

Molybdenum extraction process : An overview*

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Abstract : An ever-increasing quantity of low-grade molybdenite concentrates are being produced from secondary sources especially as by-products of copper and uranium mining. Such low-grade MoS₂ concentrates are not amenable for the extraction of Mo metal by traditional methods. A critical survey indicates that over the past three decades significant research efforts have been directed not only to improve and modify the conventional methods, but also to develop new methods for the extraction of molybdenum satisfying indigenous needs and environmental considerations. In this paper, the various methods of extracting molybdenum from its primary and secondary sources are critically reviewed. Ten distinct new approaches have been considered as potentially useful methods and a critical appraisal has been made of the new routes investigated during the past two decades. At the end, the Indian status on this subject is critically reviewed and potentially useful processes have been identified.

Keywords : *Molybdenum extraction, Molybdenite concentrates, Alternative methods of molybdenum extraction, Commercial processes.*

INTRODUCTION

Molybdenum is an important refractory metal which is mainly extracted from its sulphide ore ¹¹, molybdenite (MoS₂). Other important minerals ¹² (oxygenated ores) of molybdenum include wulfenite (PbMoO₄), powellite (CaMoO₄), ferrimolybdite (Fe₂Mo₃O₁₂.8H₂O) and molybdite (MoO₃). World mine production of molybdenum ¹³ (Table 1) in recent years has been around 140,000 tonnes, 40% of which originates from USA. China, Chile, Canada and C.I.S. are the other important producers. Of the world's 7.85 million tonnes of molybdenum reserves, the primary molybdenum porphyries account for about 59% ¹². The remainder originates from secondary sources; bulk of it as co/by-product of copper ore, some from uranium mining and a little from tungsten as well as Pb + Zn ores. Molybdenite concentrates ¹⁴ produced from primary sources (0.1–0.5% Mo) are of high-grade (50–57% Mo) whereas those obtained as co-products from secondary sources (e.g., Cu–Mo porphyries, 0.015–0.1% Mo) are of low-grade (25–45% Mo) ¹⁵. The various methods in vogue or investigated for the extraction of molybdenum are summarised in Table 2.

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Table 1 : World mine production of molybdenum¹³¹

Country	Production (thousand tonnes)			
	1980	1985	1990	1995
USA	68.4	49.2	61.1	58.0
China	2.0	2.0	14.8	24.9
Chile	13.6	18.2	16.2	17.5
USSR	10.4	11.0	11.5	—
Canada	15.2	7.9	13.6	8.9
Turkey	0.1	0.1	0.1	—
Mexico	0.5	4.3	3.2	3.6
India	0.1	0.1	0.1	0.1
Others	17.9	23.9	18.5	30.6
World Total	128.2	116.7	139.1	143.6

Table 2 : The different routes of molybdenum extraction

Item	High-grade Conce.	Low-grade Conc.
A. Commercial	(i) Ammonia Leach	(i) Leaching/fusion with Soda ash
	(ii) Distillation	(ii) Digestion with caustic/acid
B. New processes	(i) Thermal dissociation	(i) Alkali fusion
	(ii) Plasma smelting	(ii) Autoclave oxidation
	(iii) Metallothermy	(iii) Nitric acid leach
	(iv) Molten salt electrolysis	(iv) Pyrochlorination
	(v) Lime-scavenged reduction	(v) Electro-oxidation (Hypochlorite leach)
		(vi) Lime-scavenged reduction

COMMERCIAL PROCESSES

High-Grade Concentrates

High-grade concentrates are traditionally processed^{11,24,51} by roasting MoS_2 concentrates to produce crude MoO_3 which is further treated either by the ammonia leach process or the distillation route to obtain a relatively pure MoO_3 . The trioxide is then reduced by hydrogen to produce molybdenum metal.

Ammonia Leach Process^{11,41} :

Fig. 1, illustrates the commercial flow sheet for ammonia leach practice. There are six metallurgical/chemical steps involved in the production of the trioxide (MoO_3) from molybdenum disulfide concentrate. After controlled roasting of the concentrate, the product (crude MoO_3) is leached with ammonia and then purified chemically. Reduction of the pure trioxide (obtained by calcining the ammonium molybdate) is carried out in three stages by

MOLYBDENUM EXTRACTION PROCESS : AN OVERVIEW

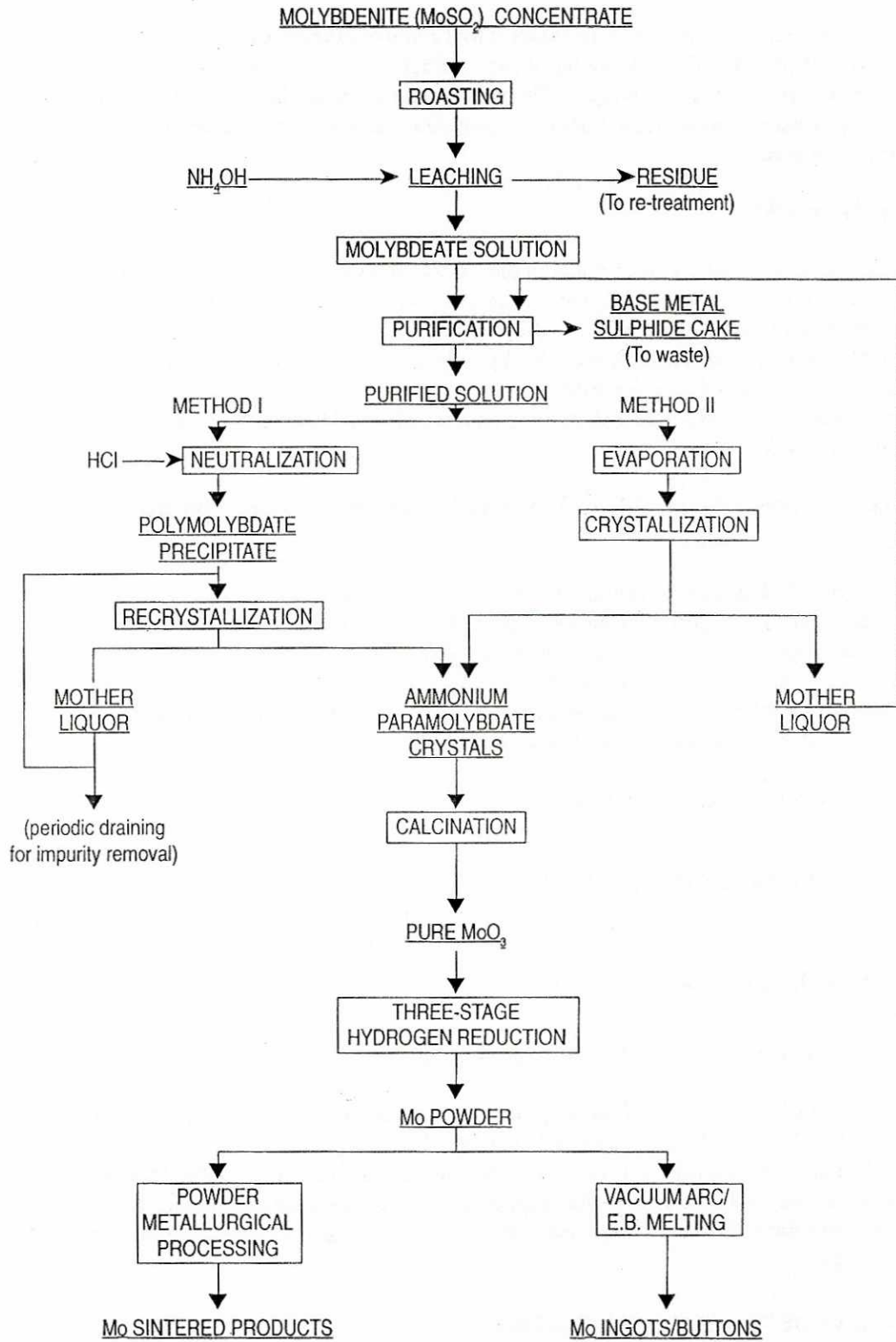


Fig. 1 : Molybdenum extraction by conventional ammonia leach method ^[1]

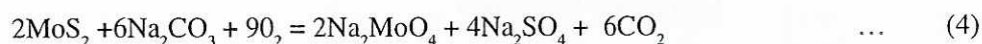
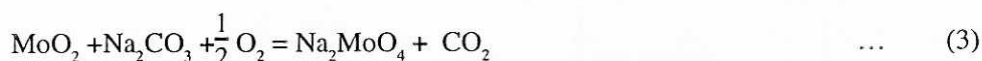
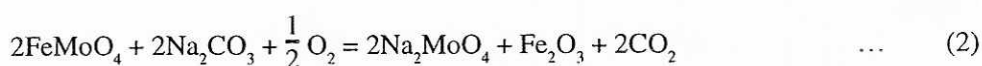
hydrogen : the first stage at 450–600°C to reduce it to the nonvolatile dioxide (MoO₂) which is then reduced at 650–900°C to obtain the metal. A final hydrogen treatment is given at 1000°C for the removal of residual oxygen. The molybdenum powder thus made is consolidated either by powder metallurgical route or consumable electrode arc (or electron beam) melting under vacuum.

Distillation Process ^[1,4] :

The distillation route varies from the ammonia leach process only with respect to the purification methods for the MoO₃ calcine. In the distillation process the impure MoO₃ is purified by its distillation at 900–1000°C employing a rotating inclined electric arc furnace assisted by blowing air over the surface of the liquid trioxide. Metal recovery in ammonia leach process is higher than that in the distillation route. In both these processes, the residues left behind contain 5–25% Mo which, therefore, require additional treatment to enhance the overall metal recovery.

Commercial Processes Applicable to Low-Grade Concentrates and Mo Bearing Residues ^[1,2,4,5,6]

A variety of techniques are in vogue for the processing of low-grade molybdenite concentrates. These include leaching/fusion with soda ash (Na₂CO₃) or digestion with caustic soda/HCl. Leaching/fusion with soda ash involves mixing the raw material with soda ash and heating in a furnace for about 6–8 hrs. at 700–750°C. During fusion all the moly compounds (CaMoO₄, FeMoO₄, MoO₂) and unoxidized MoS₂ react with soda ash and are converted into the water soluble sodium molybdate as per the reactions.



Calcines in which Mo occurs as CaMoO₄ and other molybdates (which have low MoO₂ and MoS₂) may be leached directly in autoclaves at 180–200°C at about 12–15 atm pressure (instead of fusion with soda ash). Fusion with soda ash is not a convenient method for the processing of calcines which contain 3–5% tungsten as it gets converted to sodium tungstate which passes into the solution. In such cases, the calcines are digested with 20–30% hot hydrochloric acid.

LIMITATIONS OF TRADITIONAL ROUTES

Traditional pyroroutes for the extraction of molybdenum suffer from several inherent limitations listed below.

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i) *Large Number of Processing Steps*

This includes roasting, three chemical purification steps, calcination, three-stage hydrogen reduction and finally metal consolidation.

ii) *Difficulties in Reducing the Trioxide to Metal*

A single step reduction (though most desirable) is not feasible on account of the high sublimation tendency of the trioxide even at moderate temperatures, formation of low melting eutectic (550-600°C) which retards its reduction rate and also the exothermic nature of the oxide reduction process.

iii) *Sulphur Dioxide Pollution*

A large volume of low strength SO₂ is emitted (from any molybdenite roaster) whose tolerable level in the environment is very low (5 ppm threshold limit). During past three decades strict environmental regulations have been imposed on nonferrous smelters to meet the air quality standards (AQS) by the Environmental Protection Agencies (EPAs) in most countries. Consequently, molybdenite roasters are required to install expensive pollution abatement equipment. Scrubbing [and dust (SPM) control] of large quantity of stack gas is expensive. Having sulphuric acid is no doubt attractive but the gas has to be cleaned from smoke and dust and about 6% SO₂ is necessary for efficient and economic conversion.

iv) *Low Recoveries*

5-25% Mo being left over in the residue after trioxide purification stage which necessitates additional treatment of the residue to improve the overall recovery of Mo metal.

ALTERNATIVE ROUTES OF MOLYBDENUM EXTRACTION ^[2,5-7]

Owing to the reasons outlined above, and more importantly the necessity of processing complex and significant quantities of secondary sources, a number of alternative routes, some of which are applicable only to high-grade concentrates and other to low-grade ones ^[2,5-7], have been reported in literature. Such routes range from simple thermal/plasma dissociation/smelting or metallothermy of high-grade molybdenite to complex alkali/acid processing or fused (molten) salt electro-extraction from suitable anodes made from the concentrates. The potentially useful techniques/routes that have been investigated in recent years are now critically surveyed below.

New Processes Applicable to High-Grade Concentrates

Thermal Dissociation ^[8-12]

Molybdenum can be produced by the thermal dissociation of molybdenite, as per the reaction



It is necessary to continually withdraw the sulphur (S_2 gas) produced in-situ during the reaction which occurs in two distinct steps^[12].



A few interesting studies^[9-11] have been reported on the above fascinating single step approach. At Climax Laboratories during 1952-60, Scholz and co-workers^[8] successfully processed upto 100 lb batches of molybdenite using a reactor capable of attaining a vacuum of 1-5 μ m at 1650°C and demonstrated the technical feasibility of molybdenum production. However, they reportedly faced substantial furnace failure problems.

Plasma Smelting^[13-23]

The advantage of using plasma in the reduction of concentrates largely accrues not merely from the increased reduction rates obtained at elevated temperatures but also from the more reactive species available at these temperatures in the plasma medium. Pioneering researches have been reported on this subject from 1975 onwards^[13] notably from Noranda Labs. and McGill University. Basically plasma reactors can be exploited for one or more of the following purposes :

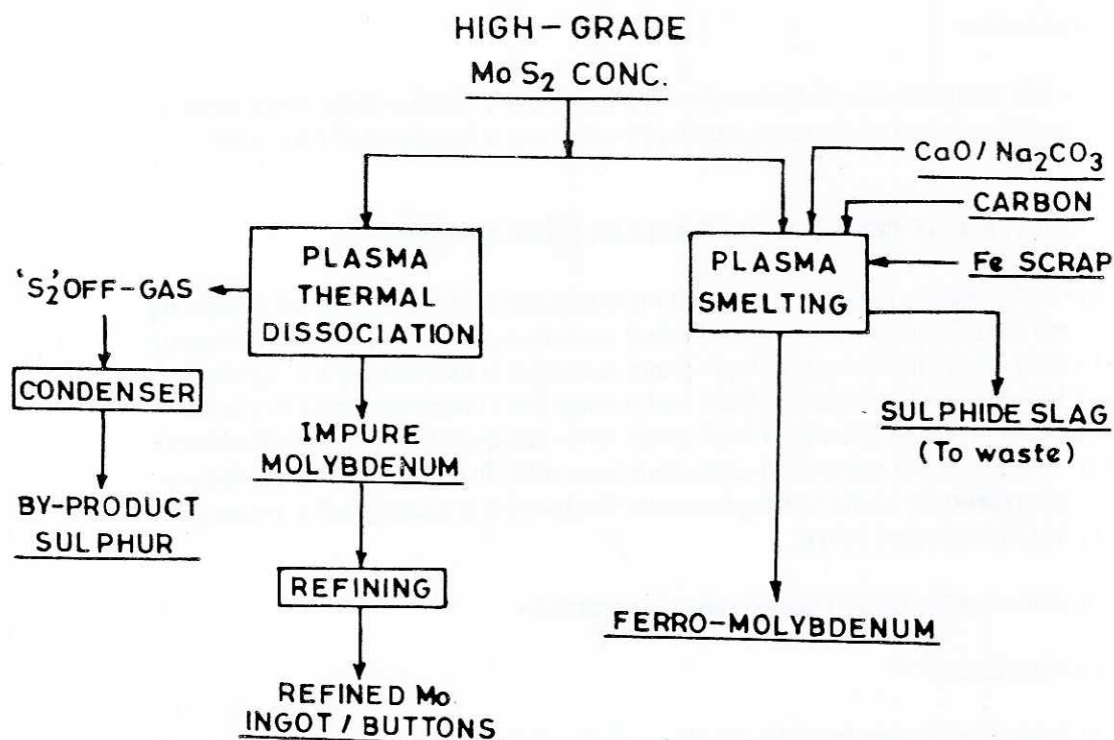


Fig. 2 : Schematic flow sheet for the production of Mo or Fe-Mo by plasma processing.

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Table 3 : Summary of results on the plasma thermal dissociation/smelting for the production of Mo and Fe-Mo

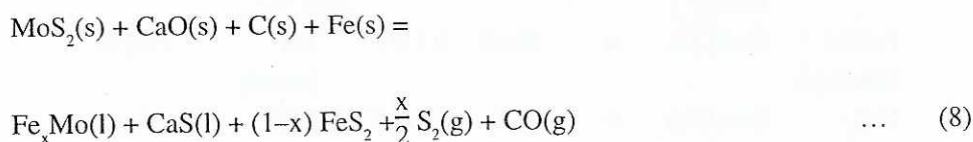
Investigator(s) (Year)	Plasma Reactor			Rating (kW)	Product purity	Conversion	Energy Comp. (kWh)
	Feed	Type	Gas				
<u>Plasma Thermal Dissociation of Molybdenite</u>							
Huska & Clump ¹⁴ (1967)	MoS ₂	Induction coupled	Ar	5	21.1%S	70%	N.A.
Noranda Res. Centre ²¹ (70's)	MoS ₂	Transf. Arc	Ar N ₂	20 20	3% S 0.03%S	N.A. 99.96%	36/kg Mo 12/kg Mo
Kubanck et al ¹⁵ (1977)	MoS ₂	3-Phase Transf. Arc	Ar+N ₂	100	3.8%S	94%	165/kg Mo
De Vynck ¹⁶ (1977)	MoS ₂	Non-transf. Arc	Ar	20-50	10%S	N.A.	15/kg Mo
	Product from above	Transf. Arc	Ar	20-25	0.1%S	N.A. (overall)	55/kg Mo
Harrington ¹⁷ (1979)	MoS ₂	Transf. Arc Transf. Arc Transf. Arc	Ar H ₂ H ₂ +Ar	50 50 50	13.7%S 0.47%S 0.45%S	88% 58% 88-99%	45/kg Mo 45/kg Mo 23-24/kg Mo
Evans et. al ¹⁸ (1988)	MoS ₂	3-Phase Transf. Arc	N.A.	47	0.15%S	100%	200/kg Mo
Mimura&Nanjo ¹⁹ (1992)	MoS ₂	N.A.	Ar	N.A.	0.6-0.7%S	N.A.	N.A.
<u>Plasma Production of Ferro-molybdenum</u>							
MacRae & Gold ²⁰ (1979)	MoS ₂ +C	Falling Film Transf. Arc	N.A.	N.A.	0.7%S 2.7%C	N.A.	9.8/kg Mo
Gauvin et al ²¹ (1981)	MoS ₂ +Re- cycled dust	Transf. Arc	N ₂ +Ar	N.A.	<0.15%S	96-99	11/kg Mo
Johnston & Pickels ²² (1989)	MoS ₂ +C CaO+Fe	3-Phase Transf. Arc	N.A.	47	1.5%S 5.0%C	>90	200/kgFeMo
Lelievre et al ²³ (1990)	MoS ₂ +C Na ₂ CO ₃ +Fe	3-Phase Transf. Arc	N.A.	47	0.2%S 7.0%C	>90	125/kgFeMo

N.A. — Data not available

- (i) Thermal decomposition of molybdenite concentrates resulting in molybdenum metal and elemental sulphur as by-product.
- (ii) Smelting of molybdenite in the presence of a potent sulphur acceptor like lime enabling production of the metal and fixing much of the sulphur as solid CaS.
- (iii) Reduction smelting of the concentrate by carbon in presence of lime and iron scrap which enables production of ferro-molybdenum.

The subject of plasma dissociation and smelting was eminently reviewed by Munz and Gauvin ¹¹³¹. A classified survey and a schematic flow sheet are presented, respectively, in Table 3 and Fig. 2. Nearly two decades ago, Harrington ¹¹⁷¹ has demonstrated the production of molybdenum ingots containing 0.45% S with a specific energy consumption of 22.9 kWh employing a transferred -arc reactor and a 1:1 mixture of H₂ + Ar. Deployment of higher temperatures and continuous feeding of molyconcentrates reportedly enabled production of the metal with <0.15% S and a specific energy consumption of only 12 kWh/kg of the Mo in the feed. Excellent results were reported on the formation of metal product (Mo) with only 0.03% S at a high conversion of 99.96%. Evans and coworkers ¹¹⁸¹ observed that it is feasible to produce high-grade moly metal containing <0.15% S but at a relatively high specific energy consumption (200 kWh/kg Mo).

Another interesting aspect refers to the direct production of ferro-molybdenum in a three phase 47 kW plasma arc furnace (at 2300°C) in the presence of lime and iron scrap as per the reactions.

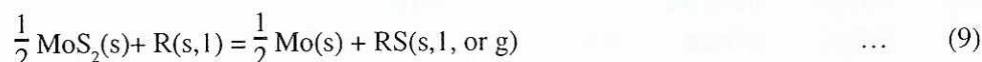


Pickles and coworkers ^{122,231} found that the specific energy consumption for the above reaction can be reduced to 125 kWh/kg Fe-Mo.

Techno-economic assessments were also made in some laboratories and it is believed that plasma smelting routes will be attractive on account of (i) low capital cost (only 10% compared to electric smelting routes), (ii) low operating cost, (iii) availability of high-purity nitrogen at a low cost, (iv) very high recoveries and (v) low specific energy consumption.

Metallothermic Reduction ^{12,5,6,24-291}

Reduction of high-grade molybdenite concentrates with cheaper metals such as Al, Sn, Pb, Na in a suitable bomb or closed furnace has been the subject of several investigators. The basic reaction is represented by



where R is the reductant metal. Jena and coworkers ^{124,251} successfully prepared molybdenum metal by reducing molybdenite concentrate with aluminium in a bomb reactor employing KClO₃ as the heat booster. Mukherjee and Gupta ¹²⁶¹ conducted the aluminothermic reduction of molybdenite using pelletized charge and potassium chlorate as heat booster. The reaction was initiated by resistance heating of a nichrome coil embedded in the charge. Buttons containing 29% Mo could be recovered which were electrorefined to higher purity molybdenum. Natchman and Poole ^{127,281} reported the preparation of molybdenum by using lead or tin as reductant in temperature range 1200-1500°C under a protective atmosphere. The production of molybdenum by reducing its sulphide with tin was also investigated on a

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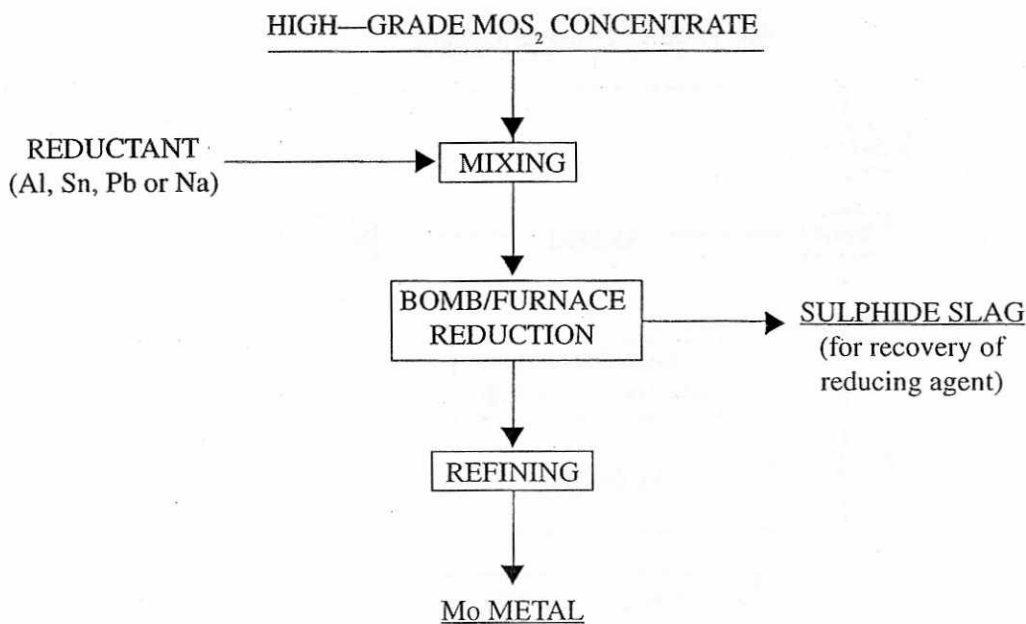


Fig. 3 : Metallurgical reduction of molybdenite.

pilot plant scale by Abraham and Krey ¹²⁹. In general, such metallurgical practices seem to be attractive because they can be simple, bypass the roasting step and the metal can be produced from small quantities of local concentrates. However, the technique is limited not only by the availability of high-grade concentrates but also poor kinetics with some of the reducing agents. A schematic flow sheet for the metallurgical production of molybdenum from molybdenite is shown in Fig. 3.

Molten Salt Electrolysis ^{12,30-33}

Electro-extraction of molybdenum from its soluble anodes with molten (fused) salt electrolysis is a novel approach which has been extensively investigated at the BARC ¹³⁰⁻³³ (Mumbai). Fig. 4 shows an illustrative flow sheet for the molybdenum extraction by the molten salt route. The soluble anodes may be in the form of oxide, sulphide or carbide. The conductivity of oxide and sulphide anodes is low which is increased by mixing them with carbon. Whereas the oxide is prepared by roasting the molybdenite concentrate, the synthesis of carbide involves carbonaceous roasting of molybdenite at 650°C followed by its carbiding at 950°C under hydrogen atmosphere. The electrolytic cell devised at BARC for molybdenum extraction was designed to permit semi-continuous operation at 900-950°C in an inert atmosphere using molybdenum cathode and a complex electrolyte (KCl-K₃MoCl₆). The soluble anodes were kept in the space between the perforated graphite crucible and the graphite lined cell to provide larger anodic area. The metal is recovered as dendrites from the cathode deposits which is leached with dil HCl to remove the adhering electrolyte. The washed molybdenum dendrites were finally consolidated and refined by electron-beam melting for the removal of trace metal impurities. The operating conditions (reported from BARC laboratories) for the electro-extraction of molybdenum using sulphide, oxide or carbide anodes is summarised ¹⁵¹ in Table 4. Direct electro-extraction

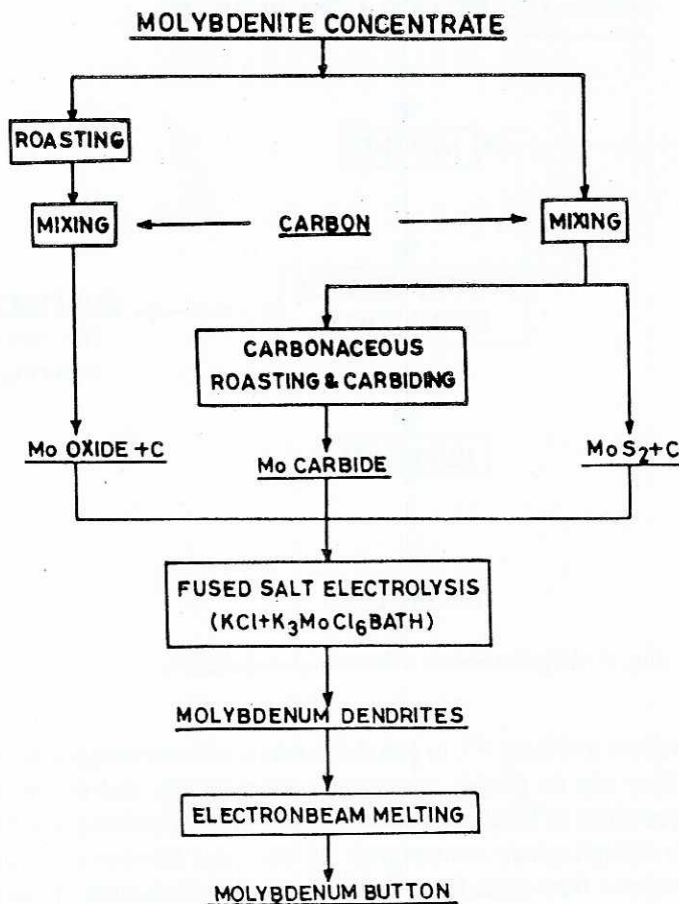


Fig. 4 : Extraction of molybdenum by molten salt electrolysis¹³⁰⁻³³¹.

from the sulphide anodes is attractive as it can bypass roasting although its current efficiency is lower and metal recovery moderate¹⁵¹.

Table 4 : Typical operating data for the electroextraction of molybdenum^{130-33.51}

Parameters	Optimum conditions for different anodes		
	MoS ₂ + C	Mo oxide + C	Mo Carbide
Electrolyte	KCl-K ₃ MoO ₆	KCl-K ₃ MoO ₆	KCl-K ₃ MoO ₆
Mo Conc. in electrolyte (%)	7.5	7.5	7.5
Electrolyte temperature (°C)	900	950	930
Voltage (V)	0.7-0.8	0.25-0.4	0.8-1.1
Cathode current density (A/Ft ²)	1350	450	720
Max. cathode current efficiency (%)	50	99	61
Metal recovery (%)	82	94	71
Hardness of consolidated Mo (DPH)	160-170	150	150-160
Metal purity	99.9+	99.9	99.95

New Processes Applicable to Low-Grade Concentrates

Alkali Fusion ^[34,35]

Alkali fusion of molybdenite concentrates enables Mo recovery in various usual forms e.g., molybdic oxide and calcium molybdate. In the process reported by Woldyka^[34], molybdenite concentrate mixed with sodium carbonate and sodium nitrate was fused at 700°C and the resultant material was solidified, crushed and leached with water. An average yield of over 99% was reported. The process has the potential to achieve some energy conservation as the fusion process can become autogeneous once the reaction temperature is attained. Sulphur from the concentrate can be converted to sulphate and no air pollution problem is envisaged. Mehra et. al. ^[35] also investigated the fusion of a molybdenite concentrate with soda ash and ferric oxide at 920°C and molybdenum was finally recovered as calcium molybdate.

Nitric Acid Leaching

Vizsolyi and Peters ^[36] reported bench scale tests on nitric acid leaching of an off-grade molybdenite concentrate, a flow sheet of which is shown in Fig. 5. Leaching with 4M HNO₃ at room temperature resulted in the formation of molybdic acid, sulphuric acid and nitric oxide, as per the reaction

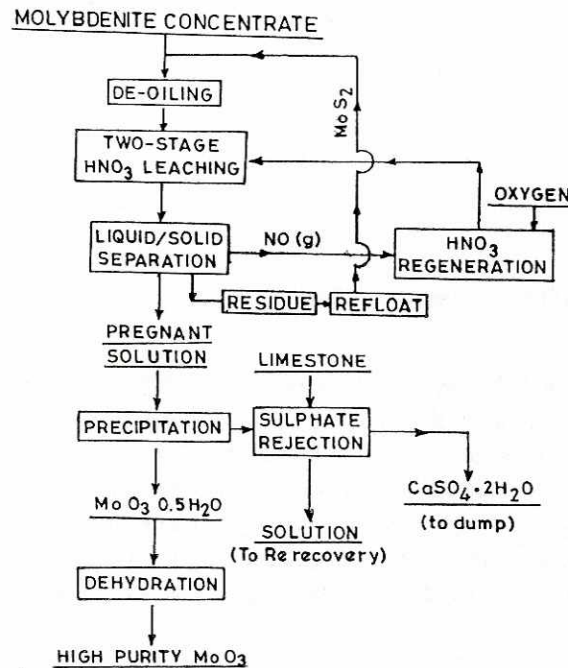
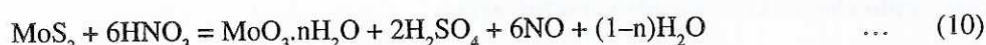


Fig. 5 : Nitric acid leaching of molybdenite concentrate ^[36].

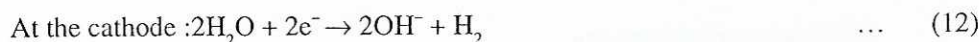


Although the process appears to be more expensive than the conventional route, it has inherent economic merits such as (i) its ability to treat low-grade concentrates; (ii) no SO_2 pollution; (iii) high purity MoO_3 product; (iv) possible recovery of Cu and Re as by-products and (v) regeneration of the acid.

Cymoly process^[37], an alternate hydrometallurgical process, consists of pressure leaching of the molybdenite concentrate with nitric acid in presence of oxygen. The impure molybdic acid is purified by solvent extraction (SX) with simultaneous recovery of copper and rhenium from the leach liquors. The process has been tested on a semi-commercial pilot plant. Parson and coworkers^[38] developed a computer model to simulate the leaching of molybdenite by dil HNO_3 . Excellent results were achieved using 1–6 M HNO_3 under conditions that permitted precipitation of high-purity $\text{MoO}_3 \cdot 0.5\text{H}_2\text{O}$.

Hypochlorite Leaching^[2,7,39-40]

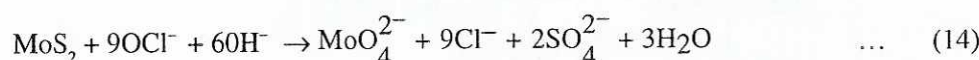
Hypochlorite leaching, also known as electro-oxidation involves electrolysis of pulps containing brine and the molybdenite concentrate. The hypochlorite is generated in-situ in leaching the molybdenite. The following reactions are presumed to take place



Cl_2 and OH^- produced combine to form the hypochlorite ions



Aqueous OCl^- ions generated, in turn, react with the MoS_2 forming soluble molybdate



In a pioneering investigation Scheiner and coworkers^[39] of US Bureau of Mines reported 99% dissolution of molybdenite with a specific energy consumption of 30 kWh/kg of Mo. The process is said to be capable of recovering Re and Na_2SO_4 as by-products. Moreover, it involves no air pollution problem. They have demonstrated the process on a pilot plant scale using a 108 kVA bipolar electrolytic cell having 41 electrodes. The leach liquor was processed by solvent extraction employing a tertiary amine and stripping with ammonia to yield an ammonium paramolybdate product. A 99% recovery was reported.

In our country a similar study was reported by Mukherjee et. al.^[40] who treated a low-grade molybdenite concentrate resulting in molybdate liquor. They investigated two routes for preparing the metal powder: (A) Precipitation as CaMoO_4 using calcium chloride and hydrogen reduction of the molybdate followed by leaching of the reduced product with dilute acid for the removal of CaO, and (B) sorption of the molybdate ions using activated charcoal, desorption with ammonia, crystallization as ammonium paramolybdate and

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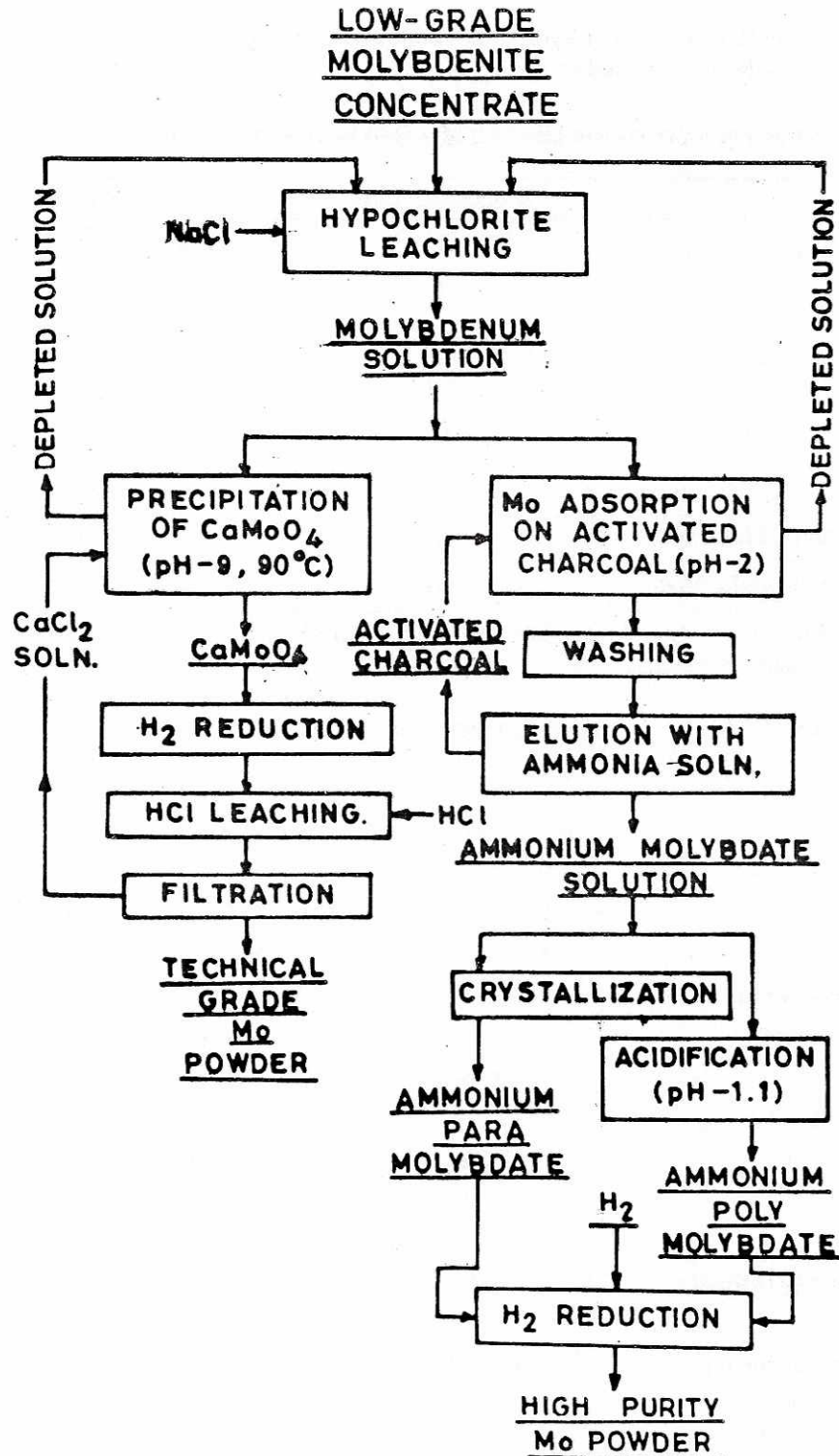


Fig. 6 : Suggested scheme for the production of molybdenum from low-grade molybdenite concentrates¹⁰¹.

finally calcination–cum–reduction under hydrogen. Their processing scheme is reproduced in Fig. 6 and typical results cited in Table 5.

Table 5 : Results of hypochlorite leaching of a molybdenite concentrate*

Type of leaching	Monopolar Cell	Bipolar Cell
Amount of Conc. (kg)	2	5
Pulp density (w/v%)	10	8.3
Current (A)	100	75
Voltage (V)	3.5	20
Duration (h)	48	28
Mo recovery (%)	95	95
Power consumption (kWh/kg Mo)	36	29
Na ₂ CO ₃ consumption (kg/kg Mo)	5	4.5

* [Mo = 30.56%, Cu = 0.58%, Ni = 0.31%, Fe = 5.1%, SiO₂ = 4.15%, and S = 22.6%, particle size = 150µm]; Adapted from Ref. 2.

Table 6 : Lime–scavenged reduction of molybdenite¹⁵⁰⁻⁵¹¹

Item	Reducing agent	
	Hydrogen	Carbon
<u>Process Parameters</u>		
1. Nature of sample	Powder mix. (MoS ₂ + CaO)	Powder mix. (MoS ₂ + CaO + C)
2. Mole ratio (a) CaO/MoS ₂	3	2
(b) C/MoS ₂	–	4 (at 1298 K)
3. Flow rate	3.33 cm ³ s ⁻¹	–
4. Temperature of reduction	1173 K	1273–1298 K
5. Time of reduction	3.6 ks	18 ks
<u>Kinetics</u>		
1. Rate	Jander's linear rate law	
2. Activation energy (kJ/mol)	169.6	361 ± 4
<u>Product Analysis</u>		
1. Product purity (as made)	97% Mo	96% Mo
2. Phases identified	Mo	Mo, traces of Mo ₂ C & CaMoO ₄
3. 'S' in the off-gas	<0.5%	N.D.
<u>Environmental</u>	Essentially non-polluting	Non-polluting w.r.t., 'S' bearing gases

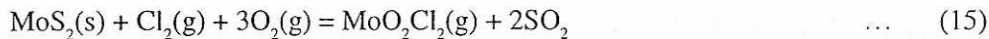
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Table 7 : Imports of molybdenum in India
(Qty. in tonnes, value – Rs. in lakhs)

Item	1991-92		1992-93		1993-94		1994-95		1995-96	
	Qty	Value	Qty	Value	Qty	Value	Qty	Value	Qty	Value
Metal & Semis	38	217.1	34	269.8	25	239.6	31	220.9	1700	4700.0
Concentrate	587	372.1	240	345.7	286	437.6	760	1746.6	3680	5632.0
Ore	325	160.9	246	279.6	338	377.7	1465	1395.5	651	858.9
Ferroalloy	-	-	-	-	669	790.6	143	199.0	307	1515.7
Oxide	-	-	-	-	57	61.4	81	128.5	-	-

Pyrochlorination ^[41-43]

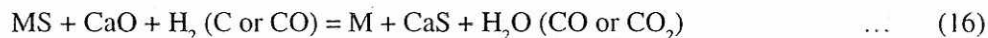
Pyrochlorination is a well known process for the treatment of various ores and minerals and has gained importance in recent times for the treatment of sulphide minerals due to the reasons such as (i) high reactivity of chlorine towards metal sulphides, (ii) high volatility of metal chlorides, (iii) high solubility of most metal chlorides in water, (iv) low operating temperatures, and (v) possibility of recovering sulphur (S°) in elemental form. The processing of molybdenite concentrate by the pyrochlorination in the presence of oxygen can be represented by



The molyoxychloride, MoO₂Cl₂ (sublimation point 156°C) product can be condensed as a yellowish white solid. Nair and coworkers ^[41-43] studied the said reaction and found that a treatment temperatures of 300°C and 275°C will be needed respectively, in static and fluid bed reactors. Recoveries in the range of 90-95% were reported depending upon the technique, nature of the concentrate and method of treating the molyoxychloride concentrate. Two approaches were attempted by them. In one, the condensate was water leached and precipitated as CaMoO₄ by CaCl₂ treatment at pH of 7. In another, 90% Mo was recovered as MoO₃ by K₂S₃O₈ treatment of the water leached MoO₂Cl₂ and the remainder as calcium molybdate by precipitation. Based on the technical feasibility, a flow sheet for the treatment of low-grade molybdenite concentrate has been proposed (Fig. 7).

Lime-Enhanced Reduction of Molybdenite

The direct reduction of metal sulphides by different reducing agents (e.g., H₂, CO or C) is not generally feasible. But by incorporating a potent sulphur scavenger e.g., lime which is inexpensive and readily available, sulphide reduction becomes an experimental reality and same has been termed as 'lime-scavenged' or 'lime-enhanced' reduction. This may be represented by the generalized reaction.



Extensive laboratory studies have been conducted on the lime-enhanced reduction of several sulphides by Prasad and Coworkers ^[44-49]. The said reaction for molybdenite ^[44,45,50-52]

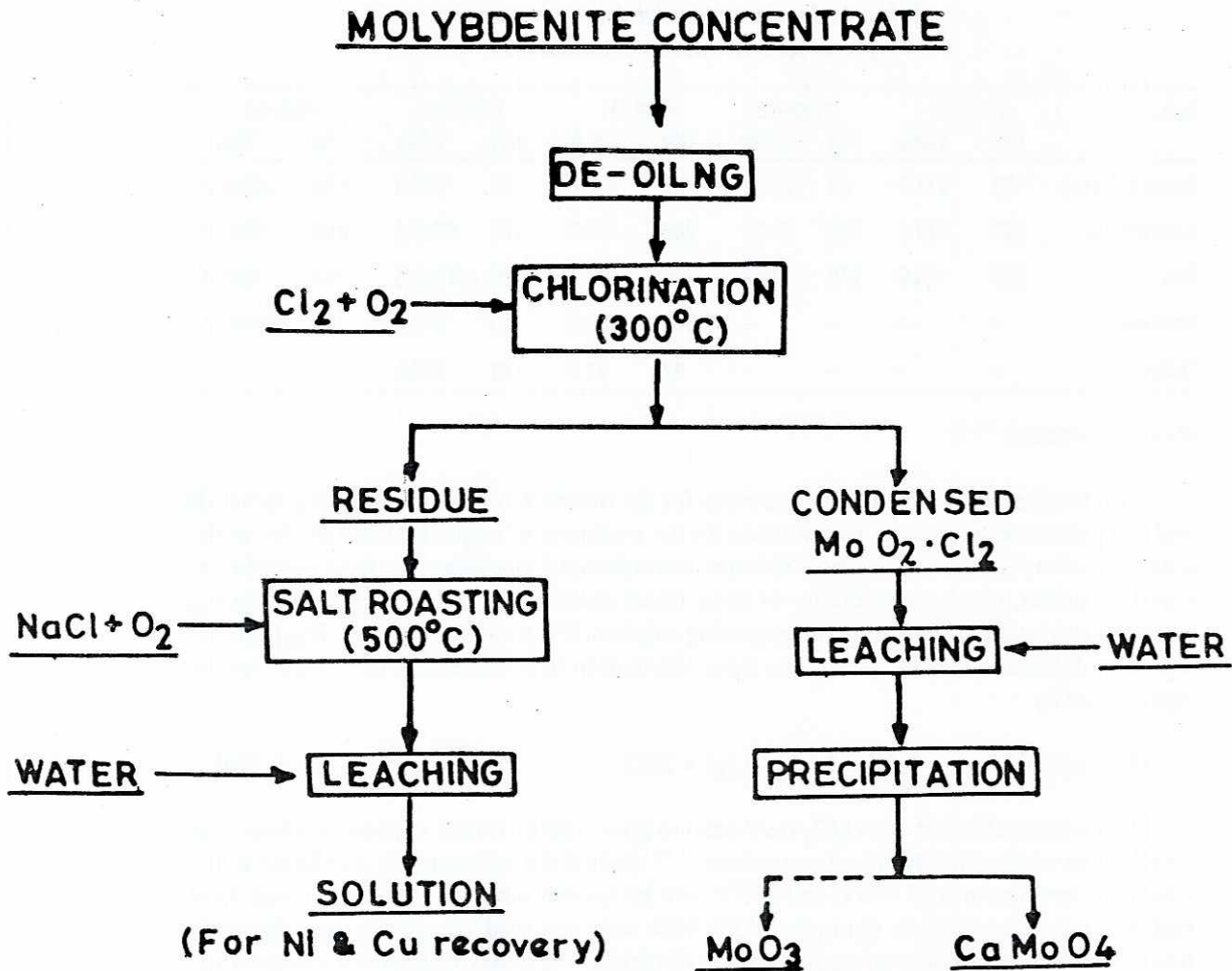
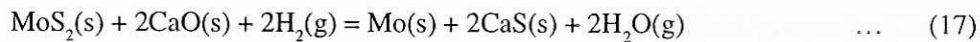


Fig. 7 : Chlorination of molybdenite concentrate ¹⁴¹⁻⁴³¹.

reduction can be represented by



It has been observed that such reactions are highly feasible, possesses favourable energetics and the presence of lime drastically cuts down the sulphur emission into the off-gas. Mankhand and Prasad proposed a novel 'Leach-Reduction-Melting' approach ¹⁵⁰¹ (Fig. 8) for the treatment of even low-grade molybdenite concentrates. The resultant metal from this approach was of 96-97% purity which could be consolidated and refined by electron-beam melting to 99.9% purity. This new approach was claimed to be patently simple, applicable to high as well as low-grade concentrates with minimal SO₂ pollution into the atmosphere and hence expected to enjoy cost benefits. Table 6 summarizes the important results on the lime-scavenged reduction of molybdenite using hydrogen or carbon.

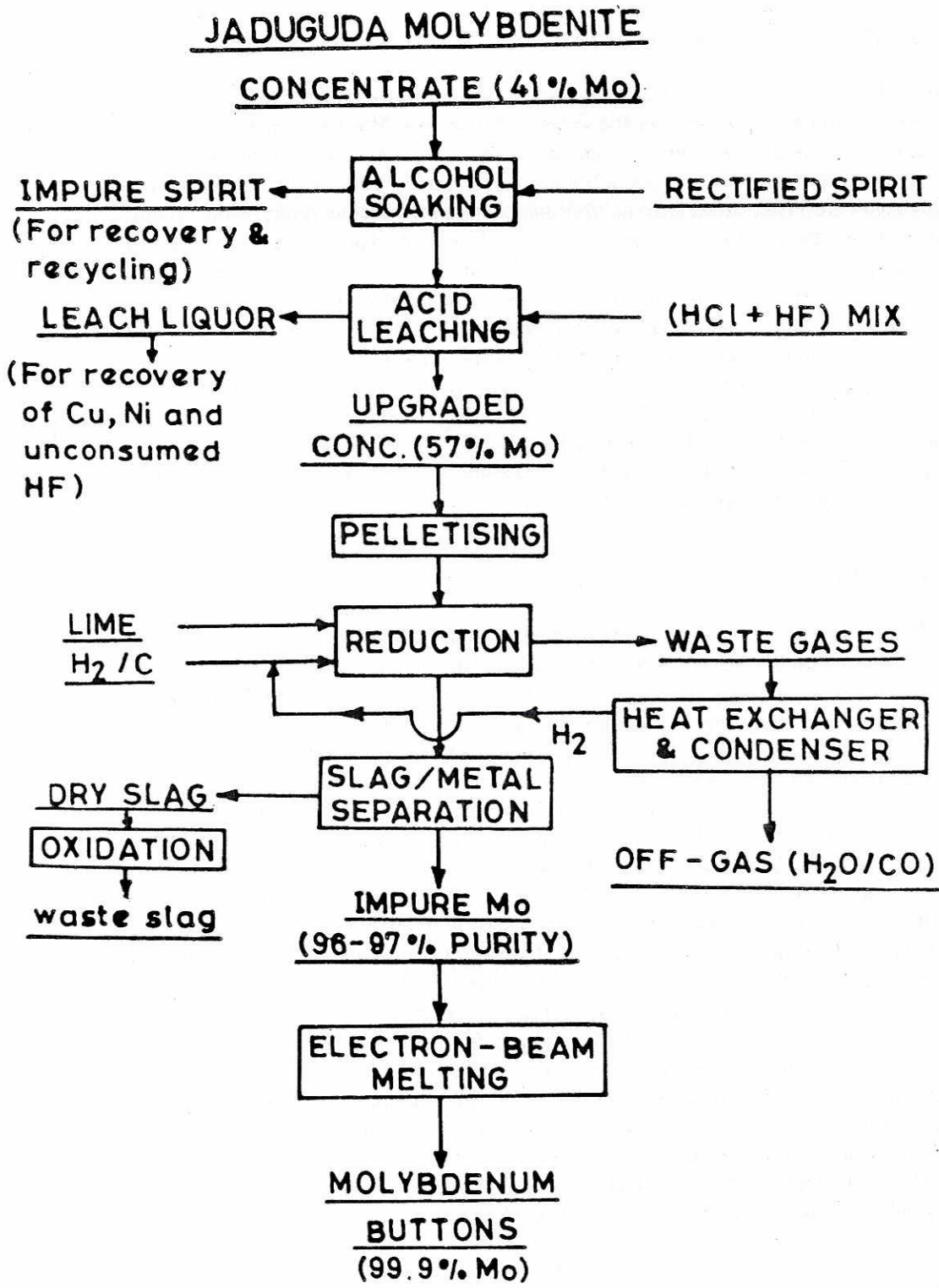


Fig. 8 : Molybdenum extraction by the lime-scavenged reduction approach¹⁵⁰¹.

STATUS OF MOLYBDENUM IN INDIA

The total recoverable resources of molybdenum in India are estimated to be 8.037 million tonnes^[53] which are spread over the states of Karnataka, Madhya Pradesh and Tamil Nadu. At present no molybdenum is produced in India and most of the requirements of various forms of molybdenum are met through imports. Table 7 presents the recent imports of molybdenum ore, concentrate, ferromolybdenum and the metal/semis, oxide by our country^[54]. It is clear that the quantities imported as well as foreign exchange spent have been increasing rapidly. During 1995-96 a sum of Rs. 1270 million was spent for importing the said items. Besides the primary molybdenite ores, there seem to be four secondary sources in India. Uranium mining at Jaduguda which can yield 78 tonnes of low-grade molybdenite concentrate per annum, copper mining at Rakha (Bihar) and Malanjkhand (M.P.) whose deposits are reported to contain 0.11 and 0.04% Mo, respectively. (A flow sheet for the production of 60 tonnes/year of molybdenite concentrate has been developed by BARC); The Dariba-Rajpura lead-zinc deposits which reportedly contain recoverable, quantities of molybdenum^[5,53]. Apart from these, another 1,740 tonnes of MoS₂ has been estimated to be available in the states of Karnataka and Tamilnadu.

CONCLUSIONS

Traditional methods of molybdenum extraction, namely, roasting of molybdenite concentrate by ammonia leach and distillation processes are applicable for high-grade MoS₂ concentrates derived from the primary molybdenum ores. An ever-increasing quantity of complex low-grade molybdenite concentrates is being produced from secondary sources as by-products of copper and uranium mining. Such secondary low-grade MoS₂ concentrates require extensive modifications (additional steps) in the already complex conventional routes. Therefore, appropriate researches have been made on the development of new moly extraction routes, ten of which have been identified as potentially useful techniques. Among the new methods, plasma smelting, molten salt electrolysis and lime-scavenged reduction are useful for high-grade concentrates only. On the other hand alkali fusion, autoclave oxidation, nitric acid leaching, hypochlorite leaching, pyrochlorination and lime-scavenged reduction appear to be suitable for the treatment of low-grade concentrates. Being essentially environment friendly the last three routes are expected to enjoy cost benefits. Though molybdenum metal is yet to be produced in India, considerable potential exists for its extraction especially as by-product of Cu, U and Pb/Zn mining. Further R & D (scale up tests) efforts are recommended on four inherently attractive routes viz., molten salt electrolysis, pyrochlorination, hypochlorite leaching and lime-scavenged reduction for the processing of indigenous low-grade molybdenite concentrates. Semi-pilot plant scale tests have been in progress at Hyderabad under the aegis of the Nonferrous Technology Development Centre (NFTDC) and the Defence Metallurgical Research Laboratory for the past five years^[55] on the hypochlorite leach process. But its status is not known.

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