Research of Technology of Processing Man-Made Waste of Molybdenum Production

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Abstract. In this work, the chemical and material composition of man-made waste from molybdenum production and the method of its processing to extract valuable components have been studied. On the basis of theoretical and experimental studies, effective methods of extracting ammonium-molybdenum acid, ammonium perrhenate and copper concentrate were selected. The production of high-purity ammonium molybdenum is carried out by a standard method. The developed technology is environmentally friendly by reducing the use of ammonia at the initial stage. It is shown that the obtained product in terms of purity and chemical properties corresponds to State standard (GOST 2677-78) and is a finished product.

1 Introduction

In the world, there is an increased interest in research that allows you to create energy-saving and environmentally sound technologies for the disposal and processing of industrial waste. This is due to the fact that the main task of today's development is the rational use of resources, since natural reserves are depleted, and the level of man-made pollution has long exceeded all permissible norms. Of the various man-made wastes, the wastes of non-ferrous and rare metals metallurgy enterprises are of particular interest. Technogenic wastes, being complex composite formations in composition, contain non-ferrous and rare metals in concentrations of industrial interest, and in some cases exceeding their content in ores.

About 1 billion tons of gaseous wastes (170 kg per 1 person) are emitted into the atmosphere annually, about 15 billion tons of liquid wastes (2.5 tons per 1 person) are released into the hydrosphere, approximately 85 billion tons of solid wastes fall on the ground waste (14 tons per person, or 567 tons per 1 km2). Waste generation per unit of production increases as one approaches the beginning of the production chain, which causes the greatest burden on ecosystems in regions with the predominant development of industries engaged in the extraction and primary processing of natural resources, and primarily mining and metallurgical industries.

In dump farms and tailings of the Navoiy and Almalyk MMC, according to calculations, more than seven billion tons of such wastes have been accumulated, containing about 1,000 tons of gold, 1,300 tons of silver, two million tons of copper, 30,000 tons of lead and other useful components.

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2 Research objects

In the sludge field of Research and Production Association "Production of Rare Metals and Hard Alloys" (PRMHA) of JSC "Almalyk MMC" for more than sixty years of existence, a huge amount of solid and liquid waste from molybdenum production has been formed, which contain, on average, molybdenum -6.7%; rhenium -0.05%; copper-5.7%, as well as gold and silver.

3 Methods

As is known [1], there are various ways of processing molybdenum concentrates and molybdenum-containing cinder waste. Enrichment of molybdenum ores is carried out mainly by the method of collective or selective flotation.

Currently, the most common in industry is the hydrometallurgical method of processing molybdenum-containing concentrates [2].

Thus, analyzing the literature reviews on the state of the issue of obtaining ammonium molybdate from various types of molybdenum-containing raw materials (from standard molybdenum concentrate to substandard molybdenum raw materials) by the hydrometallurgical method [3], we can conclude that the most common methods of opening molybdate and decomposition of poor molybdenum concentrate in industrial production are acid and ammonia methods. The cinder of molybdenum concentrate is leached with solutions of acid and ammonia. From the resulting acid and ammonia solution, after cleaning it from impurities, ammonium molybdate is produced.

In order to involve valuable waste in the production and reduce the harmful impact on the environment, a technology has been developed for obtaining copper concentrate, ammonium molybdate (AMC), ammonium perrhenate (AP) from waste solutions of molybdenum production of Research and Production Association "Production of Rare Metals and Hard Alloys".

In world practice, there are a number of technologies for the disposal of waste solutions, however, they are not complex and are aimed at extracting individual components [4–19].

Table 1. The results of the analysis of samples taken from various stages of the technology for processing initial solutions of workshop No. 5 of Research and Production Association "Production of Rare Metals and Hard Alloys"

Sample No.	**Name**	**Re** mg/l	**Cu** mg/l	**W** mg/l	**Mo** mg/l	**Fe** mg/l
1	Ref. solution 5 workshop Research and Production Association "Production of Rare Metals and Hard Alloys"	7.9	1675.0	-	28.6	23.0
2	Refined 1 cycle Research and Production Association "Production of Rare Metals and Hard Alloys"	85.3	1702.0	-	309.5	34.0
3	Refined 1 cycle Research and Production Association "Production of Rare Metals and Hard Alloys"	10.3	121.0	-	81.7	7.0

4	Refined Research and Production Association "Production of Rare Metals and Hard Alloys"	103.3	450.0	Not found	295,8	5,0
5	Eluate Research and Production Association "Production of Rare Metals and Hard Alloys"	-	64.0	1264	1264 g*	-
6	Copper concentrate Research and Production Association "Production of Rare Metals and Hard Alloys"	-	39.66%	-	-	-

Table 2. Results of the analysis of waste solutions based on averaged samples from the sludge field

Elements	**Content, mg/l**	**Elements**	**Content, mg/l**
Molybdenum	7.43-86.9	Aluminum	13.63-100.44
Copper	14.67-1320	Titanium	5.0-30.0
Lead	2.71-5.20	Iron	67.33-599.54
Rhenium	1.87-9.18	Barium	6.15-35.8
Arsenic	0.4	Tin	0.33-3.64
Sulfur total	1.59	Zinc	60.5-752.74
silicon oxide	28.2	Gallium	0.0001-0.0003
Calcium	962.4-4193.3	Gold, g/t	0.32-4.04
Magnesium	28.1- 966.1	Silver, g/t	1.03-14.09
Manganese	3.36-28.5		

The initial raw material of the technology is waste solutions of molybdenum production after sorption of productive solutions, formed after ammonia (or soda) leaching of molybdenum middlings (industrial product molybdenum) (Table 2).

In workshop No. 6, according to this technological scheme, the installation of a pilot site for the processing of waste solutions was carried out.

Table 2 shows that, in terms of content, molybdenum, copper, rhenium, gold, and silver are of industrial interest.

The density of the initial solution is not higher - 1.15.

Output parameters of separated components (intermediate product and productive solution) of the unit: mg/l): Cu – concentrate with copper content - 8375; Re - containing a solution of Mo-143; Re-39.5;

4 Discussion

The analysis of the chemical composition of the products was carried out by ICP spectroscopy, emission and X-ray fluorescence analyzes using an energy-dispersive spectrometer ES-20000 R (Oxford Inst., England), respectively. The phase composition of the products was determined by the X-ray diffraction method. Diffractograms were obtained on a Panalytical Empyrean diffractometer equipped with a Cu tube (Kα1= 1.5406 Å, Kα2=1.5443 Å, Kα2/Kα1=0.5, with 0.01o 2theta steps from 5 to 100 degrees. Pixel 1D detector in "line scan" mode.

Characteristics of the phase mineralogical composition of the products are given below.

Characterization of copper concentrate. Analysis of the diffraction pattern of copper concentrate, its qualitative and quantitative interpretation made it possible to establish the phase composition of the concentrate. The decryption result is shown in Table 3.

Table 3. Qualitative and quantitative interpretation of the phase composition of the copper concentrate

No.	Crystal phase	Quantity, %
1	CuO	4.08
2	$Cu_2O(SO_4)$ - dolerophanite	79.68
3	Fe_2O_3 - hematite	16.24

As can be seen from Table 3, the main phase is dolerophanite - 79.695, 16.24% - hematite and 4.08% - CuO.

Apparently, when the product is calcined, after the precipitation of copper with sodium sulfide, at a temperature above 800°C, the process of formation of synthetic dolerophinite occurs. The presence of a sulfate group, namely intracrystalline, is confirmed by IR spectroscopy.

IR absorption spectra were recorded on a System-2000 IR-Fourier spectrometer (Perkin-Elmer, USA) in KBr pellets and an IR-Fourier spectrometer with an attenuated total internal reflection attachment with an ATR reflection attachment in the region of 400-4000 cm-1 with a resolution of 1 cm -1 and accumulation up to 50 scans. All IR spectra presented are difference spectra.

In the IR spectrum of copper concentrate (Fig. 1), intense absorption bands are observed in the region of 400 - 1300 cm-1. The complex band at 600 cm-1 belongs to the doubly degenerate bending vibration υ4(F2) of the SO42- anion, and the band with a maximum at 1043 cm-1 belongs to the triple degenerate symmetric stretching vibration υ3(F2) of the anion. SO42.. Band, absorption υ1(A) maximum at 980 cm-1 and bands at 621 cm-1 assigned to the doubly degenerate vibration υ2(E) of the SO42- anion.

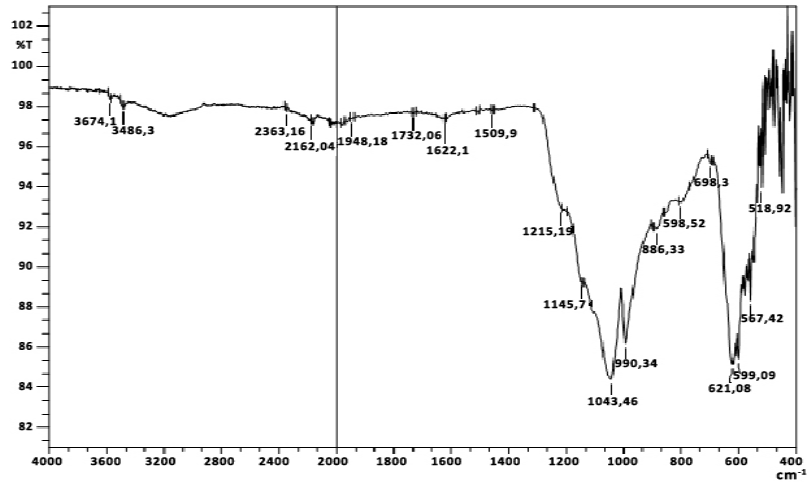

Fig. 1. IR spectrum of copper concentrate

In addition, the presence of octahedral [OCu]6 coordination polyhedra in the dolerophanite structure leads to the appearance of new lines in the spectrum in the region of 400–460 cm1. The chemical composition of copper concentrate, molybdenum and crude ammonium perrhenate is presented in table 4.

Table 4. Chemical composition of copper concentrate, molybdenum and crude ammonium perrhenate (main components are given)

Name	Mg*	K*	Ca*	Fe*	Cu	Zn	Mo	Ag	W*	Re	Au *	Pb
Copper	1875	1199	79176	36699	15.2%	1905	3740	52.4 g/t	1683	0.711	4.89 g/t	3100
Molybdenum	1715	1659	2837	994	3860	315	52.1%	0.852	32007	0.615	0.251	656
Rhenium	121	790	372	996	79.6	15.8	1997	2.05	20.0	86.3%	0.030	98.6

Precious metals gold and silver are concentrated mainly in copper concentrate, the content of which is 4.89 and 52.4 g/t.

The diffraction pattern shows 7 reflections with an intensity above I/Io = 50 and a number of reflections below 50%.

Below are the results of the study of the characteristics of the sample of ammonium perrhenate, after the operation of the second cleaning on sorbent A-170.

As can be seen from the diffraction patterns (Fig. 2), the obtained ammonium perrhenate corresponds to the standard NH4ReO4-.

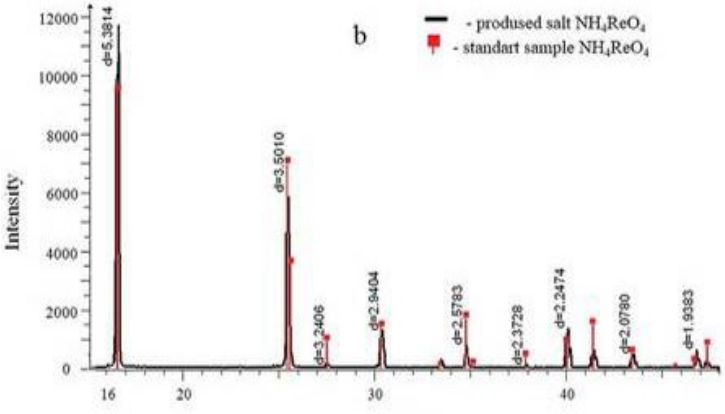

Fig. 2. X-ray diffraction pattern of ammonium perrhenate standard sample.

Ammonium perrhenate forms colorless, white) crystals of tetragonal syngony, space group I40/a, cell parameters a=0.5871 nm, c=1.2942 nm, Z=4. The structure consists of tetrahedral anions [ReO4]—.

The IR spectra of the obtained sample of ammonium perrhenate were studied in the frequency range 400-4000 cm-1. The structure of the absorption bands in the IR spectra of both samples is identical, which indicates that the resulting sample corresponds to ammonium perrhenate.

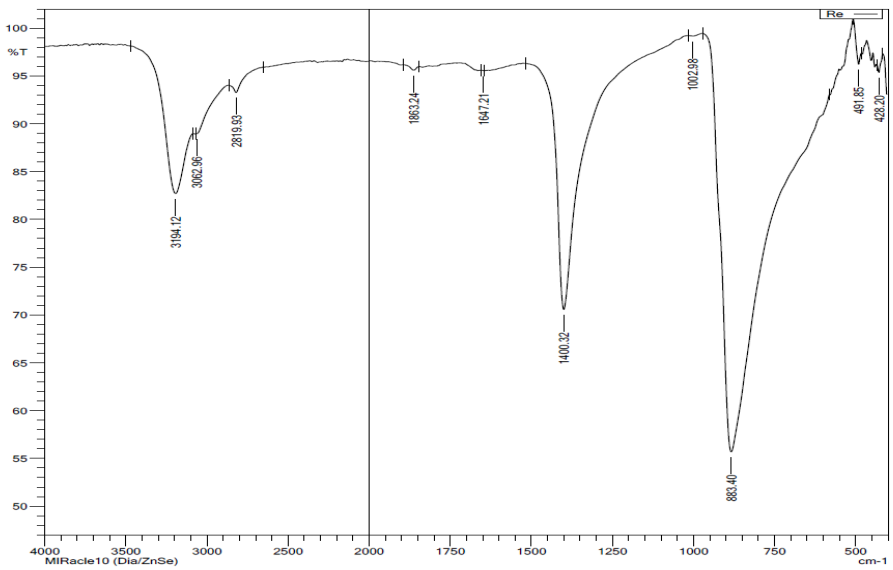

Fig. 3. IR spectrum of ammonium perrhenate obtained from waste solutions of molybdenum production of Research and Production Association "Production of Rare Metals and Hard Alloys"

The observed intense lines in the region 400–1300 cm-1 correspond to the vibration of the [ReO4]– anion. The complex line at 600 cm–1 belongs to the doubly degenerate bending vibration υ4(F2) of the [ReO4]– anion, and the line with a maximum at 1043 cm–1 belongs to the triple degenerate symmetric stretching vibration υ3(F2) of the anion. [ReO4]— line υ1(A) with a maximum at 980 cm-1 and bands at 621, assigned to the doubly degenerate vibration υ2(E) of the [ReO4]— anion.

As in the case of IR spectra, (Fig. 3) also indicate the identity of the obtained NH4ReO4 with commercial products of ammonium perrhenate produced by NMMC from productive solutions of uranium production.

The chemical elemental analysis of the obtained NH4ReO4 was performed by various methods. According to the results of the chemical determination of rhenium in the Central Laboratory of the Almalyk MMC in ammonium perrhenate, it is 69.2% (the theoretical calculated Re content in perrhenate is 69.1).

For the purpose of the purity of the experiment, the resulting ammonium perrhenate was analyzed at the Central Laboratory of Navoiy MMC, which analyzes commercial products of NH4ReO4.

Below are the results of the study of the composition of ammonium tetramolybdate, obtained by the proposed technology with modern analytical instruments.

Energy dispersive (ED) spectra were obtained ammonium tetramolybdate from two local points of the sample under study. In table 5 and 6 show the conditions for the ED spectra survey and the results of the ammonium tetramolybdate analysis at each of these points.

Table 5. Survey conditions Energy dispersive spectra and results of analysis of ammonium tetramolybdate at a local point 1.

Element	Line type	Conditional concentration	Weight, %	Reference name	Preset reference
N	K series	0.00	9.70	BN	Yes
O	K series	0.01	28.93	SiO_2	Yes
Mo	L series	0.02	61.37	Mo	Yes
Sum:			100.00		

Table 6. Survey conditions Energy dispersive spectra and results of analysis of ammonium tetramolybdate at a local point 2.

Element	Line type	Conditional concentration	Weight, %	Reference name	Preset reference
N	K series	0.04	11.23	BN	Yes
O	K series	0.08	30.71	SiO_2	Yes
Mo	L series	0.24	58.06	Mo	Yes
Sum:			100.00		

5 Conclusion

Work has been carried out on the development of scientific and patent literature on the problem of extracting molybdenum from molybdenum-containing wastes with a low content of valuable components.

ICP-spectroscopy, X-ray diffraction analysis and microprobe analysis have been used to determine the chemical and mineralogical composition of molybdenum production wastes of Research and Production Association “Rare Metals and Hard Alloys” of Almalyk MMC.

On the basis of theoretical and experimental studies, effective enrichment methods were selected and optimal conditions for the separation of iron and copper with the production of copper concentrate were determined.

Photocolorimetric methods for the analysis of molybdenum, copper, iron and rhenium in technological solutions have been developed.

The sorption of metals on various ion-exchange resins was studied, on the basis of which the low-basic anion exchangers A-100Mo for the sorption of Mo and A-170 for the sorption of rhenium of the Purolight company were selected, and a technology was developed for processing waste solutions of molybdenum production with the production of concentrates of iron, copper, molybdenum and rhenium.

According to the proposed technology for processing molybdenum middlings to obtain high purity molybdenum molybdenum, molybdenum middlings were processed according to the existing technology to obtain ammonium tetramolybdate, then the ammonium tetramolybdate solution was acidified to pH=1.5-2.5 with nitric acid. After filtration, the clarified mother liquor was fed for the sorption of molybdenum into a column with anion exchanger A100 Mo. Desorption of molybdenum was carried out with a 12% ammonia solution. The desorbent was sent to obtain ammonium tetramolybdate, from which, after dissolution in ammonia and crystallization, ammonium of molybdenum oxides was obtained, which meets the chemical composition requirements of State standard 2677-78 for ammonium of molybdenum oxides.

The proposed technology was tested at the production site of workshop No.5 of the Research and Production Association “Rare Metals and Hard Alloys” of Almalyk MMC in the amount of 50 kg of molybdenum middling product.

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