

Investigation of the sorption method of processing molybdenum-containing raw materials to extract rare metals

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Abstract. The article investigates the sorption method of concentrating rare metals on various sorbents (brands "Purolight": A-100, A-170, A-172 and BO-020) and determines the optimal conditions for their extraction. It is shown that the extraction of molybdenum on the sorbent "Purolight A-100" was 98%. The proposed sorption mechanism consists in the formation of molybdenum complexes with functional phosphor basics and sulfate groups of sorbents. Sorption of rhenium on the Purolite A-170 sorbent was 93%. Sorption of rhenium on the sorbent BO-020 is described by the Langmuir equation with a maximum static exchange capacity of 94%. Based on the sorption and desorption kinetics of molybdenum and rhenium on various ion-exchange sorbents, it was shown that the sorption of molybdenum and rhenium proceeds most efficiently on low-basic anion exchangers A-100 Mo and A-170, respectively, and after double recleaning of the “rough” rhenium concentrate, ammonium rhenium of qualification was obtained AR-0.

1 Introduction

All over 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, since natural resources are depleted, and the level of man-made pollution has long exceeded all permissible standards. Man-made 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. Of the various man-made wastes, the wastes of the metallurgy enterprises of non-ferrous and rare metals are of particular interest [1–9].

Molybdenum and rhenium are among the most widely used refractory rare metals in electronic and rocket technology in the production of most catalysts.

The sources of raw materials in the production of these metals are molybdenum concentrates obtained from copper-molybdenum ores. The content of molybdenum in copper-molybdenum ores is usually low and is expressed in hundredths, and sometimes thousandths of a percent. This type of ores includes ores of such large copper deposits

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located in the territory of the Commonwealth of Independent States, as Kounrad and Boshekul in Kazakhstan, Kalmakir in Uzbekistan, Kadjaran in Transcaucasia. These ores are an important source of molybdenum concentrates [10].

Molybdenum concentrates serve as raw materials for the production of ferromolybdenum and chemical compounds of various degrees of purity: molybdenum trioxide, ammonium molybdate, sodium molybdate, calcium molybdate, metallic molybdenum is produced from pure MoO_3 [11, 12].

Recently, for the selective extraction of metals from solutions and pulp in the metallurgy of noble and rare metals, especially developed ion-exchange sorbents are widely used, which are capable of selectively extracting metals from solutions and pulp. Ion-exchange sorbent (composite chemical reagent - sorbent) is widely used in the metallurgy of non-ferrous, noble and rare metals.

Currently, in industry, such compounds as zeolites (natural aluminosilicates) are used as ion exchangers; natural coals treated with sulfuric acid (sulfonated coals); artificial high-molecular organic compounds (sorbents). The latter are most widely used in the production of non-ferrous, rare and precious metals.

The macromolecule of an ion-exchange sorbent consists of flexible intertwining threads of polymer molecules, the carbon chains of which have cross-links - "bridges" that form a network structure, the so-called matrix. The matrix contains immobile charged groups, the nature and amount of which can be controlled during the synthesis of the sorbent.

Active (functional) groups in cation exchangers are sulfate group ($-\text{SO}_3\text{O}$), carboxyl group ($-\text{COOH}$), hydroxyl group ($-\text{OH}$) and other more complex compounds. Anion exchangers contain amino groups of various degrees of substitution ($-\text{NH}$), ($=\text{NH}$), tertiary and quaternary ammonium bases as active groups. Depending on the purpose, sorbents with particles ranging in size from 0.3 to 2.0 mm are used in industry, the total surface of which varies from 0.2 to 300 m^2/g . The most important ion-exchange characteristic of the ion exchanger is the exchange capacity. It expresses the amount of ions sorbed by the ion exchanger under the accepted conditions. There are three types of exchange capacity:

1) Static capacity is the number of ions, the number of ions sorbed by a unit of sorbent, which is in equilibrium with the electrolyte;

2) The dynamic capacity expresses the amount of ions sorbed by a unit of sorbent when the electrolyte is in contact with the sorbent under dynamic conditions (filtration) until the adsorbed ion exchanger appears (breakthrough) in the solution that has passed through the sorbent layer;

3) The total dynamic capacity expresses the amount of sorbed ions under dynamic conditions until the sorbent layer is completely saturated.

The full dynamic capacity of the sorbent is achieved if the concentration of the ion to be absorbed in the outgoing solution is equal to the concentration of this ion in the initial solution.

Usually the capacity of the sorbent is expressed in milligram equivalents ($\text{mg}/\text{eq}/\text{g}$), however, for practical purposes, the capacity of ion exchangers is expressed in units of mass per unit volume of the swollen sorbent (g/l , kg/m^3).

The exchange capacity of the sorbent largely depends on the pH of the medium. This dependence is the basis for the classification of the sorbent, and according to the nature of the dependence of the static capacity on the pH of the medium, all sorbents are divided into four classes.

2 Objects and methods of research

The objects of research are composite molybdenum-containing middling products (MCMP), molybdenum cinder of the Almalyk mining and metallurgical complex joint stock company, as well as sludge from Research and Production Association "Production of Rare Metals and Hard Alloys" of "Almalyk MMC" JSC. During the more than 60 years of the plant's existence, a significant amount of waste has accumulated in the form of sludge and waste solutions of molybdenum production.

The molybdenum middling cinder of Almalyk MMC JSC is a multicomponent composite system of complex composition in the form of molybdenum trioxide, unoxidized molybdenite, molybdates of various metals.

When conducting research, we used a complex of chemical, physical and instrumental methods for analyzing the elemental and material composition. Below is a brief description and capabilities of local and analytical instruments and mineralogical and technological research methods.

1. Quantitative and qualitative analysis of the elemental composition of objects was carried out on an electron probe microanalyzer and JXA-8800R "Superprobe" (Jeol, Japan). It allows you to determine the content of more than 70 elements (from boron to uranium) in the concentration range from 0.005 to 100% in microsections about 1 micron in size.

2. ICP - mass spectrometer Elan-6000 (Perkin Elmer, USA). Elan-6000 Inductively Coupled Plasma Mass Spectrometer (ISPMS). The limit of detection for most elements is 0.00 grams per ton.

3. Atomic absorption spectrometer Perkin Elmer AS-3300 is designed for accurate analysis of 2-3 elements of liquid samples, process solutions, solids after their chemical decomposition.

4. X-ray fluorescence analyzer, energy dispersive spectrometer ES-20000 R (Oxford Inst., England) is used for fast multi-element analysis (from sodium to uranium), quantitative and semi-quantitative analysis of solid, powder, liquid, etc. for the content of 50 elements (from 0.001 to 100%).

5. The mechanism of joint phase transformations in the composition of ore and products of their processing, as well as the regularities of the solid-gas-phase interactions occurring in this case, were studied on a Q-1500D derivatograph (Hungary). In this case, the samples were subjected to continuous heating in corundum crucibles in a derivatograph furnace from room temperature to 1000°C at a rate of 10°C/min. Aluminum oxide fired at 1200°C was used as a reference.

Chemical analysis determined the carbon content in the composition of carbonates and in the form of organic compounds. Compound of organic carbon (natural and flotation oils) - 1.8%.

Table 1. Results of mass-spectrometric analysis of the initial MCMP

Name	Li	Be	B	Na	Mg	Al
Kontr 3m	4.16	0.188	57.9	1980	14995	10979
Name	Cr	Mn	Fe	Co	Ni	Cu
Kontr 3m	23.8	257	77069	31.0	24.6	24389
Name	Zr	Nb	Mo	Ag	Cd	In
Kontr 3m	10.2	0.536	187816	47.3	80.8	64.9
Name	Pr	Nd	Sm	Eu	Gd	Tb
Kontr 3m	3.53	12.6	2.30	0.425	1.65	0.204
Name	Ta	W	Re	Pt	Au	Tl
Kontr 3m	0.051	20.1	253	0.086	2.63	0.431

Continuation of table № 1

P	K	Ca	Sc	Ti	V	Y
89	2053	11787	2.00	238	14.8	4.27
Zn	Ga	As	Se	Rb	Sr	Ce
1170	1.83	7.85	12.0	9.45	49.7	36.6
Sn	Sb	Te	Cs	Ba	La	Hf
3.64	107	8.84	0.775	77.4	16.5	0.371
Dy	Ho	Er	Tm	Yb	Lu	
1.11	0.183	0.475	0.064	0.401	0.061	
Pb	Bi	Th	U			
5953	59.1	4.65	3.87			

Incoming molybdenum middlings from “Almalyk MMC” JSC after flotation enrichment contain residues of flotation reagents, which hinder their hydrometallurgical processing. In order to purify MCMP from flotation reagents, it was washed in two stages with hot water under vigorous stirring. The flotation reagents were separated in the form of foam. The filtered sample was dried, after which sintering with soda was carried out. Samples weighing 50 g of middlings were mixed with soda, sintered in a muffle furnace at a temperature of 450-500°C for 1 hour. Speck was placed in a heat-resistant beaker and leached in a heated mechanical stirrer in two stages, the temperature of the solution reached 60-70°C. The solid:liquid (S:L) ratio was maintained at 1:4 - 1:5. Table 2 shows the data of the original MCMP sample and selected data from laboratory experiments on MCMP leaching.

Table 2. Results of analyzes of the initial content of Mo in MCMP and after soda leaching

№ experiments	content Mo, %
Initial sample MCMP	30.62
20	38.0
21	36.37
22	37.21
23	33.25

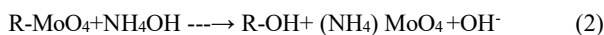
3 Results and discussion

To study the molybdenum sorption process, two sorption columns with a resin capacity of 3 kg each were prepared.

For selective sorption of the molybdate ion, an A-100 Mo type ion-exchange resin with the general formula R-NO₃ was used. Sorption of the sodium molybdate ion corresponds to the substitution reaction:



The saturated resin was washed with technical water and molybdenum was desorbed with ammonia water according to the following reactions:



The ion exchange resin was again washed with water and converted to the nitrate form with nitric acid:



The solutions leaving the columns are a strong solution of ammonium molybdate with a Mo content of 80-90 g/l.

The following preparatory operations of the resin before sorption were performed:

- flushing with technical water;
- flushing with 7–10% ammonia water solution;
- treatment with 5-7% nitric acid for 10-12 hours;
- flushing with technical water.

Solutions were fed into the columns from bottom to top with adjustable clamps. The optimal rate of passage of solutions was established experimentally and amounted to 7 l/hour. At this speed, good sorption of molybdenum onto the resin is achieved. Supplied solutions for sorption contained 40 g/l Mo, when leaving the column, the content of Mo reached the discharge content of 0.085 g/l. Figure 1 shows the output curves of A-100Mo at various specific loads (SL) of the working solution.

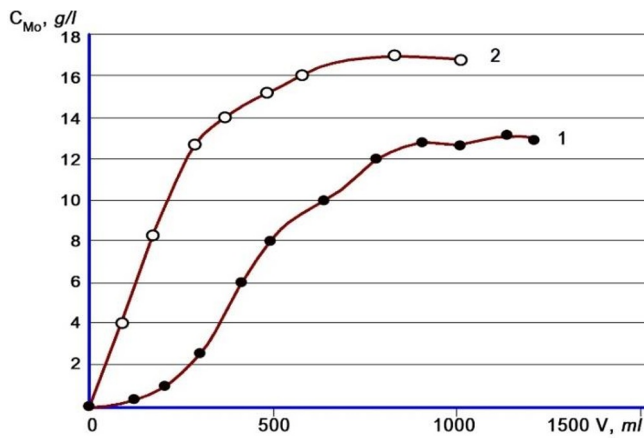


Fig. 1. Output curves of Mo sorption with Purolite A-100 Mo ion exchanger at SL=3(1) and 6/h (2) and $C_0=10\div 17$ g/l

After sorption of a certain volume of the solution, the resin was desorbed with 11-12% ammonia solution (NH_4OH). The desorption curve is shown in Fig. 2.

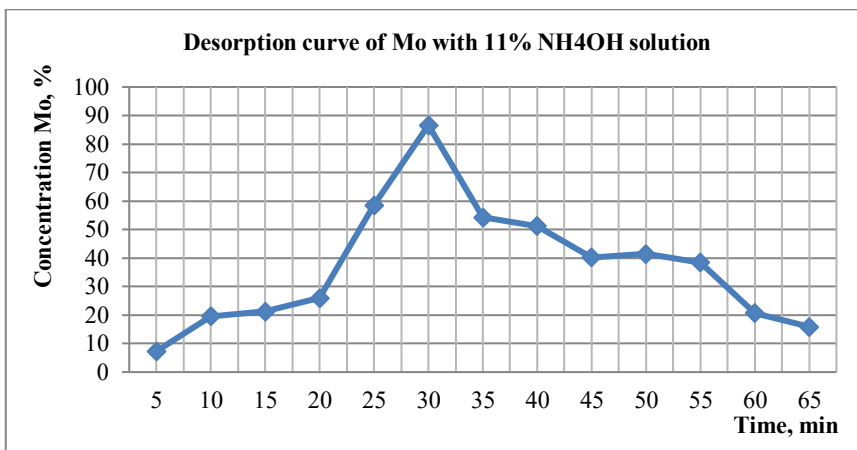


Fig. 2. Desorption curve of molybdenum containing solution

The obtained solutions of sodium moisture molybdate with a soda content of 60-65 g/l are transferred into a sour solution by adding nitric acid, pH of solutions directed to sorption should be 2-2.5.

Nitrogenic acid is supplied from 46 to 56%. Nitric acid consumption: at a concentration of 46% of nitric acid per liter of productive molybdenum -containing solution, 61.2 ml of nitric acid is consumed, and with a concentration of 56% of nitric acid per liter of productive molybdenum-containing solution, 53 ml of nitric acid is consumed.

Molibden containing solutions formed as a result of the desorption of the resin are sent to the container for evaporation to the content of 80-90 g/l in the solution. The discharge was carried out in a container equipped with a steam shirt until a solution reaches a solution of 1.11–1.19 kg/dm³.

Pumping of the depressed solution was carried out periodically upon reaching the density of the solution of 1.11–1.19 kg/dm³ (260–270 g/l). Stepping under vacuum. The pairs and gases extending from the reactor from the evaporation are sucked by one of the vacuum pumps.

Before the start of ammonium tetramolibdate crystallization (NH₄)₂O · 4MoO₃ · 2H₂O, the contents of the reactor acidified with nitric acid to pH 2.0-2.2 through a sprayer that prevents a heterogeneous increase in the concentration of the solution. After that, the solution with constant mixing was cooled up to 60 °C, supplied chilled water into the crystallizer shirt. After receiving the required pH, the solution is continued to mix for 5 minutes before the end of the crystallization operation [13, 14].

In the case of stirring mixing for some reason, the crystallizes located in the reactor must be dissolved in ammonia water.

After the crystals are ready for filtering, the pump is turned on, which pumps the suspension for filtering. The reactor is washed with technical water, after which a new portion of the solution from the reactor No. 28 is supplied to it. The resulting ammonium tetramolibdate is transmitted to determine the content of the Mo for analysis in the laboratory.

The filtrate is a uterine solution with a molybdenum content of 2-3 g/l and pH of a solution of 2.0-2.5 are directed by gravity to a container with a stirrer. For additional extraction of molybdenum from it, the solution is acidified with nitric acid to pH 0.9-1.0. At the same time, an amorphous precipitate of molybdenum acid falls, which is filtered 25-30 minutes after acidification of the uterine solution on the gutting filter installed under the container.

Next, nitric acid for neutralization was added to the wolted solution.

When sodium molybdate solutions are neutralized, precipitation occurs, after the filtration of the solutions, molybdenum acid is unloaded into a container (container).

Thus, studies on the grinding of the source molybdenum middling cinder and their processing using sintering with soda and without the use of sintering allowed to determine the best option for the effective extraction of molybdenum by processing fine-grained molybdenum middling cinder directly by leaching with a solution of soda with a concentration of 120 g/l due to the effective extraction of molybdenum in finished products. Molybdenum in the discharge pinks remains only 3% or less.

As noted in the literary review for the sorption of molybdenum and rhenium from various molybdenum's containing raw materials, depending on the form of the location of molybdenum, rhenium and other components, as well as the parameters of the medium, nitrogen-containing anionites and complex-forming ionites, amino-containing imperatives, etc.

Various sorbents are used from cationitis and anionites, from slightly acidic and strongly acidic, from highly response to low -axial ones.

In molybdenum production, VP-1P and VP-14KR, respectively, were used to extract molybdenum and rhenium. The promising ionites are low -axial sorbents produced by Purolate.

The capacity of the weakly basic A170 anion exchange resin for Re(VII) during sorption from 4 m. H₂SO₄ solution is several times higher than during sorption from 1 m. HNO₃ solution. A study of the equilibrium, kinetics, and dynamics of rhenium desorption from macroporous and gel weakly basic anion exchangers Purolite A170 and Purolite A172 with ammonia solutions shows that, under equal conditions, rhenium is quite completely desorbed from macroporous anion exchanger A170 by an aqueous solution of ammonia at room temperature at various degrees of saturation of the anion exchanger with rhenium, while from the A172 gel anion exchanger, a satisfactory degree of rhenium desorption is achieved only when it is highly saturated with rhenium. The rate of desorption of rhenium from a macroporous anion exchanger is significantly higher than from a gel one [15].

Table 3 below shows the comparative characteristics of the physical, chemical and technological properties of sorbents.

The decrease in the sorption of Mo(VI) by the gel anion exchange resin from solutions with pH<5.0 is apparently due to the onset of the transition of the heptamolybdate ion into a larger octamolybdate ion, which cannot penetrate into the grains of the gel anion exchange resin due to the sieve effect. With an increase in pH above 5.0, the depolymerization of the heptamolybdate ion begins and the transition of Mo (VI) to the form of the monomolybdate ion MoO₄²⁻ occurs. At pH = 7.0, molybdenum is completely in the form of the molybdate ion, which has a low affinity for anion exchangers [16].

In addition, with an increase in pH, the functional groups of anion exchangers are deprotonated, and they lose their ability to retain anions [17].

Table 3. Comparative characteristics of physical, chemical and technological properties of sorbents

Parameters	A-100	A-170	A-172	BO-020
The structure of the polymer matrix	Polystyrene cross-linked with divinylbenzene macroporous	The structure is macroporous	polystyrene hypercrosslinked with divinylbenzene helium	
Appearance	White opaque spherical particles	White opaque spherical particles	Translucent yellow color	Amber spherical grains
Number of whole particles, %, not less than	95			
Functional groups	Third amine -R-N ⁺ (CH ₃) ₂ H ₂ O	secondary amine		
Ionic form (in commercial product)	free base (FB)	free base		
Bulk weight, g/l	845-675		- 0.642 g/cm ³	
Scatter of particles, mm +1,2 Cl ⁻ , %	no more 20			

Continuation of table № 3

Parameters	A-100	A-170	A-172	BO-020
Specific gravity: wet anion exchange resin free base	1.03 g/ml	1.05 g/cm ³	1.07 g/ml.	
Full exchange capacity: Wet anion exchanger, by volume g-eq/l, not less; Dry anion exchanger, by weight g-eq/l, not less than	1.3 3.9	1.25		
High basic capacity, %	10-20 of total capacity			
Maximum operating temperature form Cl-, °C,	no more 100	60		
Anion exchanger stability pH range	0-14		0-14	
Working range pH	0-9			

The latter causes a decrease in the sorption of both Mo(VI) and Re(VII) at relatively high pH values. From the point of view of the separation of rhenium and molybdenum, it is important that in the pH range = 7.0÷7.5 the capacity of anion exchangers for Re(VII) has sufficiently high values, while Mo(VI) is practically not sorbed under these conditions. This explains the fact that upon contact of anion exchangers saturated with both metals with a solution having pH = 7.0–7.5, desorption of Mo (VI) will occur, while Re(VII) will remain in the anion exchanger phase [18].

Very interesting results were obtained for the sorption of rhenium on the sorbent BO-020. This sorbent is an analogue of the widely used AMP sorbent [19].

Currently, BO-020 is used in the joint sorption of uranium and rhenium, as well as before the extraction of rhenium from productive solutions of underground leaching of uranium. We have studied the sorption of ReO_4^- on TVEKS impregnated with various impregnants in the sorbent BO-020.

Figures 3-5 show the microstructure of the sorbent BO-020 impregnated with TBF, TEA in various solvents after sorption of ReO_4^- .

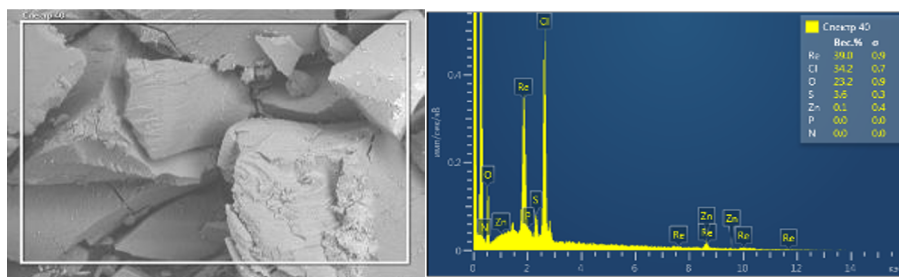


Fig. 3. Microstructure of sorbent BO-020 impregnated with TBF (in ethanol) after sorption of ReO_4^-

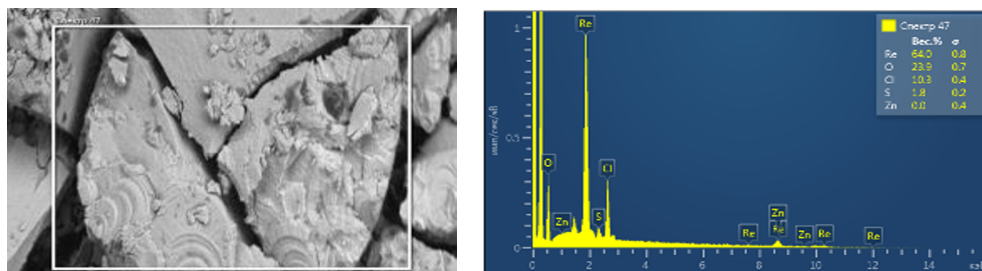


Fig. 4. Microstructure of sorbent BO-020 impregnated with TEA (in ethanol) after sorption ReO_4^-

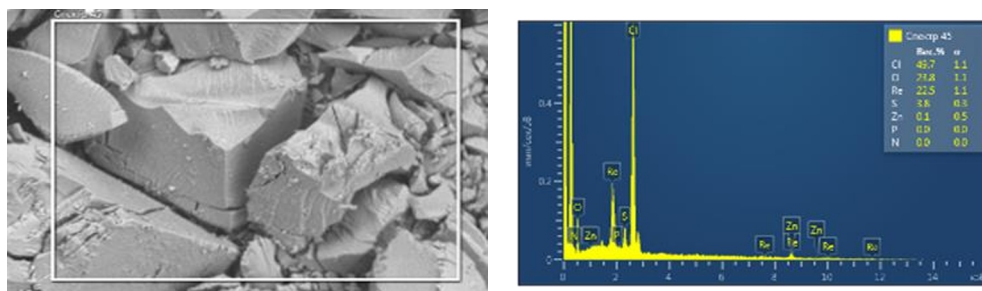


Fig. 5. Microstructure of sorbent BO-020 impregnated with TEA (in acetone) after sorption ReO_4^-

The structure of the resulting TVEKS was studied by IR spectroscopy using the data of these works. The results of comparing the TVEKS spectra with each other before and after the sorption of metal ions, as well as with the spectra of the sorbent-element complexes, confirmed the complex formation of functional groups.

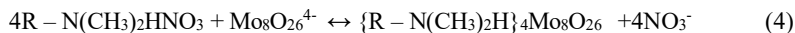
The shifts of the characteristic bands revealed the presence of interaction between organic ligands and metal ions with the formation of stable metal complexes in the solid phase.

Interesting results were obtained by us on the sorption of Au^{3+} , Pt^{2+} impregnated with alkyl-substituted P, S, N containing polymeric sorbents [20-22].

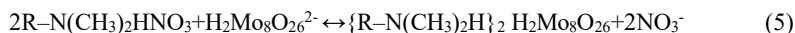
Sorption of molybdenum. When carrying out the sorption of molybdenum, columns are used with a ratio of height H to diameter $D > 5:1$, preferably $H:D=1: 8-10$. Four columns are used, operating in the "wandering" column mode: three operate in the sorption mode, of which the first - until saturation with molybdenum, the second - before the breakthrough of molybdenum, the third is used for guaranteed capture of molybdenum, if there is an accidental breakthrough of molybdenum into the solution leaving the of the second column, the fourth is on regeneration (washing, desorption of molybdenum, second washing, charging into protonated solution leaving the second column, the fourth is on regeneration (washing, desorption of molybdenum, second washing, its shape). functions change metas, namely: at the beginning, the prepared productive solution containing molybdenum is fed from the pressure tank sequentially to the first three columns, i.e. the solution is fed directly to the first column, from the first to the second, and from the second to the third. a certain period of time, the first column is saturated with molybdenum, it is disconnected from the supply of the solution and put on regeneration. The initial solution is fed to the second column with regenerated or fresh anion exchanger, etc. The solution, after passing successively through three columns, not containing molybdenum, is sent for disposal (neutralized with soda until neutral and evaporated).

The macroporous anion exchanger Purolight A100 Mo is used as a sorbent.

The process of molybdenum sorption on the anion exchanger is described by the reaction equations:



or (which is more correct).



During sorption, molybdenum, which is in solutions mainly in the form of protonated octamolybdate ion, is exchanged for nitrate ion, which is initially in the anion exchanger phase and thus passes into the anion exchanger phase.

The anion exchanger must be in protonated NO_3^- - form.

The rate of transmission of the solution during sorption should not exceed 1-2 spec. turnover/hour. The full dynamic exchange rate of the anion exchanger for molybdenum is not less than 160 kg Mo/m³ of swollen anion exchanger, the capacity up to the breakthrough of molybdenum (at a rate of transmission of a solution of 1 turnover/hour, 110 kg Mo/m³ of swollen anion exchanger (they must be specified during the start-up adjustment work).

The concentration of molybdenum in the solution at the outlet of the last column standing on the sorption operation should not exceed 0.05 g/l.

Molybdenum saturation of the first of the columns, into which the initial solution enters, is fixed by the change in the concentration of molybdenum in the solution at the outlet of the column: at the moment when the concentration of molybdenum in the solution at the outlet of the first column becomes equal to or close to its concentration in the solution supplied for sorption, switch columns and start regeneration of the first column.

Control - determination of the concentration of molybdenum in the solution after each passage of each of the three columns (after reaching the stationary mode - determination of the concentration of molybdenum in the solution after passing the first and third columns), regulation of the rate of transmission of the solution.

Washing the sorbent from the initial solution. To remove the initial solution containing molybdenum from the column with the molybdenum-saturated sorbent, the column is washed with water. The amount of water that must be passed through the column is 2-3 spec. turnover/hour. (to be specified during commissioning). Washing speed - 1-2 spec. turnover/hour. The solution after washing containing molybdenum should be combined with the acidified productive solution supplied for sorption.

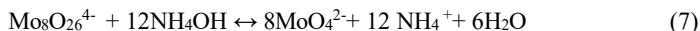
Control - before entering the mode - determination of the concentration of molybdenum in the solution at the outlet of the column (flushing can be stopped after the concentration of molybdenum <0.5 g/l), regulation of the amount of water supplied for washing, and the speed of washing.

Desorption of molybdenum. An ammonia solution is prepared by mixing a concentrated 12-14% ammonia solution with water in a ratio of ~1: 1÷1:1.5. The desorbing solution is prepared directly in the pressure tank and fed into the molybdenum-saturated sorbent column.

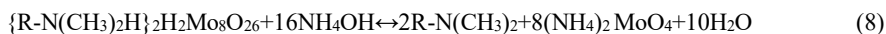
During the desorption of molybdenum, two parallel reactions occur, which are written below in ionic form: the reaction of deprotonation of the functional groups of the anion exchanger, due to which the anion exchanger loses its ability to retain anion exchangers:



and the reaction of depolymerization of polymolybdates – ions



The overall reaction describing the process of desorption of molybdenum from the anion exchanger (assuming that molybdenum is sorbed in the form of a protonated octamolybdate ion) can be represented as:



The solution flow rate is 3 l/day; the amount of solution that must be passed through the sorbent for molybdenum desorption is 2.5-3.0 r/h (to be specified during commissioning). Desorbate containing molybdenum (the concentration of molybdenum in it can reach 180 g/l) is collected and sent to obtain pure ammonium molybdate.

Control - determination of the concentration of molybdenum in the desorbate, regulation of the amount of solution supplied for desorption, and the rate of transmission of the solution.

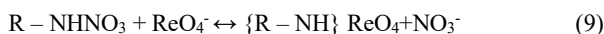
The molybdenum middling was processed according to the existing technology to obtain ammonium tetramolybdate, then the ammonium tetramolybdate solution was acidified to pH = 1.5-2.5 with nitric acid. After filtration, the clarified mother liquor was fed to the sorption of molybdenum in a column with an A100 Mo anion exchanger. Molybdenum was desorbed with 12% ammonia solution. The desorbent was sent to obtain ammonium tetramolybdate, from which, after dissolution in ammonia and crystallization, ammonium molybdate oxide was obtained, which meets the chemical composition requirements of State standard (GOST 2677-78) for ammonium molybdate.

Sorption of rhenium. Output parameters of the separated components productive solution (after 1-cycle of sorption of rhenium): Mo, Re - containing solution Mo-0.0021 mg/l, Re-1183 mmg/l.

The second cycle of sorption is carried out similarly to the 1st cycle on sorption columns (sorbent A-170).

Output parameters of the separated components of rhenium-containing productive solution: Re-0.0001 mg/l; Mo = 247.124 gr/l.

Sorption of rhenium on A-170 resin is described by the equation:



After saturation of the resin, the saturated sorbent is washed with distilled water, then the rhenium is desorbed.

Desorption of rhenium. Desorption of rhenium with 10-12% ammonia solution from Purolite A-170 anion exchanger is efficient. For one contact of the sorbent and eluent, it was possible to extract up to 98% of rhenium according to the reaction:



The eluate and wash water are subjected to evaporation up to 50% of the volume and subjected to crystallization by cooling the solution. Then carry out the secondary evaporation until dry and subjected to the first re-treatment with ammonia water. As a result, "rough" ammonium perrhenate NH_4ReO_4 CRE=68.7% is obtained. After the second re-treatment with ammonia water, the content of Re = 69.3%.

Table 4 below is presented by technological processes, which shows the main parameters of the technology.

Table 4. Balance by technological processes

№	Name operations	volume, V m ³ , kg	Initial data, raw and materials	Technological parameters of the process	Output parameters
Solution preparation area					
1	Waste solution	5 m ³	Пачбop mg/l: C _{Mo} =28.6; C _{Cu} =1675.0 C _{Fe} = 23.0; C _{Re} =7.9; ρ = 1.15 g/cm ³ .	t=90°C evaporation to ρ =1.8-1.9 g/cm ³ . V= 1m ³ after evaporation	Solution mg/l C _{Mo} =143 C _{Cu} =8375 C _{Fe} =115, C _{Re} =39.5; ρ =1.9
Collective precipitation of elements					
2	Solution C _{Mo} =143 C _{Cu} =8375 C _{Fe} =115, C _{Re} =39,5 ρ =1,9	V=1000 l	Na ₂ S = 23.4 kg	t=25-30 °C Ph=7.5-8	Solution after precipitation C _{Mo} =0.000143 C _{Cu} =0.0008375 C _{Fe} =0.000115, C _{Re} =0.000395; ρ =1.9
Filtration					
3	Precipitate, Solution after precipitation C _{Mo} =0.000143 C _{Cu} =0.0008375 C _{Fe} =0.000115, C _{Re} =0.000395; ρ=1.9	12.4 kg	Filtration cloth, suction filter	Using a vacuum pump	Sediment in % C _{Mo} =1.64 C _{Cu} = 99.56 C _{Fe} =1.32, C _{Re} =0.445
Acid leaching					
4	Sediment in % C _{Mo} =1.64 C _{Cu} = 99.56 , C _{Fe} =1.32, C _{Re} =0.445	Sediment 12.4 kg	56% HNO ₃ = 33 l flushing with water 20 l.	t=50 °C; Ph=1.8-2 ratio S:L=1:3	Solution after leaching, V=55 l, C _{Mo} =4290, C _{Cu} = 251250, C _{Fe} = 3450, C _{Re} =1185 ρ =1.3-1.4
Re-filter as needed to remove particulate matter					
Sorption of Mo, 1-cycle					
5	C _{Mo} =4290, C _{Cu} = 251250 C _{Fe} = 3450, C _{Re} =1185 ρ =1.3-1.4	V=55 l	Low base anion resin A- 100Mo = 26 l	t=50 °C; Ph=1,8-3 solution flow rate l/day = 9 l	V=70 l, Solution after sorption mg/l, C _{Mo} = 0.0021, C _{Cu} = 247135, C _{Fe} =3412, C _{Re} =1183, ρ =1.3-1.4

Continuation of table № 4

Washing of the sorbent after sorption of Mo with distilled water V = 100 l and desorption					
6	Saturated sorbent A-100Mo	4 kg	12-14% NH ₄ OH, distilled/water	Desorption rate 9l/day	
Desorption of Mo with ammonia V=50l ammonia+30 l distilled/water					
7	Saturated sorbent A-100Mo	4 kg	12-14% NH ₄ OH, distilled/water	$\tau=5$ l/day	Eluate No.1 V=70l after desorption of Mo C _{Mo} =3064 C _{Cu} =0.0035 C _{Fe} =0.00023, C _{Re} =0.0001
Sorption Re 2-cycle					
8	Solution after Mo sorption, mg/l C _{Mo} =0.0021, C _{Cu} =247135, C _{Fe} =3412, C _{Re} =1183, $\rho=1.3-1.4$	V=70 l	Low base anion resin A-170=52 kg	t=50 °C; Ph=1.8-3 solution flow rate 9 l/h	Solution after sorption of rhenium C _{Mo} =247124, C _{Fe} =3408 C _{Re} =0.0001 $\rho=1.3-1.4$
Washing of the sorbent after sorption with dis/water. Re desorption by ammonia V=50 l ammonia+30 l dis/water					
9	Saturated Resin A-170Re	3 kg	12-14% NH ₄ OH dis/water	Desorption rate 5 l/day	Eluate No. 2 after desorption, 70 l
Primary evaporation of the eluate (cooling, crystallization 5-10°C, filtration NH₄NO₃)					
10	Productive Re solution and ammonium nitrate solution after evaporation	V=7 l	12-14% NH ₄ OH dis/water	t=5-10 °C	Sediment NH ₄ NO ₃ and Productive solution Re after filtration, V= 5l
Secondary evaporation of the productive solution to a dry state					
11	Rough ammonium perhenate m _{Re} =66.3 gr	V=7 l	12-14% NH ₄ OH dis/water	Desorption rate 4 l/day	Rough ammonium perhenate NH ₄ ReO ₄ 63 gr, C _{Re} =68,7%
First repurification (dissolution, cooling, recrystallization, filtration)					
12	m _{Re} =52.2 gr after initial cleaning	V=1 l	ammonia water	t=50-60 °C	ammonium perhenate 52.2 gr, C _{Re} = 68.7 %
Second repurification (dissolution, cooling, recrystallization, filtration)					
13	Ammonium perhenate after secondary refining m _{Re} =49.6 gr	V=1 l	ammonia water	t=50-60 °C	Commercial product Ammonium perhenate 51.5 gr, C _{Re} = 69.3 %

4 Conclusions

A detailed analysis of the current state of artificial ion-exchange sorbents for the extraction of precious metals from the pulp in the laboratory and production conditions of the metallurgical industry has been carried out.

Based on the results of the study, it was revealed that the interaction of the sorbents chosen by us with noble metal ions provides a high degree of release of noble metals in the process of their extraction.

As a result of the above studies, a technology has been developed for processing molybdenum middlings to obtain ammonium molybdate of high purity. The proposed technology was tested at the production site of workshop No.5 of the Research and Production Association "Production of Rare Metals and Hard Alloys" of "Almalyk MMC" JSC in the amount of 50 kg of MCMP.

Based on the sorption and desorption kinetics of molybdenum and rhenium on various ion-exchange resins, it was shown that the sorption of molybdenum and rhenium proceeds most efficiently on low-basic anion exchangers A-100 Mo and A-170, respectively, and after double repurification of the "rough" rhenium concentrate, ammonium rhenium of qualification was obtained. AR-0, corresponding to State standard (State Standard 31411-2009).

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