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Pyrometallurgy of Molybdenum

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ABSTRACT

This paper is concerned with the pyrometallurgical aspects of molybdenum extraction. The presentation begins with properties and applications of molybdenum and its alloys, then proceeds to describe occurrences and reserves of molybdenum, followed by resource processing including physical and chemical beneficiation. We then turn to the production of metallic molybdenum starting from oxide, sulphide and industrial waste. The processes described are non-metallic reduction, metallothermic reduction, and electrolytic processes such as electrowinning and electrorefining, using thermit metal, scrap, or molybdenum compounds as soluble anodes.

INTRODUCTION

Molybdenum together with niobium, tantalum and tungsten are the most important group of refractory metals. These metals are transition elements, characterised by high strength of interatomic bond and consequently by a high melting point (over 2700K) and a very good combination of high temperature strength and other mechanical properties. These are abundant sources of raw material, assuring availability for many years. These metals are recognised as an important section of currently used engineering materials.

Molybdenum is a silvery grey metal belonging to the sixth group of the periodic table. It possesses some of the characteristic properties of this group, but in some respects a diagonal relationship exists between molybdenum, vanadium and rhenium. The outstanding feature of molybdenum /1-4/ is its extraordinary chemical versatility-oxidation states from divalent to hexavalent and coordination number from 4 to 8. Molybdenum has good thermal conductivity (0.35 cal/cm. sec. K) which is several times that of many metals, low thermal expansion and a low specific heat, thus giving it high dimensional stability or lesser tendency to thermal cracking, lower thermal stresses in rapid heating and cooling cycles. Electrical conductivity of the pure metal is also relatively high (0.2×10^6 mho-cm^{-1} at 293 K) being about one third of that of copper. Modulus of elasticity (28.5 to 30 $\times 10^3$ kg/mm^2) for pure metal is outstanding and is little affected by high temperature. Resistance to corrosion is another important property of unalloyed molybdenum. It is resistant to caustic solutions, many of the mineral acids, and to molten alkali metals. However, it oxidises very rapidly in an oxidising environment at temperatures above 800 K and also when exposed to oxidising acids like HNO_3 and oxidising molten salts.

The attractive properties – the high melting point, high modulus of elasticity, high strength at elevated temperatures, high thermal conductivity, high resistance to corrosion, low specific heat, and low coefficient of expansion – have given molybdenum its importance. This paper presents an account of the metal with emphasis on its extractive metallurgy. First there is brief coverage of its application aspects, followed by discussion of resources – occurrences and reserves, descriptions of various methods of resource processing, and of molybdenum metal production, concluding with a summary.

Molybdenum was first discovered in 1778 by C.W. Scheele /5/, but it took more than a century before the first recorded practical use was made of this metal, in armour steels in 1894. Since then, it has been considered as metal for armaments and was used in large quantities during the First and Second World Wars. The post-war period saw a rapid growth of use of this metal, not only in conventional steels but also in many of the new varieties, and in other unconventional applications /6-11/.

APPLICATIONS

Use of molybdenum today can be broadly classified in three categories: as an alloying additive; as unalloyed pure molybdenum; and in chemicals and lubricants. Molybdenum is useful as an alloying element in iron and steel, and super-alloys account for about 86% of total consumption. About 4% of unalloyed molybdenum is used in electrical, electronic, chemical and nuclear applications, about 9% is used in molybdenum compounds in paints and pigments, catalysts, lubricants, flame retardants and as micronutrients in agriculture, and the last 1% has miscellaneous applications such as welding, hardfacing, magnetic alloys, glass industry, etc. The range of molybdenum applications is presented in Table 1.

On the basis of consumption pattern as shown in Table 1, commercial molybdenum takes the forms of molybdic oxide, ferromolybdenum, pure or unalloyed molybdenum, molybdenum alloys and molybdenum chemicals such as oxides, molybdates, sulphides and sulphur-bearing compounds, in addition to the natural form, i.e., molysulphide.

The world market for molybdenum is encouraging for producers. The strongest markets are in drilling equipment and pipe line steels for securing increased supplies of oil and gas, formation of synthetic fuel from coal, newer grades of stainless steels for use as solar collectors and for applications in sea water condensers. For this reason, even in a period of severe recession of the steel industry,

TABLE I
Application Areas of Molybdenum

Application area	Applications	Proportion of total consumption
As an alloying constituent	1. Low alloy steels a) Dual phase steels for automotive applications b) Rail steels for heavy duty rail service c) Deep gas and oil wells, line pipes in HSLA steels d) Power generation-9Cr-1 Mo steel with minor additions of Ni and V – the steel will replace some applications currently served by 314 SS	47
	2. Stainless steel – in 316 variety structural steels, solar collectors (18Cr, 2Mo), food handling, water distribution	20
	3. Tool steels – molybdenum bearing tool steels and also replacing tungsten in tungsten bearing tool steels	9
	4. Cast iron – nodular cast irons and white irons for automotive parts, crusher parts, mill rolls, etc.	7
	5. Super alloys – missiles and rockets, jet engines, airframes and rocket test sleds and in combat conditions	3
	Metal working-die casting dies, hot work tools, resistance welding electrodes, moulds, thermocouples	
Molybdenum metal	1. Electrical-electrical furnaces, electrical contacts, brushes, in manufacturing lamp filaments.	4
	2. Electronic – transducers, transistors, and rectifiers, electronic tubes.	
	3. Chemical – valves, heat exchanges, reboilers, tank liners.	
	4. Nuclear – in heat exchangers, piping, heat shields, for use in handling liquid metals, as a cladding and as reflectors.	
	5. Glass industry – as electrodes.	
Chemical and compounds	1. Paints and corrosion inhibitors Molybdates, particularly $ZnMoO_4$ and 9) molybdenum orange because these are non-toxic and excellent corrosion inhibitors, dyes, inks, etc.	(appr.
	2. Catalysts - molybdic oxide, molybdates, molysulphide, moly carbonyl and organomolybdenum compounds – in oil refining and hydrosulphurisation and in synthesis of organic compounds.	
	3. Lubricants and additives – MoS_2 and Mo–S compounds as solids, suspensions in oils and greases.	
	4. Flame retardants – molybdates, complexes e.g., MoO_2dithiocarbonate/ and also as smoke retardants.	
	5. Agriculture – molybdates as micro nutrients in fertilisers for nitrogen cycle in plants.	
Miscellaneous	Welding and hard facing alloys, magnetic alloys, materials for glass metal seals, etc.	

sales of molybdenum have been quite significant, even though there have been delays in setting up and commissioning newer production facilities. With an anticipated overall annual growth rate of about 4.5 percent throughout the remainder of this century the prospects for the molybdenum industry look quite bright.

RESOURCES AND RESERVES

0.001% /12/ of molybdenum, fifty-third element in abundance, is present in the earth's crust. Molybdenum is not found in its free or native state, but always in combination with other elements in about 20 different forms. The most common molybdenum minerals are molybdenite (MoS_2), powellite ($CaMoO_4$), wulfenite ($PbMoO_4$) and ferromolybdite ($FeMoO_3H_2O$). Of these, only molysulphide has current economic importance. The oxide minerals powellite, wulfenite and ferromolybdite, may become possible source materials as the demand for molybdenum continues to rise and economic factors make it viable to process oxidised sources.

Molysulphide is widely distributed around the world but the highest concentrations are found in silica rich rocks – lenco granites, quartz veins, pegmatites and silicate deposits /13-16/. World molybdenum resources are fairly equally divided between deposits that contain molybdenum as the primary metal and those in which molybdenum is a by-product or co-product. Porphyry molybdenum and porphyry copper-molybdenum deposits contain the bulk of molybdenum resources. In porphyry deposits, the sulphide mineral occurs as disseminated grains and in quartz veins and veinlets, hydrothermally altered granitic intrusive rocks, and in intruded igneous or sedimentary country rocks. The porphyry or disseminated deposits are usually pipe-shaped bodies, circular or oval, and with steeply-inclined sides, and are located close to one or more major faults in the host rock. Average mineral content of porphyry-type deposits ranges from 0.1 to 0.5% molybdenite in molybdenum porphyries, and from about 0.015 to 0.1% molybdenite in copper-molybdenum porphyries. Currently mineable porphyry deposits range in size from a few hundred meters to several thousand meters horizontally and may extend to depths of a few thousand meters. Fractures and hydrothermally altered rocks may extend beyond the limits of mineable ore. To date, more than 95% of the world's supply of molybdenum has been obtained from porphyry molybdenum or copper-molybdenum deposits. In some cases, processing of these porphyry deposits also yields by-products like tin, tungsten and pyrites.

A few molybdenum minerals are also associated with ore deposits of uranium, tungsten, and in coal, shale, phosphorite, lignitic sandstone, etc. In fact, small quantities of molybdenum are being recovered as by-products from uranium and tungsten operations.

Molybdenum is one of the important trace elements associated with manganese nodules mined from the sea-bed. So far these small sources have not been utilized for recovering molybdenum. In addition to naturally occurring molybdenum sources, scrap and residues accruing from various industrial operations constitute a fairly large resource. Neither has this source been exploited to augment molybdenum supplies. With increasing awareness about conservation and total resource recovery, processing of these secondary sources may assume an increasingly important role.

World reserves of molybdenum are estimated at 7731 million tonnes /17/. Almost three-quarters of the world reserves of molybdenum are located in the Western Cordillera of North and South America, the mountainous regions along the western part of these continents. The remaining one-quarter is distributed among the USSR, parts of Europe (Bulgaria, Yugoslavia, Norway), China, Australia, Japan, the Philippines, etc. Table II shows identified molybdenum reserves of the world.

The United States produces over 60% of the molybdenum in the world, major production comes from Climax, a subsidiary of Amax Inc., where mining is primarily for molybdenum minerals. These primary molybdenum deposits constitute about 71.4% of the American reserves, and the by-product from copper-molybdenum accounts for 22.3%. Other deposits, which include co-product reserves of copper-molybdenum areas, by-product from tungsten ores, and by-product of uranium ores form only 6.3%. In co-product copper-molybdenum ores, neither copper nor molybdenum exists in large enough quantities for the mining operation to be economically viable for the extraction of only one mineral, but the operation becomes profitable when both are recovered. Such ores usually contain 0.6% or less of copper and are therefore termed as co-product reserves of copper and molybdenum.

Canada, Chile and Peru rank as the next three most important producers of molybdenum. Together with the US, these produce about 98% of molybdenum outside the controlled-economy countries. Canadian deposits include primary molybdenite and copper molybdenum ores, whereas the reserves of Chile and Peru are all by-products with copper. In fact, these copper ores also contain some molybdenum oxide minerals. Russian

TABLE II
Identified Molybdenum Resources

			(In Thousand Tonnes)	
		Reserves	Other	Total
NORTH AMERICA				
	United States	3348	3616	6964
	Canada	580	938	1518
	Mexico	134	357	491
	Other	–	580	580
	Total	4062	5491	9553
SOUTH AMERICA				
	Chile	2410	2946	5356
	Peru	223	446	669
	Other	–	268	268
	Total	2633	3660	6293
EUROPE				
	Bulgaria	4.5	9	13.5
	USSR	70	670	1340
	Other	–	625	625
	Total	674.5	1304	1978.5
AFRICA		–	45	45
ASIA				
	China	223	223	446
	Iran	134	134	268
	Other	4.5	174	178.5
	Total	361.5	531	891.5
OCEANIA				
	Australia	–	22	22
	Other	–	179	179
	Total	–	201	201
WORLD TOTAL		7731	11232	18963

reserves form about 12.5% of world reserves, which are mainly by-products of copper mining operations.

RESOURCE PROCESSING

Mining:

Primary molybdenum deposits are mined both by open-cast surface mining and underground mining methods. The ores are of low tenor and would require high tonnage mining methods for profitable recovery. While open-cast methods lend themselves to high tonnage operations, underground operations utilise special techniques such as block caving. At present, the Climax mine, employing the block-caving technique, is considered to be one of the largest underground mines based on the ore tonnage produced. In the United States, copper-molybdenum deposits, from which molybdenum is recovered as a by-product, are also mined, either by open-cast or block-caving methods /15/.

Physical Beneficiation:

Mined ore is sent to mills where it is crushed and ground to liberate the molybdenum from associated quartz/granite and other gangue materials. Ground ore after classification is processed by flotation – a physical beneficiation method using differences in density and surface energy properties of minerals including molybdenite, and unwanted associations. Flotation is carried out in flotation machines, wherein air is introduced into an aqueous slurry of ore particles with or without additions. Some of the minerals, which are hydrophobic, or are treated to become hydrophobic, adhere to air bubbles and float to the surface, whereas the other (hydrophillic) minerals do not float, thus resulting in separation of minerals. Flotation of molybdenum is so spontaneous that it is termed a natural floater. This natural flotability is attributed to predominant breakage of molybdenite crystals at weak vander Waal's bonds of sulphur-sulphur rendering the particles hydrophobic. Natural flotability of molybdenite can be further enhanced by adding sulph-hydrate collectors, e.g., hydrocarbons, pine oil or cresylic acid. Recoveries in flotation processes are dependent on several factors – pH, pulp density, particle size, density of ore, ore feed grade, metal value, and, of course, on the type of flotation machine. With primary ores at least, a two-state flotation scheme is normally adopted. A roughter concentrate of 3-4% Mo is produced in the first instance, which is then further treated by regrinding-reflotation in several stages, to produce the desired grade of material. A concentrate of 90-94% MoS_2 can be conveniently produced at an overall recovery of 75-90% of the in-place ore content.

Production of molybdenite concentrate from copper ores is more difficult because of the lower content of Mo in the ore (less than 0.1% Mo) and lower priority attached to its recovery. Accepted practice is bulk flotation of copper minerals and molybdenite in the first instance to achieve separation from gangue minerals. Bulk flotation utilises strong collectors like potassium amylxanthate, a sodium isopropyl xanthate and non-selective frother such as methyl isobutyl carbinol (MIBC) in alkaline media (pH 8-11.5), using lime for regulating pH and also for depressing flotation of pyrites. Bulk flotation is then followed by separation of copper and molybdenum minerals by differential flotation using specific depressants. With the exception of Utah, which uses starch for depression of molybdenum and recovers it from tailings of copper, all other operations use reagents which inhibit flotation of copper and iron sulphides without altering the flotation characteristics of molybdenite. Principal reagents used for this purpose are sodium sulphide and its mixture with polythiophosphates and polythioarsenates. Another group comprises NaCN and its complex salts with iron and zinc. Concentrates produced as a by-product from copper-moly ore processing contain 70-90% MoS_2 and the yield varies from about 20 to 80% with an average of 55% for plants in the United States. Almost half of the molybdenum values of run of mine are lost at the bulk flotation stage, due to lack of liberation, large flake size, and oxide coating on ore particles. These losses are difficult to control because the processing scheme is usually designed to affect optimum recovery of the major mineral. It is generally observed that Mo recovery increases as the copper content of the ore body decreases.

All physical beneficiation treatments essentially yield two grades of concentrates – a high grade concentrate assaying over 90% and a low grade concentrate assaying less than 90% MoS_2. Further processing by chemical methods is dependent on the starting grade of the concentrate. In addition to recovery of molybdenum from the conventional high grade and low grade concentrate sources, there has been increasing interest in the recovery of molybdenum from lean ores or even from waste from the existing ores. Consequently, much attention has been given to chemical treatment of such molybdenum as had hitherto been considered economically less exploitable. The chemical beneficiation treatments usually involve a combination of one or more metallurgical operations to yield a suitable purified molybdenum compound which may be molybdic oxide or a molybdate compound.

Chemical Processing:

Molybdenum concentrate is generally processed by chemical methods prior to usage in any industrial applications. Even when used in the form of sulphides – as a catalyst or lubricant – it requires acid leaching and drying for removal of undesirable impurities such as oxides, some metallic impurities, and oils. For any other applications the concentrate is processed either by pyro-chemical, hydrometallurgical, or electrometallurgical techniques, or a combination of these, to yield an oxide or oxidic compound which then becomes the source for any usable molybdenum products /18/. Figure 1 schematically represents processing schemes for treatment of molysulphide.

Processing High Grade Concentrate:

High grade molysulphide concentrate is usually roasted in multihearth roasters of the Nicholas Herreshoff type, to remove sulphur and convert it to technical grade

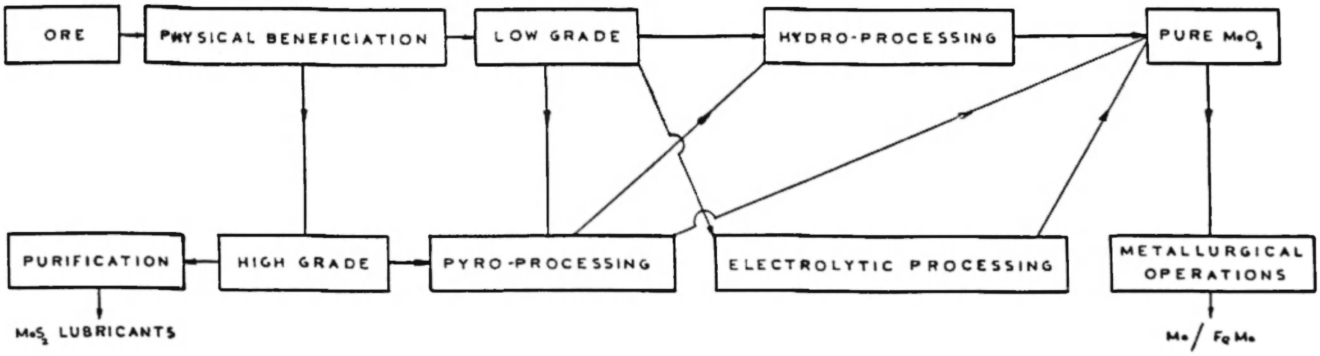

Fig. 1. Processing scheme for treatment of molysulphide.

molyoxide. The roasting operation is autogenous and requires no additional heat after initial preheating. However, the treatment requires careful regulation of temperature (about 873 K) to prevent agglomeration, melting and sublimation of oxide at higher temperature, and slow reaction kinetics and incomplete removal of sulphur at lower temperature. In recent years, greater emphasis has been laid on the adoption of fluid beds for roasting /19-22/. These processes offer many advantages such as higher throughput, excellent thermal properties and better process control. Due to optimum temperature control and near absence of solid state reactions inside the fluidized bed, calcines are generally free of molybdenum dioxide and insoluble molybdates of calcium, lead, and iron which are inevitable when using multihearth roasters. Also, the off-gases have a high sulphur dioxide content, making them suitable as a feed for use in sulphuric acid production.

Molybdic oxide (technical grade) produced either by multihearth or fluid bed roasting, retains practically all the impurities of the concentrate except the sulphur, and is considered acceptable for either direct addition to iron and steel or for addition after conversion to ferromolybdenum. The oxide, however, requires further treatment for use in producing metal. Purification can be either by a combination of sublimation and hydrometallurgical processing, or by hydrometallurgical processing alone. In the first case /22/, 99% pure molyoxide is initially prepared by sublimation in special furnaces at 1373 K – 1473 K. The sublimed oxide is then purified by a hydroprocess involving dissolution in ammoniacal solution, crystallizing ammonium paramolybdate and finally calcining it at about 773 K to yield pure oxide. In the second case /23/, the technical grade oxide is initially dissolved in ammonia solution to form ammonium molybdate and then precipitated as molybdic acid by addition of concentrated nitric acid. The molybdic acid, after washing, is redissolved in ammonia water, concentrated, crystallized and filtered. Ammonium paramolybdate crystals so obtained are then calcined at 973 K to yield pure molybdic oxide.

Processing Low Grade Concentrate and Other Sources:

The techniques of obtaining an acceptable grade oxide intermediate from the low grade molysulphide concentrates and ores have been comparatively more difficult, though many processes based on a combination of pyro-, hydro- and electro-chemical processing have been developed. Some processes that have good promise for scaling up are (a) roasting and leaching, (b) alkali fusion, (c) acid bake leaching and flotation, (d) chlorination, (e) acid leaching, (f) alkali leaching, (g) hypochlorite leaching and (h) electro-oxidation. These are shown in a simplified form in Figure 2.

(a) Roasting and Leaching

This process aims at recovery of molybdenum in the form of calcium molybdate from low grade sulphide concentrates. The process starts with molybdenite calcines being dissolved in soda ash solution and thus precipitating molybdenum in the form of calcium molybdate by addition of calcium chloride to the leach solution. For optimum recovery it is necessary to maintain the pH at 7 to 8 and the temperature of the solution at 363 K. The precipitated calcium molybdate is finally calcined at 1073 K – 1173 K /30/. A variation of this process /25/ uses iron chloride in place of calcium chloride to precipitate ferrimolybdate salts in acidic media (pH 1 to 2.8). The type of compound depends on the pH of the solution. Ferrimolybdate salts thus obtained require calcination at 773 K to remove water molecules resulting from hydration.

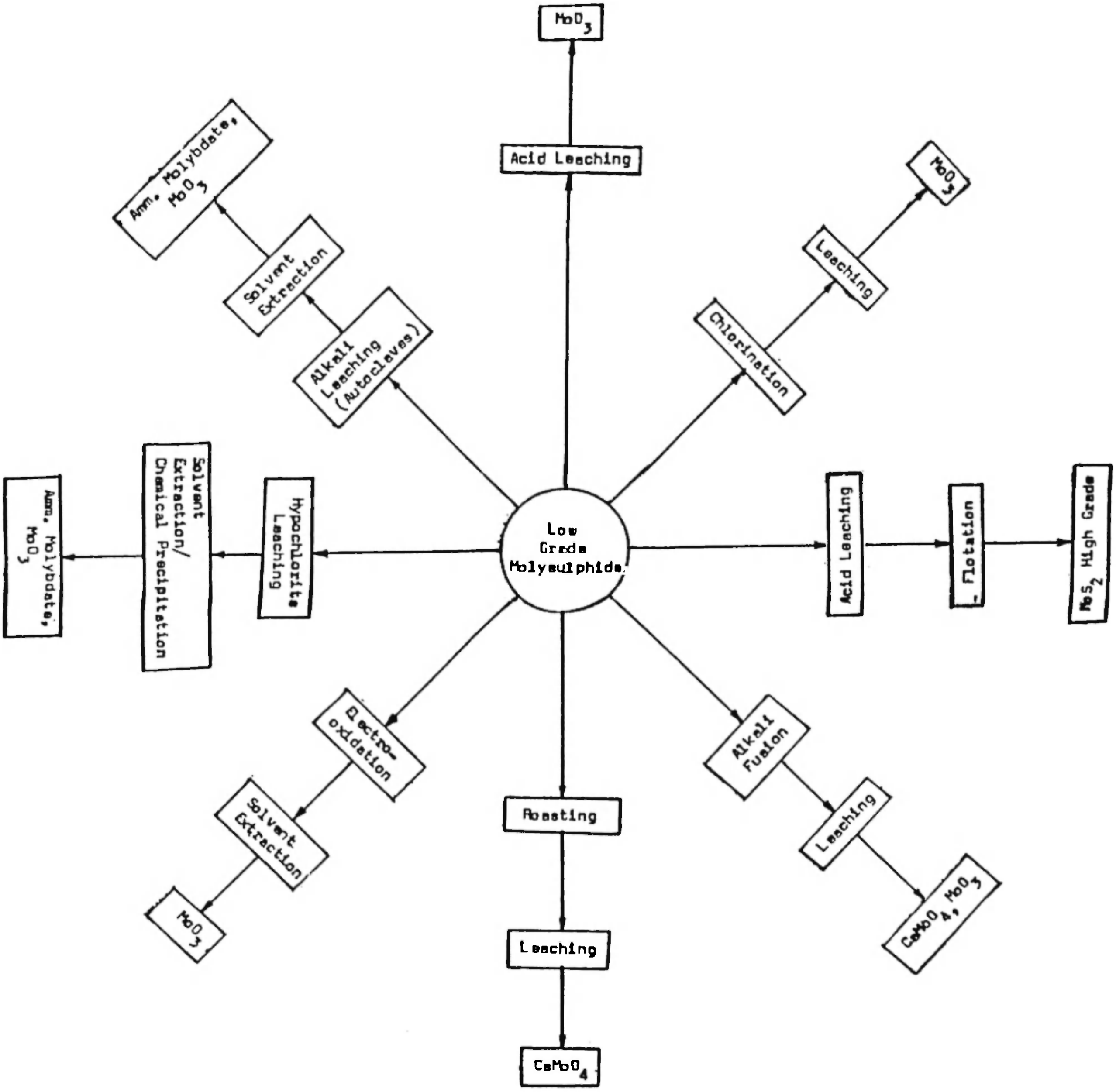

Fig. 2. Processes for the treatment of low grade molysulphide concentrate.

(b) Alkali Fusion

In this process molysulphide is fused with soda ash in the presence of either sodium nitrate or iron oxide /22,26/. The fused mass is digested with hot water to take molybdenum in solution. After liquid-solid separation, ammonia or calcium chloride is added to precipitate molybdenum either as ammonium molybdate or as calcium molybdate. One of the main attractions of this process is that no off-gases are generated, and sulphur is fixed, as sodium sulphate when using sodium nitrate additive, or as iron sulphide when using iron oxide.

(c) Acid-Bake Leaching and Flotation

Low grade and off-grade molysulphide concentrates are digested with hot concentrated sulphuric acid at 473-563 K to convert sulphides of iron, copper and lead to respective sulphates, leaving the molysulphide unaltered /27/. The molybdenum value is freed of its sulphate associations by repeated leaching with water to dissolve iron and copper sulphates, and brine solutions to solubilise lead sulphate. A high grade concentrate is finally obtained by subjecting the residue to froth flotation.

(d) Chlorination

Chlorination as an alternative to roasting for metal sulphides offers many attractions such as relatively low temperature of operation, suitability of application to low grade resources, convenience of recovering sulphur in non-polluting form and also the possibility of obtaining pure chloride by simple distillation. Development of this process for recovery of molybdenum has been rather limited. The only work which reportedly treated low grade molysulphide concentrate involved chlorination of molysulphide in the presence of oxygen at a temperature of about 573 K /28/. This treatment resulted in selective volatilisation of molybdenum oxychloride (MoO_2Cl_2). The oxychloride itself can be used for the recovery of molybdenum metal or converted to more conventionally usable forms such as molybdic oxide or oxidic compounds by simple hydrometallurgical processing.

(e) Acid Leaching

Several patented processes have been developed for the treatment of molysulphide by nitric acid. In one of the processes,molybdenite concentrate is leached with nitric acid under high pressure conditions in the presence of oxygen or oxygen-containing gases. Nitric acid, in fact, acts as a catalyst in the process. Solubilised molybdenum and rhenium (if any) are then recovered by a sequence of chemical reactions and solvent extraction. Moly-corp of America has adopted a variation of this process called Cymoly Process /30/ in a semi-commercial pilot plant. Operations of this plant have proved the chemistry and several advantages are likely to accrue from the adoption of this process. However, the economics of the plant are questionable at present. With further developments in technology and stricter control on environmental pollution, the process may receive attention in future.

(f) Alkali Leaching

This is essentially an aqueous autoclave oxidation process /29/ in which molybdenite concentrate – sodium hydroxide slurry is treated at 473 K under an oxygen overpressure of 21-28 kg/cm^2 (300-400 psi) in an autoclave. After completion of oxidation, the slurry is discharged and molybdenum recovered as ammonium di-molybdate from the leach liquor by solvent extraction and crystallisation.

(g) Hypochlorite Leaching

In hypochlorite leaching /30,31/, molybdenite is oxidized – sulphur to sulphate ions and molybdenum to molybdate ions, the leachant hypochlorite is consumed almost entirely by the molybdenite and very little, if any, by gangue minerals. The leaching rate has been observed to increase with increasing concentrations of the hypochlorite and the purity of the molybdenite. The consumption of hypochlorite and leaching rate are, however, independent of the grade of the concentrate. These characteristics have made the process attractive for molybdenum recovery from very poor molybdenum resources or even from complex ores. Molybdenum from the leach solution is usually recovered by ion exchange. Hypochlorite reagent costs have so far prevented serious consideration for commercialisation.

(h) Electro-oxidation

There have been arguments against the hypochlorite leaching process because of high reagent cost. In this context electro-oxidation /34,35/ is an interesting variation of hypochlorite leaching. The process aims at generation of hypochlorite in situ during leaching. Briefly, the treatment consists of electrolysing brine solution-ore pulp using graphite electrodes at a temperature of 303 to 323 K. In the process sodium chloride is oxidized to hypochlorite, which in turn solubilizes molybdenum, leaving the impurities unchanged. After leaching and liquid-solid separation, excess chlorite ions are chemically reduced by sulphurdioxide to prevent interferences in subsequent chemical reactions. During the leaching process, frequent additions of sodium carbonate are made to maintain the solution pH at between 6 and 8. Power consumption under optimum conditions has been estimated at about 30 kwh, and sodium carbonate consumption is about 4.5 kg per kg of molybdenum extracted. The molybdenum recovery from leach solution is affected either in the same way as that of hypochlorite or by using solvent extraction with an amine extractant and stripping with ammonium hydroxide to yield ammonium molybdate solution. Ammonium molybdate solution is then processed to ammonium salts and/or molybdic oxide. The process has extensive upgrading capabilities (it can treat ores or concentrates with as low as 0.35% MoS_2), yield very high recoveries (over 98%), is applicable for simultaneous recovery of rhenium values, and fixes sulphur as sodium sulphate, thus reducing environmental pollution.

PRODUCTION OF METALLIC MOLYBDENUM

Molybdenum from naturally occurring ores after preliminary ore processing is in the form of either sulphide, oxide or oxidic compounds, as has been shown in the previous section. These compounds serve as the starting material for producing molybdenum metal, ferromolybdenum or molybdenum compounds for commercial use. This paper is concerned only with the production of metallic forms, i.e., molybdenum metal and ferromolybdenum, which can be obtained from the said compounds by way of the chemical and/or electrochemical methods. Some of the more common methods can be classified as processes based on reduction with non-metals, metallothermic reduction, electro-metallurgical and other miscellaneous processes.

Processes Based on Reduction with Non-Metals:

Thermodynamic and thermochemical considerations indicate that molybdenum oxide and oxidic compounds are easily reducible with non-metallic reductants like hydrogen, carbon and carbonaceous gases. The reduced metal/alloy in such reduction processes is always a powdery product, due to insufficient reaction heat and non-requirement of very high temperature for completion of reduction reaction before the melting point of the metal.

Molybdenum is industrially produced by hydrogen reduction of pure molybdic oxide in static bed reactors. The reaction proceeds in two stages as indicated below:

$$MoO_3 + H_2 \; 783K \; MoO_2 + H_2O + 22150 \text{ Cal} \; .... \; (1)$$
$$MoO_2 + H_2 \; 1088K \; Mo + 2\,H_2O + 20500 \text{ Cal} \; ... \; (2)$$

The reaction (1) is highly exothermic and, if not properly controlled, is likely to result in fusion or sintering of the oxide beds, causing reduction mainly due to the lack of access of reductant to the reaction site. These difficulties of dissipation of excess heat and fusion or sintering of particles can be conveniently avoided by using the fluid bed reduction processes which have now appeared on the industrial scene /34/. These fluid bed processes have also found application in molybdenum production. In addition to molybdic oxide, oxidic compounds like calcium molybdate /37/ and ferrimolybdate /25/ have also been used for production of molybdenum and/or ferromolybdenum. The use of these compounds not only makes it possible to treat the intermediates derived from processing of low grade ores but also offers the benefit of modifying the deleterious effects of high exothermicity. Direct hydrogen reduction of molysulfide is apparently not feasible, but the use of a fluid hydrogen makes the reaction thermodynamically feasible. In a process reported by Srinivasan, Mukherjee and Gupta /38/, the reduction was performed at a temperature of 1623 K using a large excess of hydrogen. In another work, Habashi and Dugdale /39/ have shown that hydrogen reduction of molysulphide can be accomplished at lower temperature using lime as a getter for sulphur. Reduction at 1073 K in the presence of stoichiometric amounts of lime resulted in the removal of about 40% of sulphur from the sulphide concentrates.

The hydrogen reduction process, particularly that based on static bed or fluid bed reduction of molybdic oxide, is commercially well-established, but suffers from a drawback in that it yields a non-uniform product of varying purity. Considerable efforts are therefore being made to explore alternative processes for metal extraction.

Reduction of molybdenum compounds with carbon is another approach for producing molybdenum powder. Here, of course, the removal of residual carbon is extremely difficult. However, use of carbon as a reductant is made in deoxidising the mtal, which is an important step in refining to obtain consolidated metal. For example, tonnage quantities of arc-cast molybdenum metal and its alloys are currently being made by adding a computed quantity of carbon and the alloying elements, if necessary, to the consumable electrode metal prior to melting. The arc-cast ingots are usually extruded, rolled or forged to the desired shapes and sizes.

Metallothermic Reduction:

Metallothermic reduction processes have been extensively investigated for the production of molybdenum metal in a consolidated form. The choice of reduction is dependent on the starting material and on the post-reduction refining process to be employed.

Tables III and IV show free energy /40-46/ data for various compounds which can be used for selecting the reductants. For oxide and oxidic compounds calcium, magnesium, aluminium, silicon, are usually employed, whereas such additional reductants as sodium, manganese, zinc, lead, tin, could also be used for carrying out reduction of sulphides.

Metallothermic reduction of molybdic oxide was first reported thirty years ago by Gilbert and Block /44/. The process involved calciothermic reduction of molybdic oxide in a closed reactor (bomb) using iodine as a thermal booster. Good quality metal was finally obtained

TABLE III
Standard Free/Energy of Formation of Oxides
(Expressed per g - Atom of Oxygen)

Oxide	$-\Delta G^\circ_T$, Kcal/g-atom of Oxygen			
	298°K	500°K	1000°K	1500°≫
□°O_3	54.01	49.9	40.3	32.67
MoO_2	59.15	55.75	47.0	38.5
$CaMoO_4$	86.25	–	–	–
H_2O	56.72	52.15	45.8	38.65
CO_2	47.12	47.2	47.3	47.38
CO	32.8	37.1	47.95	58.4
A12O3	126.0	120.67	108.33	95.37
MgO	136.1	131.0	118.05	101.70
CaO	143.2	138.25	126.05	113.35

TABLE IV
Standard Free Energy of Formation of Sulphides
(Expressed per g – Atom of Sulphur)

Sulphide		$-\Delta G^\circ_T$, Kcal/g-atom of sulphur				
	298°K	1073°K	1173°K	1273°K	1373°K	1500°K
MoS_2	–	21	20.25	19.75	19.0	–
Mo_2S_2	–	24.6	–	–	–	15.53
H_2S	19	8.75	7.5	6.75	5.5	4.0
SnS	19.7	–	–	–	–	–
PbS	32	17.5	15.25	13.0	11.0	–
ZnS	53.5	36	33.5	28.5	23.5	21.0
MnS	59.5	47.5	46.0	44.5	42.5	40.7
Al_2S_3	66.0	–	–	–	–	–
MgS	93	77.5	72.5	70.9	67.5	–
Na_2S	95.5	72	68	65	55.25	49.4
CaS	123	105	102.5	100	97.5	90.1

by remelting and purifying the reduced metal. In a variation of this process, a mixture of molybdic and molybdenum dioxide was reduced with magnesium /45/ using lime as a heat diluent to decrease the effect of pressure rise (due to high volatility of magnesium) during the reduction process. First recorded work on the use of aluminium as a reductant for obtaining consolidated molybdenum was by Gupta and Jena /46/. The process essentially involved reduction of molybdic oxide in an externally heated closed reactor to yield consolidated molybdenum, which was further purified and consolidated by melting. Wilhelm et al /47/ further investigated a metallothermic process based on aluminium, silicon and aluminium-silicon as reductants. The results showed that the use of aluminium in excess of stoichiometric requirements increased the yield of molybdenum but resulted in increased contamination of the metal by residual aluminium. The use of silicon as such was not successful, but co-reduction with aluminium and up to 50% silicon did yield molybdenum in a consolidated form. The metal associated with excess reductants was finally refined by a combination of vacuum degassing and electron beam melting. In fact, the use of aluminium offers many advantages such as relatively low cost per chemical equivalent, availability in high purity, ease of handling and relatively low vapour pressure. These have therefore led to the development of new aluminothermic processes based on open vessel reduction which are relatively simple to carry out and easy to scale up. Open vessel reduction, however, imposes a limitation on the starting material. Molybdic oxide, while suitable and widely used for closed bomb reduction, is prohibited in open vessel reduction processes because of excessive losses due to its high volatility. The choice of molybdenum oxide compounds for open aluminothermic reduction has therefore been restricted to relatively non-volatile compounds like molybdenum dioxide and calcium molybdate for the production of molybdenum, and any of these or ferrimolybdate for the production of ferromolybdenum. The use of calcium molybdate and ferrimolybdate which are generated as intermediate compounds during processing of low grade ores, would also avoid extraneous addition of either lime or iron oxide. The processes based on the technique of open aluminothermic reduction using molybdenum dioxide /48/, calcium molybdate /47/ and ferrimolybdate /25/ have been recently published in the literature. Ferromolybdenum, the form in which molybdenum is mostly used, is industrially produced by aluminothermic reduction of oxide or oxidic compounds. Some quantities of reductant aluminium are usually substituted by ferrosilicon with great advantages in costs and processing conditions. The process essentially consists of charging the reaction feed comprised of molybdic oxide, iron oxide, aluminium, ferrosilicon and fluxes like lime and fluorspar into the reaction furnaces. The reaction furnace is a bottomless, brick-lined steel shell placed on a sand bed in a mould box. The reaction is initiated by electrical firing or by a trigger mixture of potassium chlorate and aluminium. A variation of the procedure of running the thermit charge involves starting the reaction with part of the charge and, after the reaction stabilises, adding progressively the remainder of the main charge.

In the metallurgical processing scheme, recovery directly from molysulphide would be a more attractive proposition than through oxides. The table on free energy data shows that molysulphide is reducible with calcium, magnesium, aluminium, sodium, manganese and zinc. In the case of other reductants, such as lead or tin, production of molybdenum is feasible by continuously removing the respective volatile sulphides from the reaction site. Nachtman and Poole developed two metallothermic processes, one based on lead /50/ as the reductant in a flowing atmosphere of hydrogen, and the other based on tin /51/ as a reductant in a dynamic vacuum. In both the processes the reduction reactions were carried out at a temperature of 1523-1773 K. In a variation of these processes, Abraham and Krey /52/ examined the use of tin as a reductant on a pilot scale, using flowing hydrogen as a carrier gas for the removal of reaction products. These processes, however, did not receive any consideration for industrial applications because of economical disadvantages of the high volatility of lead, which resulted in excessive losses and the very high cost of tin as a reductant. Fosse and Hobin /53/, patented a process on the reduction of molysulphide with sodium in the presence of sodium chloride. The first attempt to produce massive molybdenum from molysulphide concentrate by aluminothermic reduction was by Mehra, Gupta and Jena /54/. In the process, an aluminothermic charge was admixed with adequate amounts of calcium and sulphur to provide sufficient heat and also to facilitate low temperature initiation of the reaction inside an externally heated reactor. Good quality metal was finally obtained by electron-beam melt refining. Venkataramani, Bose and Jena /55/ succeeded in preparing molybdenum in powder form by vacuum thermal reduction of molysulphide with aluminium. The reacted product was acid-leached for metal recovery. Haver, Uchida and Wong /22/ reported a process on aluminothermic reduction of stoichiometrically composed pellets of molysulphide and aluminium at a temperature of about 1073 K. The reaction products, an impure molybdenum alloy and aluminium sulphide, were subsequently treated with water. The hydrolysis of aluminium sulphide resulted in the formation of hydrogen sulphide which was considered suitable for further conversion to elemental sulphur. The residue from the hydrolysis was oxidised, then treated with aqueous ammonia and finally calcined to recover high purity molybdic oxide. Mukherjee and Gupta /56/ successfully demonstrated a process for producing consolidated molybdenum by open aluminothermic reduction of molysulphide using potassium chlorate as a heat booster. The product analysed at 29% aluminium was subsequently purified to 99.99% pure molybdenum by electrorefining in a molten halide electrolyte.

Table IV sums up the results on metallothermic reduction processes developed for production of molybdenum. From the results it can be seen that the metallic product invariably requires further treatment to remove excess reductant and/or unreduced starting compound. This has been achieved mostly by adopting a melting route wherein the impurities volatilise off preferentially. Excess oxygen, if present, can be removed either by sacrificial deoxidation through volatilisation of molybdenum oxides or by addition of calculated amounts of carbon. In some cases electrorefining has been employed in place of melting, but the product in such cases is molybdenum powder.

In the process metallurgy of molybdenum there has been an increasing interest in the use of electrolytic methods for metal production, mainly from the point of view of developing a continuous or semi-continuous

TABLE V
Data on Metallothermic Reduction of Molybdenum

Reductant	Mode of reduction	Molybdenum compound for reduction	Procedure	Stoichiometric reductant %	Yield %	Analysis		Post reduction refining	Reference
						Reductant %	Oxygen %		
Calcium	Closed	MoO_3	Externally heated using thermal booster	100	–	0.01-0.1	0.007	Arc melting	44
Magnesium	Closed	MoO_3,MoO_2	By trigger mixture	–	97	0.01-0.70	0.025	Arc melting	45
Aluminium	Closed	MoO_3	External heating	100	71	0.18	0.09	Arc and electron beam melting	46
	Closed	MoO_3	By trigger mixture	100	82	0.08	2.1	Arc and electron beam melting	47
	Closed	MoS_2 conc.	External Heating	100	90	0.27	–	Arc and electron beam melting	54
55	Under vacuum	MoS_2 conc.	By heating to 1773K	110	90	0.31	–	Pyro vacuum treatment and electron beam melting	
	Open	MoS_2 conc.	By trigger mixture	150	90	29	–	Fused salt electrolysis and electron beam melting	56
	Open	$CaMoO_4$	By preheating and trigger mixture	120	98.5	3.1	0.1	Electron beam melting; fused salt electrolysis	49
24	Open	$CaMoO_4$	By trigger mixture	100	96	0.8	–	Ferromolybdenum	
25	Open	Ferrimolybdate	By trigger mixture	120	–	1.0	–	Ferromolybdenum	
Aluminium-Silicon (Al-50% Si)	Closed	MoO_3	By trigger mixture	113	93	0.1 Al 5.3 Si	0.27	Electron beam melting	47
Lead	Flowing H_2 reactor	MoS_2	By heating at 1523-1773K	–	–	–	–	–	50
Tin	Vacuum	MoS_2	By heating at 1523-1773K	–	–	–	–		51
Sodium	Closed	MoS_2	By heating	–	–	–	–		53

processing scheme. Early attempts to produce pure molybdenum electrodeposits from aqueous or organic baths either results in no deposition at all or deposition of small amounts of oxidised metal /57,58/. This was due to the fact that the deposition potential of molybdenum oxide is lower than that of the metal. Successful molybdenun electrodeposition has only been accomplished in fused electrolyte systems comprising either oxyanionic or halide salts. The oxyanionic salts have relatively low electrochemical stability, but even then these are suitable for use in electrodeposition of molybdenum because of the very low decomposition potential of molybdenum oxides. The oxyanionic electrolytes are considered suitable for electrowinning of molybdenum only, and not for electrorefining. In the latter process, with the progress of electrolysis, there would be considerable depletion of molybdenum through simultaneous ion transfer from soluble anode and from the electrochemical decomposition of molybdenum oxide from the electrolyte, thus making it impossible to continue electrolysis after a while. The halide electrolytes offer the advantage of low-temperature operation, better conductivity and stability as compared to the oxides. The main difficulty, however, is the retention of highly volatile molybdenum halide in the bath. This was first resolved by Senderoff and Brenner /59/ by complexing the molybdenum trichloride. This type of electrolyte could be successfully used for electrorefining and electroplating, i.e., in the processes using soluble anodes in which the electrolyte acts as a vehicle to transport molybdenum from anode to cathode. The halide electrolyte was found unsuitable for electrowinning because the decomposition of electrolyte resulted in generation of chlorine at the anode, which in turn led to the oxidation of trichloride salt to highly volatile pentachloride, thus causing depletion of molybdenum salt. Considering all these aspects it can be said that oxyanionic electrolytes have established themselves as the most suitable for electrowinning, while the halide electrolytes are found in processes based on the use of soluble anodes. To date an impressive record of work has been reported in the field of electrochemical behaviour in halide baths /60-65/ and electrodeposition of molybdenum from both the oxyanionic and halide fused salts. The developed processes can be broadly defined as electrowinning and electrorefining.

Electrowinning:

Molybdenum electrowinning processes based on the use of molybdic oxide or oxidic compounds or molysulphide dissolved in oxide bath have been extensively investigated. The first reported work on the electrowinning of molybdenum is credited to Zadra and Gomes /66/. The process essentially involved deposition of pure tungsten and molybdenum from molybdenum-bearing scheelite concentrate dissolved in a molten sodium pyrophosphate-sodium metaphosphate-sodium chloride bath in open electrolytic cells. This process was later extended by Heinen and Zadra /67,68/ to the use of molybdic oxide of varying purity. A high purity molybdenum metal was deposited on the cathode of high current efficiency. But the degradation of the electrolyte and erratic metal to cathode adherence did not permit smooth operation of the cell for prolonged periods. In a subsequent work Heinen and Baker /69/ circumvented these problems by altering the electrode configuration. They operated the cell continuously for prolonged periods without any deterioration in the quality of the metal deposited or of the electrolyte. The use of calcium molybdate for electrowinning of molybdenum was demonstrated by Khlebnikov and Nadol'skii /70/. The metal was produced in a laboratory by inert atmosphere electrolysis of calcium molybdate dissolved in calcium chloride. Heinen, Barbar and Baker /71/ reported the recovery of molybdenum as dimolybdenum carbide by electrolysis of molysulphide dissolved in fused halide-carbonate-tetraborate electrolyte. The electrolysis was conducted in an open atmospheric electrolytic cell at a temperature of 1273 K. Electrosynthesised carbide was reacted with molybdic oxide at 1773 K in an inert atmosphere to produce molybdenum metal. Suri, Mukherjee and Gupta /72/ demonstrated a workable process for the preparation of molybdenum from sodium molybdate. The process involved electrosynthesis of molybdenum carbide from sodium carbonate, sodium tetraborate, sodium fluoride and potassium fluoride. The carbide was then admixed with monitored amounts of molybdenum dioxide and subjected to vacuum thermal sintering treatment, to yield good purity molybdenum metal.

Electrorefining:

Electrorefining of molybdenum essentially comprises two different processes — one concerned with the dissolution of molybdenum and the less noble impurities (more noble impurities being left behind in the anode sludge) from the anode and the other involving electrodeposition at the cathode of molybdenum and the more noble metals present in the electrolyte. The refining process is therefore highly selective. The purity of product and the success in operation are dependent on the potential of the operating electrode and the relative concentration of the various species at the electrodes. Extensive studies on electrorefining of molybdenum in various molten halide electrolytes in inert atmospheric electrolytic cells have been reported by Cummings, Cattoir and Sullivan /73/. Metal with 99.99% purity can be obtained from halide electrolytes composed of a mixture of alkali metal chlorides and a molybdenum-bearing complex of molybdenum trichloride with one of the alkali metal chlorides. Amongst the electrolytes investigated, the KCl-K_3MoCl_6 electrolyte was considered the best from the point of view of ease of preparation, product quality and the type of the deposit. The results of these findings have been further substantiated by several investigators /49,56,74/, who have independently carried out electrorefining studies on different types of anode feed. In practically all the cases, high purity metal was readily obtainable, though the anode feed and/or electrolyte contained substantial quantities of one or more of impurities such as tin, iron, copper, nickel, silicon, aluminium, oxygen and sulphur.

An interesting variation of the electrorefining process is the soluble anode electrolysis of molybdenum, in which compounds of molybdenum serve as soluble anodes in place of impure or scrap molybdenum. In these processes, molybdenum solubilises from the anode and is deposited at the cathode without electrochemical decomposition of the electrolyte, as is the case in the conventional electrorefining process with impure metal. Extensive work on electrolytic processes using carbide /75,76/, oxide /77,78/ and sulphides /59,76/ has been reported from the authors' laboratories. The theoretical energy requirement for the conduct of the process can be estimated from the free energy of formation of the chosen compound. Considering a typical case of electrodeposition from molybdenum carbide the requirement of voltage can be computed:

$$½Mo_2C = Mo + ½C$$

$$\Delta G^{\circ}_T = -nFE^{\circ}_T \text{ x } 0.24$$

where ΔG°_T = standard free energy of formation of the metal compound at T K in calories

n = number of electrons involved in the reaction = 3 in this case

F = Faraday constant, 96500 coulombs

E°_T = standard emf for decomposition of metal compound at T°_K in volts

$$E^{\circ}\text{-}6_T = -1.445 \text{ x } 10^{-5} \text{ x} \Delta G^{\circ}_T$$

For Mo_2C at 1200 K, E°_T = 0.0217 volt

Theoretical potentials required for deposition from different compounds are presented in Table VI. The actual deposition potentials are substantially higher than these values on account of polarisation and other losses. The applicability of such a process is dependent not only on the decomposition potential of the chosen compound and that of the electrolyte, but also on the physical and chemical properties of the soluble mode. The anode material should have good electrical conductivity, and be chemically compatible with the electrolyte. Among the compounds that have been investigated, molybdenum carbide and molybdenum sesquisulphide have good electrical conductivity, but the oxide and disulphide do not. For imparting electrical conductivity to the electrodes formed from these compounds, a compacted mix of the compound and carbon was prepared in which carbon provided conducting pathways, thus enabling the molybdenum compounds to loose electrons at the anode. The electrochemical reactions for the deposition of molybdenum can be presented as /77/:

At the anode

For carbide:

$Mo_2C+9Cl^- \rightarrow Mo_2Cl_9^{3-}+ 6\text{ e-} + C$ . . . . (3)

For Oxide:

$MoO_3+C \rightarrow MoO_2+CO/CO_2$

$MoO_2+C\beta MO + CO/CO_2$

$2\text{ Mo} + 9\text{ Cl-} \beta Mo_2Cl_9^{3-} +6e-$ . . . . (4)

For sulphide:

$2\text{ MoX}_2+9Cl\text{-} \beta\ Mo_2Cl_9^{3-}+6e\text{-} + 4S(5)\ Mo_2S_3+9Cl\text{-} \beta\ Mo_2Cl_9^{3-}$
$+ 6\text{-} + 3S$ . . . . (6)

All these anodic reactions furnish molybdenum anions at the anode. The cathodic reaction corresponding to all the anodic processes is essentially the metal deposition reaction, which, after the work of Senderoff and Mellors /80/ can be represented as:

$Mo_2Cl_9^{3-}+ 3Cl\text{-} = 2(MoCl_6)^{3-}$ . . . .(7)
$\square^{\propto=}l_6^{3-} 3CL\text{-} = Mo + 6Cl\text{-}$. . . . . (8)

In all cases, a good quality metal was obtained at high efficiency and yield.

Table VII presents a brief summary of all the investigations carried out in the electrolytic methods for the preparation of molybdenum. The results clearly show that the methods based on soluble anode electrolysis of molybdenum compounds offer attractions for scaling up.

Miscellaneous Processes:

It is known that molysulphide can be thermally decomposed /81/ to produce metallic molybdenum and

TABLE VI

Values of Standard E.M.F. for Decomposition of Various Molybdenum Compounds

Compound	Decomposition Reaction	ΔG°_{1200K},Cal	$-E^{\circ}_{1200K}$,Volts
Mo_2C	$½Mo_2C=Mo^{\circ}+½C$	1500	0.0217
MoO_2	$MoO_2=Mo^{\circ}+2O$	87500	1.264
Mo_2S_3	$½Mo_2S_3=Mo^{\circ}+3/2\ S$	31845	0.46
MoS_2	$MoS_2=Mo^{\circ}+2S$	20370	0.60

TABLE VII
Data on Electrometallurgical Methods for Preparation of Molybdenum

Process	Electrolyte	Molybdenum content %	Anode	Temperature of operation K	Voltage	Metal recovery %	Current efficiency %	Purity of product %	Reference
Electrowinning	$NaCl$-NaF-Na_2B_4O7	10 MoO_3	Graphite	1273	4.7	–	98	99.9	68
	$NaCl$-NaF-$Na_2B_4O_7$	7.5 MoO_3	Graphite	1273	8-12	88	91	99.8	69
	$CaCl_2$-$CaMoO_4$	15-70 $CaMoO_4$	Graphite	1323	–	>80	–	99.9	70
	KCl-KF-Na_2SiO_3	7.5 MoS_2	Graphite	1273	1.0	0.3g/Amp-hr Mo_2C	–	–	71
	NaF-KF-$Na_2B_4O_7$ Na_2CO_3	10 MoS_2	Graphite	1273	1.0	0.42g/Amp-hr Mo_2C	–	–	71
	NaF-KF-$Na_2B_4O_7$ Na_2Co_3	16 Na_2MoO_4	Graphite	1233	0.5-1.0	0.50g/Amp-hr-Mo_2C		–	72
Electrorefining	$NaCl$-KCl-K_3MoCl_6	2.9-10.5 Mo	Mo Scrap	1073-1113	–	–	54-91	99.99	73
	$RbCl$-Rb_3MoCl_6	0.8-3.8 Mo	Mo Scrap	1123-1173	–	–	13-95	99.99	73
	KCl-K_3MoCl_6	1.7-5.9 Mo	Mo Scrap	1043-1173	–	–	60	99.99	73
	KCl-K_3MoCl_6	7.5 Mo	Thermit Mo	1173	0.6-0.75	60	70	99.9	49
Soluble anode electrolysis	KCl-K_3MoCl_6	7.5 Mo	Mo_2C	1200	0.8-1.1	71	60	99.95	75
	KCl-K_3MoCl_6	7.5 Mo	MoS_2-C	1173	0.7-0.8	82	50	99.9+	56
	KCl-K_3MoCl_6	7.5 Mo	Mo_2S_3-C	1173	1.0-1.2	75	84	99.9+	78
	KCl-K_3MoCl_6	7.5 Mo	MoO_3-C	1223	0.25-0.40	94	97	99.95	78

sulphur. A process based on such thermal decomposition would be more attractive as it would avoid conventional oxidation, purification of oxides and reduction steps. The quality of product through such a direct sulphide process is likely to be quite superior as compared to the conventionally produced metal because of the total elimination of oxygen through the processing scheme. Based on these considerations, Scholz, Doane and Timmons /82/ reported results of investigations carried out on a fairly large scale. The process involved thermal decomposition of molysulphide under a dynamic vacuum at a temperature of 1773-1873 K. The process could not be commercialised mainly because of operating difficulties, non-availability of suitable container materials at operating temperatures, reactions kinetics, etc. Since the decomposition reaction becomes more favourable at higher temperatures due to favourable energetics and kinetics, this prompted Husaka and Clump /83/ to investigate decomposition of molybdenum disulphide in an induction-coupled argon plasma. The laboratory studies showed the possibility of obtaining a conversion as high as 70% with almost quantitative recoveries. They further suggested that direct production of molybdenum would require plasma reactors with much larger diameter than the one they had used.

RECYCLING OF MOLYBDENUM

The electrical furnace industry and the lamp filament industry generate substantial quantities of molybdenum waste, in the form of scrap and acid leach liquor respectively. With increasing awareness of the need for total resource utilisation, and ecological and economic considerations, it has become important to recover and recycle molybdenum. Fresh scrap is usually routed through a melting process whereas used scrap is first oxidised, and then passes through the entire sequence of the normal process flowsheet. The oxidation step poses difficulties for massive types of scrap, so an alternate wet route was developed by Mukherjee, Bidaye and Gupta /84/. In this process the scrap is dissolved in an acid mixture comprising sulphuric acid and nitric acid under a total reflux system. The leach liquor is then processed for recovery of molybdenum.

Leach liquor from the lamp filament industry contains about 200 g/litre of molybdenum with 33% nitric acid and 37% sulphuric acid. Kulkarni /85/ had devised a method of recovering 98% of molybdenum by neutralising the spent acid with ammonia and precipitation of ammonium tetramolybdate. The process required large quantities of ammonia and was not considered applicable to recovery of acid, thereby adversely affecting the economics. An alternate system was developed by McCarty /86/ which involved precipitation of molybdic oxide from the spent acid by heating leach liquor to boiling for a long enough time. The oxide is then filtered and separated from the original liquor which is then reconstituted by adding small amounts of fuming nitric acid and sulphuric acid for re-use as a dissolving acid. An overall recovery of over 96% is easily obtainable.

SUMMARY

In this paper, an attempt has been made to discuss all the aspects of molybdenum extraction based on pyrometallurgical processing. The presentation begins with properties and applications of molybdenum metal and its alloys. In this section important applications of molybdenum in conventional and strategic areas are listed. The vast range of these applications is mainly due to the right combination of high temperature metallurgical, physical and chemical properties. Molybdenum in nature occurs as a sulphide and also as a complex oxide. These occurrences may be described either as primary ores or as a by-product, depending on the mineral association. In addition to these resources, recycling of industrial waste constitutes another major source for molybdenum.

Of all these resources, sulphide ores currently meet over 90% of all molybdenum requirements, therefore its processing by physical and/or chemical methods to a suitable intermediate is dealt with. Physical beneficiation is essentially based on flotation. The processing scheme depends on the type of the ore and other mineral associations – the final product of physical beneficiation is a high grade concentrate assaying up to 90% MoS_2. High grade concentrate can be treated in two ways, in one the concentrate is processed directly to metallic molybdenum by metallothermic reduction followed up with post reduction refining/sulphide purification and then thermal dissociation; in the other, it is first roasted and the roasted calcines are reduced after purification with hydrogen/metal reductants to molybdenum powder or alloys. The process based on roasting – purification – hydrogen reduction has long been in industrial use, though many modifications have taken place recently. Low grade concentrate is usually subjected to chemical processing to obtain a pure intermediate such as molybdic oxide, calcium molybdate, ferrimolybdate, which then serve as starting materials for the production of metallic molybdenum or its alloys. Besides these chemical reduction processes, several molten salt electrolytic processes have also been developed for molybdenum, these include electrowinning and electrorefining. The electrowinning processes are based on oxyanionic types of electrolytes which can be operated in an open atmosphere. The electrorefining processes must be conducted in an inert atmosphere because they are based on chloride electrolytes with a complex potassium hexachloromolybdate as a functional electrolyte. In electrorefining, the soluble anode may be crude metallothermically reduced metal, scrap or molybdenum compounds, such as carbides, sulphides and oxide-carbons.

In the case of crude metal or scrap the operating potentials are very low, but the compounds require a certain minimum potential higher than that required for refining crude metal/scrap but lower than that required for decomposing the electrolyte.

The last section of the paper is concerned with miscellaneous processes including plasma processing for thermal decomposition of molysulphide and the recovery of molybdenum from industrial waste such as molybdenum scrap and molybdenum liquor from the lamp filament industry. The processes for industrial waste are essentially based on hydrometallurgical processing to obtain pure oxidic compounds which can then be used for production of metallic molybdenum or its alloys. Though so many new processes have been developed, the economics of the alternative processes have not yet justified the displacement of the well-established roasting-purification-hydrogen reduction process. The economics of any process which depends on such local factors as availability of raw materials, capital, capital goods and construction, electrical power and fuels, put pressure on extraction metallurgists to develop processes that are economically advantageous to their countries.

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