Multi-Stakeholder Platform for a Secure Supply of Refractory Metals in Europe

FACTSHEET

MOLYBDENUM

SHORT DESCRIPTION

Molybdenum is a shiny silvery metal, which is moderately dense and moderately hard and has the sixth highest melting point of all equal elements, at 2623°C. Of all the engineering materials, it has the lowest thermal expansion coefficient, and fairly high thermal conductivity [29]. Although the EU does not consider Molybdenum a critical raw material, the current supply of it in the EU is lower than 1%.

Fig. 1 Mo Metal [30]

APPLICATIONS

The widespread use of Molybdenum in metallurgical applications is due to its effectiveness as an alloying element; it is not susceptible to oxidation and influences the mechanical properties of alloys, has solid solution strengthening properties and enhances hardenability. For these reasons, it is used in the production of steels, metals and alloys and, to a lesser degree, in the production of chemicals (Fig.1). End-use of Molybdenum, however, is found in a wide array of industries (Fig.2). The most important end-use applications of Molybdenum include the machinery, electrical, transportation, automotive, chemical and oil and gas industries.

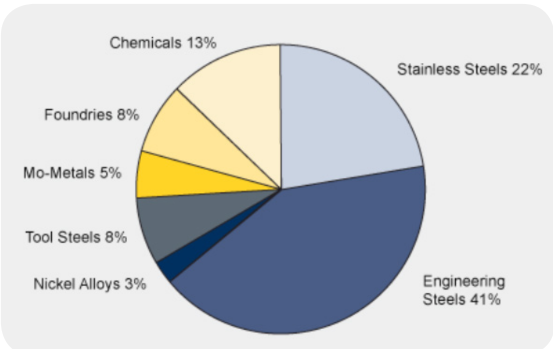

Fig. 3 Use of Molybdenum produced from mined ore [1] and worlwide by industries

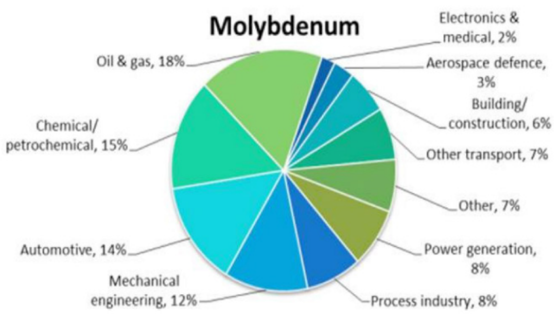

Fig. 2. Worldwide use of Molybdenum in different industries [2]

For chemical applications, there are several different Molybdenum products on the market, such as ammonium heptamolybdate, ammonium octamolybdate, ammoniumdimolybdate, MoS_2 and sodium molybdate, among others.

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Table 1 shows Molybdenum applications and grades:

Material type		Mo grades	Reference
Steel products	Stainless steels	1-6.1%	[3]
	Tool & high speed steels	0.5-9%	[4]
	Maraging steels	4-5%	
	Other steels	0.2-0.5%	
Mo super alloys		2-28.5%	[5]
Mo metal and alloys	Mo metal	99.5-99.97%	[6]
	Mo-W alloys	10-50%	
	Mo-Re alloys	52.5-97%	
	Mo-Ta alloys	89.3%	
	Mo-Nb alloys	90.3-97%	
	Carbide-stabilized alloys	~99%	
	Dispersion-strengthen alloys	~99%	
	Cu-Mo-Cu laminate	75-87%	
	Mo-Ni laminate	95%	
	Mo-Cu powder	70/85%	
	Mo-Ti	50 atomic%	
	Mo-Na powder	97-99%	
	Pure Mo metal powder	99.0%	
	Mo-C powder	>94%	
	17.8Ni-4.3Cr-1.0Si-0.8B powder	76.1%	
Mo chemicals	Lubricant grade MoS_2 (> 98%)	MoS_2 > 98%	[7]
	Desulphurization catalysts	~ 8%	[8]

Table 1. Mo grades in different materials/applications

EU SUPPLY AND DEMAND: CURRENT AND FUTURE

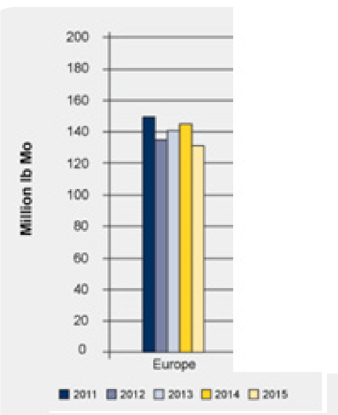

Fig. 4 Mo consumption in Europe [9]

Europe produced four metric tons (metal content) of Molybdenum in 2012 and eight tons in 2013, all from Norway. Molybdenum consumption in Europe in 2013 was 63.5 kt. Europe is the world's second biggest consumer of Molybdenum, with an average annual consumption of 63,500 tons in 2011 and 2012, which represents 25 % of annual worldwide production.

In 2015, total worldwide production of Molybdenum was approximately 267,000 tonnes.

As for imports to the EU, Molybdenum waste and scrap account for the largest quantities of imported products with 3,221,019 imported tons followed by Molybdenum bars and rods (830,667 tons), unwrought Molybdenum (59,1937 tons), Molybdenum powders (231,320 tons) and Molybdenum wire (163,663 tons), mainly from the USA, China, and Armenia.

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The EU's main Molybdenum product export is waste and scrap (336,738 exported tons), followed by Molybdenum powder (229,751 tons) and unwrought Molybdenum, including bars and rods (136.367 tons), usually to the USA, Brazil and Mexico.

Ferro-Molybdenum (FeMo) is one of the most important Molybdenum alloys, with a 60-75% Molybdenum content, and is the main resource used in Molybdenum alloying of high-strength low-alloy steels. In the EU, Austria is the only country that produces a low amount of FeMo. Belgium is the biggest exporter of FeMo, followed by the UK and the Netherlands, while Germany is the biggest importer, followed by Italy, Belgium, Spain, and Sweden. The iron and steel industries are very likely to continue driving Molybdenum consumption in Europe and worldwide. Molybdenum is primarily used as an alloying element in steel, cast iron and non-ferrous metals. The EU is the second largest steel producer in the world after China, with an output of over 177 million tonnes of steel a year (11% of global output), which means that the EU will need to continue importing Molybdenum.

A large amount of Molybdenum comes from recycling. According to a study conducted by *Steel and Metal Market Research* in 2011, almost 80,000 tonnes (26%) of all Molybdenum produced was from recycled materials, which means that scrap is very important for the supply chain. Europe is the region with the highest first use of Molybdenum scrap, at a rate of about 3,000 tonnes/year.

The International Molybdenum Association (IMOA) [32] estimates that end-user demand for Molybdenum could increase by an average of 3.6% in the period to 2024, and a similar estimated growth-rate value of 4.6% was published in the “Molybdenum Market Outlook” [33]. Roskill has analysed the evolution of this metal as well and has predicted an increase for Europe of about 105 kt /year between now and 2025, and that current capacity is insufficient to meet this growth in demand [34]. As the market for the main applications of Molybdenum is growing and there are no potential substitutes for Molybdenum in terms of its applications in mechanical engineering and in the automotive, oil and gas, chemical/petrochemical, power generation, processing, aerospace, defence, electronics and medical industries, the demand for Molybdenum is expected to grow accordingly. Molybdenum has also been proposed as potential substitute for Tungsten and Niobium, both considered CRMs [35] [36].

Given the good trade relationships that the EU has with producing countries, its strong industrial base and the relatively low cost and high abundance of Molybdenum, the balance between supply and demand should not be of high concern for Europe in the medium term. Resources of Molybdenum are sufficient to supply world needs for the foreseeable future [35].

MAIN PRIMARY AND SECONDARY RESOURCES

PRIMARY RESOURCES

Although Molybdenum is contained in various minerals, only molybdenite (MoS_2) is suitable for the industrial production of marketable molybdenum products. Molybdenum content in molybdenite ranges between 0.01 and 0.25%. Worldwide mine production of Molybdenum in 2014 was concentrated in three countries: China (41.73%), the United States (22.22%) and Chile (16.55%). Minor contributions came from Peru (5.77%) and Mexico (4.88%). The contribution of the European Union to worldwide mine production of Molybdenum was negligible. Only Norway produced 2 tonnes of Molybdenum in 2014.

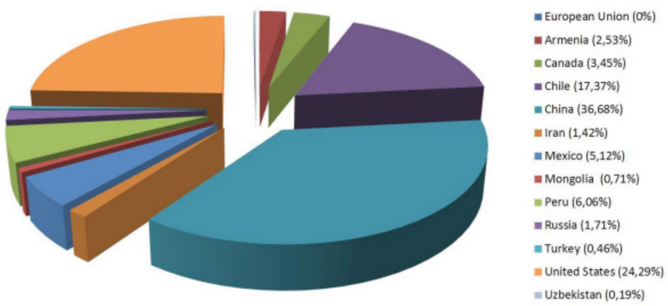

Fig. 5 Mo production worldwide countries

Molybdenum is recovered as a by-product of Copper and and Tungsten mining. Approximately 50% of the world’s molybdenum production comes from Cu-Mo ore. In Europe there are Copper mines whichcontain Molybdenum: Herzogenhügel (Belgium), Elatsite (Bulgaria), Karlievo (Bulgaria), Kimmeria (Greece), Recsk (Hungary), Polkowice, Sieroszowice, Rudna, Gaworzyce, Lubin-Malomice, Niecka Retkow and Wartowice (Poland), Aitik and Laver-nya(Sweden), Majdanpek, Borska Reka and Veliki (Macedonia).

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SECONDARY RESOURCES

Several Molybdenum-containing wastes used as secondary resources are shown in Table 2.

Molybdenum is a fully recyclable metal. About 60% of Molybdenum scrap is used to produce stainless steel and structural steel. The rest is used to produce alloy tool steel, super-alloys, high-speed steel, cast iron and chemicals.

Name of residual	Main industry	Estimated content of Mo
Spent acid	Lamp industry	40-70 g/L
Fly ash	Heavy oil-fired power station	~ 0.35%
Flue dusts from steelmaking	Steel industry	0.02 – 1.2% (depends on dust)
Mill scale	Steel industry	Similar as the steel products except its oxygen content
Copper slag	Copper production industry	0.3%
Aqueous waste waters	Copper, molybdenum and uranium flotation mills	Cu mine in Arizona (1 – 30 mg/L); Uranium mill in Colorado (900 mg/L); Mo mills in Colorado (25 mg/L)
Radioactive wastes	Production of ^{99}Mo/^{99m}Tc generators	-
Molybdenite Roasting Dust	Roasting of Mo concentrate	-

Table 2. Mo Secondary Resources

MAIN PROCESSING AND EXTRACTING TECHNIQUES FOR PRIMARY AND SECONDARY RESOURCES

PRIMARY RESOURCES

Mining of primary resources

Molybdenum is mined as an important ore and is also recovered as a by-product of copper and tungsten mining activities. Molybdenum is contained in various minerals, but only molybdenite (MoS_2) is suitable for the industrial production of marketable molybdenum products.

Depending upon the minerals contained in the ore body and their quality, molybdenum mines are grouped into three classes: 1) Primary mines; 2) By-product mines (50% of the world's molybdenum production comes from Cu–Mo ore as a by-product); and 3) Co-product mines.

If the ore lies close to the surface, open cast pit technology is employed. The overburden is excavated to reveal the ore body for easy extraction. If the ore lies deep underground, the underground block caving technique is employed, and large blocks or ore are undercut and allowed to collapse under their own weight. The resulting rock is brought to the surface for processing.

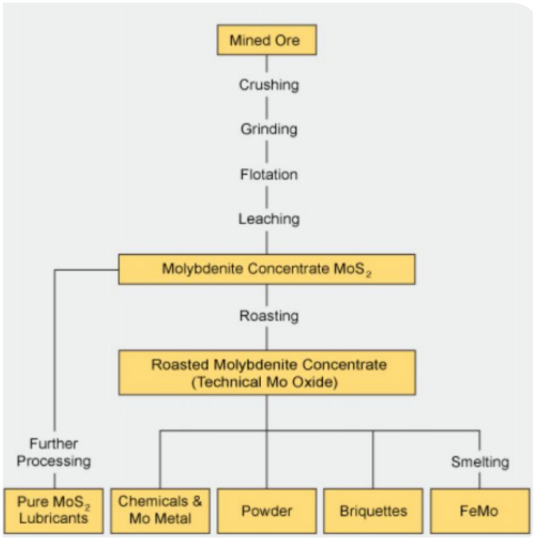

Fig. 6 Typical flowsheet for Mo production from ores

Mineral processing

Normally, crushing and grinding are performed, converting the ores to fine particles, which are subsequently subjected to flotation in order to separate the metallic minerals, including molybdenite, from the gangues. In the case of copper/molybdenum ores, molybdenite is separated, by flotation, from copper sulphide. The resulting concentrate contains between 85% and 92% MoS2. An acid-leaching treatment can then be used to dissolve impurities like copper and lead if necessary. The concentrate is roasted in the air at temperatures between 500 and 650°C, and the resulting molybdenite usually contains a minimum of 57% molybdenum with a sulphur content of less than 0.1%.

Extractive metallurgy

Once a concentrate is obtained, a small portion of it is directly applied to produce pure molybdenite chemicals and the remaining larger portion is transformed into molybdenum oxide, an important starting compound for powders and ferro-molybdenum. Most of the concentrate is roasted to a technical grade and then used directly in steel and iron industry, while the remainder undergoes additional processing to produce a high-grade molybdenum oxide suitable for use in catalysts, pharmaceuticals, fertilizers, pigments, etc.

There are several hydrometallurgical techniques that can be used to recover molybdenum from beneficiation concentrates.

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In many cases, pretreatment stages are performed to reduce the impurities before roasting. Normally, sodium cyanide is used to remove copper and gold, ferric chloride to remove copper, lead and calcium and hydrochloric acid to remove lead and bismuth. Oxidative pressure leaching is becoming the most popular hydrometallurgical technique for Molybdenum recovery because of its environmental friendliness and versatility in treatment of high/low-grade concentrates.

SECONDARY RESOURCES

From waste rock and tailings

Mo-Cu is separated by flotation and the coarser Mo concentrate undergoes a Mo re-cleaning flotation process to obtain a final Mo concentrate. A jet flotation system is recommended for old tailings. The initial slurry is separated into 3 flows: 1) Rough concentrate, or flow 1, is mixed with the initial feed from flow 2; 2) The rough concentrate from flow 2 is mixed with the initial feed from flow 3; 3) The rough concentrate from flow 3 is fed for scavenging. It is efficient to use flotation with a mixture of heat-saturated water steam and air [27].

Mo recycling

As for the recycling of Mo-containing steel scrap, one common method involves re-melting of the steel scrap, for example, in an Electric Arc Furnace (EAF). Before being subjected to re-melting, however, the scrap normally needs to be pre-treated in order to: 1) ensure that the scrap is of suitable size to be charged into the furnace; 2) ensure homogenous composition of the scrap; 3) remove the impurities from the scrap.

In the case of spent catalysts, they are normally recycled by roasting them in order to eliminate C and S content (de-oiling and de-coking) and/or facilitate the transformation of the refractory metal oxide into other forms. Crushing/grinding are subsequently performed to obtain finer materials, which are then subjected to a leaching process [38].

THE ENVIRONMENTAL AND SOCIAL IMPACTS OF MOLYBDENUM EXPLOITATION

The release of Molybdenum into the environment due to extraction activity is unavoidable. This can occur [37]:

1. During mining and mineral processing activities, when Molybdenum is released into the environment from waste rock and tailings.
2. During the metallurgical process (e.g., in the slag and dust)
3. During end-use applications as a result of corrosion and product wear and disposal.

The leaching of metals that occurs during sulphide oxidation reactions in mining waste rock dumps presents a global environmental challenge. Molybdenum metal can be released at elevated concentrations as sulfidic waste rock weathers and can produce toxic effects at elevated environmental concentrations. Molybdenum is particularly harmful to ruminants which are susceptible to molybdenosis. Nuss & Eckelman performed a life cycle assessment of metals in 2014, including refractory metals. The results for Molybdenum, compared with those for other refractory metals, are very low: 5.7 kg Co_2 eq/kg of global warming potential, 0.16 kg SO_2 eq/kg of terrestrial acidification, 0,54 kg P eq/kg of freshwater eutrophication and 0,009 CTUh/kg of Human Toxicity. The only result that is slightly higher is cumulative energy demand, at 117 MJ eq/kg.

To prevent any environmental and social damage that Molybdenum-associated activities may cause, all mining activity must be conducted in accordance with the regulations set forth in European Directive 85/337/CEE concerning Environmental Impact Assessment. Directive 2006/21/EC also provides several references for measures, procedures and guidance to reduce any adverse effects on the environment (water, soil, air, fauna, flora and landscape) stemming from extractive industry waste management activities. One of the objectives of this Directive is for Member States to take the necessary measures to ensure that extractive waste is managed without endangering human health and without using processes or methods which could harm the environment. Uncontrolled disposal of extractive waste must also be avoided.

Molybdenum is not included in the reference document entitled Best Available Techniques for Management of Tailings and Waste-Rock in Mining Activities, which is focused on ores with potentially significant environmental impacts. As for secondary resources, however, FeMo has been included in Best Available Techniques Reference Document for the Non-Ferrous Metals Industries [39].

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This document addresses several important environmental performance issues:

- In Ferro-Molybdenum production, fluorspar may be used to improve slag and metal separation. Fluorspar is a calcium fluoride ore that is used as a flux and lowers the melting point and the viscosity of the slag, resulting in an enhanced fluidity of the slag. Additionally, when mixed with lime, it reduces the phosphorus and sulphur content of the metal. The use of fluorspar as a fluxing agent results in emissions of fluorides within the range of 150 – 260 mg/Nm_3. Due to the biotoxic nature of fluoride, fluorspar use should be kept to a minimum.

- During Ferro-Molybdenum production, 1.5-3 tons of slag are produced per ton of alloy. To minimize the environmental impact of slag treatment and disposal, slag can be used as a construction material. Moreover, the dust generated in the process can be recycled to the smelting process or sent to special waste disposal or processed for the recovery of Molybdenum.

SUBSTITUTION POSSIBILITIES

The substitutability of Molybdenum in current applications is rather low (with a high substitutability index) which may be due to the fact that most of the alternative applications are closely related to loss in performance, higher cost and potential harmfulness of possible substitutes.

Application	Share	Megasector	Substitutability index
Oil and Gas	18%	Oil	1.0
Chemical/Petrochemical	15%	Chemicals	1.0
Automotive	14%	Transport-Road	1.0
Mechanical Engineering	12%	MechEquip	1.0
Power Generation	8%	Electrical	1.0
Process Industry	8%	MechEquip	1.0
Other Transportation	7%	Transport-Other	1.0
Others	7%	Other	0.5
Building / Construction	6%	Construction	0.3
Aerospace & Defence	3%	Transport-Other	1.0
Electronics & Medical	2%	Electronics	1.0

Substitutability of Molybdenum by application

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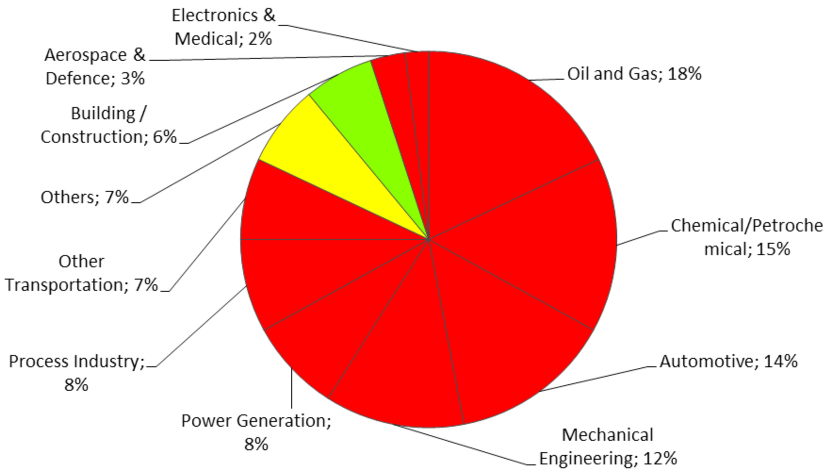
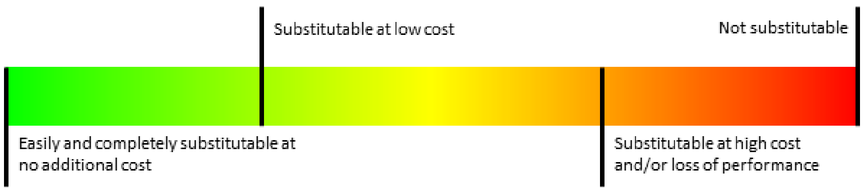
The data in the previous table is presented in visual format in the following graph:





The substitution potential of Molybdenum in steels is related mainly to switching among hundreds of different steel grades. Stainless steel grade 316 can be substituted with Grade 445M2 (with a higher Cr content), as it is a product/by-product substitution. In alloy steels, potential substitutes are: B, Cr, Nb, and V. In tool steels, Molybdenum can be substituted with Tungsten. Refractory materials in high temperature electric furnaces, apart from graphite, are mainly substituted with other refractory metals, such as Tantalum or Tungsten. In those applications where Molybdenum is used because of its refractory properties, Niobium is a potential substitute. When the aim is material strengthening, Niobium is also a potential substitute, with lower and stable prices, but it is considered as Critical Raw Material. In super-alloys, W-alloyed and Ni-and Co-based super-alloys can substitute Molybdenum, with high thermal fatigue resistance, good oxidation resistance, excellent hot corrosion resistance, air melting capability, air or argon re-melting capability and good welding properties [11-16].

As for pigments, possible substitution with harmful, toxic chromium and cadmium-based substances are a questionable alternative. In the case of catalysts used for HDS, depending on the application of the HDS and nature of the feed, Ru, Ni, Co and W are potential substitutes, as they are product/by- product substitutions [13-15].

HEADING TOWARDS THE FUTURE: RECENT RESEARCH ACTIVITIES

PROCESSING TECHNOLOGIES

Primary resources

Research in this field to date has been dedicated mainly to flotation processes and flotation reagent development [10].

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Secondary resources

Research has been conducted on the recovery of molybdenite from ultra-fine waste tailings using oil agglomerate flotation (OAF). Neutral oils like kerosene, diesel, transformer and rapeseed oil have been used as collectors or bridging reagents in OAF. Conventional flotation froth cannot catch ultra-fine particles and is thus ineffective as a process to recover molybdenum metal from waste tailings, underscoring the relative strengths of OAF methods in the recovery of fine minerals. The study showed that the best results were obtained with transformer oil, due to its appropriate carbon chain length, kinematic viscosity and cyclical structure. Mo recovery was 95% [17]. Experiments have also been carried out to recover Molybdenum by cleaning concentration tailings in a Molybdenum concentrator using an unconventional flotation column with fine bubbles. This technique is called the cyclone-static micro-bubble flotation column procedure. Mo recovery was 74% [18].

HYDROMETALLURGY

Primary resources

Different novel leaching methods include alkaline pressure leaching, oxidant- additive leaching and bio-leaching. Precipitation, solvent extraction and ion exchange have also been developed [10]. Pressure leaching of Ni-Mo shales under alkaline conditions has been studied, achieving a Mo recovery rate of >98% for 10 hours at 80°C and a NaOH concentration of 2.5 mol/L. The main advantage is that Molybdenum is completely solubilized and Ni remains in the solid residue, although NaOH consumption is high and large amounts of Na_2SO_4 waste are produced [23].

Molybdenum from low-grade Ni-Mo ore using hypochlorite leaching under mechanical activation in a planetary ball mill has been studied, yielding high Molybdenum recovery at 70 °C and a pH of 11[24]. High recovery rates of Molybdenum (>99%) can be reached with molybdenite concentrate at room temperature, with a current density of 800 A/m2 in 4 M NaCl and a pH of 9, and the NaCl is recycled [25]. Another innovative high-Mo recovery process involves bioleaching Molybdenite ores with Acidithiobacillus and Leptospirillum culture, which results in a Mo recovery of 85%, contained in finely ground high-purity MoS_2 samples [26].

Secondary resources

Cyanex 600, a new extractant from Cytec, is proven to have good properties for the recovery of Molybdenum from a copper SX raffinate containing 75 ppm Mo and 40 g/L of sulphuric acid [19].

To steel making dusts, water leaching is applied to obtain an alkaline solution containing about 2 g Mo/L, which then undergoes solvent extraction to obtain a pure Mo solution. The leachate is then purified using Aliquat 336 [21].

After roasting pre-treatment, spent catalysts can be leached under acidic or alkaline conditions. Soda ash roasted at 600 °C has been used to recover 92% of Mo contained in hydro-refining catalysts. After leaching, a Na-molybdate solution is obtained and converted to high-purity Molybdenum oxide through adsorption on activated carbon to purify the pregnant leach solution before it crystallizes into ammonium molybdate [22].

PYROMETALLURGY

Liquidation smelting of Cu-Mo concentrates, oxychlorination for processing low-grade Mo concentrates, low temperature oxidizing-chlorinating roasting, direct reduction by Mn, co-roasting Mo concentrate and pyrolusite, plasma smelting for direct FeMo production and direct reduction of MoS_2 have been developed [10].

For recycling Mo-containing mill scale, microwave heating is a potentially effective process, as the reaction rate is very high and there is no need to pelletize the mill scale. An innovative process mixes the mill scale with carbonaceous materials and heats the mixture in a microwave oven. Thus, the mill scale is reduced to metallic droplets in 15 minutes and can easily be separated from carbonaceous materials [20].

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