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Review

Molybdenum Recovery from Mineral Raw Materials by Hydrometallurgical Methods

A.G. Kholmogorov[1], O.N. Kononova[2]*, G.L. Pashkov[1],
S.V. Kachin[2], O.N. Panchenko[1], O.P. Kalyakina[2]

[1] Institute of Chemistry and Chemical Technology, Siberian Department of the Academy of Science,
Karl Marx Pr., 42, Krasnoyarsk, 660049, Russia
[2] Department of Chemistry, Krasnoyarsk State University, Svobodny Pr., 79, Krasnoyarsk, 660041, Russia

ABSTRACT

The present review is focused on technological processes used in the industrial practice of molybdenum production from raw materials, i.e. on pyro-metallurgical (oxidative roasting) and hydrometallurgical methods. It was shown that the hydrometallurgical methods have the advantages over the pyro-metallurgical ones: ecological safety and opportunities for production of pure molybdenum salts owing to sorption on acrylic and styrene macroporous anion exchangers with long-chained cross-linking agents. © 2002 SDU. All rights reserved.

Keywords: Molybdenum; Hydrometallurgy; Sorption; Macroporous anion exchangers; Long-chained cross-linking agents

1. INTRODUCTION

Molybdenum (sulfide and oxidized), copper-molybdenum and uranium ores as well as secondary raw materials are the sources for molybdenum production. In 1940-1970, the pyro-metallurgical methods (Zelikman, 1970) were used for molybdenum breakdown from sulfide ores and concentrates. These methods are environmental dangerous and do not allow to isolate completely the useful components of raw materials. In 1970-1990, the chemical technologies for production of molybdenum and its salts were rapidly developing (Klyachko *et al.*, 1979; Kholmogorov *et al.*, 1985; Short Communications, 1971 and 1998). At present time the application fields for molybdenum high purity alloys, single crystals, complex inorganic and organic salts are being widening. It is fostered by extraction and sorption methods for isolation and purification of metals.

2. PYRO- AND HYDRO-METALLURGICAL PROCESSES FOR BREAKDPOWN OF MOLYBDENUM-CONTAINING RAW MATERIALS

Molybdenum-containing raw materials can be classified by their composition in useful components): as mono-mineral and multi-mineral materials. The oxidized ores fall into the first group, from which only molybdenum is recovered. The sulfide ores belong to the second group, from which molybdenum, sulfur, rhenium, copper and other elements can be recovered.

Table 1 shows technological processes, which are used or tested in industry for molybdenum production from raw materials.

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* Corresponding author. E-mail: cm2@ktk.ru

Table 1
Technological processes of molybdenum production from raw materials

Key technological process	Method of processing and Mo recovery from solutions	Salt composition of exhausted solutions, g/L
1	2	3
1. Molybdenum ores beneficiation	a) Chlorine-soda leaching of sulfide industrial products	Mo=0.5÷3.5; Cu = 0.02÷0.1; Fe=0.003÷0.02; SO_4^{2-}=45÷55; ($NaCl+Na_2SO_4$)=285÷320
	b) Electrochemical leaching of copper-molybdenum-containing industrial products	Mo = 0.4÷3.0; Cu = 0.05÷0.1; Re = 0.01÷0.1; Fe = 0.002÷0.05; Cl^- = 150÷180; SO_4^{2-} = 10.3÷30.5; CO_3^{2-} = 2.5÷3.6; ($NaCl+Na_2SO_4$) = 270÷290
	c) Sulfuric acidic leaching of oxidized industrial products	Mo = 0.6÷0.7; Cu = 0.5÷0.8; H_2SO_4 = 10÷13; Fe = 12÷15; P_2O_5 = 0.2÷0.4; SO_4^{2-} = 40÷50
	d) Closely grouped leaching of oxidized ores	Mo = 0.1÷0.8; H_2SO_4 = 5÷20; Fe = 0.01÷0.15
2. Molybdenum concentrates processing A. Paramolybdate production according to pyro-hydrometallurgical scheme	a) Oxidative roasting of molybdenum concentrates. Ion exchange recovery of Mo and Re from hyrochloric acidic solutions	Mo = 0.51÷1.5; Cu = 0.1÷0.3; Fe = 0.2÷4.5; Cl^- = 35÷100; SO_4^{2-} = 7÷15; Re = 0.01÷0.02; pH = 2.5÷3
	b) Ion exchange recovery of Mo and Re from sulfuric acidic solutons	H_2SO_4 = 40÷180; Re = 0.3÷0.9; Cu = 0.1÷0.6; Mo = 4÷17; Fe = 0.05÷0.5; As = 0.01÷0.05
	c) Ion exchange purification of ammonium molybdate solutions	Mo = 80÷125; NH_3 = 25÷60; Cu = 0.05÷0.8; Fe = 0.01÷0.05; Na = 0.2÷3; K = 0.1÷0.5; Ca, Mg = 0.01÷0.05
	d) Ion exchange recovery of molybdenum from solutions after acidic and salt leaching	Mo = 1÷2; NH_4Cl = 100÷150; HCl = 25÷40; Fe = 7÷15; Cu = 2÷5; Ca = 2÷4
B. Paramolybdate production according to hydrometallurgical scheme	a) Nitric acidic breakdown of molybdenite concentrates. Ion exchange recovery of Mo and Re from mother nitric acidic solutions	Mo = 0.5÷1.9; Re 0.05÷0.1; NO_3^{2-} = 120÷150; SO_4^{2-} = 100÷135
	b) Purification of ammonium molybdate solutions from impurities	Mo = 75÷100; Cu = 0.1÷1.5; Fe = 0.2÷0.3; Ni = 0.05÷1; Na, K, Ca, Mg = 0.5; NH_3 = 25÷50
	c) Ion exchange recovery of Mo from pulps and solutions (including solutions with PO_4^{3-} ions)	Mo = 10÷20; Fe = 10÷25; HNO_3 = 100÷150; H_2SO_4 = 100÷150; H_3PO_4
	d) Ion exchange recovery of Mo and sulfuric acidic dissolution of MoS_2 by autoclave-cured leaching	Mo = 15÷25; H_2SO_4 = 35÷90; Fe = 0.5÷5.6
	e) Autoclave-cured leaching of ($MoS_2+MnO_2+H_2SO_4+ H_2O+O_2$). Ion exchange recovery of Mo from aqueous ($Mo-H_2SO_4-MnSO_4-H_2O$) system	Mo = 5÷90; H_2SO_4 = 35÷120; Mn = 45÷55; Fe = 3÷12

Continued (Table 1)

| Key technological process	Method of processing and Mo recovery from solutions	Salt composition of exhausted solutions, g/L
1	2	3
C. Calcium molybdate production	Autoclave-cured breakdown of [MoS_2-NaOH-H_2O-O_2]. Ion exchange recovery of Mo and Re from mother solutions	Mo = 0.05÷0.1; Re = 0.35÷0.8; SO_4^{2-} = 0.1÷15
3. Processing of secondary Mo-Re-containing raw materials (catalysts, solid-alloys wastes)	a) Basic and acidic breakdown of molybdenum raw materials. Ion exchange recovery of Mo	Mo = 10÷30; HCl, H_2SO_4 = 10÷50; (Na_2SO_4 + NaCl) = 100÷200
	b) Ion exchange recovery of Re and Mo	Mo = 5÷15; Re = 0.5÷3; NaCl = 150÷220
4. Processing of special alloys and parts	Ion exchange recovery of Mo from electrolytes solutions after processing of molybdenum-containing alloys	Mo, W = 0.1÷0.5; Cr = 0.2÷1.5; Ni = 0.1÷0.8; Fe = 0.5÷1.5; ($NH_4Cl+NH_4NO_3$) = 120÷170; oxiacids salts = 15÷20

2.1. Pyrometallurgical process

It should be noted that molybdenum is mostly used for production of ferromolybdenum, which, in turn, is applied for manufacture of alloyed steels. Hence, it is required to obtain the pure products (in terms of S content) – molybdenum(VI) oxide MoO_3 or calcium molybdate $CaMoO_4$ – from MoS_2 concentrates. During the oxidative roasting, MoS_2 is converted to MoO_3 under complete removal of sulfur: SO_2 is volatilized as a gas and H_2SO_4 is withdrawn by an aqueous leaching of residue after burning (Zelikman, 1970; Klyachko *et al.*, 1979; Kholmogorov *et al.*, 1985).
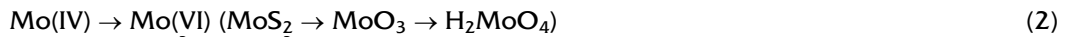
2.2. Hydrometallurgical processes

2.2.1. Autoclave-oxidative leaching of MoS_2 concentrates in aqueous medium

This kind of leaching proceeds in a three-phase system (Klyachko *et al.*, 1979; Kholmogorov *et al.*, 1985):

$$MoS_{2(s)} + 4.5O_{2(g)} + 3H_2O_{(l)} \underset{\leftarrow}{\overset{\rightarrow}{}} H_2MoO_{4(s)} + 2H_2SO_{4(l)} \tag{1}$$
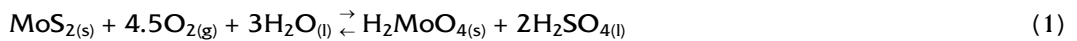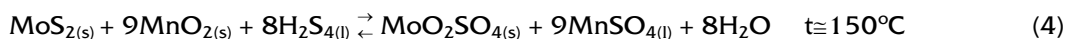
where indexes s, g and l are solid, gaseous and liquid phases, respectively.

Autoclave-cured decomposition of molybdenite concentrate in aqueous phase under oxygen atmosphere includes oxidation

$$Mo(IV) \rightarrow Mo(VI) \ (MoS_2 \rightarrow MoO_3 \rightarrow H_2MoO_4) \tag{2}$$
$$S(II) \rightarrow S(VI) \ (S^{2-} \rightarrow SO_4^{2-}) \tag{3}$$

The presence of iron and copper has a positive (catalytic) effect on acceleration of MoS_2 oxidation process, but it influences negatively the Mo(VI) dissolution in sulfuric acid formed ($H_2MoO_4 - MoO_3 - MoO_2SO_4$). The product ($MoO_3 + SiO_2$) is obtained by means of precipitate heat treatment at $450 \div 470^{\circ}C$. It contains $59 \div 61\%$ Mo and $11 \div 11.5\%$ SiO_2 and is applicable for ferromolybdenum production.

2.2.2. Autoclave-oxidative leaching of MoS_2 concentrates with pyrolusite product
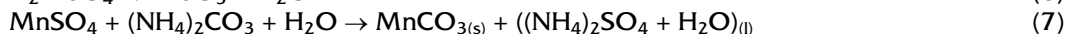
According to Kholmogorov *et al.* (1985, 1994), this kind of leaching can be described by the following reaction:

$$MoS_{2(s)} + 9MnO_{2(s)} + 8H_2S_{4(l)} \underset{\leftarrow}{\overset{\rightarrow}{}} MoO_2SO_{4(s)} + 9MnSO_{4(l)} + 8H_2O \quad t \cong 150^{\circ}C \tag{4}$$

Then manganese and molybdenum are separated:

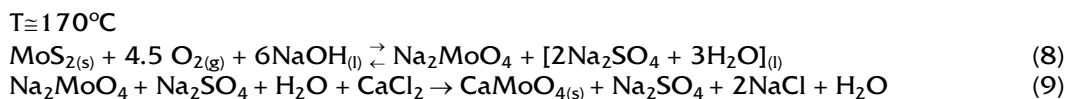$$MoO_2SO_4 + MnCO_3 + H_2O \rightarrow H_2MoO_4\downarrow + MnSO_4 + CO_2\uparrow \tag{5}$$

The manganese sulfate solution is separated from H_2MoO_4 precipitate and then the pure compounds MoO_3 and $MnCO_3$ are obtained:

$$H_2MoO_4 \rightarrow MoO_3 + H_2O \tag{6}$$
$$MnSO_4 + (NH_4)_2CO_3 + H_2O \rightarrow MnCO_{3(s)} + ((NH_4)_2SO_4 + H_2O)_{(l)} \tag{7}$$

It should be noted that ion exchange processes were investigated in technological cycle of Mo and Mn recovery (Kholmogorov and Patrushev, 1994; Kholmogorov *et al.*, 1995; 1999; Patrushev *et al.*, 1996).

2.2.3. Autoclave-oxidative processes in basic medium

Rumyantsev and Kulakova (1999) have determined that these processes result in formation of calcium molybdenite according to the next two reactions:

$$T \cong 170^{\circ}C$$
$$MoS_{2(s)} + 4.5\ O_{2(g)} + 6NaOH_{(l)} \underset{\leftarrow}{\rightarrow} Na_2MoO_4 + [2Na_2SO_4 + 3H_2O]_{(l)} \qquad (8)$$
$$Na_2MoO_4 + Na_2SO_4 + H_2O + CaCl_2 \rightarrow CaMoO_{4(s)} + Na_2SO_4 + 2NaCl + H_2O \qquad (9)$$

The ready product $CaMoO_4$ conforms to the standards of ferromolybdenum production (sulfur content is less than 0.1%).

2.2.4. Nitric acidic breakdown

Nitric acid is broadly applied in molybdenum salts production technologies as a reagent for molybdenite breakdown (Potashnikov *et al.*, 1984; Kholmogorov, 1980):

$$MoS_2 + 6HNO_3 \rightarrow H_2MoO_4 + 2H_2SO_4 + 6NO\uparrow \qquad (10)$$

The MoS_2 oxidation and H_2MoO_4 dissolution in sulfuric acid are maintained due the autocatalytic reaction. The catalysis is caused by nitrogen oxides (NO, NO_2), which are present on the surface of molybdenite species. NO_2 promotes the MoS_2 oxidation process up to 5.5 times in comparison with NO. The simultaneous formation of NO_2 and HNO_2 means that oxidation of MoS_2 proceeds under the mixed conditions. That is why special equipment is required. For instance, tubular autoclaves are used at plants for the MoS_2 oxidation in nitric acid. Such autoclaves provide a necessary contact of species of MoS_2 and oxidants (HNO_3, HNO_2, NO_2, NO). In the solutions obtained, the most of molybdenum is concentrated in the form of MoO_2^{2+} and $[MoO_2(SO_4)_2]^{2-}$.

During the recovery of molybdenum ions on anion exchangers, the ionic equilibrium is shifted as follows:

$$2SO_4^{2-}$$
$$MoO_2^{2+} \rightarrow [MoO_2(SO_4)_2]^{2-} \qquad (11)$$
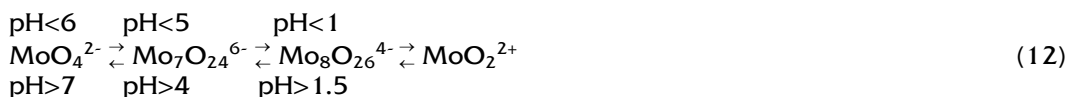$$H^+$$

3. ION EXCHANGE PROSESSES IN TECHNOLOGICAL SCHEME OF MOLYBDENUM SALTS PRODUCTION

Ion exchange processes have found a broad application field in the molybdenum technology (Kholmogorov and Patrushev, 1994; Kholmogorov *et al.*, 1994; Patrushev *et al.*, 1996; Short Communications, 1998), which can be seen from Table 1 and Figure 1. After the MoS_2 concentrates processing by acidic methods, the sorption methods of isolation and concentration of molybdenum are tested. That allows to obtain the high-purified molybdenum salts (ammonium molybdate as well as complex inorganic and organic compounds).

3.1. Ionic state of molybdenum in acids solutions

It is known (Kholmogorov *et al.*, 1985) that the size and type of molybdenum ions depend on pH value of salt system:

$$pH<6 \qquad pH<5 \qquad pH<1$$
$$MoO_4^{2-} \underset{\leftarrow}{\rightarrow} Mo_7O_{24}^{6-} \underset{\leftarrow}{\rightarrow} Mo_8O_{26}^{4-} \underset{\leftarrow}{\rightarrow} MoO_2^{2+} \qquad (12)$$
$$pH>7 \qquad pH>4 \qquad pH>1.5$$

In the hydrochloric acidic media ($C_{HCl} > 0.2$ mol/L), the anions $MoO_2Cl_3^-$, $MoO_2Cl_4^{2-}$ are formed; in the sulfuric acidic and phosphoric acidic solutions, $[MoO_2(SO_4)_2]^{2-}$ and $PMo_{12}O_{40}^{3-}$ are formed, respectively.

In the pH range 1-6, the molybdenum anions exist as polyanions with the larger size than the monomeric MoO_4^{2-} ions.

The molybdenum ionic state in the mineral acids solutions should be taken into account during development of sorption processes.

3.2. Structure of ion exchangers and its effect on molybdenum recovery from solutions

The synthesis of novel macroporous anion exchangers, including the resins on the non-styrene basis with long-chained cross-linking agents, is the reason for rapid introduction of ion exchange technologies into the production of molybdenum salts (Kholmogorov *et al.*, 1982; 1983; 1986; 1989; 1991; 1997; 1999).

The characteristics of some anion exchangers are summarized in Table 2. The increase in the internal porosity of methylacrylate copolymers beads facilitates the high chemical activity of anion exchangers (e.g. AN-108P, AN-106P), which possess the exchange capacity to chloride ions on a level of 6.1÷8.3mmol/g. That is why the problem of the molybdenum recovery from the acidic solutions can be solved.
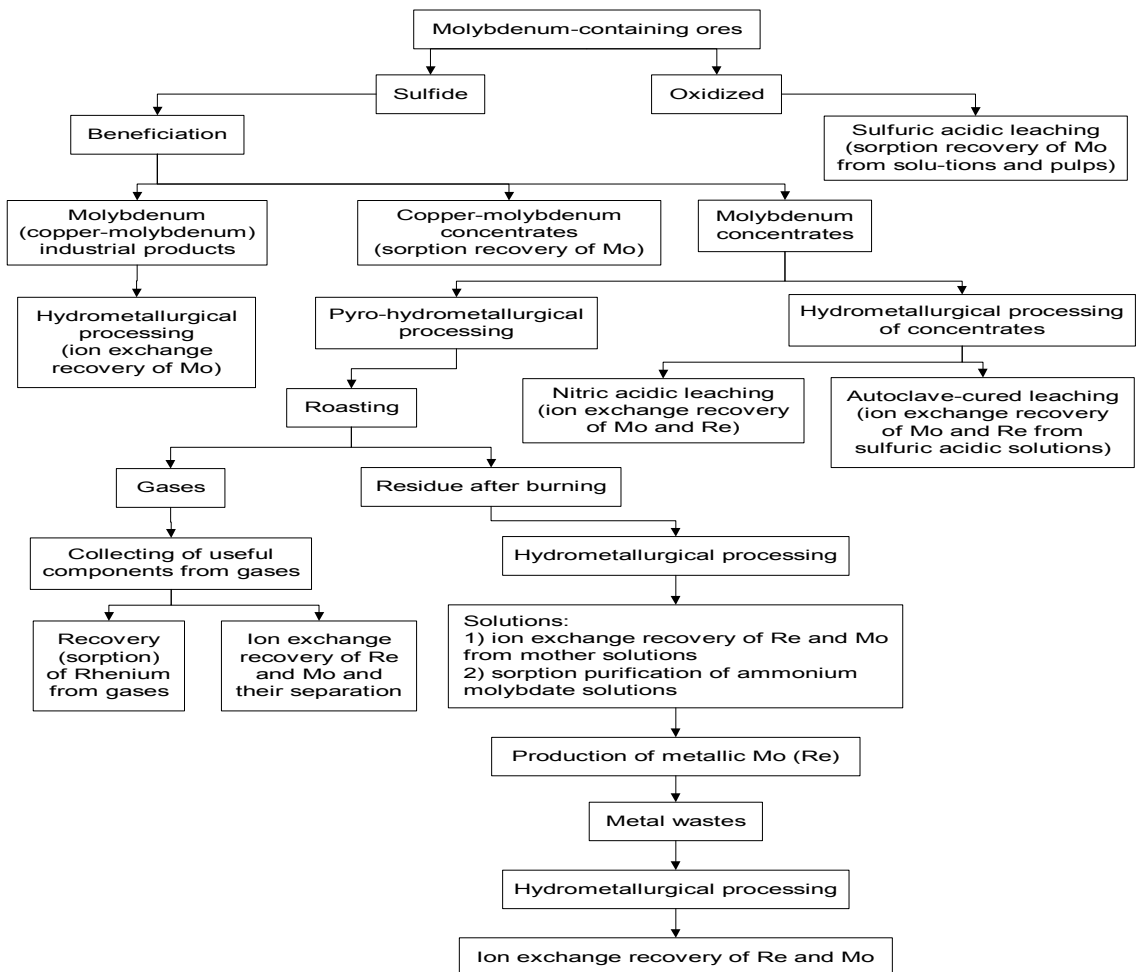

Figure 1. Principal technological schemes of processing of molybdenum-containing raw materials using ion exchange processes

Table 2
Physical-chemical and sorption properties of aminopolymers

Trade name	Copolymer	Cross-linking agent	Functional group	Structure	Total pore volume cm³/g	Specific swelling volume ml/g	Static exchange capacity in Cl⁻ - form mmol/g	Na⁺ - form mmol/g	Specific surface m²/g
AN-221	St	DVB, 8%	-CH-NH-(CH₂)₂-NH₂	P	0.31	3.6	4.9	-	45
AN-80P	MA	DVB, 7%	-CH-CO-NH-(CH₂)₂-NH₂	P	0.36	4.1	6.1	1.2	36
ANS-80	MA	DVS, 3%	-CH-CO-NH-(CH₂)₂-NH₂	NP	-	2.3	5.9	0.9	-
AN-108P	MA	TVEPE, 4%	-CH-CO-NH-(CH₂)₂-NH₂	P	0.46	3.8	6.9	0.4	41
AN-108M	MA	DVEDEG, 7%	-CH-CO-NH-(CH₂)₂-NH₂	MN	-	2.3	6.3	0.4	-
AN-511	St	DVB, 10%	-NH-(CH₂)₂-NH-CH₂-NH₂	P	0.38	3.9	5.1	-	58
AN-106P	MA	DVEDEG, 7%	-NH-(CH₂)₂-NH-CH₂-NH₂	P	0.41	3.8	6.8	-	34
AN-106MP	MA	TVEPE, 4%	-NH-(CH₂)₂-NH-CH₂-NH₂	MP	0.36	3.7	8.6	-	43
AN-85P	AN	DVB, 7%	$-CH-C=N-CH_2$ / $HN-CH_2$	P	0.49	5.1	5.8	-	49
ANE-80P	AN	DVB, 7%	$-CH-C=N-CH_2$ / $N-CH_2$ / $(CH_2)_2-NH_2$	P	0.52	4.2	8.2	-	31
ANKF-80	MA	DVB, 7%	$-CH-CO-NH-(CH_2)_2$ / $NH-CH_2-P(=O)-OH$ OH	P	-	3.9	1.9	4.2	29
AMF-2	MA	DVB, 7%	$-CH-$ / $O=C-NH-CH_2-NH-(CH_2COONa)_2$	P	-	4.1	2.3	4.1	33

St = styrene; MA = methylacrylate; AN = acrylonitrile; DVB = divinylbenzene; DVS = divinylsulfide; TVEPE = tetravinyl-ester of pentaerythritol; DVEDEG = divinyl-ester of diethyleneglycol; P = porous; NP = non-porous; MN = macronetwork; MP - macroporous

3.3. Ion exchange processes in molybdenum production technology

The technological processes using organic ion exchangers were approved in the different stages of molybdenum salts production (Figure 1). The effect of physical-chemical structure of ion exchangers investigated on their saturation degree with the molybdenum ions can be seen from Table 3. The anion exchangers, based on acrylic copolymers with long-chained cross-linking agents (DVEDEG and TVEPE) and aminated by diethylenetriamine, compare favorably in their sorption properties to molybdenum polyanions the styrene anion exchangers AN-221, AN-521 (Table 3).

Table 3
Sorption properties of anion exchangers with different physical-chemical characteristics to molybdenum

Trade name	Copolymer	Cross-linking agent	Aminating agent	Static exchange capacity in Cl^- - form mmol/g	Exchange capacity to molybdenum, mmol/g in acids		
					0.01 M H_2SO_4	0.5 M H_2SO_4	0.2 M HNO_3
AN-80P	MA	DVB, 7%	EDA	6.1	6.4	3.1	1.5
AN-108P	MA	TVEPE, 4%	EDA	6.9	6.7	3.2	1.6
AN-108TP	MA	DVEDEG, 7%	EDA	6.8	7.3	3.4	1.6
AN-221	St	DVB, 8%	EDA	4.9	4.5	2.9	1.3
AN-106P	MA	DVEDEG, 7%	DETA	6.8	7.6	3.6	1.9
AN-106	MA	DVB, 7%	DETA	6.2	6.9	3.4	1.8
AN-106TP	MA	TVEPE, 4%	DETA	8.6	7.8	3.9	2.1
AN-521	St	DVB, 12%	DETA	5.1	4.7	3.1	1.4

MA = methylacrylate; St = styrene; DVB = divinylbenzene; TVEPE = tetravinyl-ester of pentaerythritol; DVEDEG = divinyl-ester of diethyleneglycol; EDA = ethylenediamine; DETA = diethylenetriamine

In the [Mo(VI)-H_2SO_4-$MnSO_4$-H_2O] solutions, the porous anion exchangers are saturated in dependence on sulfuric acid concentration according to the molybdenum ionic state in strong acidic media. Formation of MoO_2^{2+} cations excludes sorption of molybdenum on anion exchangers.

A similar pattern remains for nitric acidic solutions too (Figure 2, curve 2).

In the mineral acids investigated, the molybdenum distribution coefficients decrease in the following row:
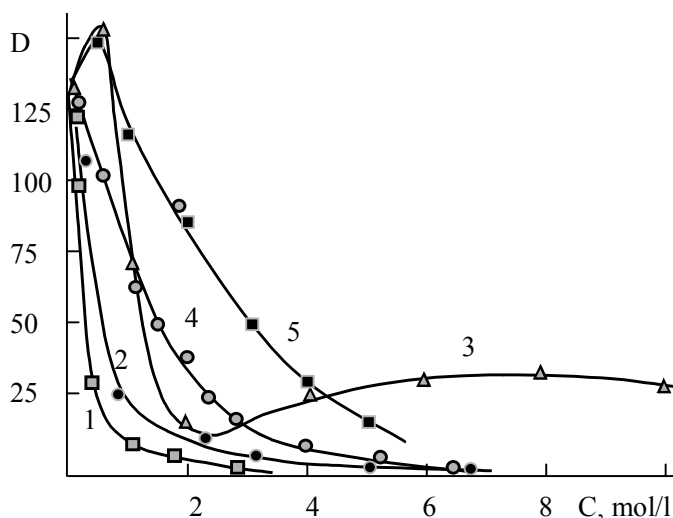
$$HCl>H_3PO_4>H_2SO_4>HNO_3>HClO_4$$

Figure 2. Change of distribution coefficients of molybdenum (D) on anion exchanger AN-85P in mineral acids solutions: $HClO_4$ (1); HNO_3 (2); HCl (3); H_2SO_4 (4) and H_3PO_4 (5)

In strong acidic media (pH<2), the MoO_2^{2+} cations are formed being in equilibrium with the anionic forms $Mo_8O_{26}^{4-}$, $MoO_2Cl_4^{2-}$, $[MoO_2(SO_4)_2]^{2-}$, $PMo_{12}O_{40}^{3-}$. Formation of complex anions in hydrochloric, phosphoric and sulfuric acids increases molybdenum recovery degree from acidic solutions. Formation of anion boundaries depends on molybdenum concentration (Kholmogorov *et al.*, 1985). This concentration affects both ion exchange process and change of polyanion composition. If $0.5Mo$ corresponds to one charge of MoO_4^{2-} ion, then $2Mo$ corresponds to one charge of $Mo_8O_{26}^{4-}$ polyanion, i.e. the exchange capacity of the resin increases up to 4 times during sorption of $Mo_8O_{26}^{4-}$ ion. It was determined (Kholmogorov, 1980; Kholmogorov and Burakova, 1991) that the ionic state of the molybdenum anions sorbed changes similarly with the solutions:

$$\overset{H^+}{MoO_4^{2-} \rightarrow Mo_8O_{26}^{4-}} \tag{13}$$

what can be seen from Figure 3.

At pH=2.9, the $Mo_8O_{26}^{4-}$ polyanions are sorbed (spectrum 2) and at pH=7 and pH=6, the MoO_4^{2-} anions are sorbed (spectra 3 and 4), which are converted to $Mo_8O_{26}^{4-}$ ions with decrease of pH value up to 3.0 (spectrum 5).
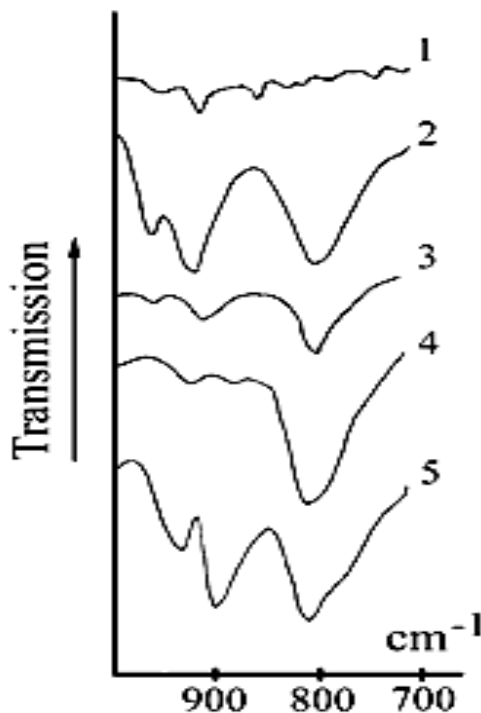

Figure 3. IR spectra of anion exchanger AN-85P after saturation with molybdenum ions from hydrochloric acidic solutions at pH 2.9 (2); 7.0 (3); 6.0 (4) and 3.0 (5). Spectrum 1 is the initial anion exchanger in Cl⁻ form.

In the nitric acidic media, the mixed nitric-sulfuric acidic solutions (0.2÷3.5 mol/L) are formed after breakdown of molybdenite concentrates. Molybdenum is recovered from such weak acidic solutions on vinylpyridine anion exchangers (VP-1, VP-14K) and from strong acidic solutions – on anion exchanger AM-2B. The saturation degree of these anion exchangers depends on concentrations of molybdenum ions and nitric acid. The isotherms of molybdenum sorption in strong acidic solutions (Figure 4) are S-shaped (curves 1-3). With the decrease in HNO_3 concentration, they become convex. It should be noted that the iron sorption on the investigated anion exchangers does not occur.
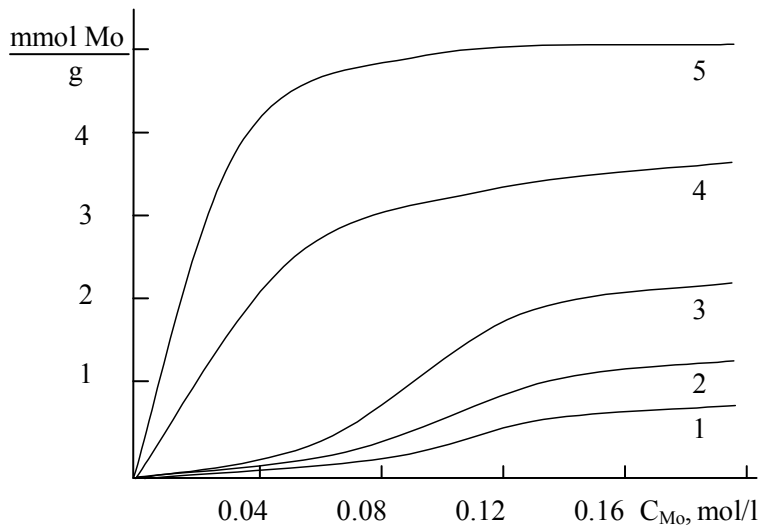
Figure 4. Isotherms of molybdenum sorption on anion exchanger AN-85-10P at HNO₃ concentration (mol/L): 1.7 (1); 1.2 (2); 1.0 (3); 0.5 (4) and 0.05 (5)

The molybdenum sorption on porous anion exchangers proceeds rapidly (the resin is saturated to 92÷96% during 1.5÷2h) and depends on molybdenum concentration (Figure 5).

It should be also noted that molybdenum sorption proceeds efficiently under the dynamic conditions using ion exchange columns with a stationary resin bed and with a mobile bed (underflow of solution and sorbent) as well, under these conditions, the saturation of anion exchangers with Mo ions adds up to $115÷136 kgMo/m^3$. The molybdenum desorption from the investigated anion exchangers is carried out by 15÷25% ammonia solutions. As a result, ammonium molybdate solutions (75÷55gMo/L) are obtained, which are applicable for production of crystalline ammonium paramolybdate. The Mo desorption degree is ~99.9% under these conditions.
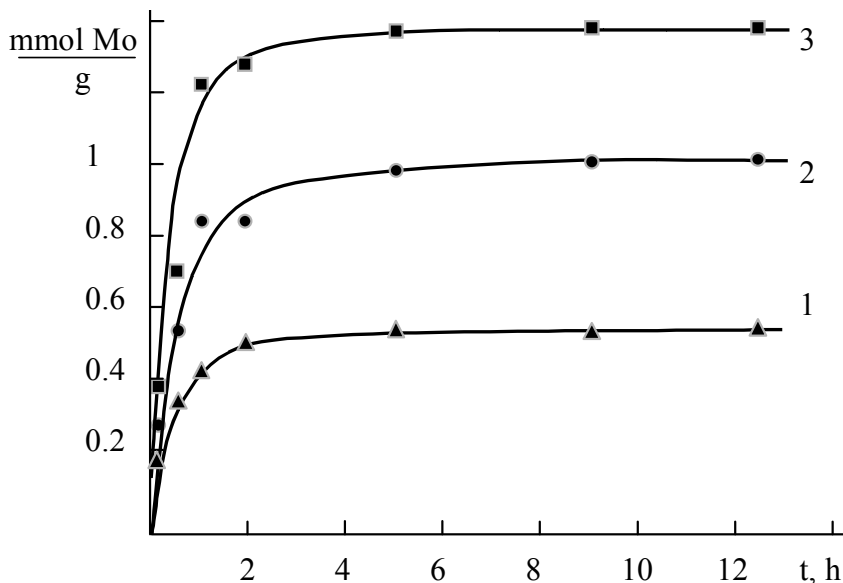
Figure 5. Kinetic curves of molybdenum sorption on anion exchanger AN-85-10P from nitric acidic solutions (0.5 M HNO₃) at molybdenum concentration (mol/L): 0.05 (1); 0.1 (2) and 0.4 (3)

4. CONCLUSIONS

- Pyrometallurgical (oxidative roasting) and hydrometallurgical methods are developed for molybdenum recovery from mineral and secondary raw materials.
- Pyrometallurgical process is ecologically dangerous and does not allow to utilize raw materials.
- Hydrometallurgical methods (nitric acidic breakdown of MoS_2 concentrates and molybdenum salts production as well as autoclave-cured breakdown in acidic and basic media) can be used under the industrial conditions.
- Molybdenum recovery and concentration can be effectively carried out using macroporous anion exchangers with long-chained cross-linking agents.

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