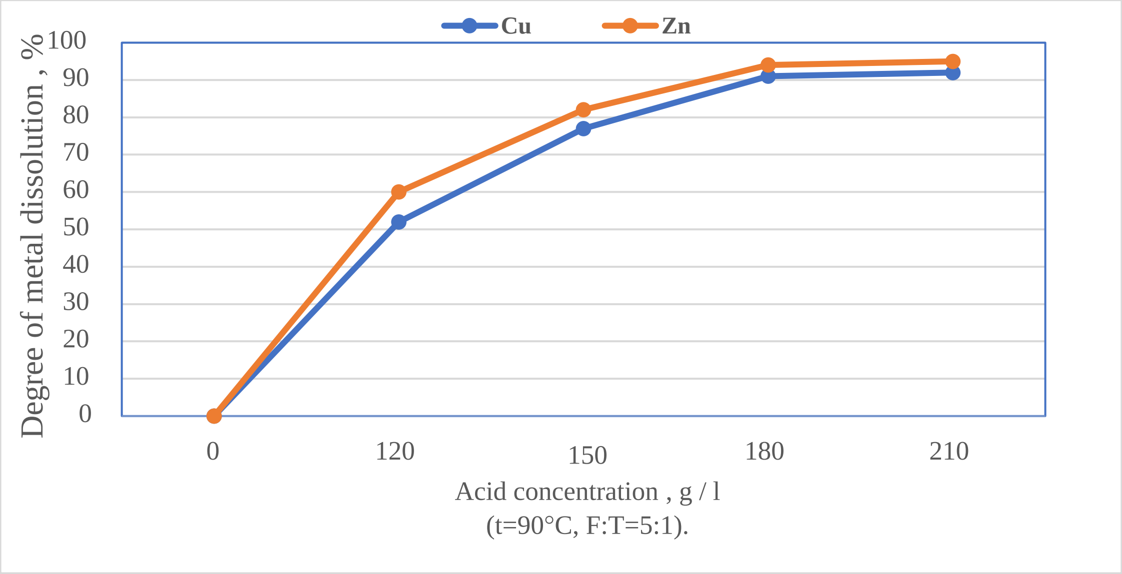

Fig. 2 - The degree of zinc and copper`s dissolution during the process of zinc cake`s leaching at 90 ˚C depending on the concentration of sulfuric acid

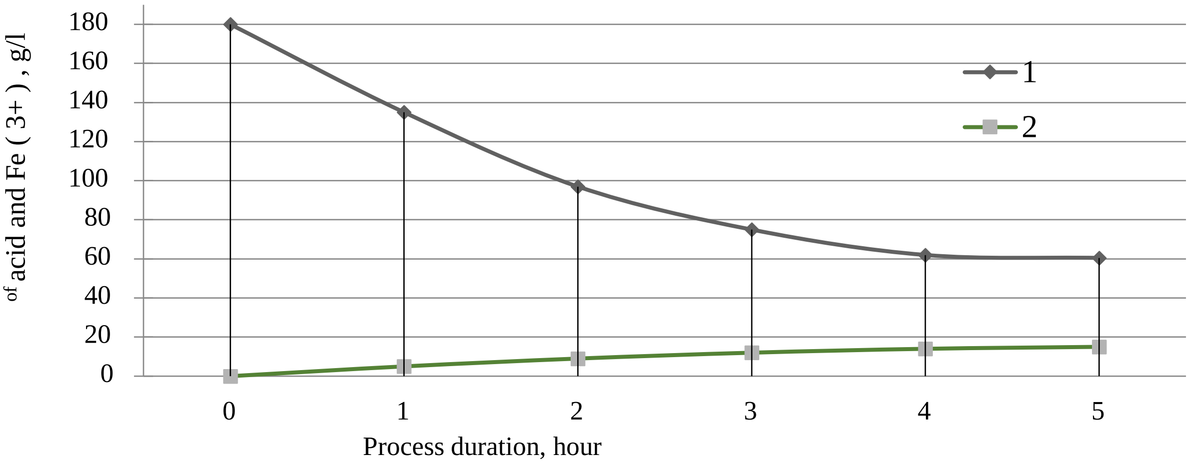

Fig. 3 - Dependence of the change in the concentration of sulfuric acid (1) and iron (2) on the duration of the process

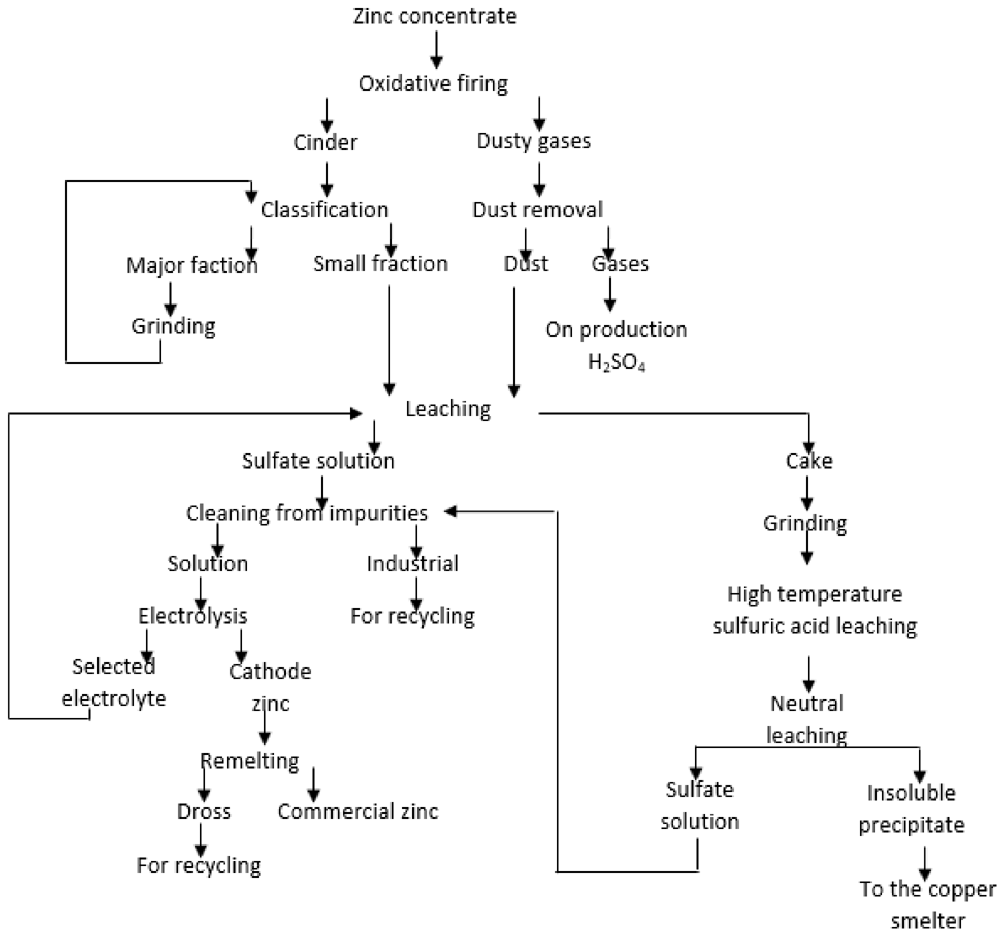

Fig. 4 - Improved technological scheme for processing zinc concentrates by hydrometallurgical method.

To clean the high-temperature sulfuric acid leaching solution from copper, cadmium, cobalt, antimony, nickel and other impurities, three-stage neutral leaching with zinc dust is carried out in mixers with mechanical stirring. The resulting sediment (copper cake) is transferred to cadmium production.

In the improved technological scheme for processing zinc concentrates using the hydrometallurgical method, Figure 4 shows a section in the scheme of processing zinc cakes using a high-temperature sulfuric acid leaching process.

In Figure 4 shows a scheme for processing zinc cakes using a high-temperature sulfuric acid leaching process, instead of the Waelz process used in many zinc plants around the world.

Thus, the following optimal conditions for leaching zinc cake were established: sulfuric acid concentration 180–190 g/l, temperature 90 ^{0} C, duration 4–4.5 hours. Under these conditions, the degree of extraction of zinc into solution is 97–98.5%, copper 92–93%, cadmium 78–80% and iron 72.5–75.2%. In the resulting sulfate solution, the concentration of zinc in the solution is sufficient to transfer it to the zinc electrolysis workshop; the impurities contained in the solution are first purified by the hydrolytic method used at the zinc plant of Almalyk MMC JSC.

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«Алмалық ТМК» АҚ-да мырыш концентраттарын гидрометаллургиялық әдіспен өңдеудің технологиялық сызбасын жетілдіру

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ТҮЙІНДЕМЕ

Концентраттардан мырыш алу пирометаллургиялық және гидрометаллургиялық әдістермен жүзеге асырылады. Ал жоғары сортты мырыш гидрометаллургиялық әдісті қолдану арқылы алынады, онда күйдірілген сульфид концентраты күкірт қышқылды мырыш ерітіндісімен күкірт қышқылды шаймалауға ұшырайды, нәтижесінде қайта өңдеу өнімі – қоқымды (сүзіндіні) шаймалау процесінің қатты қалдығы түзіледі. Тазартудан кейін мырыш сульфаты ерітіндісі электролиттік тазартуға ұшырайды, ал қоқым пиро - немесе гидрометаллургиялық жолмен өңделеді. «Алмалық ТМК» АҚ-да мырыш концентраттарын гидрометаллургиялық өңдеу процесінде алынған мырыш қоқымын пирометаллургиялық әдіспен – илектеу арқылы өңдейді. Илектеу процесі ұзындығы 50 метр және диаметрі 3,5 метр екі құбырлы пеште (илектеу пеші) 1100–12000^{0}С температурада, тотықсыздандырғыштың, кокс ұсағының және мұнай коксының қатысуымен өтеді. Мырыш қоқымын илектеу нәтижесінде возгондар мен қатты техногендік қалдық, құрамында мыс, алтын, күміс бар клинкер түзіледі. Клинкерден қымбат металдарды алу үшін, ол зауытта балқыту пештерінде өңделеді. Қазір 450 мың тоннадан астам клинкер жинақталып тұр. Осыған байланысты қазіргі уақытта мырыш қоқымдарын өңдеудің қымбат илектеу процесінің орнына, гидрометаллургиялық әдіспен мырыш қоқымдарын өңдеу бойынша ғылыми зерттеулер жүргізілуде. 4-4,5 сағат шаймалау кезінде мөлшері 0,074 мм қоқымдарды жоғары температурада (9000^0 С) күкірт қышқылымен шаймалау игерілді, ерітіндіге мырыштың алынуы 98,5% құрайды; мыс 92,8%; темір 75,2%; кадмий 79,2% болады.

Түйін сөздер: мырыш, қоқым (сүзінді), процесс, шаймалау, концентрат, қож, экстракция, ерітінді, клинкер, кокс.

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Совершенствование технологической схемы переработки цинковых концентратов гидрометаллургическим способом на АО «Алмалыкский ГМК»

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АННОТАЦИЯ

Извлечение цинка из концентратов осуществляется двумя способами: пирометаллургическим и гидрометаллургическим, а получение чистого цинка высших марок возможно гидрометаллургическим методом, при котором прокаленный сульфидный концентрат подвергают сернокислотному выщелачиванию раствором сернокислого цинка и образуется рециркуляционный продукт – твердый остаток процесса выщелачивания кека. После очистки раствор сульфата цинка подвергают электролитическому рафинированию, а кек перерабатывают пиро- или гидрометаллургическим способом. На АО «Алмалыкский ГМК» в процессе гидрометаллургической переработки цинковых концентратов полученный цинковый кек перерабатывается пирометаллургическим методом – прокаткой. Процесс прокатки происходит в двух трубчатых печах (прокатных печах) длиной 50 метров и диаметром 3,5 метра при температуре 1100-12000С, в присутствии восстановителя, коксовой мелочи и нефтяного кокса. В результате прокатки цинковых кеков образуются возгоны и твердый техногенный остаток — клинкер, содержащий медь, золото и серебро. Клинкер перерабатывается на заводе в плавильных печах с целью извлечения драгоценных металлов, но на данный момент его накапливается более 450 тысяч тонн. В связи с этим в настоящее время проводятся научные исследования по переработке цинковых кеков гидрометаллургическим методом с целью исключения дорогостоящего прокатного процесса переработки цинковых кеков; освоено высокотемпературное (900 С) сернокислотное выщелачивание кеков размером 0,074 мм при выщелачивании в течение 4-4,5 часов, извлечение цинка в раствор составляет 98,5%; медь 92,8%; железо 75,2%; кадмий 79,2%.

Ключевые слова: цинк, кек, процесс, выщелачивание, концентрат, огарок, экстракция, раствор, клинкер, кокс.

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Earth sciences

Methodological principles of searching for disposal sites of radioactively contaminated materials by geophysical methods

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ABSTRACT

This article is devoted to radiometric studies at one of the sites of the Chornobyl nuclear power plant (the “Sandy Plateau” site), which is located on the south-eastern outskirts of the city of Pripyat. Radioactive substances, both artificial and natural, resulting from incidents and disasters at nuclear facilities pose the greatest danger. The disposal sites for radioactively contaminated materials considered in this work are sources of groundwater pollution. Currently, there is a problem of searching for their location for reburial in specialized stationary burial grounds, to solve which detailed complex geophysical studies are used. Various geophysical methods are considered, including micro-sensing and radiometric studies, to determine the location of burials. Particular attention is paid to the analysis and interpretation of geophysical data, as well as the economic and practical aspects of the application of these methods. As a result of the study, it was established: that when searching and studying burial sites of radioactively contaminated materials, the use of surface gamma photography makes it possible to assess the level of radioactive contamination of the upper layers of the soil (to a depth of 0.8-1 m). However, if the thickness of buried radioactively contaminated materials exceeds a certain level, which leads to weak contamination of rocks at a depth of more than 1-1.5 m, then burial objects may go undetected when using only gamma-ray imaging. In such cases, microgamma probing becomes an effective method. Increased values of exposure dose rate and the nature of microgamma sounding curves serve as indicators of the presence (increase in exposure dose rate with depth) or absence (sharp decrease in exposure dose rate with depth) of radioactively contaminated materials in the studied area.

Keywords: radioactive contamination, geophysics, research, complexing, micro gamma sounding, decontamination.

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Introduction

One of the greatest dangers is the radioactive pollution of the environment by man-made and natural radionuclides after accidents and catastrophes at nuclear cycle facilities. By-products of nuclear energy production pose long-term risks to human health and the environment [1]. The accident on April 26, 1986, at the Chornobyl nuclear power plant, which led to the release of large amounts of radionuclides into the environment, led to serious contamination of the surrounding area [[2], [3]].

As a result of the clean-up efforts of the accident in 1986-87, waste dumps containing approximately

106 m3 of low-level waste were created [4]. These waste dumps largely do not comply with regulatory requirements for low-level waste disposal sites and pose a radiation hazard to the environment.

According to an assessment by the Nuclear Energy Agency Committee on Radiation Protection and Public Health, “...all of these wastes are a potential source of groundwater contamination that will require careful monitoring until safe disposal in an appropriate repository can be achieved.” and that "...large uncertainties remain which require correspondingly greater characterization efforts" [5].

In 1999-2003, an international team of French and Ukrainian institutes studied the behavior of radionuclides from the Chornobyl fallout at an experimental site in the area of the “Red Forest” landfill near the Chornobyl nuclear power plant. The Chornobyl Pilot Site (CPS), established as part of the project, became a field installation for in-situ confirmation and development of models of radionuclide migration in soils and the geosphere [[6], [7]].

In 1986-1988, temporary disposal sites of radioactively contaminated materials, decontamination waste, radioactively contaminated structures and equipment were carried out in the Chornobyl exclusion zone without proper engineering training for special burial grounds. Due to the emergency, the work was carried out urgently, while in almost most cases, proper topographic mapping of the disposal sites of radioactively contaminated materials was not ensured. In this regard, at this time, the location of many of them is unknown. Meanwhile, these disposal sites are sources of groundwater pollution that feed the Pripyat River and its tributaries. Nowadays, there is a problem of searching for them to reburial them in specialized stationary burial grounds.

The task of finding disposal sites for radioactively contaminated materials can be solved only through the use of detailed integrated geophysical studies. From the point of view of geophysics, the main types of pollution of the geological environment are radioactive and geochemical. As a result of studying the geological environment by geophysical methods, static and dynamic (time-varying) geophysical anomalies over pollution sources are detected [[8], [9]].

Tasks and complex of geophysical research

Geophysical methods are widely used in engineering-geological, geoecological and archaeological research. Analyzing the experience of using geophysical methods in solving engineering problems, it was determined that the tasks of searching for disposal sites of radioactively contaminated materials are practically similar to the tasks that are set before geophysical methods in the process of archaeological research.

The possibility of using geophysical research is based on a noticeable difference in the electromagnetic and radiometric parameters of both archaeological and man-made objects, compared with the surrounding host rocks. At the same time, the following basic tasks are solved using geophysical methods:

- mapping of trenches, mine workings, dams, ditches;
- search and exploration of disposal grounds, necropolises, underground structures, armament depots, and disposal sites of radioactively contaminated materials [[10], [11]].

A specific feature of the search for disposal sites of radioactively contaminated materials is the determination of radiometric parameters of radioactively contaminated materials and host soils. The experience of using geophysical methods for this purpose and the analysis of literary data indicates that the solution to the above tasks is a rather complex problem and requires the use of detailed integrated geophysical studies, as well as experimental and methodological work to improve the selected complex [[1], [2], [3], [4], [5], [12]].

From our point of view, a set of geophysical methods for searching and exploration of natural reserves should include:

- micro-electrical profiling using the electrical resistance method in various modifications, based on measuring the resistance of soils and rocks using electric currents;
- electrical profiling using the natural electric field method, which allows identifying zones with anomalous conductivity, which may indicate the presence of radioactive waste or changes in the composition of soils;
- microelectric sounding for detailing detected anomalous areas, allowing to localize of the sources of anomalies and determining their nature using point measurements of electrical resistance at shallow depths;
- the induced polarization method using the median gradient method is used to assess the polarizability of rocks and identify zones with

increased content of metals or organic substances, which may be associated with the disposal of radioactive waste;

- GPR sensing is effective for searching for containers with radioactive waste and mapping the structures of underground voids. The method uses radio waves to obtain images of underground structures, making it possible to detect various objects and anomalies at depths of up to several tens of meters with high resolution;
- micromagnetic studies involve measuring the Earth's magnetic field to identify local anomalies caused by the presence of magnetic materials or changes in the magnetic properties of rocks;
- surface and borehole gamma survey - measures the level of natural radioactivity of rocks and soils;
- as well as laboratory radiometric studies.

At the same time, the rational complex of specialised geophysical research in each specific case is determined by the tasks and economic factors.

Geophysical surveys are carried out in a profile-area version and should be sufficiently detailed, the observation step is several meters, and when anomalies are detailed – tens of centimeters. Parametric observations are performed on known objects and serve as exemplary models for interpreting the results of observations on ordinary profiles [[13], [14]].

Some positive experiences of such work have been accumulated. An example is the search for military equipment that sank in the swamps in 1941-1944 and the disposal sites of German soldiers on the fields of the Korsun-Shevchenko Battle. At the same time, detailed magnetometric surveys, as well as studies using natural electric field and microelectroprofiling methods (searching for craters from explosions of aerial bombs, artillery shells, remnants of iron structures, and weapons) turned out to be quite effective [[15], [16], [17]].

The processing of the received materials consists in their complex interpretation and analysis of the entire data set. As a result, anomalous zones are highlighted, which may be related:

- with a violation of the integrity of rocks (based on the materials of micro electroprofiling, microelectrosonding and GPR studies);
- with the presence of steel fragments (based on the materials of micromagnetic survey);
- with electrochemical processes (oxidation of metal fragments) occurring in the body of the disposal (based on the methods of natural electric field and induced polarization);
- with the presence of soils and materials intensively contaminated with radioactive substances – products of nuclear accidents and waste from radiochemical production (based on materials from surface and spur gamma-ray surveys).

Based on the results of the performed geophysical studies, a set of geophysical maps and sections is being built, which allow us to conclude that there is a disposal of radioactively contaminated materials in the studied area, as well as to determine the points of opening the body of disposal by wells and pits.

Experimental part

As an example of such work, we will present some materials of radiometric studies at one of the sites of the Chornobyl nuclear power plant (the Sandy Plateau site). The site is located on the southeastern outskirts of the city of Pripyat. Before the accident at the Chornobyl nuclear power plant, this area was washed with river sand 2 m thick and was planned for the construction of a new massif in Pripyat. Uncontaminated river sand is characterized by an exposure dose rate of 4-8 μR/h. Figure 1 shows a fragment of the 137Cs surface pollution map of the Chornobyl exclusion zone with the research area marked on it.

In 1988, experimental decontamination works were carried out at the research site by removing the top layer of soil with a thickness of 10 cm. In accordance with technical specifications, highly active soil should be buried on the same site, but information about the location of the disposal turned out to be lost. Many years later, the urgent task of searching for temporary disposal of radioactively contaminated soil removed during decontamination works arises. To solve this problem, areal studies were performed at the work site using the biolocation method over a network of 20×10 m. Based on the materials of these works, elongated anomalies were identified, the nature of which at the first stage was associated with the presence of trenches with radioactively contaminated soil. However, selective drilling of individual biolocation anomalies did not yield positive results [[18], [19], [20]].

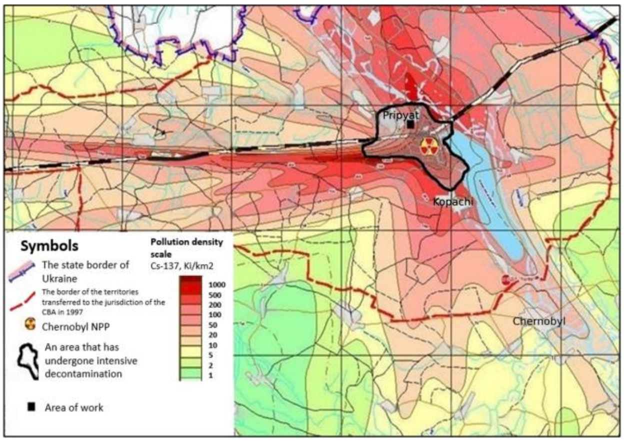

Figure 1 - Fragment of 137Cs surface contamination map: The scale 1:200 000

To check the detected anomalies, a surface gamma survey was performed over a 20×5 m network using a SRP-68-01 radiometer, the results of which are shown in Figure 2. At points where the exposure dose rate of γ-radiation (P) exceeded 3000 µR/h, measurements were repeated using the SRP-68-03 spur radiometer.

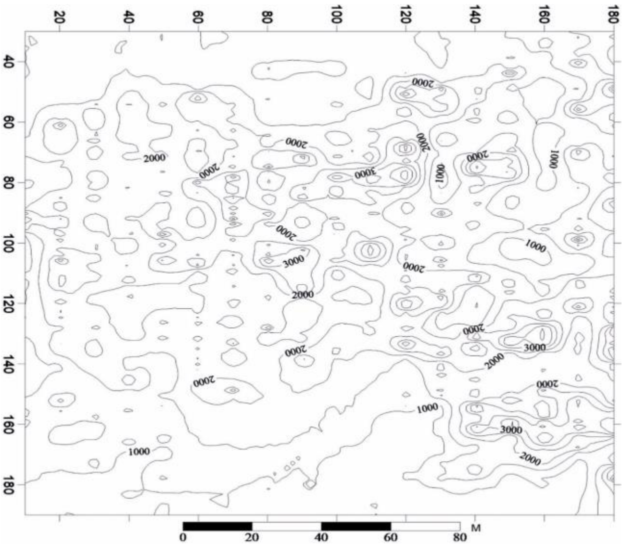

Figure 2 - Map of the exposure dose rate of γ-radiation (P). The «Sandy Plateau» site: The scale is 1:2 000. The isolines are drawn through 500 µR/h.

The exposure dose rate of γ-radiation at the research site varies from 350 µR/h to 4250 µR/h. The areas with increased exposure dose rates (2000 – 4000 µR/h) are localized in the central and southeastern parts of the research area, and the areas with reduced P values (350 – 1500 µR/h) are located in the northern, northeastern, southern and western parts of the site. The average values of the exposure dose rate of γ-radiation at the research site are 1800 µR/h. According to the materials of the «Kirovgeologiya» production association, the background values of the exposure dose rate of γ-radiation of territories composed of river sands in the research area ranged from 4 µR/h to 8 µR/h.

The gamma field has a mosaic, sometimes backstage nature, which may be the result of uneven removal of the upper highly active layer by earthmoving machines during decontamination. At the same time, the negative forms of the microrelief were partially «sprinkled» with highly active soil, and the positive ones, on the contrary, were cut to a great depth.

To assess the degree of radioactive contamination, the specific activity of ^{137}Cs was calculated using the well-known formula:

$$A_{Cs} = \frac{P \cdot \mu_{эф}}{2 \cdot \pi \cdot K_{\gamma Cs} \cdot \rho},$$

where *P* – exposure dose rate, µR/h; $\mu_{эф}$ – effective attenuation coefficient of γ-radiation; $K_{\gamma Cs}$ – gamma equivalent of ^{137}Cs; ρ – density of rocks, g/cm^3. A fragment of the pollution assessment map of the ^{137}Cs site is shown in Figure 3.

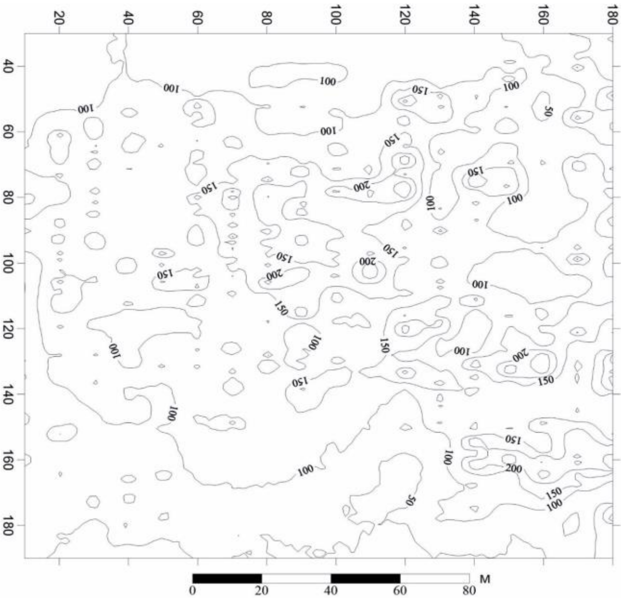

Figure 3 - Map of the specific activity of 137Cs (ACs) of the topsoil. The «Sandy Plateau» site: The scale is 1:2000. The isolines are drawn through 500 kBq/kg.

For the study area, the specific soil activity caused by ^{137}Cs in the depth range of 0-50 cm varies from 24 kBq/kg to 291 kBq/kg with an average value of 121 kBq/kg.

For operational analysis of gamma survey materials, graphs of exposure dose rate and specific activity of 137Cs were constructed along profiles that stretched from south to north. The exposure dose rate is related to the level of radiation exposure and is taken into account when planning radiation protection measures and environmental monitoring. The specific activity of cesium shows how much a specific mass of material is contaminated with the radionuclide. High specific activity may indicate significant radioactive contamination requiring decontamination measures or access restrictions. These indicators are used to assess current conditions, plan protection measures and respond to radiation accidents.

Figure 4 shows the materials of the surface gamma-ray survey according to profile 8 (graph of exposure dose rate and specific activity of ^{137}Cs), typical for the research area.

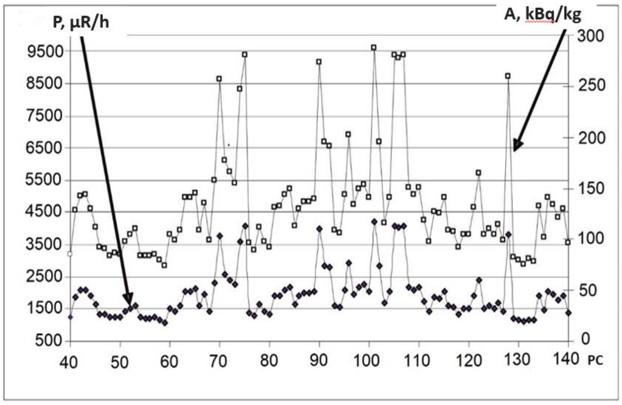

Figure 4 - Graphs of the exposure dose rate (P) and specific activity of 137Cs of the topsoil (A) according to profile 8

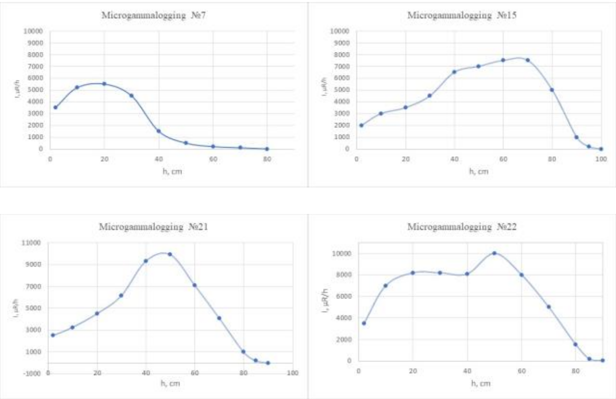

Figure 5 - Graphs of the dependence of the change in the exposure dose rate (I) on the depth (h), characteristic of microgammasondings performed at the «Sandy Plateau» site.

A comprehensive analysis of the γ-radiation exposure dose rate map and the biolocation research scheme revealed that the correlation of biolocation and surface γ-anomalies is often absent [20].

To check the anomalous zones identified by biolocation and surface γ-survey, microgammasonding was performed, the characteristic types of which are shown in Figure 5.

Results and Discussion

The materials of the microgammasonding curves show that the value of the exposure dose rate at depths of 2-10 cm ranges from 1300 µR/h to 7000 µR/h and tends to increase with depth. With a further increase in the measurement depth (up to 50 – 70 cm), different behaviors of the exposure dose rate graph are observed, depending on the depth of penetration of technogenic radionuclides into the soil: the values remain at the same level, increase or in some cases decrease. The final branch of all microgammasondings has a descending nature, and the exposure dose rate decreases to tens of µR/h, i.e. almost to the background. Analysis of microgammasonding data shows that the penetration depth of technogenic radionuclides is up to 50-60 cm. The nature of the behavior of microgammasonding curves (a sharp decrease in the exposure dose rate after 30-60 cm with a depth) allows us to conclude that there is no disposal of radioactively contaminated soil in the surveyed area.

Conclusions

The complex of geophysical methods in the search and exploration of disposal sites of radioactively contaminated materials includes surface and spur gamma-ray surveys, microelectroprofiling by the process of electrical resistance in various modifications, electroprofiling by the method of natural electric field, microelectrosonding when detailing detected anomalous areas, the method of induced polarization by the method of median gradient, micromagnetic and geolocation studies, as well as laboratory radiometric studies. The tasks and economic factors determine a rational complex of specialised geophysical research in each specific case, while geophysical surveys should be sufficiently detailed.

During the search and exploration of disposal sites for radioactively contaminated materials, surface gamma-ray surveys allow us to assess the radioactive contamination of the topsoil (up to a depth of 0,8-1 m), but with the capacity of overlapping disposal sites for radioactively contaminated materials of slightly contaminated rocks of more than 1-1,5 m, the search object may not be fixed.

Microgammasonding is an effective method for determining the disposal of radioactively contaminated materials. High values of exposure dose rate and the behavior of microgammasonding curves are criteria for the presence (increase in exposure dose rate with depth) or absence (sharp decrease in exposure dose rate with depth) of disposal of radioactively contaminated materials at the surveyed site.

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

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Радиоактивті ластанған материалдар көмілген жерлерді геофизикалық әдістермен іздеудің әдістемелік принциптері

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ТҮЙІНДЕМЕ

Бұл мақала Припять қаласының оңтүстік-шығыс шетінде орналасқан Чернобыль атом электр станциясы учаскелерінің біріндегі («Құмды үстірт» учаскесі) радиометриялық зерттеулерге арналған. Ядролық қондырғылардағы апаттардың әсерінен пайда болған жасанды және табиғи радиоактивті заттар үлкен қауіп төндіреді. Радиоактивті ластанған материалдар көмілген орындар жер асты суларын ластайды Қазіргі уақытта мамандандырылған стационарлық қорымдарда қайта көму мақсатында олардың орналасқан жерін іздеу мәселесі тұр, оны шешу үшін егжей-тегжейлі кешенді геофизикалық зерттеулер қолданылады. Жерлеу орындарының орнын анықтау үшін әртүрлі геофизикалық әдістер қарастырылады, соның ішінде микро-сенсорлық және радиометриялық зерттеулер. Геофизикалық мәліметтерді талдау мен түсіндіруге, сондай-ақ осы әдістерді қолданудың экономикалық және практикалық аспектілеріне ерекше назар аударылады. Зерттеу нәтижесінде анықталғаны: радиоактивті ластанған материалдар көмілген жерлерді іздестіру және зерттеу кезінде жер үсті гамма-фотосуретін пайдалану топырақтың жоғарғы қабаттарының (тереңдікке дейін) радиоактивті ластану деңгейін бағалауға мүмкіндік береді. 0,8-1 м). Алайда, егер көмілген радиоактивті ластанған материалдардың қалыңдығы белгілі бір деңгейден асып кетсе, бұл 1-1,5 м-ден астам тереңдіктегі тау жыныстарының әлсіз ластануына әкеліп соқтырса, онда көму объектілері тек гамма-сәулелік бейнелеуді қолданғанда анықталмай қалуы мүмкін. Мұндай жағдайларда микрогамма зондтау тиімді әдіске айналады. Экспозиция дозасының жылдамдығының жоғарылауы және микрогамма зондтау қисықтарының сипаты зерттелетін аумақта радиоактивті ластанған материалдардың болуы (тереңдікпен экспозициялық доза жылдамдығының жоғарылауы) немесе жоқтығы (тереңдікпен экспозициялық доза жылдамдығының күрт төмендеуі) көрсеткіштері ретінде қызмет етеді.

Түйін сөздер: радиоактивті ластану, геофизика, зерттеу, комплекстеу, микрогаммалық зондтау, залалсыздандыру.

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Методические принципы поисков пунктов захоронения радиоактивно загрязненных материалов геофизическими методами

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АННОТАЦИЯ

Данная статья посвящена радиометрическим исследованиям на одном из участков Чернобыльской АЭС (участок «Песчаное плато»), который расположен на южно-восточной окраине г. Припять. Радиоактивные вещества, как искусственного, так и естественного происхождения, возникшие из-за инцидентов и катастроф на ядерных объектах, представляют наибольшую опасность. Рассматриваемые в данной работе пункты захоронения радиоактивно загрязненных материалов являются источниками загрязнения подземных вод. В настоящее время существует проблема поисков их местоположения с целью перезахоронения в специализированные стационарные могильники, для решения которой используются детальные комплексные геофизические исследования. Рассматриваются различные геофизические методы, включая микрогаммазондирование и радиометрические исследования, для определения местоположения захоронений. Особое внимание уделяется анализу и интерпретации геофизических данных, а также экономическим и практическим аспектам применения этих методов. В результате исследования установлено: при осуществлении поиска и исследовании мест захоронения радиоактивно загрязненных материалов использование поверхностной гамма-съемки позволяет оценить уровень радиоактивного загрязнения верхних слоев грунта (до глубины 0,8-1 м). Однако, если мощность захороненных радиоактивно загрязненных материалов превышает определенный уровень, что приводит к слабому загрязнению пород на глубине более 1-1,5 м, то объекты захоронения могут остаться незамеченными при использовании только гамма-съемки. В таких случаях эффективным методом становится микрогаммазондирование. Повышенные значения мощности экспозиционной дозы и характер кривых микрогаммазондирования служат индикаторами наличия (увеличение мощности экспозиционной дозы с глубиной) или отсутствия (резкое снижение мощности экспозиционной дозы с глубиной) радиоактивно загрязненных материалов в изученном участке.

Ключевые слова: радиоактивное загрязнение, геофизика, исследования, комплексирование, микрогаммазондирование, дезактивация.

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