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OPPORTUNITIES FOR BY-PROCESS EXTRACTION OF MOLYBDENUM FROM BLACK SHALE ORES

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Abstract

The article presents the results of a study of the possibility of extracting molybdenum from the products of processing refractory black shale ores. The analysis showed high molybdenum concentrations in the recycled ammonia-carbonate solutions at the stripping stage. A liquid extraction method was studied to extract molybdenum from these solutions. A process flow chart for molybdenum extraction is described, including the following main stages: deoxidation of carbonate solutions with sulfuric acid to pH = 1, joint extraction of uranium and molybdenum, selective stripping of molybdenum, neutralization of strips and production of ammonium paramolybdate.

Keywords: Black shales, molybdenum, ammonia-carbonate solution, organic phase, extract, strip, trioxide, precipitation, ammonium paramolybdate.

Introduction

Molybdenum is a rare element. According to Vinogradov, its average content in the earth's crust is $1.1 \cdot 10^{-4}$% by weight [1]. Due to the low concentration of molybdenum in ores, only ores containing tenths and hundredths of a percent of this element can be processed. Flotation and gravity enrichment methods are used to enrich molybdenum ores.

The ores of the Altyn-Tau deposit are complex and include uranium, molybdenum, vanadium, and other elements. Increased uranium, molybdenum, and vanadium concentrations are observed in the oxidation zone. The molybdenum content in ores reaches 350–400 g/t. When opening the ore with sulfuric acid using the vat method (CHV) or heap leaching (HL), non-ferrous metals, including molybdenum, are extracted simultaneously with uranium. Studies that were previously conducted allowed us to develop a combined process flow chart for processing black shale ores. According to this flow chart, the ore material is crushed to a class of -10 mm and then screened through a sieve with 5 mm cells. The +5 mm fraction is sent to the crushing unit, and the -5 mm class material is crushed to 2.0–1.5 mm and subjected to crushing. Crushing for the +5 mm fraction is carried out using sulfuric acid solutions with a 5–6 g/l concentration.

Productive heap leaching solutions are strengthened with sulfuric acid to 20 g/l and sent to the crushing unit.

Leaching produces productive solutions with pH=0.95 and residual acidity of 15.6 g/l, subject to extraction processing. Extraction is performed in countercurrent mode using a triple extraction mixture of the composition [TBF-0.08M + TAA-0.15M + Di-2EGFK-0.18M] based on diesel fuel. The saturated organic phase is re-extracted with an ammonia-carbonate solution. According to the study, molybdenum accumulates in the circulating ammonia-carbonate solutions (pH > 12), the concentration of which reaches 0.6–1.2 g/l. This can lead to contamination of the finished uranium oxide product with molybdenum. In addition to molybdenum, the solutions contain uranium in significant concentrations (0.4–1.3 g/l). The extraction of molybdenum from uranium-containing carbonate solutions, with its subsequent conversion into a commercial product, is of practical interest since molybdenum is a valuable component of modern heat-resistant steels, the demand for which is constantly growing.

The article presents the results of studies to determine the possibility of extracting molybdenum from circulating ammonia-carbonate solutions by liquid extraction.

The literature reveals that molybdenum can be extracted from nitric acid [2], hydrochloric acid [3], sulfuric acid [4], and phosphoric acid [5] media. Organic compounds of neutral, acidic, and basic nature are used as extract ants.

Extraction experiments were conducted to determine the organic mixture's optimal composition and the process's equilibrium pH. The carbonate solution was prepared by deoxidation with concentrated sulfuric acid. Diesel fuel was used as a diluent to prepare the extraction mixture. Extraction was carried out under the following conditions: ratio of organic and aqueous phases (O:A) = 1:1, temperature—room temperature (23 °C), stirring time—10 minutes. The results of the experiment are presented in Table 1 and Figure 1.

Table 1

Dependence of the degree of extraction of molybdenum and uranium by various mixtures of extractants on the equilibrium pH of the solution

(Composition of the initial solution, g/l: U-0.62; Mo-0.97)

Extraction agent composition, mol/l	**pH of solution, g/l**											
	8,0		**4,0**		**3,0**		**2,0**		**1,5**		**1,0**	
	Extraction degree, %											
	U	**Mo**	**U**	**Mo**	**U**	**Mo**	**U**	**Mo**	**U**	**Mo**	**U**	**Mo**
0,1M TBF	84	25	50	20	-	2,0	35	1.0	23	1,0	27	1,0
0,1M Di2EGFK	95	28	53	8,0	64	38	66	67	76	69	92	68
0,1M TAA +0,1M TBF	61	74	75	81	78	82	87	84	63	76	52	89
0,2M Di2EGFK + 0,1M TBF	95	24	72	10	93	37	92	63	98	63	95	63
0,1M Di2EGFK +0,1M TBF +0,1M TAA	95	69	99	80	98	86	99	87	97	86	98	74

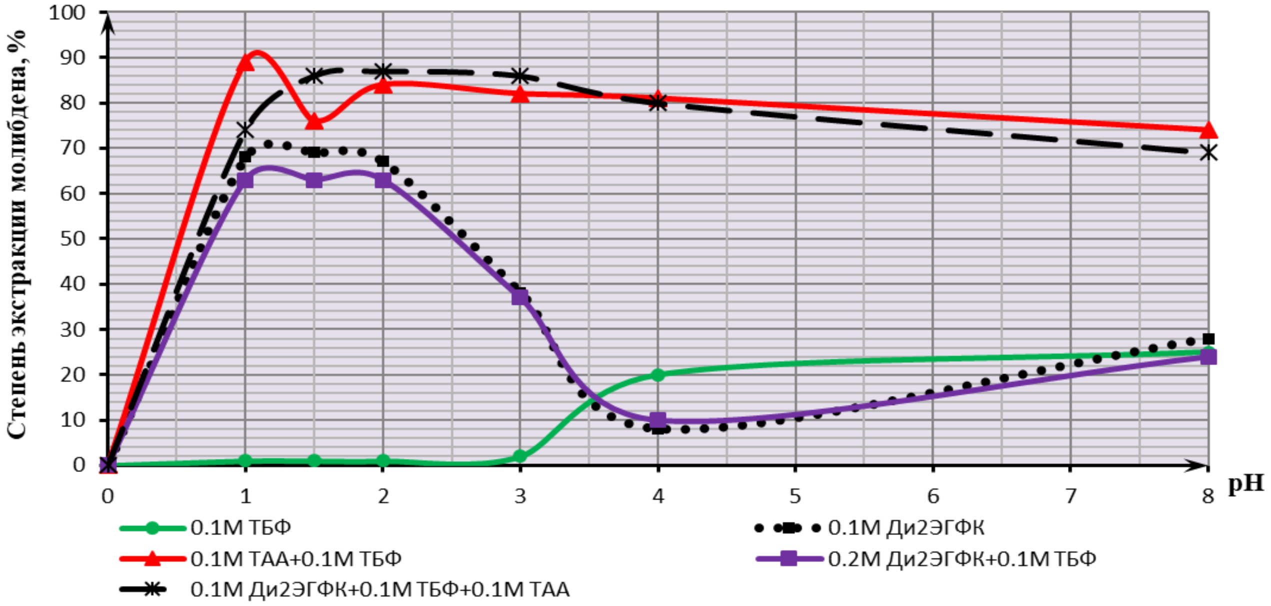

Fig. 1. Dependence of the degree of extraction of molybdenum by various mixtures of extract ants on the equilibrium pH of the solution

As can be seen from the data in Table 1 and Figure 1, the extractant mixtures of the composition [0.1 M TAA + 0.1 M TBP] and [0.1 M Di2EHP + 0.1 M TBP + 0.1 M TAA] demonstrate a high capacity for molybdenum. The mixture of the composition [0.1 M TAA + 0.1 M TBP] has a capacity for molybdenum in the range from 74% to 89%, with the maximum value achieved at pH = 1.0. The mixture of the composition [0.1 M Di2EHP + 0.1 M TBP + 0.1 M TAA] shows a capacity for molybdenum from 69% to 86%, with maximum values achieved in the pH range = 1.5–3.0. In addition, it is evident from the table data that the mixture of the composition [0.1 M TAA + 0.1 M TBP] extracts 52% of uranium into the organic phase at pH = 1. In contrast, the mixture of the composition [0.1 M Di2EGFK + 0.1 M TBP + 0.1 M TAA] extracts uranium at a level of 97–99% at pH = 1.5–3.0. Thus, the optimal mixture for molybdenum extraction is the mixture of extractants of the composition [0.1 M TAA + 0.1 M TBP], the pH of the solution is equal to 1. To determine the optimal conditions for extracting molybdenum from ammonia-carbonate solutions, extraction studies were carried out in continuous mode on a laboratory extraction unit (Fig. 2). The experiment was carried out on an eight-stage extraction cascade with settling tanks for separating the aqueous and organic phases. Peristaltic pumps fed the organic and aqueous phases into the extraction cascade. The piping diagram of the laboratory extraction unit is shown in Figure 3.

Fig. 2. Laboratory continuous extraction plant

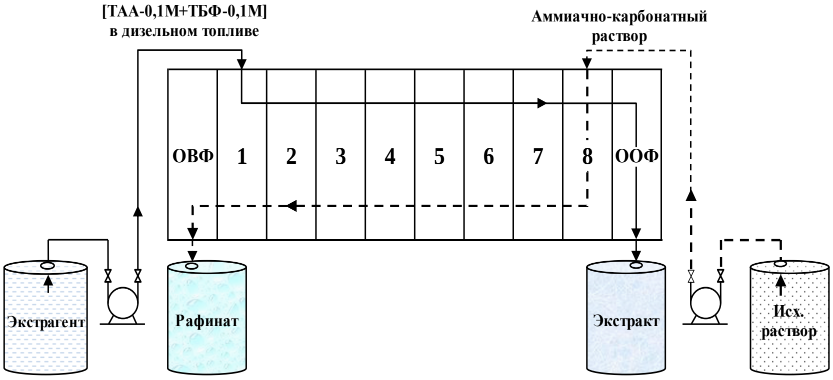

Fig. 3. Scheme of piping of laboratory extraction cascade

Extraction was carried out at a total phase feed rate of 1 l/h and an organic to aqueous phase (O:A) ratio of 1:5 until stable molybdenum concentrations in the raffinates were achieved, i.e. equilibrium in the cascade. After equilibrium, the extraction process was stopped, and the aqueous phase was collected from the chambers for molybdenum concentration analysis. If molybdenum was detected in the discharge raffinates (chamber No. 1), the O:A phase ratio was reduced, and the extraction process was continued. The results of experiments on molybdenum extraction from an ammonia-carbonate solution at different O:A ratios are presented in Table 2.

Table 2 Extraction of metals from ammonia-carbonate stripping solutions

(Composition of the initial solution, g/l: U-0.62; Mo-0.97; pH=0.95)

Camera No.	**Metal concentration in aqueous phase, mg/l**					
	O : B = 1 : 5		**O : B = 1 : 2.5**		**O : B = 1 : 1.5**	
	U	**Mo**	**U**	**Mo**	**U**	**Mo**
1	0.29	0.19	0.09	0.07	0	0
2	0.33	0.25	0.19	0.18	0.05	0
4	0.41	0.57	0.26	0.37	0.09	0.08
6	0.47	0.67	0.32	0.48	0.18	0.27
8	0.52	0.79	0.49	0.63	0.37	0.41

According to the data in Table 2, the optimal ratio of the organic and aqueous phases (O:A) for efficient extraction of molybdenum from the ammonia-carbonate solution is 1:1.5. In this case, 4-5 extraction stages are required for complete extraction of molybdenum from the aqueous phase. The saturated organic phase analysis revealed a molybdenum content of 3.6 g/l and uranium of 2.1 g/l. According to literature data, molybdenum re-extraction from saturated extracts can be carried out using alkali [6], sodium hypochlorite [7], soda [8] or ammonia [9]. The authors indicate that separating uranium and molybdenum after their joint extraction with amines is possible through successive selective re-extraction. In this case, at the first stage, uranium is extracted by washing with sodium chloride or a mixture of sodium chloride and sodium sulfate. Then, the second metal is re-extracted with a solution of soda or ammonia. Conversely, molybdenum is re-extracted first, and then uranium. This approach ensures the production of both metals as finished products. To develop a process for the selective re-extraction of molybdenum, the effect of equilibrium pH on the degree of its extraction was studied. A 3% ammonia solution was dosed into a reactor with saturated extract and stirred to various pH values during the experiments. The results of the studies are given in Table 3.

Table 3

Selective reextraction of molybdenum with ammonia solutions
(Content in the initial organic phase: molybdenum - 4.8 g/l; uranium - 2.1 g/l; pH = 0.95)

pH	$V_O:V_B$	Content, g/l		Extraction into re-extract, %	
		Mo	U	Mo	U
2	10 : 0,45	3,2	<0,005	4	0
3	10 : 0,62	12,2	<0,005	21	0,01
4	10 : 0,81	21,3	<0,005	48	0,01
5	10 : 0,11	29,8	<0,005	91	0,01
6	10 : 0,12	26,1	<0,005	87	0,02
7	10 : 0,13	19,1	<0,005	69	0,02

As can be seen from the data in Table 3, the optimal conditions for molybdenum reextraction are achieved at an equilibrium pH value in the range of 5÷6. Under these conditions, selective reextraction of molybdenum from the saturated organic phase is ensured. The extraction of molybdenum into the reextract was 87÷91%, its concentration in the reextract reached 26÷29 g/l, while the uranium content did not exceed 0.005 g/l. Molybdenum was isolated from ammonia reextracts by the neutralization method. Ammonia desorbates were heated to a temperature of 55–60 0C, and hydrochloric acid was added with vigorous stirring. At a pH value of <1, paramolybdate crystals were formed. Thus, more than 97.5% of molybdenum was isolated from the solution as a precipitate. The obtained paramolybdate crystals were filtered, dried and calcined in a muffle furnace at 400 0C. Chemical analysis of the precipitate showed that it contained at least 98.2% molybdenum oxide.

Thus, the studies confirmed the possibility of extracting molybdenum from recycled ammonia-carbonate solutions formed during the processing of black shale ores. The extraction of molybdenum from ammonia-carbonate reextracts includes the following main stages: deoxidation of carbonate solutions with sulfuric acid to pH=1; joint extraction of uranium and molybdenum; selective reextraction of molybdenum; neutralization of reextracts; and obtaining ammonium paramolybdate. The developed process allows for the efficient extraction of molybdenum from recycled solutions and its production as a high-quality commercial product in demand on the market.

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