Molybdenum production: the innovation pathways

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Based on contribution from REFRAM partners
1 Innovation potential in mineral processing

- Enrichment techniques, such as:
  - Oil agglomerate flotation process to recover molybdenite from ultrafine waste tailings;
  - Dispersion-selective hydrophobique floculation to recover molybdenite from ultrafine waste tailings;
  - Using cyclone-static micro bubble flotation column to recover Mo and Cu from the cleaning concentration tailings.
Comprehensive utilization, such as:

- Recovery of non-metallic minerals including quartz and feldspar from a Mo mine tailings;

- Recovery of potassium feldspar by further beneficiation of molybdenum mine tailings.
2 Innovation potential in metallurgical processing

Metallurgical processing of primary resources

Molybdenum processing flowsheet (from IMOA)

High volatility at ~ 800 °C: loss of MoO$_3$ in the dust and then low Mo recovery.

Normally high grade concentrate (48-56% Mo), then what about low grade concentrate (20-45% Mo)?

Any alternatives? Any countermeasures?

- Roasting in air at temperatures 500-650°C;
- Emission of dust and sulfurous gas.
• Innovative potential of processing low-grade Mo concentrates

  o Oxy-chlorination of low-grade Mo concentrates

  The reaction mechanism:
  \[
  \begin{align*}
  \text{MoS}_2 + \text{Cl}_2 + 3\text{O}_2 & \rightarrow \text{MoO}_2\text{Cl}_2 + 2\text{SO}_2 \\
  \text{MoS}_2 + \text{Cl}_2 & \rightarrow \text{MoCl}_5 + \text{SO}_2\text{Cl}_2
  \end{align*}
  \]

  Characterization of the process

  • The chlorinated products can be treated by following-up hydro-metallurgical process to extract Mo;
  • Due to the exothermic reaction, less energy is required.

  Extraction of Mo from low-grade concentrate by oxychlorination.
Liquation smelting Cu-Mo concentrates

• **Why:**
  Liquation smelting makes it possible to concentrate selectively the rock-forming and molybdenum ore components.

• **How:**
  Fusing Cu-Mo concentrate with sodium carbonate and silicate in an electrothermic furnace at 950–1150 °C.

• **Effect:**
  Extraction of molybdenum into the liquation salt.
• **Innovative potential of alternative oxidative roasting**

  o **Co-roasting molybdenum concentrate and pyrolusite (MnO2)**

  Roasting: molybdenum ore (MoS$_2$) + pyrolustite (MnO$_2$) + air at 450 – 600 °C.

  The reaction mechanism:

  $\text{MoS}_2 + \frac{7}{2}\text{O}_2 \rightarrow \text{MoO}_3 + 2\text{SO}_2$
  $\text{MoS}_2 + 3\text{O}_2 \rightarrow \text{MoO}_2 + 2\text{SO}_2$
  $9\text{MnO}_2 + \text{MoS}_2 \rightarrow \text{MnMoO}_4 + 6\text{MnO} + 2\text{MnSO}_4$
  $\text{MnO}_2 + \text{SO}_2 \rightarrow \text{MnSO}_4$
  $\text{MnO}_2 + \text{MoO}_2 \rightarrow \text{MnMoO}_4$

  • **Advantages**: lower roasting temperature; less emission of gases (CO, CO$_2$ and SO$_2$); co-production of ammonia molybdate and manganese sulfate; high Mo recovery.
Low temperature oxidizing-chlorinating roasting

- The reaction mechanism:
  
  \[
  \begin{align*}
  \text{MoS}_2 + 3.5\text{O}_2 &= \text{MoO}_3 + 2\text{SO}_2 \\
  2\text{NaCl} + \text{SO}_2 + \text{O}_2 &= \text{Na}_2\text{SO}_4 + \text{Cl}_2 \\
  \text{MoO}_3 + 2\text{NaCl} + 1/2\text{O}_2 &= \text{Na}_2\text{MoO}_4 + \text{Cl}_2 \\
  \text{MoO}_3 + \text{Cl}_2 &= \text{MoO}_2\text{Cl}_2 + 1/2\text{O}_2
  \end{align*}
  \]

- ~60 - 75% molybdenum in ash: Mo extracted by two stage leaching;
- others in the gas phase and caught by absorbers: dissolution in alkali.
- Advantages: reducing the emission of \(\text{SO}_2\); lower roasting temperature; high Mo recovery.
- Disadvantages:?
Direct reduction by Mn

- **The feasibility:**
  Comparably lower price for Mn;
  High affinity of Mn to S.

- **The reaction mechanism:**
  \[ \text{MoS}_2 + 2\text{Mn} = 2\text{MnS} + \text{Mo} \]

- **Implementation:**
  Converting molybdenite concentrate to **ferro-molybdenum** with the help of a melt of ferromanganese or a mixture of ferromanganese and iron in an electric arc furnace, induction furnace or converter.
Plasma smelting for direct FeMo production

- **Implementation:**
  Charging Mo concentrates, carbonaceous material, lime and iron scrap into the plasma arc furnace.

- **The reaction mechanism:**
  \[
  \text{MoS}_2 + \text{CaO} + \text{C} + \text{Fe} \rightarrow \text{FeMo} + \text{CaS} + \text{FeS}_2 + \text{CO}
  \]

- **Characterization of the process:**
  Decomposition of MoS\(_2\) at \(\sim 2300\) °C and S is generated as by-product; high Mo recovery; low specific energy consumption.
Direct reduction of MoS\textsubscript{2}

- **Implementation:**
  Direct reduction \(\text{MoS}_2\) in the presence of powerful sulfur acceptors, such as lime, by reducing agents (CO, H\textsubscript{2} or C).

- **The reaction mechanism:**
  \[
  \text{MoS}_2 + \text{CaO} + (\text{H}_2, \text{CO} \text{ or } \text{C}) = \text{Mo} + \text{CaS} + (\text{H}_2\text{O}, \text{CO}_2 \text{ or CO})
  \]

- **Characterization of the process:**
  Single step extraction process.
• Innovative potential of adding MoO₃ to the steel

- Refraining the volatilization of MoO₃

Adding MoO₃ to steel accounts for the major use of MoO₃.

Mo: high volatility of MoO₃ at temperatures above ~ 800 °C; Mo loss can be more than 7% when adding MoO₃ into EAF.

Using “mill scale + MoO₃ + coke” as an alloying precursor can refrain the volatilization of MoO₃ due to in-situ formation of more stable compounds of Mo.

Mo recovery can reach **up to 98%**.

This process is know to be industrialized.
Metallurgical processing of secondary resources

Primary resources
- Primary Mo ore
- Cu-Mo ore

Secondary resources
- Waste rock/tailings
- Copper slag
- Mill scale

Primary use of Mo
- ~ 80% Mo for steel production
- ~ 10% Mo for catalysts

How to effectively and economically recycle Mo from these secondary resources?
• Innovation potential in Mo extraction from copper slag
  o Direct reduction: a pyro-metallurgical process

Mo in copper slag: 2FeO•MoO2 - Fe3O4 spinel

Carbothermic reduction of the copper slag: FeMo alloy.

Leftover slag: used as cement.

Flowchart of the process
Roasting-leaching process: a hybrid pyro- and hydro-metallurgical process

Why not direct leaching:
Mo in copper slag (2FeO•MoO₂ - Fe₃O₄ spinel): difficult to be processed by hydro-metallurgical process due to low leaching degree.

The new proposed process:

- Copper slag
- Oxidative roasting at 700 °C (Oxidation of Mo and Fe to their highest states)
- H₂SO₄ Selective leaching
- Mo recovered

Mo recovery from the slag was influenced by the magnetite content in the slag during the leaching process (low magnetite content leads to a high recovery of molybdenum). > 80% Mo recovery was achieved.
• Innovation potential in Mo extraction from Mo-containing mill scale

- Sponge iron production from mill scale

In proposed process mill scale is recycled and the Mo content is used.
- Smelting reduction Mo-containing mill scale in EAF

According to our experience, ~ 5 wt.% mill scale can be charged into EAF with no operation problem.
Carbothermic reduction of Mo-containing mill scale by microwave heating

Mo-containing mill scale can be reduced into metallic beads in a short time (~ 15 minutes).

The reduced Mo-containing beads can be used for Mo-containing steel production by charging it into, for example, EAF.
• **Innovation potential in Mo extraction from steelmaking dusts**

- Particle size has significant effect on the filtration process;
- Choosing extractant is crucial for selective extraction;
- The process should be up-scaled and the cost-efficiency should be verified.

Other alternatives for Mo recovery from dusts: smelting reduction, similar to mill scale recycling.
Metallurgical processing of urban mines (EoL products)

- Innovation potential in Mo extraction from steel scrap
  - Alloy steels (0.5-9 wt.% Mo): higher Mo content but lower production volume;
  - Stainless steels (1-6.1 wt.% Mo): higher Mo content but lower production volume;
  - Carbon steels (0.2-0.5 wt.% Mo): lower Mo content but higher production volume.

Mo-containing steels recycling: re-melting in the Electric Arc Furnace

Innovation potential in recycling Mo-containing steel scrap:

- Improving the sorting of Mo-containing steel scrap;
- Improving the impurity control (Cu, Zn, etc. removal).
• Innovation potential in Mo extraction from spent catalysts

**Pyro-metallurgical process- smelting reduction:**
- Mo and other metals are reduced and recycled as ferroalloys;
- The non-reducible materials are left in the slag.
- High processing capacity, but also high energy consumption.

**Hydro-metallurgical process:**
- Mo in the spent catalysts is converted into soluble compounds and leached out.
- Possible to extract Mo as pure element.
- The process is of high complexity, accompanied by the generation of hazardous wastes.

**Bio-metallurgical process:**
- The spent catalysts are treated by bacteria in the aqueous solution.
- Leaching solution can be used to extract Mo.
- Environment-friendly, low cost but less effective process.
Various processes for processing catalysts

Innovation potential:
Development of hybrid pyro- and hydro- processes;
Further investigation into the bio-metallurgical process;
Development of the separation and purification process.
4 Mo production: the future value chains

Key processes (highlighted in orange) in the innovative pathway:
1. Applying alternative roasting route to recover not only MoO3 but also the sulfurous/sulfate;
2. Establishing more efficient sorting system to increase the Mo recycling to 50% or even more;
3. Improving the Mo recovery from slag, dust, mill scale, etc;
4. Utilizing the generated residuals as other industrial by-products.

- Primary Mo ore
- Innovative roasting and processing
- Residual materials
  - Construction materials, etc.
  - Sulfurous or surface materials

- Waste rock & tailings
  - Mineral Re-processing

- Mo loss in environment or other materials
- Sorting system (according to grades)

- Metallurgical processing
- Products and EOL products
  - Steels in various grades
  - Catalysts
  - Special alloys/metals
  - Others

- Slag, mill scale, dust, etc.
- FeMo alloy
- Steelmaking and processing

- Technical grade MoO3
  - ~ 50% as recycled
  - ~ 50% as input from primary ore
Thank you!