

HYDROMETALLURGICAL PROCESSING OF MOLYBDENUM MIDDINGS FROM SHATYRKUL-ZHAYSAN CLUSTER ORE

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Abstract

This research investigates the hydrometallurgical processing of molybdenum middlings extracted from copper-molybdenum ore in the Shatyrcul-Zhaysan cluster in Kazakhstan. A molybdenum intermediate obtained after selective flotation of the copper-molybdenum concentrate was used, with a recovery of 0.07%, a molybdenum content of 22.23% and an extraction of 74.91%. The mineralogical analysis shows molybdenite and chalcopyrite as the main minerals. In experiments, atmospheric leaching with nitric acid in single-stage and two-stage countercurrent processes was investigated to optimize molybdenum extraction and reduce acid consumption. The optimum conditions obtained were: 300 g/L nitric acid, 100 g/L sulfuric acid, 90°C temperature and 2 hours leaching time in the single-stage leaching, which extracted 98.8% molybdenum. The two-stage leaching under optimized conditions allows the extraction of 94.3% molybdenum in solutions with lower residual acidity (0.89 g-eq/L) and redox potential (550 mV) without reducing the extraction of valuable component. Molybdenum extraction reaches 94.3% in the subsequent solvent extraction stage from two-stage leaching solutions. The final product, calcium molybdate with a molybdenum content of 46.83%, meets commercial grade specifications. This research demonstrates an effective process for hydrometallurgical production of commercial grade calcium molybdenite from copper-molybdenum ore, with high molybdenum recovery, reduced acid consumption through two-stage leaching, and minimal hazardous discharges.

Keywords: Leaching; Nitric acid; Extracting; Environmental friendliness; Minerals

1. Introduction

Due to the global ongoing worldwide depletion of natural resources, high prices, high demand, and future scarcity, it is extremely important to recycle ores, by-products, secondary materials and waste. In addition, it is necessary to use more efficient and cost-effective technologies to produce marketable products in order to minimize capital costs and protect the environment. To improve the extraction of molybdenum from the ore to finished molybdenum industrial products and the intention of overall resource utilization, it is beneficial to obtain molybdenum industrial products with maximum separation of the molybdenum in them with the following metallurgical processing and highly selective extraction of minerals [1]. Hydrometallurgical nitric acid leaching technology can treat both complete and incomplete concentrates, intermediates, and other products with high molybdenum recovery [2]. Innovative intensive methods, such as very fine crushing, and high-

temperature autoclave leaching, do not reach the average in the selection of colour and rock resources [3]. One of the promising ways of revealing high-sulphur quartz-sulphide products turn out to be sulfurization in the substance of mineral acid [4]. The nitric acid method helps to transfer valuable components into the solution [5].

Nitric acid leaching is applied in various parts of the world for extracting valuable metals and minerals from ores and concentrates. This hydrometallurgical process is commonly used in the mining and metallurgical industries to extract metals such as copper, nickel, and uranium from their respective ores. It is also employed in the production of fertilizer-grade phosphoric acid from phosphate rock, as well as in the purification of precious metals such as gold and silver. The method's versatility and effectiveness in metal extraction make it a widely used technique in regions with significant mining and mineral processing activities, including but not limited to North America, South America, Europe, Africa, and Asia.

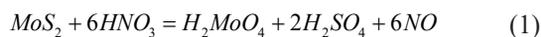
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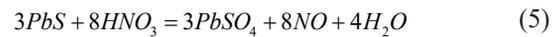
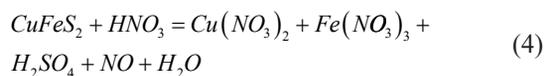
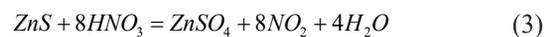
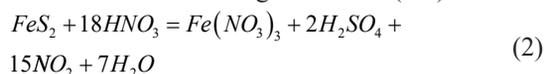


D. Dreisinger [1] noted, that the outcomes of treating limonitic laterite ores with nitric acid pressure leaching (NAPL) were impressive, with over 82% recovery rates for both Ni and Co, production of Ni/Co hydroxide with 25.4% Ni and 2.6% Co, over 85% HNO₃ regeneration/recycling, and the generation of valuable by-products. The marketability of the sulfur-free leaching iron residue for iron production and the production of fibrous calcium sulfate for papermaking during HNO₃ regeneration was remarkable. Additionally, the NAPL technology achieved over 98% nickel and cobalt extractions and less than 1.5% iron extraction in high magnesium-bearing laterite ores, demonstrating its profitability based on preliminary economic analysis. Researchers B. Ma et al. [2] explored the potential of hydrometallurgical processing to unlock valuable minerals from complex ores and concentrates, and presented two notable developments as examples of the integration of new science and technology into processing methods. The authors concluded, that the Boleo process demonstrates the ability to extract copper, cobalt, zinc, and manganese from a complex, clay-bearing ore, aided by high-rate thickener technology for separating and washing clay-bearing leach residue.

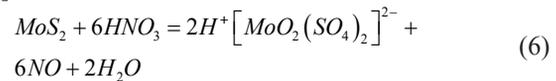
The decomposition of molybdenite concentrates can be carried out by hydrometallurgical methods that exclude pre-oxidation roasting. The treatment of molybdenite concentrate with nitric acid at 90°C oxidizes molybdenite to form molybdenum acid [6]. One of the advantages of the nitric acid method is the complete extraction of by-product metals (rhenium and copper), and harmful discharges are practically eliminated since a mixture of ammonium sulphate and nitrate is crystallized from the nitric-sulphuric acid mother liquor after evaporation [7]. The interaction of MoS₂ with nitric acid is described by the overall reaction equation (1) [8]:



In this early period and all the oxidized molybdenum turns into a solution, containing the composition of cations MoO₂²⁺, Mo₂O₅²⁺. When the number of sulphuric acids in the solution increases, the molybdenum particle transform into anionic sulphate aggregates (for example, [MoO₂(SO₄)₂]²⁻). The characteristic of low-grade molybdenite products is that they contain many associated sulfides, which react with nitric acid through reactions (2-5):



In this case the reactions described above (4, 5) produce nitrogen monoxide, which exposes molybdenite to oxidation, and by reactions (2, 4) produce sulphuric acid comes out, which makes it possible to retain molybdenum, which is oxidized in the mixture. Nitric acid leaching of molybdenite in this case is represented by the reaction equation (6) [8]:



However, the processing of industrial products rich in molybdenum requires the additional introduction of sulphuric acid, the addition of which forms the complex [MoO₂(SO₄)₂]²⁻, which allows the molybdenum to be completely retained in the mixture and increases the rate of oxidation of MoS₂ by utilizing of the initial source reaction (MoO₂²⁺, Mo₂O₅²⁺). In addition, H₂SO₄ is known to increase the wettability level of the product, which ensures that the molybdenite oxidation reaction operates at an increased rate from the first step. The progressive use of nitric acid as a leaching agent is indicated by the following attributes:

- the energy potential of the ongoing hydrochemical reactions;
- increased oxidative progression of the system;
- high probability of utilization of the escaping nitrous fumes during the regeneration of the nitric acid.

Y. E. Agapitov et al. [9] found that in the hydrometallurgical processing of minerals, working mixtures formed during nitric acid leaching of sulphide ores and products must generally be characterized by increased properties such as exact acidity (4-6 g eq/l), redox potential (ORP) -900 mV [9]. This complicates further processing of such solutions and reduces the service life of the reagents (extractants, sorbents) and the irrational consumption of nitric acid [10]. Nitrous gases formed by the interaction of sulfides and nitric acid are captured with further regeneration of nitric acid [11]. This corresponds to the proven scheme in which water-ore slurries, water, concentrated sulphuric acid, and ammonia water are used as absorbers [12].

2. Materials and Methods

The aim of the trial is to produce commercial calcium molybdate from industrial molybdenum products using hydrometallurgical methods applied to copper-molybdenum ore from the Shatyrcul-Zhaysan cluster in Kazakhstan. Initial ore processing involves collective and selective flotation to obtain copper and molybdenum concentrates. Prior to leaching, the



mechanical preparation of the molybdenum product is performed to break down the mineral associations and improve subsequent hydrometallurgical processing. The leaching experiments are carried out in a reactor with controlled parameters, including temperature, acid concentrations (varying nitric acid at constant sulfuric acid), and leaching time, with the goal of optimizing molybdenum extraction. This comprehensive approach aims to develop an efficient process for the production of commercial calcium molybdate from available raw materials.

Studies have been conducted to produce a commercial product – calcium molybdate from molybdenum industrial products by hydrometallurgical methods from copper-molybdenum ore of the Shatyrkul-Zhaysan cluster. The Shatyrkul deposit is in the Shuisky district of the Zhambyl region (Republic of Kazakhstan) 35 km east of Birlik station and is one of the sites of the Shatyrkul-Zhaysan cluster. The technology of copper-molybdenum ore processing developed by NOVOMEK Engineering LLC includes obtaining collective copper-molybdenum concentrate and its subsequent selection. The final products of the technology are copper and molybdenum concentrates. The technological scheme for ore processing includes two main operations: collective flotation (main flotation, control flotation, and three refinings) and selective flotation (main flotation, three refining operations, and additional flotation of the first refining tailings) [13-17]. The separation of copper-molybdenum concentrates was based on the application of sodium sulphide with prior oxidative steaming, kerosene was used as a molybdenite collector [18-22].

The chemical analysis of the solid and liquid samples was conducted using atomic absorption spectroscopy (AAS) and inductively coupled plasma optical emission spectrometry (ICP-OES). AAS was pivotal in determining the concentrations of various metals such as molybdenum, copper, and iron in the leach solutions. Concurrently, ICP-OES was also used to analyze the metal concentrations in these solutions. These methodologies were integral in providing comprehensive insights into the elemental composition of the samples, thereby playing a crucial role in optimizing the hydrometallurgical process and ensuring effective metal extraction.

Extractant performance studies were carried out by experimentally constructing extraction isotherm curves. This involved contacting equal volumes of organic and aqueous phases with varying initial metal concentrations in the aqueous phase. The equilibrium pH and metal concentrations in each phase were analyzed to plot the extraction isotherms. Studies on the leaching of molybdenum middlings in a direct flow single-stage and two-stage counter-current mode

were conducted. To intensify the process to reduce the leaching time and increase the extraction before each experiment the operation of mechanical preparation of the molybdenum product in the flotation complex was carried out [23]. Mechanical preparation of molybdenum was carried out to reveal molybdenum from all mineral associations (sulfides, oxides, silicates) and therefore can be considered as one of the possible methods of preparation of this type for the subsequent hydrometallurgical processing. For mechanical activation, a sample of the initial concentration was placed in a plastic cup with a rubber insert and metal balls, water was added in an amount equal to a sample of the concentrate and a turbine stirrer stirred the pulp for 8 minutes at a speed of 1000 rpm, provided by a mechanical drive.

Then, using a metal sieve, the pulp was separated from the metal balls and quantitatively transferred to the reactor. After sedimentation of the solid phase the L:T ratio was brought to the value required for the conditions of the experiment. L = liquid volume, typically of water, leach solutions, or other process fluids (in ml or L), T = amount of solid material - ore, concentrates, tailings etc. (in g or kg). Under these conditions the disclosure of minerals of molybdenum intermediate product with a grade of -0.045mm from 72.2 to 91%. In the laboratory leaching studies, the reactor was filled with pre-prepared pulp (L:T = 1:1/3) and mechanically activated. The pulp was then heated to the temperature required by the conditions of the experiment at constant stirring ($n_{\text{arr}}=140-170$ rpm). Then nitric and sulphuric acids were injected into the reactor. At the end of dosing the reagents, the time of the beginning of leaching was fixed. Studies on the selection of the optimum concentration of nitric acid in the agitation leaching of molybdenum from the concentrate were conducted with a concentration of sulphuric acid 100 g/L, temperature 90°C, leaching time of 2 hours, ratio L:T=7:1, in the range of nitric acid concentration from 100-800 g/L.

In the extraction process CYANEX® 600 Molybdenum extractant was used in combination with Elixore 205 thinner as a diluent, with a ratio of approximately 25% extractant and 75% diluent. Extraction was performed with leach solutions obtained from both single-stage and two-stage leaching experiments, with varying key parameters such as acid concentration and metal ion concentrations. Extraction performance was evaluated by generating extraction isotherms, and the data was employed to model the extraction-reextraction process in a closed cycle. For re-extraction, molybdenum was re-extracted using a 10% sodium hydroxide (Na_2CO_3) solution, to obtain a purified solution suitable for the precipitation of calcium molybdate products. The optimization of the solvent extraction process was based on the composition of the initial leach liquors, with the two-



stage leaching solution exhibiting improved extraction efficiency attributed to lower acidity and redox potential. The concentrations of metals in the leach solutions like molybdenum, copper, iron etc. were determined using standardized analytical techniques such as atomic absorption spectroscopy or inductively coupled plasma optical emission spectrometry.

3. Results

The leaching conditions in the study were determined based on laboratory studies designed to optimize the leaching process. The pulp, prepared in a specific liquid-to-solid ratio (L: T) of 1:1/3, underwent mechanical preparation before being heated to the experimentally required temperature, with constant stirring (140-170 rpm). Both nitric and sulphuric acids were then added to the reactor. The study particularly focused on finding the optimal concentration of nitric acid for the agitation leaching of molybdenum from the concentrate. This was explored under the conditions of a sulphuric acid concentration of 100 g/L, a temperature of 90°C, a leaching time of 2 hours, and a L: T ratio of 7:1, with nitric acid concentration varying from 100-800 g/L. As a result of selective flotation of copper-molybdenum concentrate according to the developed technological scheme and selected reagent plan a molybdenum intermediate was produced with a yield of 0.07% with a molybdenum content of 22.23% and a recovery of 74.91% was produced. The chemical composition of the sample for hydrometallurgical processing is shown in Table 1.

The content of the main valuable components was molybdenum 22.23%, copper – 7.516%, gold 10.6 g/t, and silver 167 g/t. The ore minerals were studied in reflected light using an OLYMPUS BX53 microscope, SIMAGIS XS-3CU video camera, and the Mineral C7 Image Study Software from SIAMS. The mineralogical study of the molybdenum intermediate product visually established the approximate ratio of ore and non-ore minerals as 80:20%, respectively. The ore mineralization of the Mo concentrate is represented by:

- major ore minerals – molybdenite (40%) and chalcopyrite (22%);

- minor – magnetite, hematite, iron hydroxides (10% in total), and pyrite (10%);
 - rare – covellin;
 - singular – chalcosine, bournite;
 - non-metallic minerals (20%);
 - all ore minerals are almost 80% in the open state, free of aggregates;
 - the most frequent accumulations of molybdenite with chalcopyrite;
 - preferential grain size of molybdenite 0.003-0.5 mm, chalcopyrite 0.003-0.06 mm.

Molybdenite is quantitatively one of the main ore minerals. Molybdenite is finely scaly in the form of lamellar, tabular, foliated, in some places deformed, and sometimes barrel-shaped. Molybdenite is well-preserved, without signs of oxidation. The overwhelming majority of grains (80% of the total content) are free of clusters 0.003-0.5 mm in size. Accordingly, about 20% of grains of molybdenite are in aggregates with other ore minerals, most often with chalcopyrite, very rarely with hematite, pyrite, and non-ore minerals, forming simple and complex intergrowths, mainly in the form of binary, occasionally polymineral aggregates with the above minerals (Figure 1).

Chalcopyrite is the main copper sulphide, which is less frequently diagnosed than molybdenite and is characterized by a high opening. Almost all of the chalcopyrite (80% of the total content) is in a freely-fragmented state. The predominant grain size of chalcopyrite is within 0.003-0.06 mm, less frequent are segregations up to 0.1 mm in elongation. Approximately 20% of the total content in the concentrate, chalcopyrite forms close associations with molybdenite and hematite, less commonly with pyrite and magnetite, and occasionally with non-metallic minerals, forming both simple and complex intergrowths. Rarely, chalcopyrite is subjected to substitution by covellite to varying degrees. Relicts of molybdenite, pyrite, and hematite plates occur as inclusions in chalcopyrite. The conditions and results of studies on the analysis of nitric acid concentration dependence are presented in Table 2 and Figure 2.

At a nitric acid concentration of 100 g/L the molybdenum extraction was 41.73%. With increasing nitric acid concentration, the oxidation rate increases

Table 1. Chemical structure of the molybdenum product

Component	Content, %	Component	Content, %	Component	Content, %
Mo	22.23	As	0.018	Ni	0.0143
Cu	7.516	Co	0.0278	CaO	1.617
Au, g/t	10.6	P	0.12	C	9.57
Ag, g/t	167	Cd	<p.e.	Stotal.	27.85
Fe	16.54	Re, g/t	62.3	Sulfide.	27.6
Zn	0.049	Bi	<p.e.	Sulfide.	0.256
Pb	0.053	SiO ₂	11.422	Sb	0.000635
Al ₂ O ₃	2.128	MgO	1.23	U	0.0304



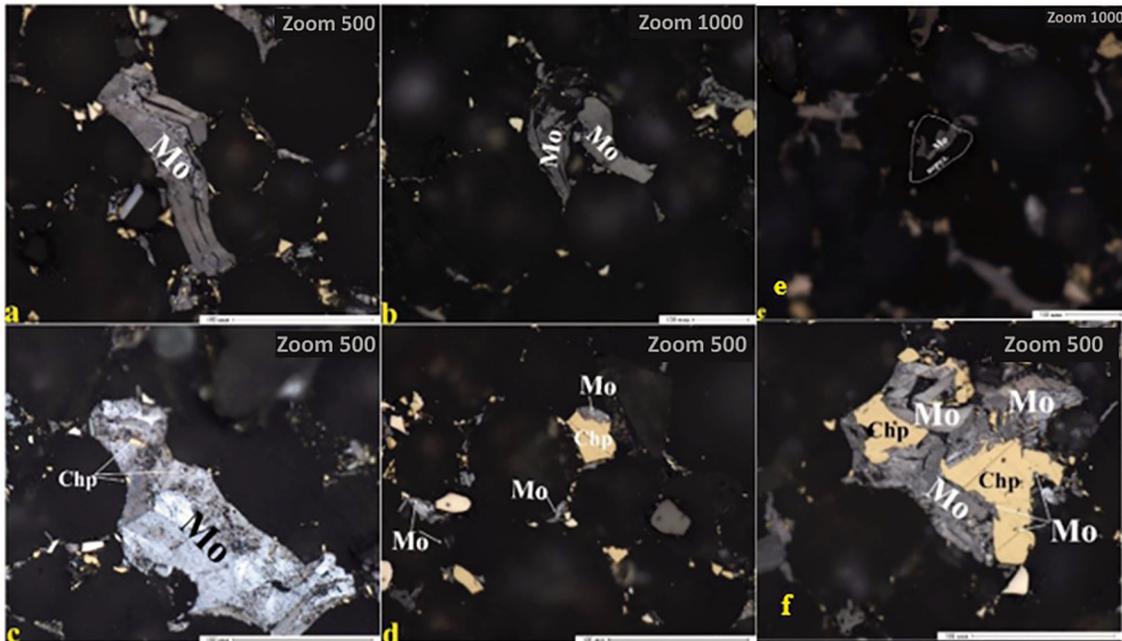


Figure 1. Characteristics of molybdenite excretions
 Note: Mo – molybdenite; Chp – chalcopyrite

Table 2. Conditions, plan, and results of molybdenum concentrate leaching

Nitric acid concentration, g/L	Result of cake, %	Cake elements content, %						Extraction into solution, %		
		Mo	Cu	Fe	Zn	Re, g/t	Ca	Mo	Cu	Fe
100	52.667	24.595	2.68	10.013	0.016	86.6	0.131	41.73	81.221	68.116
200	30.333	8.892	0.946	13.412	0.008	39.11	0.259	87.867	96.182	75.403
300	25.667	1.0033	0.389	13.285	0.005	16.77	0.158	98.842	98.672	79.384
400	24.333	1.763	0.178	14.027	0.003	7.19	0.169	98.07	99.424	79.364
500	25.333	4.813	0.098	13.098	0.002	1.17	0.159	94.515	99.67	79.939
600	25.333	8.164	0.118	12.349	0.002	1.71	0.141	90.696	99.602	81.086
800	30.33	10.509	0.035	9.442	0.001	0.63	0.114	85.66	99.859	82.685

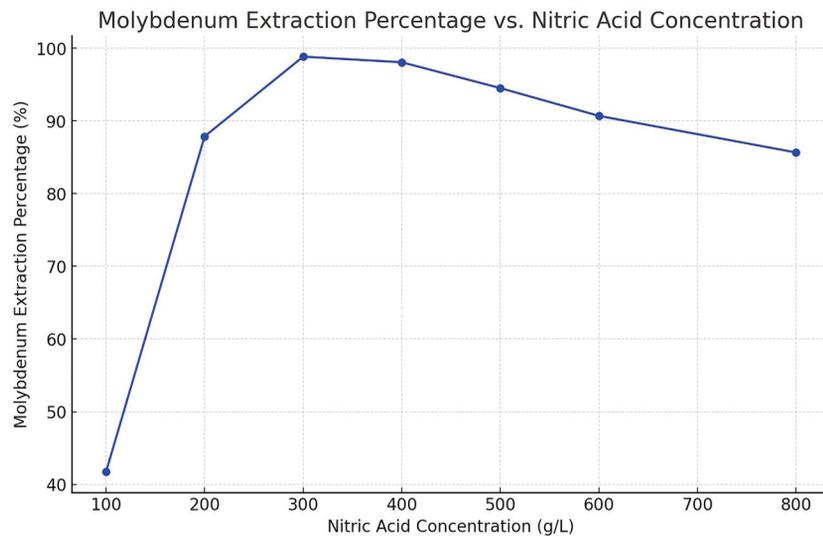


Figure 2. Percentage of extraction as a function of nitric acid concentration



and already at 300 g/L an almost complete oxidation of the molybdenum is achieved, with the placement of molybdenum in the mixture showing 98.842%. A further increase in concentration up to 800 g/L leads to a slight decrease in molybdenum oxidation, which contributes to coagulation of the molybdenum acid and deterioration of the oxidation of molybdenum minerals. The chemical composition of the residue (cake) after leaching with a nitric acid concentration of 300 g/L is presented in Table 3.

When carrying out further research on atmospheric leaching of the intermediate product, it is necessary to consider that to provide extraction of molybdenum at a level $\geq 98\%$, the concentration of nitric acid at the initial time should be 300 g/L. At the same time, the residual acidity of the productive solution was 2.3 g-eq/l, which can cause certain difficulties in the extraction of valuable components from the leaching solutions at the extraction stage. The processing of such productive leaching solutions requires additional operations of conditioning-

neutralization (with significant consumption of alkaline agents), thickening, sedimentation, and filtration. In order to reduce the consumption of nitric acid and, consequently, reduce the residual acidity of productive solutions, aimed at the extraction of valuable components by extraction/re-extraction of the solution and precipitation of calcium molybdate, studies on two-stage nitric acid leaching of molybdenum industrial product have been carried out. The leaching of molybdenum industrial products in a stepped counter-current mode involves two stages of leaching:

Soft leaching: the initial concentrate is in contact with the leaching solution from the second stage; the productive solution is sent for further processing.

Hard leaching: the cake from the first stage contacts with leaching agents – nitric and sulphuric acids; the leaching cake is sent for further processing or disposed of.

The two-stage leaching scheme is shown in Figure 3.

Table 3. Chemical composition of the leaching cake, %

Mo	S	P	Ca	As	Al	SiO ₂	MgO	Au, g/t	Ag, g/t	Bi
1	14.422	-	0.158	-	2.424	19.244	4.221	24.6	495	-
Cd	Re, g/t	Pb	Ni	Co	U	Ba	Zn	Cu	Fe	F
-	16	0.015	0.0171	0.0053	0.002	0.042	0.005	0.389	13.285	-

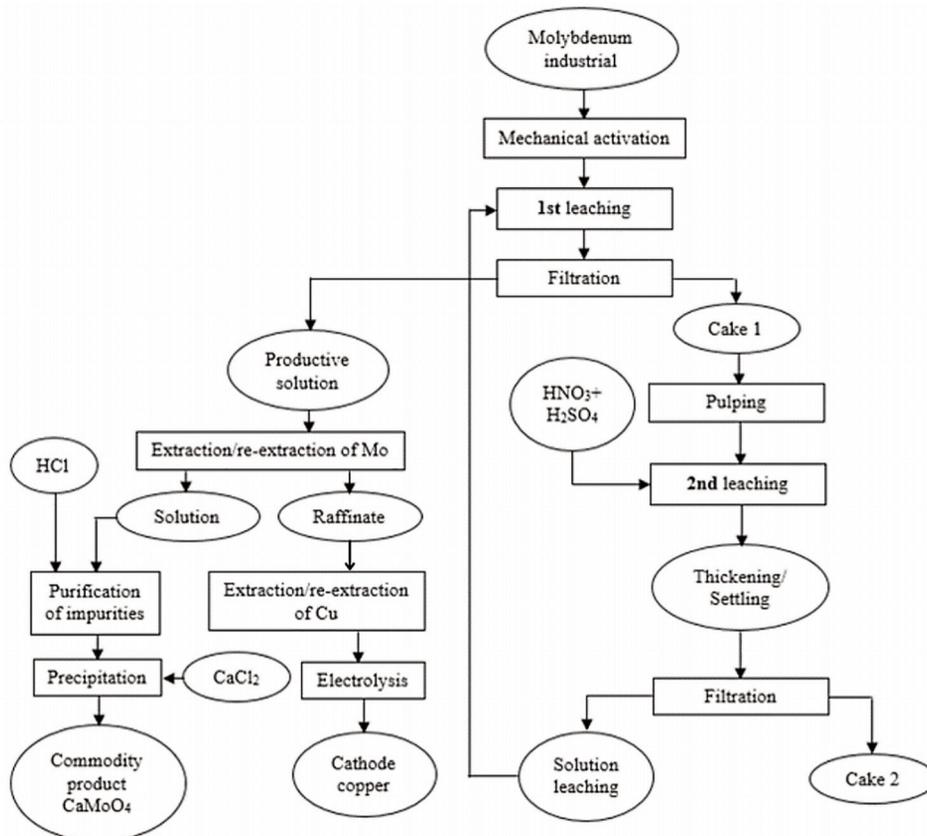


Figure 3. Two-stage counter-current leaching scheme for molybdenum milling product

For the two-stage leaching, studies were carried out with a nitric acid solution and the pre-processed solution, the composition of which is shown in (Table 4). Silver sulfide minerals do not dissolve in nitric acid medium. Instead, the silver probably forms an insoluble residue during the leaching process, which turns into the solid leach residue. Silver is detected in the leach cake analysis (16.77-495 g/t Ag in Table 2), but is absent from the post-leach solution (Table 4). The presence of sulfur in the cake (14.22% S) indicates that insoluble silver sulfide compounds rather than metallic silver are formed.

This solution (sample PR_{avg}) was obtained by leaching the concentrate with a nitric acid solution – 300 g/L and used for the initial treatment of the concentrate at the first stage of leaching. Subsequently, the leaching of the molybdenum intermediate product in the first stage was carried out with the solution from the 2nd stage of leaching, at a ratio of L:T=7:1, temperature 90°C. The cakes obtained from the experiments were used for the 2nd stage leaching studies with the addition of nitric acid. The conditions and the results of research on the leaching of molybdenum middlings in the stepped counter-current mode in two stages with recycled and nitric acid solution are shown in Table 5.

The 1st stage studies of molybdenum product leaching showed that by selecting the leaching conditions it is possible to obtain solutions with residual acidity of 1.7 equiv. g/L, with molybdenum extraction into the solution amounting to 88.81%, and copper extraction – 95.706%. The recovery in the second stage of the leaching was 91.688% of molybdenum and 87.448% of copper. The molybdenum extraction in the throughput after 2

leaching stages (test No. 1) was 99.07%. As can be seen from the data in Table 5 (test No. 2), the recovery of molybdenum in the 2nd stage of leaching with a circulating solution was 94.12%, with a residual acidity of 1.5 g-eq/l. The recovery of molybdenum in the throughput was 99.36%. In tests No. 3 and No. 4, the end-to-end molybdenum recovery was 98.92% and 88.61%, respectively. In all cases, high molybdenum recovery rates were obtained in solution (99.07%; 99.36%; 98.92%; 88.61%), with residual acid concentrations of (1.7; 1.5; 0.95; 0.89 eq/L).

The productive solution after nitric acid leaching was directed to molybdenum extraction by liquid extraction. The chemical behavior of the molybdate-ion is difficult to predict, particularly in nitric acid multicomponent systems. With increasing acidity (pH<1), the decrease in extraction parameters is explained by the predominant presence of molybdenum cations [24]. The observed increase in molybdenum extractability with further increase in acidity is most likely due to the formation of anionic complexes of [MoO₂(SO₄)₂ type [25]. The influence of various parameters on the extraction process, such as the concentration of nitric acid, CYANEX 923, hydrogen ions, nitrate ions, and molybdenum (VI) [26]. Re-extraction was performed with different desorbing agents, and the maximum desorption reached 99% with 2M sodium acetate [27].

The task of the research is the extraction of molybdenum from a multicomponent nitric acid solution after one- and two-stage leaching. The extraction studies were performed at a ratio of ~25% CYANEX@600 Molybdenum extraction agent and 75% Elixore 205 diluent. The technical data of the CYANEX@600 Molybdenum extraction agent used

Table 4. Chemical structure of the leaching solution, g/L

Cu	Fe	SO ₄ ²⁻	Zn	Mo	Ca, mg/L	As	Au, mg/L	Ag, mg/L	H ⁺ , equiv. g/L	Re, mg/L	ORP, mV
10.8	19.5	6.8	0.0696	21.3	25.7	-	-	-	2.8	8.627	621

Table 5. Conditions and results of the double leaching of molybdenum middlings

No.	Leaching position	Nitric acid concentration, g/L	Cake result, %	Cake elements content, %					Extraction into solution, %			
				Mo	Cu	Fe	Zn	Re, g/t	Ca	Mo	Cu	Fe
1	first	200	53	4.692	0.609	11.255	0.006	27.87	0.188	88.814	95.706	63.935
	second	200	78	0.5	0.098	12.129	0.002	12.8	0.241	91.688	87.448	15.943
2	first	Rotation, RPM	33.86	7.128	0.928	10.399	0.016	54.04	0.257	89.144	95.82	78.711
	second	200	67.3	0.623	0.123	12.171	0.003	10.64	0.206	94.12	90.192	13.39
3	first	100	51.429	10.41	2.17	9.397	0.011	72.73	0.21	75.917	84.822	70.133
	second	180	33.67	1.384	0.221	12.614	0.004	15.19	0.204	95.524	96.571	54.803
4	first	100	51.429	10.41	2.17	9.397	0.011	72.73	0.21	75.917	84.822	70.133
	second	100	69.33	7.1	0.401	9.765	0.005	15	0.21	52.71	85.956	21.023



for molybdenum extraction as well as the technical data of the Elixore 205 diluent are given in Tables 6 and 7.

Studies on the performance of the extractant were carried out by plotting isotherm extraction curves. Based on the data obtained, a simulation of the extraction-re-extraction technological scheme in a closed cycle was carried out. Molybdenum re-extraction was carried out with a sodium hydroxide solution (10%). Studies of molybdenum extraction from single-stage and two-stage nitric acid leach solutions with concentrations of nitric acid 300 and 100 g/L, respectively, and sulphuric acid 100 g/L were conducted. The chemical composition of single-stage solutions is given in Table 4 and two-stage leaching solutions are given in Table 8.

Considering the presented results, the progressive mixture of two-step leaching is justified by the lowered values of ORP, and acidity in contrast to the productive mixture acquired in the one-step cycle. However, molybdenum recovery is very elevated and for several cycles differs imperceptibly. Based on the data obtained, the modeling of the technological scheme of extraction-reextraction in a closed cycle, with the determination of molybdenum extraction in the liquid extraction step was carried out (Table 9).

The Solvay company MinChem program was used to simulate the extraction process. Based on the obtained data presented in Table 9, the McCabe-Thiele diagram from the solution of one-stage and

two-stage leaching was constructed (Figure 4). The operating line was selected based on the optimal aqueous to organic ratio of 1:1 determined from the extraction experiments. At this ratio, the highest extraction of molybdenum was achieved while maintaining phase separation. The organic to aqueous ratio dictated the slope of the operating line on the McCabe-Thiele diagram used to model the multistage extraction process.

The horizontal axes represent the concentration of Mo in the aqueous phase, while the vertical axes represent the concentration of Mo in the organic phase. This setup is indicative of a partitioning process where Mo is distributed between the two phases. The curves on the graph represent the equilibrium distribution of Mo between the organic and aqueous phases at different concentrations. The point at which the curve forms a plateau indicates the saturation limit of Mo in the organic phase. As a result of the conducted research, the extraction/re-extraction stage molybdenum extraction was 57.8% and 94.28%, respectively. Reducing the residual acidity of the productive solution (from 2.3 to 0.89 g-eq/l) at the expense of performing a 2-stage leaching, allows to considerably increase an extraction/re-extraction extraction of molybdenum (from 58.46% to 94.28%). The solution after re-extraction was directed to the precipitation of calcium molybdate. The chemical structure of the solution is shown in Table 10.

Table 6. Technical characteristics of the CYANEX@600 Molybdenum extractant

Chemical and physical properties	
Appearance	Liquid of no colour to bright-amber colour
Overall mass	0.92 in 24°C
Brookfield viscosity	o<150 sP on 25°C
	o<50 sP on 50°C
Boiling temperature	>300°C
Ignition temperature in closed space	>108°C
CYANEX 600 selectivity	High molybdenum selectivity at low pH

Table 7. Main characteristics of Elixore 205 Thinner

Characteristic	Measuring unit	Method	Elixore 205
Density at 15°C	kg/m ³	ASTM D 4052	820
Viscosity at 20°C	mm ² /s	ASTM D 445	2.4
Viscosity at 25°C			-
Viscosity at 40°C			1.7
Ignition temp	°C	ASTM D 93	76
Content of aromatic compounds	ppm (x10 ⁻⁴ % mass.)	SMS 2728	-
UV			40

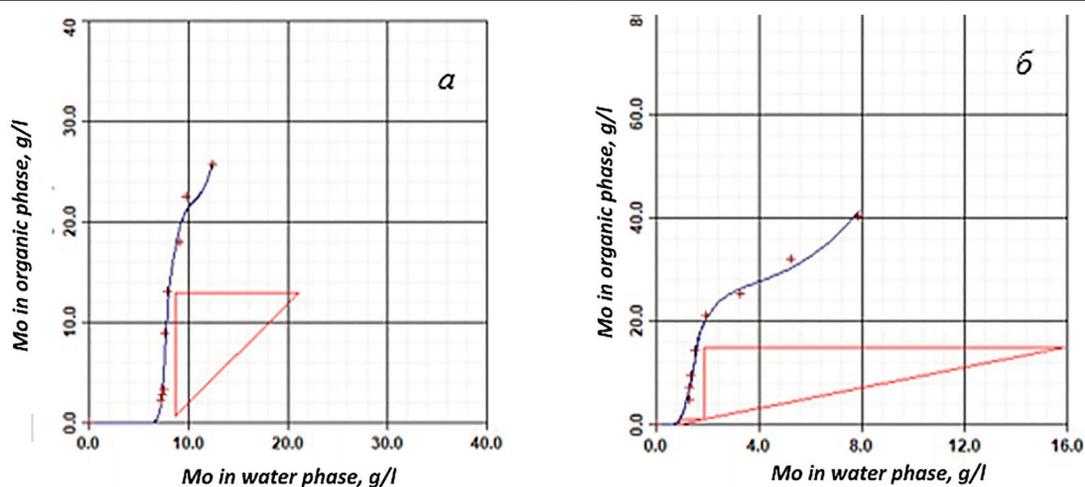
Table 8. Chemical composition of solutions after two-stage leaching, g/L

Cu	Fe	Zn	Mo	Si	SO ₄ ²⁻	H ⁺ , equiv. g/L	pH	ORP, mV
3.72	10.597	0.04	16.4	0.168	6.5	0.89	0.2	550



Table 9. Results of analysis of molybdenum extraction solutions

Volume, ml		V/V correlation	One-stage leaching		Two-stage leaching		
Organic phase	Aqueous phase		Content, g/L		Content, g/L		
			Organic phase	Aqueous phase	Organic phase	Aqueous phase	
				Mo	Mo	Mo	Mo
50	25	2:1	7.22	2.297	0	1.26	
45	30	1.5:1	7.31	2.738	2.297	1.29	
35	35	1:1	7.51	3.373	2.738	1.33	
30	45	1:1.5	7.34	4.553	3.373	1.47	
25	50	1:2	7.59	8.94	25.8	1.93	
20	60	1:3	7.91	13.09	4.553	3.25	
12	60	1:5	9.03	17.955	8.94	5.25	
12	120	1:10	9.71	22.58	13.09	7.83	

**Figure 4.** The McCabe-Thiele diagram

Note: a – one stage; b – two stages of leaching

For purification from copper, iron, and silicic acid solutions were neutralized by adding HCl to pH=7-7.5 and subjected to boiling for 30 minutes. At the same time, excess sodium hydroxide decomposes (by removing CO₂), copper carbonate complexes are destroyed, sodium silicate is hydrolysed with the release of silicic acid, and colloidal iron impurities are coagulated. Precipitation of calcium molybdate was carried out by adding calcium chloride solution (500 g/L) to a solution heated to 80-90°C, neutralized to pH=8.5-8.7 with stirring (with an excess of 10-15%). After the precipitation is completed, the solution is boiled with stirring for 1 hour to improve the structure

of the precipitate. To reduce the sulphur content, the sediment is washed with distilled water. This dissolves CaSO₄. The washed sludge is filtered on a vacuum filter, dried, and calcined. The chemical composition of the sludge is shown in Table 11.

The quality of CaMoO₄ obtained, containing 46.83% molybdenum, 0.0448% phosphorus, and 0.136% sulphur, corresponds to the MDK-1 grade. The extraction of molybdenum from the solution into calcium molybdate was 99.8%. Table 12 shows the chemical analysis of solutions after the precipitation of calcium molybdate, mother liquor, and wash water.

The mother solutions after precipitation of

Table 10. Chemical composition of the mixture, g/L

pH	Mo	Cu	Fe	SO ₄ ²⁻	Zn	P	Si	As	Ca
9.1	76.5	0.0432	0.0108	4.26	<	0.091	0.279	<	0.031

Table 11. Chemical composition of calcium molybdate, %

Mo	S	P	Ca	As	Al ₂ O ₃	SiO ₂	Mg	Au	Ag	Bi	F
46.83	0.136	0.0448	21.46	0.0029	0.32	0.18	-	-	-	-	-
Cd	Re, g/t	Pb	Ni	Co	Sb	Ba	Zn	Cu	Fe	C	U
-	-	-	-	-	-	-	-	0.002	0.004	-	-



Table 12. Chemical composition of solution after precipitation of calcium molybdate, g/L

Solution name	pH	Mo	Cu	Fe	SO ₄ ²⁻	As	P	Si	Ca
Mother solution	7.5	0.034	0.0075	0.000185	-	<	0.0081	0.0014	29.8
Washing water	7.2	0.013	0.00093	0.00014	-	<	0.007	0.005	1.62

calcium molybdate containing 0.034 g/L Mo, are returned to the leaching cycle and/or regenerated by sorption.

4. Discussion

The two-stage nitric acid leaching process demonstrated high molybdenum recovery of 94-99% under optimized conditions, significantly higher than from single stage leaching under similar acid concentrations. The improved extraction is likely due to the lower redox potential and acidity of the two-stage process, resulting from introducing components from the first stage leach solutions. The reduced acidity also allows higher ultimate recovery of 94% Mo during solvent extraction/re-extraction compared to only 58% in single stage process solutions. Although the results are promising, further analysis using techniques such as XRD and SEM-EDS are required to determine changes in mineral composition and morphology between the leaching stages and confirm the proposed mechanisms. Kinetic studies should ascertain rate-limiting factors in the countercurrent process. Since iron and silica impurities could reduce solvent extraction and final product purity, their behavior needs to be investigated. Pilot testing with actual plant feeds will determine the viability for industrial implementation.

The environmental impact of the intensive use of acid warrant evaluation through life cycle assessment. Nitric acid regeneration as demonstrated in other work could mitigate risks and costs. Energy consumption, chemical losses via aqueous effluents, and recyclability of solvents require additional focus to improve sustainability. The countercurrent methodology shows potential for integration into existing copper-molybdenum concentrator flows, but necessitates holistic techno-economic and environmental feasibility analysis before adoption. Further exploration of auxiliary process stages could enhance its commercial viability.

Recent studies by Z. Liu et al. indicate that there are currently reliably known reserves of molybdenum in the Republic of Kazakhstan in the order of 5 million tons, which corresponds to about 20.96% of the world reserves and puts the country in the 4th place in the world ranking [28]. There are numerous molybdenum deposits in the country; however, almost all of them are closed because of low enrichability, because of the great losses of the basic metal at the stage of finishing to a certain condition. However,

there is almost no operating production of molybdenum in the region of Kazakhstan. Currently, it is necessary to improve the quality of different methods and devices for the hydrometallurgical processing of molybdenum middlings from the Shatyrcul-Zhaysan cluster ore, for efficient operation of the whole mechanism. The whole mechanism of hydrometallurgical processing of molybdenum middlings from Shatyrcul-Zhaysan cluster ore was analysed, and as a result, it was decided that to apply different constructions, especially theoretical, it is necessary to have the basic knowledge to indicate losses of the main metal and their quantity, which will help to understand the process of developing the right molybdenum concentration for efficient hydrometallurgical processing under proper conditions.

According to the definition of T. Chmielewski, the value of the country's mineral reserves is predetermined at 5.7 trillion USD, of which more than 1 trillion USD, the price of already explored resources and prepared deposits, while the terrain of Kazakhstan is explored only by 20% and there is a huge chance of identifying new deposits [29]. In connection with the continuous depletion of raw materials from several natural resources, to provide the economy with stable support of mineral resources, to increase the financial attractiveness of the geological sector, and given the various challenges, the best decisions should be made to further improve the geological exploration of mineral resources and the involvement of public options for the development and production of mineral resources in the future. Also, in complex with the search for undiscovered deposits, it is necessary to put the question on the preparation of certain proposals on deep processing and utilization of technogenic emissions and to organize their form production of required products. This demonstrates that when designing and modeling the hydrometallurgical processing of molybdenum middlings from the Shatyrcul-Zhaysan cluster ore, all the factors that affect the quality of the presented ore type must be considered. Also, the fact that currently the molybdenum product and flare are processed by hydrometallurgical type to provide ammonium tetramolybdate was not taken into account.

G. Zhang et al. determined that in the intermediate product, the tailings of the retreatment and foam product of the main flotation of the intermediate collective copper-molybdenum flotation are combined and the pre-flotation fractions are collected



[30]. If you pay attention to the classical scheme, the intermediate product moves to the head of the cycle. This leads to the accumulation of preflotation fractions and weighting of the intermediate product process. But, for the more correct operation of hydrometallurgical processing of molybdenum industrial product from the ore of the Shatyrkul-Zhaysan cluster, it is necessary to apply the results of studies of initial ore, industrial products, and final tailings. Therefore, it is very important to consider the specifics of using this type of processing, the timely study of data, and possible causes of failures in the process, for further promising development of hydrometallurgical processing applications in Kazakhstan.

S. Du and Z. Luo determined that an important scientific problem arising in the development and use of combined technology is the choice of the technological scheme product for which the use of combined enrichment and hydrometallurgical technology will be most effective [31]. The traditional objects for today are the oxidized off-balance ores of the current open-cast mining and hypergene-exchanged stockpiled tailings of ore enrichment in the previous periods. Schemes for the enrichment of waste products of metallurgical production are developed. The results of this characterization study have been analysed and reviewed more precisely; it can be concluded that at present considerable attention is given to other technical products, mainly collective superconcentrates and intermediate products of polymetallic ores flotation enrichment devices.

G. Zakrzewska-Koltuniewicz et al. showed that molybdenum can be extracted from polymetallic ores, which include copper-molybdenum, phosphramic-molybdenum, lead-molybdenum, vanadium-molybdenum ores [32]. These ores are molybdenum concentrates after the appropriate enrichment stages. Molybdenum ores are enriched mainly by collective or selective flotation. However, it was not indicated that oxidized molybdenum ores are present in huge quantities. It can also be noted that these oxidized molybdenum ores have low enrichability by flotation, as well as their waste and tailings, which occupy a significant place in the metallurgy of molybdenum. As I. Silin stated, several types of concentrate processing are used in the productions [33].

It is should also be mentioned that the choice of a certain method depends on the type of raw material, production size, technological requirements for the purity of molybdenum trioxide and its structural qualities, as well as several specific stages determining the price of the processing of minerals. It is necessary to increase the funding and qualification of employees, to introduce new technologies to improve the design and modeling of facilities for

hydrometallurgical processing of molybdenum industrial products from ores, and to reduce errors during the complex technological process in these facilities.

5. Conclusions

In the study on hydrometallurgical processing of molybdenum middlings, atmospheric leaching experiments were conducted with nitric acid in single-stage and two-stage countercurrent modes to optimize molybdenum extraction and minimize acid consumption. The most effective conditions for single-stage leaching included a nitric acid concentration of 300 g/L and sulfuric acid concentration of 100 g/L at 90°C for 2 hours, resulting in 98.8% molybdenum extraction. The two-stage leaching process further refined this, achieving 94.3% molybdenum extraction with solutions of lower residual acidity and redox potential. Additionally, the solvent extraction stages using CYANEX® 600 Molybdenum extractant and Elixore 205 thinner were optimized based on initial leach liquor compositions. The final product was commercial-grade calcium molybdate with 46.83% molybdenum content. This research demonstrated a successful method for producing commercial calcium molybdenite from copper-molybdenum ore, achieving high molybdenum recovery, reducing acid consumption, and minimizing hazardous discharges.

Studies were carried out to obtain a commercial product – calcium molybdate from molybdenum industrial product by hydrometallurgical methods from copper-molybdenum ore of the Shatyrkul-Zhaysan cluster. Molybdenum intermediate product, obtained after the selective flotation of copper-molybdenum concentrate with a yield of 0.07% with a molybdenum content of 22.23% with a recovery of 74.91%. For the mineral composition of the intermediate product, the approximate ratio of ore to non-metallic minerals was visually determined to be 80:20%, respectively. The main ore minerals are molybdenite (40%), and chalcopyrite (22%); minor minerals are magnetite, hematite, iron hydroxides (in total, 10%), pyrite (10%); non-metallic minerals (20%). All ore minerals are almost 80% in the open state, free of clumps; the most common clumps are molybdenite with chalcopyrite.

Investigations of the nitric acid leaching process of molybdenum industrial products showed that conducting work in the cycle of two-stage countercurrent makes it possible to obtain functional mixtures with low final acidity and redox progression without reducing the output of necessary components in contrast to the same plans occurring in the cycle of single-stage leaching. As a result of the conducted studies, molybdenum recovery in the extraction/re-



extraction stage was 57.8% and 94.28%, respectively. A decrease in residual acidity of a productive solution (from 2.3 to 0.89 g-eq/l) at the expense of carrying out 2-stage leaching, allows a considerable increase in the extraction/re-extraction of molybdenum (from 58.46% to 94.28%). As a result of the research, calcium molybdate containing 46.83% molybdenum, 0.0448% phosphorus, and 0.136% sulphur was obtained.

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None.

Author's contributions

L. Karimova: conceptualization, methodology, data curation, writing-original draft preparation. Ye. Kairalapov and T. Tussupbekova: visualization, investigation, and supervision. T. Oleinikova and G. Makasheva: software, validation, writing-reviewing, and editing. All authors read and approved the final version of the manuscript.

Data availability

The data that support the findings of this study are available on request from the corresponding author.

Conflict of interest

There is no conflict of interest.

References

- [1] D. Dreisinger, Keynote address: Hydrometallurgical process development for complex ores and concentrates, *Journal of the Southern African Institute of Mining and Metallurgy*, 109 (5) (2009) 253-271.
- [2] B. Ma, W. Yang, B. Yang, C. Wang, Y. Chen, Y. Zhang, Pilot-scale plant study on the innovative nitric acid pressure leaching technology for laterite ores, *Hydrometallurgy*, 155 (2015) 88-94. <https://doi.org/10.1016/j.hydromet.2015.04.016>
- [3] A. Shakhlov, Y. A. Ospanov, S. S. Naboychenko, I. V. Fomenko, Features of the process of hydrothermal treatment of sulphide copper-zinc concentrates, *Tsvetnye Metally*, 2 (2019). <https://doi.org/10.17580/tsm.2019.02.04>
- [4] Y. W. Xu, X. Q. Hou, Y. Shi, W. Z. Zhang, Y. F. Gu, C. G. Feng, K. Volodymyr, Correlation between the microstructure and corrosion behaviour of copper/316 L stainless-steel dissimilar-metal welded joints, *Corrosion Science*, 191 (2021) 109729. <https://doi.org/10.1016/j.corsci.2021.109729>
- [5] V. G. Prokopov, N. M. Fialko, G. P. Sherenkovskaya, V. L. Yurchuk, Y. S. Borisov, A. P. Murashov, V. N. Korzhik, Effect of coating porosity on the process of heat-transfer with gas-thermal deposition, *Powder Metallurgy and Metal Ceramics*, 32 (2) (1993) 118-121. <https://doi.org/10.1007/BF00560034>
- [6] K. Dikanbayeva, A. P. Auyeshov, M. S. Satayev, K. T. Arynov, Ch. Z. Yeskibayeva, Researching of sulfuric acid leaching of magnesium from serpentines, *News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences*, 5 (449) (2021) 32-38. <https://doi.org/10.32014/2021.2518-170X.95>
- [7] N. A. Bobyrenko, E. Y. Meshkov, A. A. Soloviev, S. V. Zakharyan, Laboratory tests of the hydrometallurgical method for processing polymetallic raw material in Central Kazakhstan, *Gornyi Zhurnal*, 3 (2021). <https://doi.org/10.17580/gzh.2021.03.04>
- [8] D. A. Rogozhnikov, S. V. Mamyachenkov, O. S. Anisimova, Nitric acid leaching of copper-zinc sulphide middlings, *Metallurgist*, 60 (2016) 229-233. <https://doi.org/10.1007/s11015-016-0278-7>
- [9] Y. E. Agapitov, L. M. Karimova, T. A. Khazhimukhametov, E. Y. Meshkov, N. A. Bobyrenko, Development of a scheme for hydrometallurgical processing of high-sulphur copper sulphide concentrates, *Scientific and Technical Bulletin of the Volga Region*, 7 (2019) 32-36.
- [10] D. A. Rogozhnikov, S. V. Zakharyan, O. A. Dizer, K. A. Karimov, Nitric acid leaching of the copper-bearing arsenic sulphide concentrate of Akzhal, *Tsvetnye Metally*, 8 (2020). <https://doi.org/10.17580/tsm.2020.08.02>
- [11] P. V. Aleksandrov, A. S. Medvedev, R. I. Kamkin, Absorption of nitrous gases evolving during nitric acidic decomposition of sulphide minerals, *Russian Journal of Non-Ferrous Metals*, 52 (2011) 140-145. <https://doi.org/10.3103/S1067821211020027>
- [12] E. Y. Meshkov, N. A. Bobyrenko, I. A. Parygin, A. A. Soloviev, Trapping nitrous gases during nitric acid leaching of sulphide concentrates, *Tsvetnye Metally*, 2 (2011). <https://doi.org/10.17580/tsm.2021.02.04>
- [13] Ansari, M. Pawlik, Floatability of chalcopyrite and molybdenite in the presence of lignosulfonates. Part II. Hallimond tube flotation, *Minerals Engineering*, 20 (6) (2007) 609-616. <https://doi.org/10.1016/j.mineng.2006.12.008>
- [14] S. M. Bulatovic, *Handbook of flotation reagents: Chemistry, theory and practice*, Elsevier, Amsterdam, 2015, p.127.
- [15] G. Liu, Y. Lu, H. Zhong, Z. Cao, Z. Xu, A novel approach for preferential flotation recovery of molybdenite from a porphyry copper-molybdenum ore, *Minerals Engineering*, 36 (2012) 37-44. <https://doi.org/10.1016/j.mineng.2012.02.008>
- [16] M. Zanin, I. Ametov, S. Grano, L. Zhou, W. Skinner, A study of mechanisms affecting molybdenite recovery in a bulk copper/molybdenum flotation circuit, *International Journal of Mineral Processing*, 93(3-4) (2009) 256-266. <https://doi.org/10.1016/j.minpro.2009.10.001>
- [17] G. P. W. Suyantara, T. Hirajima, H. Miki, K. Sasaki, Floatability of molybdenite and chalcopyrite in artificial seawater, *Minerals Engineering*, 115 (2018) 117-130. <https://doi.org/10.1016/j.mineng.2017.10.004>
- [18] Y. Semoto, G. P. W. Suyantara, H. Miki, K. Sasaki, T. Hirajima, Y. Tanaka, Y. Aoki, K. Ura, Effect of sodium metabisulfite on selective flotation of chalcopyrite and molybdenite, *Minerals*, 11(12) (2021) 1377. <https://doi.org/10.3390/min11121377>
- [19] M. Li, D. Wei, Q. Liu, W. Liu, J. Zheng, H. Sun, Flotation separation of copper-molybdenum sulfides



- using chitosan as a selective depressant, Minerals Engineering, 83 (2015) 217-222.
<https://doi.org/10.1016/j.mineng.2015.09.013>
- [20] H. Miki, H. Matsuoka, T. Hirajima, G. P. W. Suyantara, K. Sasaki, Electrolysis oxidation of chalcopyrite and molybdenite for selective flotation, Materials Transactions, 58(5) (2017) 761-767.
<https://doi.org/10.2320/matertrans.M-M2017807>
- [21] H. Miki, T. Hirajima, Y. Muta, G. P. W. Suyantara, K. Sasaki, Effect of sodium sulfite on floatability of chalcopyrite and molybdenite, Minerals, 8(4) (2018) 172. <https://doi.org/10.3390/min8040172>
- [22] S. Medvedev, P. V. Alexandrov, Variants of processing molybdenite concentrates involving the use of preliminary mechanical activation, Russian Journal of Non-Ferrous Metals, 53 (2012) 437-441.
- [23] A. Abdrakhmanov, R. A. Yagudin, A. V. Zimin, E. P. Kalinin, L. A. Nemchinova, Improving the technological performance of the zinc cycle at the enrichment plant of OAO Uchalinsky Mining and Processing Plant, Gornyi Zhurnal, 10 (2010) 17-21.
- [24] O. V. Knyazkina, G. G. Kuznetsova, V. F. Travkin, Extraction of molybdenum with bis(2,4,4-trimethylpentyl) with phosphinic acid (cyanex-272), Russian Journal of Non-Ferrous Metals, 6 (2010) 15-19.
- [25] RF patent 2195510, Method for extracting molybdenum from acidic solutions, 2002.
<https://patents.google.com/patent/RU2280088C2>
- [26] C. Marie, V. Vanel, S. Watanabe, M. T. Duchesne, N. Zorz, L. Berthon, Behavior of molybdenum (VI) in {DMDOHEMA-HDEHP/nitric acid} liquid-liquid extraction systems, Solvent Extraction and Ion Exchange, 34(5) (2016) 407-421.
<https://doi.org/10.1080/07366299.2016.1208029>
- [27] M. M. Zeid, B. A. Masry, A. T. Kassem, H. G. Noweir, E. A. Saad, J. A. Daoud, Extraction of molybdenum (VI) from nitric acid medium and its recovery from Gattar granite ore using CYANEX 923 in kerosene, Hydrometallurgy, 176 (2018) 139-146.
<https://doi.org/10.1016/j.hydromet.2018.01.013>
- [28] Z. H. Liu, Y. Li, X. X. Zhou, J. Du, C. Y. Tao, Research progress of electro-oxidation intensification leaching for refractory ore, Advanced Materials Research, 236 (2011) 775-780.
<https://doi.org/10.4028/www.scientific.net/AMR.236-238.775>
- [29] T. Chmielewski, Development of a hydrometallurgical technology for production of metals from KGHM Polska Miedz SA concentrates, Physicochemical Problems of Mineral Processing, 51(1) (2015) 335-350.
<http://dx.doi.org/10.5277/ppmp150120>
- [30] G. Zhang, W. Guan, L. Xiao, Q. Zhang, A novel process for tungsten hydrometallurgy based on direct solvent extraction in alkaline medium, Hydrometallurgy, 165 (2016) 233-237.
<https://doi.org/10.1016/j.hydromet.2016.04.001>
- [31] S. Du, Z. Luo, Flotation technology of refractory low-grade molybdenum ore, International Journal of Mining Science and Technology, 23(2) (2013) 255-260. <https://doi.org/10.1016/j.ijmst.2013.04.010>
- [32] G. Zakrzewska-Koltuniewicz, I. Herdzik-Koniecko, C. Cojocar, E. Chajduk, Experimental design and optimization of leaching process for recovery of valuable chemical elements (U, La, V, Mo, Yb and Th) from low-grade uranium ore, Journal of Hazardous Materials, 275 (2014) 136-145.
<https://doi.org/10.1016/j.jhazmat.2014.04.066>
- [33] Silin, K. M. Hahn, D. Gursel, D. Kremer, L. Gronen, S. Stopic, B. Friedrich, H. Wotruba, Mineral processing and metallurgical treatment of lead vanadate ores, Minerals, 10(2) (2020) 197.
<https://doi.org/10.3390/min10020197>

HIDROMETALURŠKA PRERADA SRASLAKA MOLIBDENA IZ RUDE ŠATIRKUL-ŽAJSAN KLASTERA

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Abstract

Ovo istraživanje istražuje hidrometaluršku preradu sraslaka molibdena ekstrahovanih iz rude bakra-molibdena u klasteru Šatirkul-Žajsan u Kazahstanu. Korišćen je molibdenski intermedijer dobijen selektivnom flotacijom koncentrata bakra-molibdena, sa iskorišćenjem od 0,07%, sadržajem molibdena od 22,23% i ekstrakcijom od 74,91%. Mineraloška analiza pokazuje molibdenit i halkopirit kao glavne minerale. U eksperimentima je ispitivano atmosfersko luženje azotnom kiselinom u jednostepenim i dvostepenim protivstrujnim procesima da bi se optimizovala ekstrakcija molibdena i smanjila potrošnja kiseline. Dobijeni optimalni uslovi su: 300 g/L azotne kiseline, 100 g/L sumporne kiseline, temperatura 90°C i 2 sata luženja u jednostepenom luženju, kojim je ekstrahovano 98,8% molibdena. Dvostepeno luženje pod optimizovanim uslovima omogućava ekstrakciju 94,3% molibdena u rastvorima niže rezidualne kiselosti (0,89 g-ek/L) i redoks potencijala (550 mV) bez smanjenja ekstrakcije vredne komponente. Ekstrakcija molibdena dostiže 94,3% u sledećoj fazi ekstrakcije rastvaračem iz dvostepenih rastvora za luženje. Finalni proizvod, kalcijum molibdat sa sadržajem molibdena od 46,83%, zadovoljava komercijalne specifikacije. Ovo istraživanje demonstrira efikasan proces za hidrometaluršku proizvodnju kalcijum molibdenita komercijalnog kvaliteta iz rude bakra-molibdena, sa visokim iskorišćenjem molibdena, smanjenom potrošnjom kiseline kroz dvostepeno ispiranje i minimalnim opasnim ispuštanjima.

Ključne reči: Luženje; Azotna kiselina; Ekstrakcija; Ekološka prihvatljivost; Minerali

