Molybdenum production: the state of the art

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Based on contribution from REFRAM partners
1 Mo production from primary resources

- **What are the primary resources?**

  Mo ore: Mo exists in the ore as molybdenite (MoS$_2$).

  - **Primary Mo ore**: only Mo in the ore is considered; account for around 40-45% of the world’s Mo production.

  - **Cu-Mo ore**: both Cu and Mo are considered; account for around 50% of world’s Mo production;

  - **Other ores**: such as W-Mo ore.

  The concentrate of Mo in the ore is quite low: ~ 0.01-0.25 wt.%.

  **Mineral processing is needed.**
Mineral processing

- **Primary Mo ores:**
  - Crushing → Grinding → Flotation
  - Product: molybdenite with 48-56% Mo.
  - By-product: tailing, sludge, etc. → Secondary Mo resources.

- **Cu-Mo ore:**
  - Crushing → Grinding → Bulk flotation
  - Selective flotation to separate molybdenite from copper sulphide
  - Product: Copper ore concentrate with 30% Cu; Molybdenite with > 55% Mo.
  - By-product: tailing, sludge, etc. → Secondary Mo resources.
Extraction and application

Primary use of Mo, which determines the Mo production
Roasting molybdenite concentrate in air

- A small part of molybdenite concentrate is directly used to produce lubricant grade MoS$_2$.
- A large part of molybdenite concentrate is used to produce technical grade MoO$_3$ by roasting molybdenite concentrate in air.
The roasting furnace: Multiple hearth furnace
Roasting temperature: 500 and 650°C
The chemical reactions:

\[2\text{MoS}_2 + 7\text{O}_2 \rightarrow 2\text{MoO}_3 + 4\text{SO}_2\]
\[\text{MoS}_2 + 6\text{MoO}_3 \rightarrow 7\text{MoO}_2 + 2\text{SO}_2\]
\[2\text{MoO}_2 + \text{O}_2 \rightarrow 2\text{MoO}_3\]

Roasting product: \(\text{MoO}_3\) with Mo > 57% and S < 0.1%.
By-product: Dust → Secondary resources
Sulfurous gas

**Challenge of the roasting process:** emission of sulfurous gas and dust to the environment.
• **Direct alloying steel with tech-grade MoO₃**
  Account for the major use of MoO₃; MoO₃ is charged into the molten steel in the EAF, AOD converter, BOF, etc. to directly alloy steel with Mo.

  **Challenge of the process:**
  Volatilization of MoO₃ and therefore loss of Mo in the dust → secondary resource

• **Ferromolybdenum production**

  30-40% of tech-grade MoO₃ is processed into FeMo alloy

  The process: commonly by silico-/alumino- thermic reduction;
  The product: FeMo alloy with 60 and 75% Molybdenum;
  Byproduct: slag with very low Mo content → secondary resource
  Advantage of the process: high Mo recovery

  **Challenges of the process:**
  Relatively high cost of silicon and aluminum compared with the carbonaceous.
• **Mo Powder production**

Two step process:

1. Reduction of \textbf{MoO}_3 \textbf{to MoO}_2 at 450-650 °C to prevent the caking and volatilization of MoO3;
2. Reduction of \textbf{MoO}_2 \textbf{to Mo} at around 1050 °C.

**Product:** Mo powder with desired particle size and high specific surface area.

**Challenges:**
Use of high quality MoO3;
Use of H2 with two reduction steps.

• **Use MoO3 concentrate to produce Mo-containing chemicals: miscellaneous**

Dominantly used to produce catalysts.
2 Mo production from second resources

- What are the secondary resources?
  - Waste rock and tailings from the mining and mineral processing;
  - Mo-containing mill scale and dust from the steelmaking industries;
  - Mo-containing fly ash from certain type of power stations
  - Copper slag of certain type
  - Mo-containing spent acid from incandescent lamp making industries
  - Aqueous waste water
  - Radioactive wastes from Mo/Tc generators production
Mo extraction from secondary resources

- Waste rock and tailings

  - Mo tailings from molybdenum mine
    Flotation or jet flotation to concentrate Mo.

  - Flotation tailings from Cu-Mo mine
    Processes including one or several processes of desliming, bulk flotation (recleaner flotation) of Cu and Mo in the coarse fractions, separation of Cu-Mo, washing, separating S from bulk flotation tailings and low-intensity magnetic separation of Fe from S flotation tailings were used to recover Cu, Mo, S and Fe minerals.

Step 1 Flotation to get the concentrate
Step 2 Hydro extraction

- Hydrometallurgical process is preferable: Attractive especially for low-grade Mo sources.

- Existing industrial hydrometallurgical routes to recover molybdenum from mineral wastes consists of:
  
  i) Pressure oxidative leaching (POX) or acidic/alkaline leaching;
  ii) Precipitation/crystallization, ion-exchange and solvent extraction.
• **Mo-containing mill scale**
  
  o Crushing/grinding, for oily mill scale also de-oiling, then briquetting/pelletizing;
  o Smelting reduction of the briquettes in the EAF or other reactors.

• **Mo-containing steelmaking dust**
  
  o Briquetting or pelletizing.
  o Reduction in different processes:
    
    • The *rotary hearth kiln pre-reduction* of pellets followed by *submerged arc furnace smelting* (Inmetco USA, other plants in Japan Nippon Steel and Taiwan);
    • The non-transferred *plasma arc heated coke-filled shaft kiln* with dust injection via tuyeres (Scandust Sweden);
    • The smelting of briquetted dust in a conventional *submerged arc furnace* (Metal Europe France);
    • The reduction in **DC transferred open arc furnace** (Heckett Multiserv Italy and Mogale Alloys South Africa);
    • **DC arc process** for the reduction of selected metal oxides at high temperatures by means of carbonaceous reducing agents (Mintek).
Mo-containing fly ash from heavy oil-fired power station

Two-stage leaching process: (i) alkaline leaching to dissolve V and Mo and (ii) sulfuric acid leaching to recover Ni.

For Mo recovery:
- **Leaching** with NaOH to dissolve V and Mo;
- **Filtration** to get the leaching solution;
- **Alkali-precipitation** to precipitate V;
- **Filtration** to get the V compounds and Mo-containing filtrate;
- **Acidification** of the filtrate to facilitate the transformation and precipitation of molybdic acid;
- **Filtration** to get the molybdic acid.
• Copper slag
  • Carbothermic reduction of the slag;
  • Mo is recovered as Fe-Mo alloy.

Proposed Mo recovery process from Chilean copper slag
• Spent acid

  o Exothermic **neutralization** by NH$_3$;
  
  o **Precipitation** of Mo compound as ammonium molybdate;
  
  o **Filtration** to collect ammonium molybdate;
  
  o **Roasting** of ammonium molybdate to obtain MoO$_3$ powder;
  
  o Two stage H$_2$ **reduction** to get Mo powder.

Mo recovery from spent acid
3 Mo production from urban mine

- What are the dominant urban mine (EoL products) for Mo?

Mo-containing steel scrap + Spent Mo-containing catalyst
Mo extraction from urban mine

- Mo-containing steel scrap
  - Re-melting in the Electric Arc Furnace

  **Challenge**: Mo is downgraded in the steel without using its Mo content.

- Spent Mo-containing catalysts
  - Process: roasting; leaching; smelting; reduction
    - Product: Mo metal and/or ferroalloys (depending on the process)
    - By-product: slag

  **Challenge**: Less cost-efficient, especially when considering the low price of Mo at the moment
4 Mo production: the present value chain

Global mine production

Available Mo ore/concentrate

Mo ore/concentrate processing in Europe

Intermediate products

End-use products

End-use by industries

Mo Metal and oxide export in Europe (13534 MT in 2013)

Mo Metal and oxide import in Europe (17478 MT in 2013)

Mo mining production in Europe

Available Mo ore/concentrate in Europe

Mo ore/concentrate processing in Europe

Ferromolybdenum

Technical-grade MoO3

Mo Powder

Mo chemicals

Tool steels (8%)

Foundries (8%)

Stainless steels (22%)

Engineering steels (41%)

Nickle alloys (3%)

Mo metals (5%)

Chemical products (13%)

Oil & gas (18%)

Chemical/petrochemical (15%)

Automotive (14%)

Mechanical Engineering (12%)

Process industry (8%)

Power generation (8%)

Building and construction (6%)

Aerospace defense (3%)

Electronics and medical (2%)

Others (the left)

Mo reserves in EU: Munka Mine in Sweden, with the reserve of 1.7 Mt of molybdenum ore at 0.156% Mo.

Waste rock & tailings

Other industrial wastes and residues (such as Mo-containing fly ash from the powder station)

Recycled but not for its Mo content

Mo loss in the wastes/residues to the environment

~25-33% of Mo Supply

MT = Metric Tonne

56707 MT ore export in 2013

116384 MT ore import in 2013

~8 MT in 2013

Global information

Mo ore and concentrates (~ 230 000 Mt Mo production in 2015)

United States

Armenia

Australia

Canada

Chile

China

Iran

Kazakhstan

Kyrgyzstan

Mexico

Mongolia

Peru

Russia

Turkey

Uzbekistan
Thank you!