Review

Molybdenum Recovery from Mineral Raw Materials by Hydrometallurgical Methods

A.G. Kholmogorov¹, O.N. Kononova²*, G.L. Pashkov¹, S.V. Kachin², O.N. Panchenko¹, O.P. Kalyakina²

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

Received 28 April 2002; accepted 29 May 2002

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 pyrometallurgical 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 pyrometallurgical 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 BREAKDOWN 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.

* Corresponding author. E-mail: cm2@ktk.ru
Table 1
Technological processes of molybdenum production from raw materials

<table>
<thead>
<tr>
<th>Key technological process</th>
<th>Method of processing and Mo recovery from solutions</th>
<th>Salt composition of exhausted solutions, g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Molybdenum ores</td>
<td>a) Chlorine-soda leaching of sulfide industrial products</td>
<td>Mo = 0.5 ± 3.5; Cu = 0.02 ± 0.1; Fe = 0.003 ± 0.02; SO$_4^{2-}$ = 45 ± 55; (NaCl + Na$_2$SO$<em>4$)$</em>{(aq)}$ = 285 ± 320</td>
</tr>
<tr>
<td></td>
<td>b) Electrochemical leaching of copper-molybdenum-containing industrial products</td>
<td>Mo = 0.4 ± 0.3; 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$_2$SO$<em>4$)$</em>{(aq)}$ = 270 ± 290</td>
</tr>
<tr>
<td></td>
<td>c) Sulfuric acid-leaching of oxidized industrial products</td>
<td>Mo = 0.6 ± 0.7; Cu = 0.5 ± 0.8; H$_2$SO$_4$ = 10 ± 13; Fe = 12 ± 15; P$_2$O$_5$ = 0.2 ± 0.4; SO$_4^{2-}$ = 40 ± 50</td>
</tr>
<tr>
<td></td>
<td>d) Closely grouped leaching of oxidized ores</td>
<td>Mo = 0.1 ± 0.8; H$_2$SO$_4$ = 5 ± 20; Fe = 0.01 ± 0.15</td>
</tr>
<tr>
<td>2. Molybdenum concentrates</td>
<td>a) Oxidative roasting of molybdenum concentrates. Ion exchange recovery of Mo and Re from hydrochloric acid solutions</td>
<td>Mo = 0.5 ± 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</td>
</tr>
<tr>
<td>processing</td>
<td>b) Ion exchange recovery of Mo and Re from sulfuric acid solutions</td>
<td>H$_2$SO$_4$ = 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</td>
</tr>
<tr>
<td>A. Paramolybdate production</td>
<td>c) Ion exchange purification of ammonium molybdate solutions</td>
<td>Mo = 80 ± 12.5; 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</td>
</tr>
<tr>
<td>according to pyrometallurgical scheme</td>
<td>d) Ion exchange recovery of molybdenum from solutions after acidic and salt leaching</td>
<td>Mo = 1 ± 2; NH$_4$Cl = 100 ± 150; HCl = 25 ± 40; Fe = 7 ± 15; Cu = 2 ± 5; Ca = 2 ± 4</td>
</tr>
<tr>
<td>B. Paramolybdate production</td>
<td>a) Nitric acid breakdown of molybdenite concentrates. Ion exchange recovery of Mo and Re from mother nitric acid solutions</td>
<td>Mo = 0.5 ± 1.9; Re = 0.05 ± 0.1; NO$_3^{-} = 120 ± 150$; SO$_4^{2-} = 100 ± 135$</td>
</tr>
<tr>
<td>according to hydrometallurgical scheme</td>
<td>b) Purification of ammonium molybdate solutions from impurities</td>
<td>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</td>
</tr>
<tr>
<td></td>
<td>c) Ion exchange recovery of Mo from pulps and solutions (including solutions with PO$_4^{3-}$ ions)</td>
<td>Mo = 10 ± 20; Fe = 10 ± 25; HNO$_3$ = 100 ± 150; H$_2$SO$_4$ = 100 ± 150; H$_3$PO$_4$</td>
</tr>
<tr>
<td></td>
<td>d) Ion exchange recovery of Mo and sulfuric acid dissolution of MoS$_2$ by autoclave-cured leaching</td>
<td>Mo = 15 ± 25; H$_2$SO$_4$ = 35 ± 90; Fe = 0.5 ± 5.6</td>
</tr>
<tr>
<td></td>
<td>e) Autoclave-cured leaching of (MoS$_2$ + MnO$_2$ + H$_2$SO$_4$ + H$_2$O + O$_2$). Ion exchange recovery of Mo from aqueous (Mo-H$_2$SO$_4$-MnSO$_4$-H$_2$O) system</td>
<td>Mo = 5 ± 90; H$_2$SO$_4$ = 35 ± 120; Mn = 45 ± 55; Fe = 3 ± 12</td>
</tr>
</tbody>
</table>
Continued (Table 1)

<table>
<thead>
<tr>
<th>Key technological process</th>
<th>Method of processing and Mo recovery from solutions</th>
<th>Salt composition of exhausted solutions, g/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C. Calcium molybdate production</td>
<td>Autoclave-cured breakdown of [MoS$_2$-NaOH-H$_2$O-O$_2$]. Ion exchange recovery of Mo and Re from mother solutions</td>
<td>Mo = 0.05-0.1; Re = 0.35-0.8; SO$_4^{2-}$ = 0.1-15</td>
</tr>
<tr>
<td>3. Processing of secondary Mo-Re-containing raw materials (catalysts, solid-alloys wastes)</td>
<td>a) Basic and acidic breakdown of molybdenum raw materials. Ion exchange recovery of Mo</td>
<td>Mo = 10-30; HCl, H$_2$SO$_4$ = 10-50; (Na$_2$SO$_4$ + NaCl) = 100-200</td>
</tr>
<tr>
<td></td>
<td>b) Ion exchange recovery of Re and Mo</td>
<td>Mo = 5-15; Re = 0.5-3; NaCl = 150-220</td>
</tr>
<tr>
<td>4. Processing of special alloys and parts</td>
<td>Ion exchange recovery of Mo from electrolytes solutions after processing of molybdenum-containing alloys</td>
<td>Mo, W = 0.1-0.5; Cr = 0.2-1.5; Ni = 0.1-0.8; Fe = 0.5-1.5; (NH$_4$Cl+NH$_4$NO$_3$) = 120-170; oxiacids salts = 15-20</td>
</tr>
</tbody>
</table>
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$_2$SO$_4$ 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):

$$\text{MoS}_2(s) + 4.5\text{O}_2(g) + 3\text{H}_2\text{O}_l \rightarrow \text{H}_2\text{MoO}_4(s) + 2\text{H}_2\text{SO}_4(l)$$

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

$$\text{Mo(OIV)} \rightarrow \text{Mo(VI)} \ (\text{MoS}_2 \rightarrow \text{MoO}_3 \rightarrow \text{H}_2\text{MoO}_4)$$

$$\text{S(II)} \rightarrow \text{S(VI)} \ (\text{S}_2^2- \rightarrow \text{SO}_4^{2-})$$

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$_2$MoO$_4$ – MoO$_3$ – MoO$_2$SO$_4$). The product (MoO$_3$ + SiO$_2$) is obtained by means of precipitate heat treatment at 450-470°C. It contains 59-61% Mo and 11-11.5% 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:

$$\text{MoS}_2(s) + 9\text{MnO}_2(s) + 8\text{H}_2\text{S}_4(l) \leftrightarrow \text{MoO}_2\text{SO}_4(s) + 9\text{MnSO}_4(l) + 8\text{H}_2\text{O} \ \text{t} = 150^\circ\text{C}$$

Then manganese and molybdenum are separated:

$$\text{MoO}_2\text{SO}_4 + \text{MnCO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{MoO}_4 + \text{MnSO}_4 + \text{CO}_2$$

The manganese sulfate solution is separated from H$_2$MoO$_4$ precipitate and then the pure compounds MoO$_3$ and MnCO$_3$ are obtained:

$$\text{H}_2\text{MoO}_4 \rightarrow \text{MoO}_3 + \text{H}_2\text{O}$$

$$\text{MnSO}_4 + (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{MnCO}_3 + ((\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O})$$

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:

\[
\begin{align*}
T \cong 170^\circ C \\
MoS_2(s) + 4.5 O_2(g) + 6NaOH(l) & \rightarrow Na_2MoO_4 + [2Na_2SO_4 + 3H_2O](l) \quad (8) \\
Na_2MoO_4 + Na_2SO_4 + H_2O + CaCl_2 & \rightarrow CaMoO_4(s) + Na_2SO_4 + 2NaCl + H_2O \quad (9)
\end{align*}
\]

The ready product CaMoO₄ 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):

\[
MoS_2 + 6HNO_3 \rightarrow H_2MoO_4 + 2H_2SO_4 + 6NO↑ (10)
\]

The MoS₂ oxidation and H₂MoO₄ dissolution in sulfuric acid are maintained due to the autocatalytic reaction. The catalysis is caused by nitrogen oxides (NO, NO₂), which are present on the surface of molybdenite species. NO₂ promotes the MoS₂ oxidation process up to 5.5 times in comparison with NO. The simultaneous formation of NO₂ and HNO₂ means that oxidation of MoS₂ proceeds under the mixed conditions. That is why special equipment is required. For instance, tubular autoclaves are used at plants for the MoS₂ oxidation in nitric acid. Such autoclaves provide a necessary contact of species of MoS₂ and oxidants (HNO₃, HNO₂, NO₂, NO). In the solutions obtained, the most of molybdenum is concentrated in the form of MoO₂²⁺ and [MoO₂(SO₄)₂]²⁻.

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

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

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 MoS₂ 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:

\[
\begin{align*}
pH<6 & \quad pH<5 & \quad pH<1 \\
MoO_4^{2-} & \quad Mo_7O_{24}^{6-} & \quad Mo_8O_{26}^{4-} & \quad MoO_2^{2+} \\
pH>7 & \quad pH>4 & \quad pH>1.5 
\end{align*}
\]
In the hydrochloric acidic media ($C_{HCl}>0.2$ mol/L), the anions $\text{MoO}_2\text{Cl}_3^-$, $\text{MoO}_2\text{Cl}_4^{2-}$ are formed; in the sulfuric acidic and phosphoric acidic solutions, $[\text{MoO}_2(\text{SO}_4)_2]^2-$ and $\text{PMo}_{12}\text{O}_{40}^{3-}$ are formed, respectively.

In the $pH$ range 1-6, the molybdenum anions exist as polyanions with the larger size than the monomeric $\text{MoO}_4^{2-}$ 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 6.1-8.3 mmol/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](image-url)
Table 2
Physical-chemical and sorption properties of aminopolymers

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Copolymer</th>
<th>Cross-linking agent</th>
<th>Functional group</th>
<th>Structure</th>
<th>Total pore volume cm$^3$/g</th>
<th>Specific swelling volume ml/g</th>
<th>Static exchange capacity in Cl$^-$ form mmol/g</th>
<th>Na$^+$ form mmol/g</th>
<th>Specific surface m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN-221</td>
<td>St</td>
<td>DVB, 8%</td>
<td>-CH-NH-(CH$_2$)$_2$-NH$_2$</td>
<td>P</td>
<td>0.31</td>
<td>3.6</td>
<td>4.9</td>
<td>-</td>
<td>45</td>
</tr>
<tr>
<td>AN-80P</td>
<td>MA</td>
<td>DVB, 7%</td>
<td>-CH-CO-NH-(CH$_2$)$_2$-NH$_2$</td>
<td>P</td>
<td>0.36</td>
<td>4.1</td>
<td>6.1</td>
<td>1.2</td>
<td>36</td>
</tr>
<tr>
<td>ANS-80</td>
<td>MA</td>
<td>DVS, 3%</td>
<td>-CH-CO-NH-(CH$_2$)$_2$-NH$_2$</td>
<td>NP</td>
<td>-</td>
<td>2.3</td>
<td>5.9</td>
<td>0.9</td>
<td>-</td>
</tr>
<tr>
<td>AN-108P</td>
<td>MA</td>
<td>TVEPE, 4%</td>
<td>-CH-CO-NH-(CH$_2$)$_2$-NH$_2$</td>
<td>P</td>
<td>0.46</td>
<td>3.8</td>
<td>6.9</td>
<td>0.4</td>
<td>41</td>
</tr>
<tr>
<td>AN-108M</td>
<td>MA</td>
<td>DVEDEG, 7%</td>
<td>-CH-CO-NH-(CH$_2$)$_2$-NH$_2$</td>
<td>MN</td>
<td>-</td>
<td>2.3</td>
<td>6.3</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>AN-51I</td>
<td>St</td>
<td>DVB, 10%</td>
<td>-NH-(CH$_2$)$_2$-NH$_2$-CH$_2$-NH$_2$</td>
<td>P</td>
<td>0.38</td>
<td>3.9</td>
<td>5.1</td>
<td>-</td>
<td>58</td>
</tr>
<tr>
<td>AN-106P</td>
<td>MA</td>
<td>DVEDEG, 7%</td>
<td>-NH-(CH$_2$)$_2$-NH$_2$-CH$_2$-NH$_2$</td>
<td>P</td>
<td>0.41</td>
<td>3.8</td>
<td>6.8</td>
<td>-</td>
<td>34</td>
</tr>
<tr>
<td>AN-106MP</td>
<td>MA</td>
<td>TVEPE, 4%</td>
<td>-NH-(CH$_2$)$_2$-NH$_2$-CH$_2$-NH$_2$</td>
<td>MP</td>
<td>0.36</td>
<td>3.7</td>
<td>8.6</td>
<td>-</td>
<td>43</td>
</tr>
<tr>
<td>AN-85P</td>
<td>AN</td>
<td>DVB, 7%</td>
<td>-CH-NHNH-(CH$_2$)$_2$</td>
<td>P</td>
<td>0.49</td>
<td>5.1</td>
<td>5.8</td>
<td>-</td>
<td>49</td>
</tr>
<tr>
<td>ANE-80P</td>
<td>AN</td>
<td>DVB, 7%</td>
<td>N HN-(CH$_2$)$_2$</td>
<td>P</td>
<td>0.52</td>
<td>4.2</td>
<td>8.2</td>
<td>-</td>
<td>31</td>
</tr>
<tr>
<td>ANKF-80</td>
<td>MA</td>
<td>DVB, 7%</td>
<td>-CH-CO-NH-(CH$_2$)$_2$-NH$_2$</td>
<td>P</td>
<td>-</td>
<td>3.9</td>
<td>1.9</td>
<td>4.2</td>
<td>29</td>
</tr>
<tr>
<td>AMF-2</td>
<td>MA</td>
<td>DVB, 7%</td>
<td>-CH- O-C-NH-(CH$_2$)$_2$-NH$_2$-(CH$_2$COONa)$_2$</td>
<td>P</td>
<td>-</td>
<td>4.1</td>
<td>2.3</td>
<td>4.1</td>
<td>33</td>
</tr>
</tbody>
</table>

St = styrene; MA = methylacrylate; AN = acrylonitrile; DVB = divinylbenzene; DVS = divinylsulfide; TVEPE = tetravinyl-ester of pentaerythritol; DVEDEG = divinyl-ester of diethylene glycol; 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

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Copolymer</th>
<th>Cross-linking agent</th>
<th>Aminating agent</th>
<th>Static exchange capacity in Cl⁻ form mmol/g</th>
<th>Exchange capacity to molybdenum, mmol/g in acids</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.01 M H₂SO₄</td>
<td>0.5 M H₂SO₄</td>
</tr>
<tr>
<td>AN-80P</td>
<td>MA</td>
<td>DVB, 7%</td>
<td>EDA</td>
<td>6.1</td>
<td>6.4</td>
</tr>
<tr>
<td>AN-108P</td>
<td>MA</td>
<td>TVEPE, 4%</td>
<td>EDA</td>
<td>6.9</td>
<td>6.7</td>
</tr>
<tr>
<td>AN-108TP</td>
<td>MA</td>
<td>DVEDEG, 7%</td>
<td>EDA</td>
<td>6.8</td>
<td>7.3</td>
</tr>
<tr>
<td>AN-221</td>
<td>St</td>
<td>DVB, 8%</td>
<td>EDA</td>
<td>4.9</td>
<td>4.5</td>
</tr>
<tr>
<td>AN-106P</td>
<td>MA</td>
<td>DVEDEG, 7%</td>
<td>DETA</td>
<td>6.8</td>
<td>7.6</td>
</tr>
<tr>
<td>AN-106</td>
<td>MA</td>
<td>DVB, 7%</td>
<td>DETA</td>
<td>6.2</td>
<td>6.9</td>
</tr>
<tr>
<td>AN-106TP</td>
<td>MA</td>
<td>TVEPE, 4%</td>
<td>DETA</td>
<td>8.6</td>
<td>7.8</td>
</tr>
<tr>
<td>AN-521</td>
<td>St</td>
<td>DVB, 12%</td>
<td>DETA</td>
<td>5.1</td>
<td>4.7</td>
</tr>
</tbody>
</table>

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

In the [Mo(VI)-H₂SO₄-MnSO₄-H₂O] 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 MoO₂²⁺ 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:

\[
\text{HCl} > \text{H₃PO₄} > \text{H₂SO₄} > \text{HNO₃} > \text{HClO₄}
\]

![Figure 2. Change of distribution coefficients of molybdenum (D) on anion exchanger AN-85P in mineral acids solutions: HClO₄ (1); HNO₃ (2); HCl (3); H₂SO₄ (4) and H₃PO₄ (5)](image-url)
In strong acidic media (pH<2), the MoO$_2^{2+}$ cations are formed being in equilibrium with the anionic forms Mo$_8$O$_{26}^{4-}$, MoO$_2$Cl$_4^{2-}$, [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$_8$O$_{26}^{4-}$ polyanion, i.e. the exchange capacity of the resin increases up to 4 times during sorption of Mo$_8$O$_{26}^{4-}$ ion. It was determined (Kholmogorov, 1980; Kholmogorov and Burakova, 1991) that the ionic state of the molybdenum anions sorbed changes similarly with the solutions:

\[
\text{H}^+ + \text{MoO}_4^{2-} \rightarrow \text{Mo}_8\text{O}_{26}^{4-}
\]  

what can be seen from Figure 3.

At pH=2.9, the Mo$_8$O$_{26}^{5-}$ 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$_8$O$_{26}^{4-}$ 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÷136kgMo/m³. 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 MoS₂ 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.

REFERENCES


Rumyanzev, V.K., and Kulakova, V.V., Industrial processing breakdown products of molybdenum concentrates by ion exchange methods. Technologiya Metall (Metals Technology), 1999, 7, 4-8 (in Russian, with English Abstract).

Short Communications "Extraction and Sorption in Metallurgy of Molybdenum, Tungsten and Rhenium", 1971, Tsvetmetinformatsiya, Moscow, Russia, 216 pp. (in Russian).
