

## **Production of Ferromolybdenum from Indian Resources**

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### **ABSTRACT**

*In India, the resources of molybdenum are limited – primary sources are very low grade molysulphide deposits, molybdenum in low concentration co-occurs with copper and uranium deposits, processing of such deposits for copper and uranium yields small quantities of low grade molysulphide concentrate. Besides these, some quantities of molybdenum scrap and molybdenum bearing effluents are generated as secondary sources in the country. This paper is concerned with the development of processes for treating these indigenous sources. The first part of the paper describes the chemical processes for preparing pure compounds of molybdenum which could be utilized as starting materials for various metallurgical products of molybdenum. The second part of the paper deals with the production of ferromolybdenum using these molybdenum intermediate compounds.*

**Keywords :** Ferro-molybdenum, Molybdenum, Molysulphide.

### **INTRODUCTION**

In the world, over 85% of molybdenum is used as an alloying additive in iron, steel and superalloys. In some of the alloys, particularly those grades of iron and steel which contain less than 0.5% molybdenum, addition may be made either as molybdic oxide—carbon briquettes or as calcium molybdate. In most of the other alloys addition of molybdenum is in the form of ferromolybdenum. The conventional process for production of ferromolybdenum starts with molysulphide concentrate analysing over 55% molybdenum. Molysulphide concentrate is roasted to molybdic oxide which is either used as such or is further purified. The purification treatment involves a combination of oxide distillation followed by hydrometallurgical processing. The technical grade oxide or pure oxide is then admixed with iron scrap or iron oxide and metallothermally reduced to ferromolybdenum using aluminium or a combination of aluminium and silicon as the reductants. Addition of lime as a flux during ferroalloy smelting has been

found to improve the yield. High carbon ferromolybdenum has also been produced by carbothermic smelting in electric furnace.

The current requirement of molybdenum in the country is estimated to be about 50 tonnes as unalloyed metal and about 450 tonnes as ferroalloy. Besides these, there is some requirement in the form of chemicals, compounds and some alloys. Most of the current requirement of molybdenum in its various forms is met through imports. In India, the sources of molybdenum are very much limited, total availability is estimated to be only 22500 tonnes of contained molybdenum. The deposits of molysulphide are known to occur in low concentrations at Palani and Madurai in Tamilnadu; Ambamata, Gujarat; Kalankhard, Madhya Pradesh; Khasi hills, Assam; and Sikkim. Most of these resources are yet to be developed. Molysulphide is known to occur together with pyrites, and with copper–nickel sulphide in uranium deposits at Jaduguda <sup>[1]</sup> (Singhbhum, Bihar). During mining and milling of uranium at Uranium Corporation of India Ltd., (UCIL) at Jaduguda, the sulphide minerals are recovered by bulk flotation and the nonfloatable fraction is used for uranium extraction. The floated sulphide concentrate is then subjected to a sequence of differential flotation and cleaning steps to produce separated molysulphide and nickel–copper sulphide concentrates. Molybdenum also co–occurs with chalcopyrite at Rakha mines of Hindustan Copper Ltd., (HCL). In the deposit molybdenite plates are generally associated with gangue minerals and very rarely intimate intergrowth is observed between chalcopyrite and molysulphide mineral <sup>[2]</sup>. Conventional flotation methods have been developed at HCL for flotation of molysulphide using sodium bisulphide as a depressor for chalcopyrite. By adopting a suitable combination of roughing and cleaning flotation cells an intermediate grade molysulphide concentrate has been produced. Typical chemical analysis of the concentrates produced at Jaduguda and at HCL are shown in Table 1.

*Table 1 : Typical analysis of molysulphide concentrates*

	From UCIL		From HCL
Mo	30.56	45.50	50.00
Cu	0.58	0.48	0.70
Ni	0.31	0.39	0.04
Fe	5.10	—	1.80
SiO <sub>2</sub>	4.15	7.90	<1.00
S	22.60	30.00	34.00
Al <sub>2</sub> O <sub>3</sub>	not analysed	not analysed	1.40
Bi	not analysed	not analysed	0.20

These concentrates are relatively low in molybdenum and have high association of copper as compared to the internationally available concentrates. These concentrates therefore cannot be utilized as such for the production of either the metal or ferromolybdenum by adopting the conventional industrial processes. While the efforts have been directed in some laboratories to reduce the copper concentration by a combination of physical and chemical processes, simultaneous work was also initiated to develop alternate processes suitable for treating these types of concentrates. In addition to the naturally occurring sulphide sources, some quantities of secondary molybdenum sources are also generated in the country — these are the effluents of molybdenum mandrel dissolution during the making of tungsten lamp filaments and molybdenum scrap of high temperature furnaces.

This paper describes various processes that have been developed at BARC for the recovery of molybdenum from indigenous natural low or intermediate grade molysulphide concentrates and also from the secondary sources. The paper is essentially divided into two parts, the first part deals with the chemical processing of the sources to pure intermediate compounds and the second part with the production of ferromolybdenum.

## **PROCESSING OF MOLYBDENUM SOURCES**

Molybdenum from the sulphide and the secondary sources is recovered in the form of oxide either as molybdic oxide or as a molybdate such as ammonium molybdate, calcium molybdate or as ferrimolybdate. Where as all of these compounds excepting ferrimolybdate can be used for production of molybdenum metal and ferromolybdenum. Ferrimolybdate can be utilized only for the preparation of ferromolybdenum. The purity specification of these compounds for the production of molybdenum metal and that for ferromolybdenum are however, different. The critical impurity for ferromolybdenum is copper. If copper is present in the starting compound then ultimately it will find its way to the ferroalloy. Several processing scheme have been developed to prepare molybdenum oxide or its intermediate compounds and these are described separately for the low grade molysulphide concentrate and for secondary sources respectively.

## **TREATMENT OF LOW GRADE MOLYSULPHIDE CONCENTRATE**

Four different processing schemes have been developed for the treatment of low grade molysulphide concentrate these are summarised in Fig. 1.

One of the first processes <sup>[1]</sup> which was considered was based on roasting of the concentrate at about 600°C for few hours in a static bed furnace. The roasted

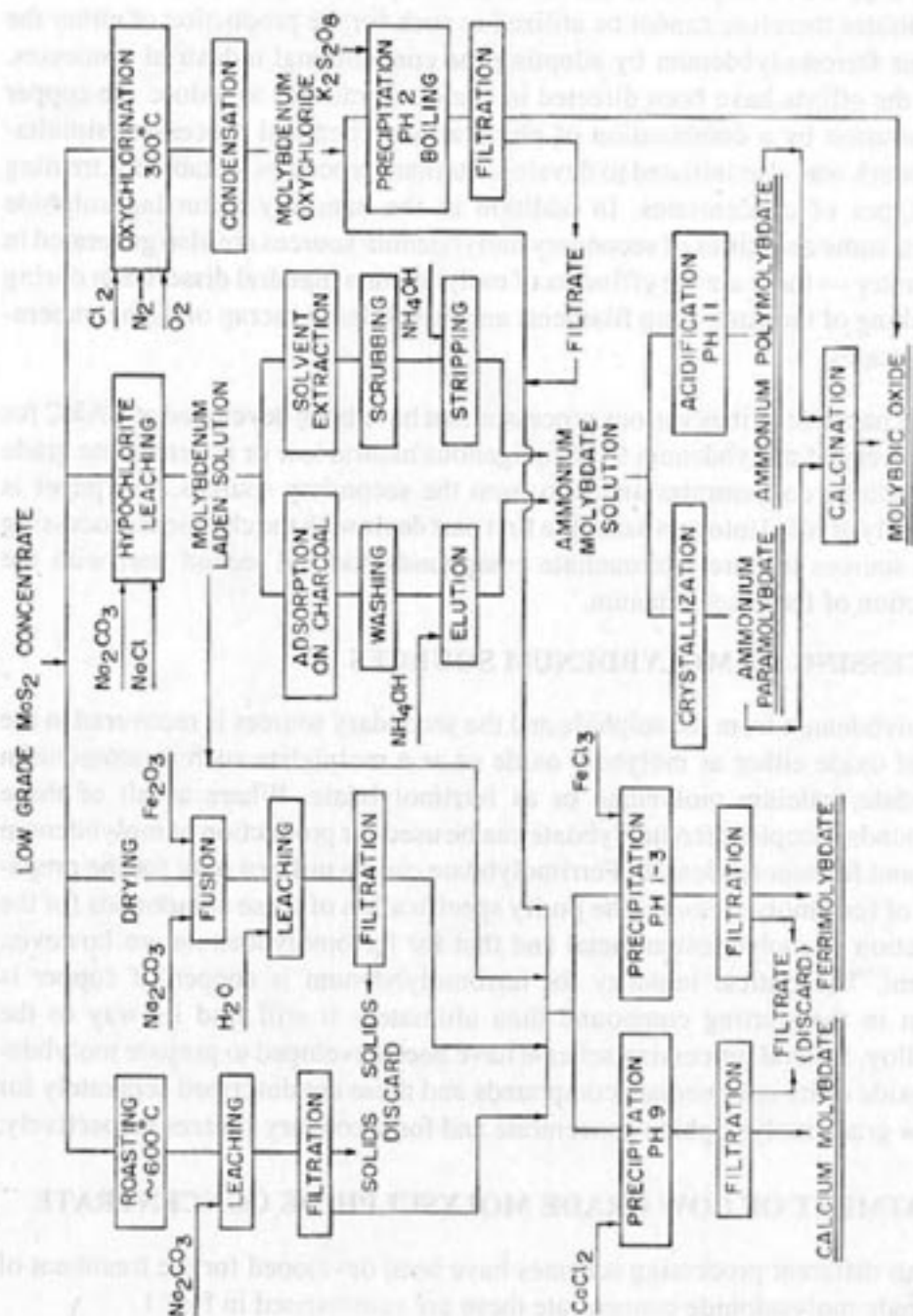
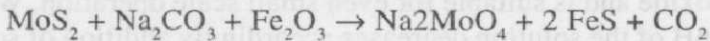


Fig. 1 : Various chemical processing routes for the treatment of low grade molybdenum concentrate

calcines were then leached in 10% soda ash solution at about 90°C. Most of the molybdenum is extracted as sodium molybdate whereas most of silica, iron and copper remain in the undissolved residue. Some amount of copper and silica impurities however get co-extracted. The removal of these impurities was accomplished by neutralizing the solution to precipitate these as basic carbonate of copper and as silica. Molybdenum from the solution was then precipitated and recovered as calcium molybdate by addition of calcium chloride to the hot solution. As an alternate to this, another process was considered which involved soda ash fusion of the concentrate at about 920°C in presence of ferric oxide. The fusion resulted in conversion of molysulphide to sodium molybdate. Next the fused mass was water leached to solubilize molybdenum and then the solution was treated essentially in the same way as that for the process based on roasting and leaching. This process offers the advantage of mixing sulphur as sulphide thereby eliminating the problem of sulphur dioxide emission. The reaction can be represented as :



Molybdenum laden solution has also been utilized to recover molybdenum as ferrimolybdate <sup>[3]</sup> and molybdic oxide <sup>[4]</sup>. Recovery of hydrated ferrimolybdate precipitate was accomplished by the addition of ferric chloride to molybdenum solution maintaining a pH of 2.8. The precipitate after calcination at 500°C typically analysed 56% MoO<sub>3</sub>. The use of different precipitation conditions in the pH range of 1–3 yielded other ferrimolybdate complexes. Recovery of molybdenum as molybdic oxide was accomplished by precipitation of molybdic acid and then calcination to oxide. For this small amount of potassium thiosulphate was added to the concentrates solution of sodium molybdate (~ 400 g/dm<sup>3</sup>) to ensure that all of molybdenum is present in hexavalent state. Molybdenum was then precipitated as molybdic acid by acidifying the solution to pH of 2 at a temperature of 20°C. Next the solution was boiled for few minutes after addition of some additional potassium thiosulphate to form a readily filterable molybdic acid precipitate. The precipitate was finally calcined to yield molybdic oxide. In the process nearly 90% molybdenum precipitated as molybdic acid but the filtrate still contained about 10% of molybdenum. Molybdenum from the filtrate was recovered as calcium molybdate by the addition of calcium chloride.

Hypochlorite leaching <sup>[5]</sup> of the molysulphide concentrate was carried out in polypropylene lined FRP bipolar cell having an anode, a cathode and seven intermediate electrodes, all made out of graphite with proper insulation on all the edges to reduce the leakage current. The assembly as such is equivalent to eight electrolytic cells connected in series. The leaching of molysulphide was accom-

plished by sodium hypochlorite which was generated insitu by the electrolysis of brine solution. The reactions at the electrodes are shown below :



The dissolution of molybdenum takes place by the following reaction :



Slurry of molysulphide in brine is agitated in a separate tank and fed from the bottom of the bipolar cell. The cell is operated at a current density of 6.5 A/dm<sup>2</sup>, temperature of 32–34°C and a pH of 7 to 8. This process offers the advantage of treating any grade of molysulphide concentrate. Moreover it eliminates the emission of sulphur dioxide and is suitable for even small scale operation. With the passage of current pH of the solution decreases accordingly addition of soda ash is continuously necessary for maintaining the pH and retaining molybdenum as sodium molybdate in the solution. Molybdenum laden solution was then processed for the recovery of molybdenum by adopting processing schemes that have been described earlier. For obtaining high purity molybdenum metal it was necessary to purify the solution by solvent extraction. Molybdenum from the purified solution was then crystallized as ammonium paramolybdate which on calcination yielded pure molybdic oxide suitable for hydrogen reduction to produce molybdenum powder.

A yet another process <sup>161</sup> which has been developed for the treatment of low grade molysulphide concentrate involves oxychlorination. The process essentially consisted of chlorination of molysulphide in presence of oxygen to form volatile molybdenum oxychloride. The reaction was carried out at low temperature in the range of 200–300°C as compared to 500°C for conventional chlorination. The use of such low temperature is beneficial because it not only reduces the problem of reactor materials it also eliminates an additional purification step due to the formation of chlorides of impurity elements such as copper, iron and nickel which are nonvolatile under these conditions. The oxychloride has been directly reduced with hydrogen to molybdenum powder. It has also been converted to molybdic oxide or calcium molybdate by hydrometallurgical processes cited earlier. To sum up it can be said that low grade molysulphide concentrate can be readily processed to yield pure oxide compounds such as molybdic oxide, calcium molybdate, ammonium molybdate and ferrimolybdate. All these have

been utilized for the production of ferromolybdenum.

### TREATMENT OF SECONDARY SOURCES OF MOLYBDENUM

Molybdenum from the secondary sources – effluent of molybdenum mandrel dissolution and molybdenum scrap was processed to molybdic oxide [7,8]. The processes that have been developed are shown in a simplified form in Fig. 2.

The spent acid analysing about 125 g/dm<sup>3</sup> of molybdenum also contained 5 M HNO<sub>3</sub> and 5.5 M H<sub>2</sub>SO<sub>4</sub>. The solution was treated in two different ways. One of

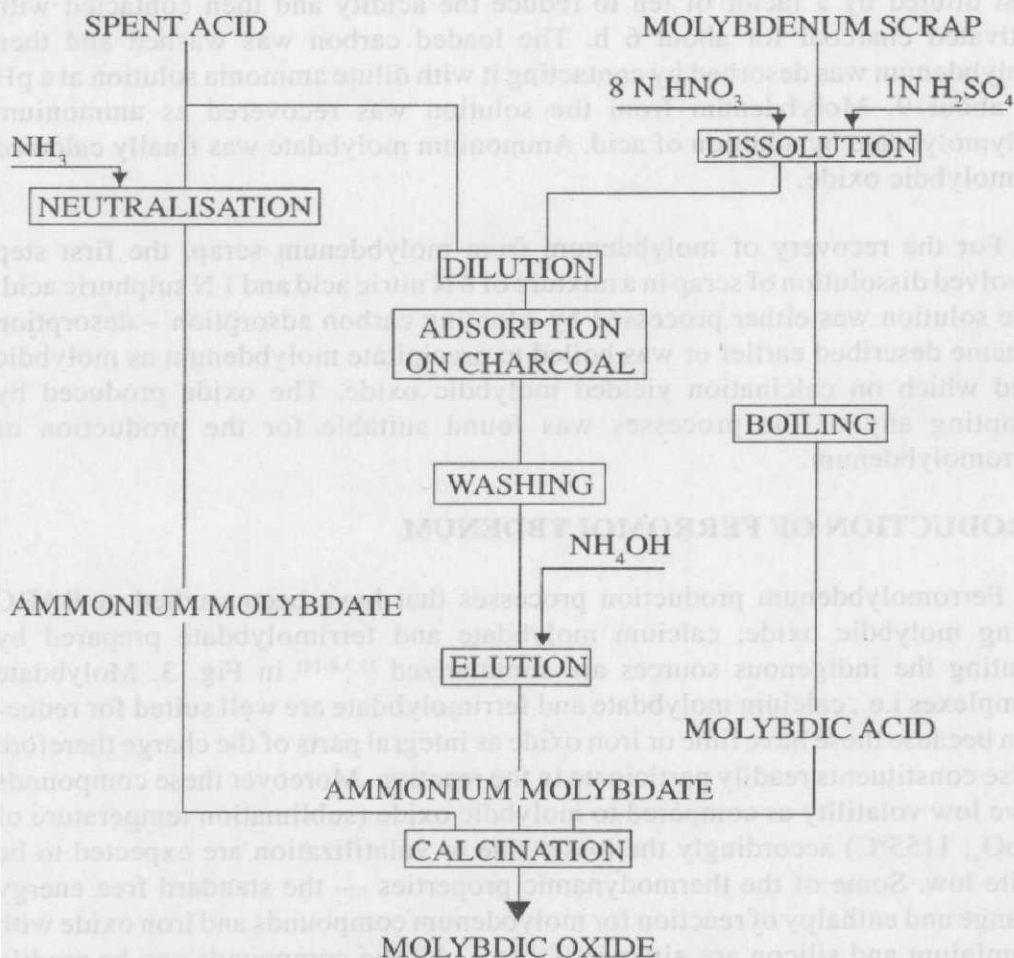


Fig. 2 : Schematic flowdiagram for treatment of secondary sources of molybdenum

the processes involved neutralization of acids and precipitation of molybdenum as ammonium molybdate. The neutralization of the solution was carried out either directly with ammonia to form ammonium molybdate or alternatively the neutralization was carried out in two stages. The first step being partial neutralization by the addition of lime or soda ash or caustic soda and then final neutralization with ammonia. The second approach yielded a final product which contained some amount of calcium or sodium. The product although is not suitable for producing pure molybdenum but is acceptable for ferroalloy production. The second approach is therefore preferred because it results in significant saving of costlier chemical i.e., ammonia. Another process that was considered was based on adsorption — desorption of molybdenum on activated charcoal. The solution was first diluted by a factor of ten to reduce the acidity and then contacted with activated charcoal for about 6 h. The loaded carbon was washed and then molybdenum was desorbed by contacting it with dilute ammonia solution at a pH of about 9. Molybdenum from the solution was recovered as ammonium polymolybdate by addition of acid. Ammonium molybdate was finally calcined to molybdic oxide.

For the recovery of molybdenum from molybdenum scrap, the first step involved dissolution of scrap in a mixture of 8 N nitric acid and 1 N sulphuric acid. The solution was either processed by adopting carbon adsorption — desorption scheme described earlier or was boiled to precipitate molybdenum as molybdic acid which on calcination yielded molybdic oxide. The oxide produced by adopting any of the processes was found suitable for the production of ferromolybdenum.

## PRODUCTION OF FERROMOLYBDENUM

Ferromolybdenum production processes that have been studied at BARC using molybdic oxide, calcium molybdate and ferrimolybdate prepared by treating the indigenous sources are summarized [1,3,8-14] in Fig. 3. Molybdate complexes i.e., calcium molybdate and ferrimolybdate are well suited for reduction because these have lime or iron oxide as integral parts of the charge therefore these constituents readily participate in the reaction. Moreover these compounds have low volatility as compared to molybdic oxide (sublimation temperature of  $\text{MoO}_3$ , 1155°C) accordingly the losses due to volatilization are expected to be quite low. Some of the thermodynamic properties — the standard free energy change and enthalpy of reaction for molybdenum compounds and iron oxide with aluminium and silicon are given in Table 2. All the compounds can be readily reduced in open reactors with aluminium but the reduction of calcium molybdate with silicon under identical conditions is not feasible.



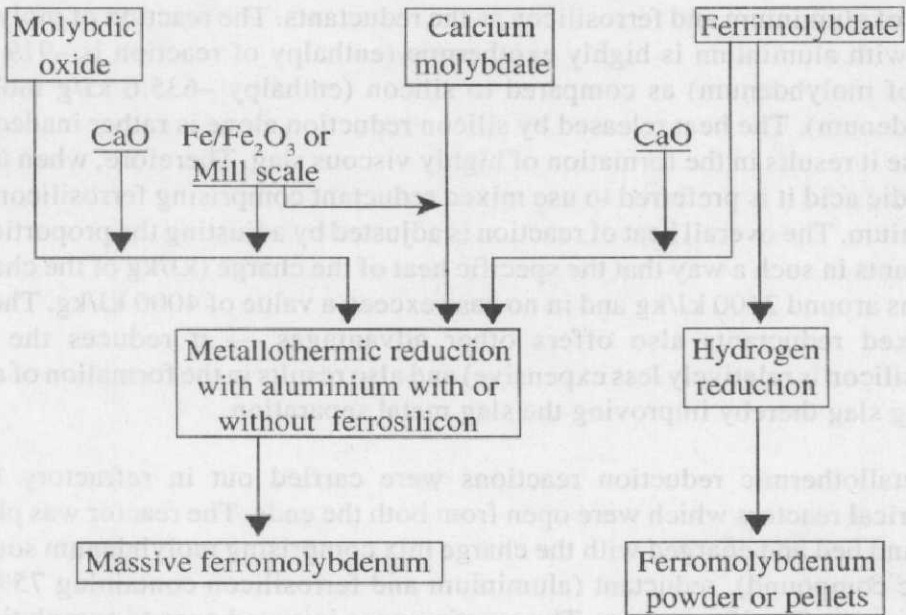


Fig. 3 : Processes for production of ferromolybdenum

Table 2 : Metallothermic reduction reactions relevant to ferromolybdenum production

Oxide	Reaction	$-\Delta G_{298}^{\circ}$ kJ/g atom of $O_2$	$-\Delta H_{298}^{\circ}$ kJ
$MoO_3$	$MoO_3 + 2 Al \rightarrow Mo + Al_2O_3$	301	919.5
$MoO_3$	$2MoO_3 + 3Si \rightarrow 2Mo + 3SiO_2$	185	1271.3
$Fe_2O_3$	$Fe_2O_3 + 2 Al \rightarrow 2Fe + Al_2O_3$	279.5	850.6
$Fe_2O_3$	$2Fe_2O_3 + 3Si \rightarrow 4Fe + 3SiO_2$	163.4	980.6
$CaO.MoO_3$	$CaO.MoO_3 + 2Al \rightarrow Mo + CaO.Al_2O_3$	-	752.4
$CaO.MoO_3$	$CaO.MoO_3 + 1.5Si \rightarrow Mo + CaO.1.5SiO_2$	-	1458.8
$0.416MoO_3$	$0.416MoO_3.0.25Fe_2O_3 +$		
$0.25Fe_2O_3$	$1.32Al \rightarrow 0.416Mo.0.5 Fe + 0.66Al_2O_3$	-	-

Production of massive ferromolybdenum was accomplished by the metallothermic reduction of the oxidic compounds using aluminium or a combi-

nation of aluminium and ferrosilicon as the reductants. The reaction of molybdic oxide with aluminium is highly exothermic (enthalpy of reaction is  $-919$  kJ/g mole of molybdenum) as compared to silicon (enthalpy  $-635.6$  kJ/g mole of molybdenum). The heat released by silicon reduction alone is rather inadequate because it results in the formation of highly viscous slag. Therefore, when using molybdic acid it is preferred to use mixed reductant comprising ferrosilicon and aluminium. The overall heat of reaction is adjusted by adjusting the proportion of reductants in such a way that the specific heat of the charge (kJ/kg of the charge) remains around 2400 kJ/kg and in no case exceed a value of 4000 kJ/kg. The use of mixed reductants also offers other advantages — it reduces the cost (ferrosilicon is relatively less expensive) and also results in the formation of a low melting slag thereby improving the slag metal separation.

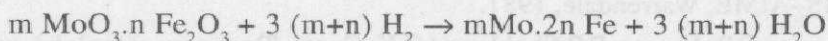
Metallothermic reduction reactions were carried out in refractory lined cylindrical reactors which were open from both the ends. The reactor was placed on a sand bed and charged with the charge mix comprising molybdenum sources (oxidic compound), reductant (aluminium and ferrosilicon containing 75% Si) and lime as a flux if necessary. The reaction once initiated goes to completion in a very short time. The reaction was triggered with a trigger mixture composed of

*Table 3 : Typical results of production of ferromolybdenum from various molybdenum compounds*

	Molybdic oxide		Calcium molybdate		Ferrimolybdate	
Charge	MoO <sub>3</sub>	1.00	CaO.MoO <sub>3</sub>	1.00	.416MoO <sub>3</sub> .	0.4
	Fe <sub>2</sub> O <sub>3</sub>	0.40	CaO	0.20	.25Fe <sub>2</sub> O <sub>3</sub>	
	CaO	0.10	Fe <sub>2</sub> O <sub>3</sub>	0.68	Al	0.17
	CaF <sub>2</sub>	0.08	Al	0.60		
	FeSi(75%Si)	0.525				
	Al	0.06				
Specific heat, kJ/mg	2541.4		2814.7		n.a.	
Alloy Composition %	Mo	60.0		51.5		54.0
	Al	0.4		0.8		1.0
	Fe	bal.		bal.		bal.
Metal Recovery, %	90		95		86	

KC10<sub>3</sub>-Al which was placed on the charge surface and then ignited with either magnesium ribbon or an electrical resistance. The reaction once initiated goes to completion in a very short time. The reacted mass was allowed to cool overnight and the ferroalloy recovered. Typical charge composition and the alloy analysis for molybdic oxide, calcium molybdate and ferrimolybdate are given in Table 3. From the table it can be seen that all the compounds could be utilized for the production of ferromolybdenum with a molybdenum recovery of over 85%.

The production powder or pelletized ferromolybdenum was accomplished by direct hydrogen reduction of ferrimolybdate powder or powder compacts<sup>[3]</sup>. The reduction reaction can be represented.



The yield or the recovery of molybdenum depended on the composition of ferrimolybdate complex (MoO content) and the reduction temperature. The ferrimolybdate complex which analysed 54.6% MoO<sub>3</sub> yielded highest recovery of 99% during hydrometallurgical processing, also it could be reduced with hydrogen to alloy powder at temperature of 800°C. The overall yield in the hydrogen reduction of ferrimolybdate was about 97% and the alloy produced analysed 54% Mo. Other complexes which analysed 75.2% and 83.9% MoO<sub>3</sub> gave lower recoveries during hydroprocessing and also required higher reduction temperature. The alloy produced in these two cases analysed 74 to 75% molybdenum respectively.

## CONCLUSIONS

The paper has demonstrated the technical feasibility of production of ferromolybdenum from indigenously available low grade molysulphide concentrate and secondary sources. Various chemical processing schemes have been suggested for obtaining pure molybdenum intermediate compounds which serve as the start materials for production of ferromolybdenum. The selection of a chemical route would depend on various techno-economic considerations.

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