Environmental and Waste Management (ISSN : 0971-9407)
Eds. - A. Bandopadhyay, N.G. Goswami and P.R. Rao
© NML, Jamshedpur - 831 007, 1998, pp. 92-99

Environmental considerations in the selection of metallurgical processes for the extraction of molybdenum from low grade molybdenite concentrate

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ABSTRACT

Environmental considerations are necessitating the development of new extractive processes for the production of various non-ferrous metals from their sulphide ores. The current industrial practice, which involves roasting of the sulphide ores, releases SO_2 *and particulates to the atmosphere. These pollutants require expensive emission control and off-gas cleaning to environmentally acceptable limits before for their discharge to the atmosphere. Of late, a need has been felt to develop new processes which not only can control the air pollution but also avoid the subsequent off-gas treatment measures. The present paper deals with the development of two alternate processes, soda ash roasting and lime enhanced carbothermic reduction, for processing the Rakha molybdenite concentrate. The effect of various experimental parameters on the recovery as well as purity of* MoO_3 *and Mo has been discussed. These processes convert the sulphide content of molybdenite to sulphates, thereby avoiding the release of pollutants to the atmosphere.*

Keywords : Enhanced carbothermic reduction, Environment friendly routes, Molybdenum extraction, Soda ash roasting.

INTRODUCTION

The conventional pyrometallurgical process for the production of molybdenum is the roasting of molybdenite concentrate to MoO_3 followed by its subsequent reduction to metal by hydrogen [1]. The roasting of the concentrate to MoO_3 although appears to be a chemically simple process, a careful control of temperature is required to accomplish this reaction. A temperature of 600°-650°C is considered to be optimum as above 650°C the calcines start sintering. In addition to this, an increase in the loss of molybdenum content also takes place through volatilization of MoO_3. The desired temperature control, during roasting, is achieved with the use of Herreshoff type multiple hearth roaster [2]. This process is well suited to those concentrates which posses at least 90% $MoS_2.MoO_3$. Products from these sources by conventional roasting process, is found to contain sulphur is the range 0.1 to 0.5% [3]. The stack gas contains SO_2 in the range of 0.9 to 1.5% and the concentration of particulates is about 20% of the feed [4]. Despite the technical improvements made in the art of roasting of the concentrate and also by providing an efficient dust catching system, it has been observed that the off-gases still carry particulates to the extent of 10% of feed. Even if an alternative method of heat dissipation is provided to increase the concentration of SO_2 in the flue gas, its concentration still remains in the range of 3 to 5% which is too low for conversion to H_2SO_4 [5]. The particulate and SO_2 are harmful air pollutants that affect human beings, vegetation and materials [6]. When this process is applied to low grade concentrates, the flue gas will have a large quantity of particulates and low concentration of SO_2. Thus, the emission control and cleaning of off-gas will be an expensive proposition because of the high cost and large load on the equipment [7]. With the growing concern for environmental pollution, new extractive process should be developed which may not either release SO_2 or recover sulphur in elemental form, to be converted later to H_2SO_4 [8].

In recent years, a number of hydro and pyrometallurgical processes have been developed for processing low grade molybdenite concentrates [9-11]. The hydrometallurgical processes are (i) electro-oxidation (ii) nitric acid and (iii) alkali leaching whereas pyrometallurgical processes are (i) alkali fusion (ii) lime or soda ash roasting (iii) chlorination and (iv) lime enhanced reduction. Among the hydrometallurgical processes, electro oxidation requires critical control of process parameters such as pH, pulp density, salt concentration, temperature and consumes reasonably large DC power. Nitric acid and alkali leaching processes require complex and costly equipment to dissolve molybdenum from the concentrate and thus are capital intensive. On account of these difficulties, hydrometallurgical processes have not been considered for commercial operation.

Among the pyrometallurgical processes, chlorination process uses either chlorine or a mixture of chlorine and oxygen to convert Mo, in the concentrate, to $MoCl_5$ and MoO_2Cl_2 respectively. This process releases S_2Cl_2 and SO_2 as air pollutants that require off-gas treatment. Roasting of the concentrate with lime/soda ash produces molybdates and converts sulphur content of the molybdenite to sulphate. Lime roasting produces insoluble molybdates and an additional leaching step is required to convert insoluble molybdate to solubles. Soda ash roasting process produces soluble molybdate in a single step operation and is thus preferable. Lime enhanced reduction process uses H_2, CO and carbon as reductants to convert molybdenum content directly to the metal. Because of the low cost and ready availability in pure form, carbon has been preferred over the other two reductants. This paper describes the development of soda ash roasting and lime enhanced carbothermic processes for the recovery of molybdenum from Rakha molybdenite concentrate.

EXPERIMENTAL

Materials

Molybdenite concentrate, used in these investigations, was supplied by Non-Ferrous Materials Technology Centre, DMRL, Hyderabad. The composition and particle size distribution of the concentrate are given in Tables 1 and 2 respectively. Soda ash and graphite were of GR grade. GR grade $CaCO_3$ was used as the source of lime, which upon in situ decomposition, forms CaO.

Table 1 : Chemical analysis of Rakha molybdenite concentrate (wt%)

Mo	Cu	Ni	Fe	S	SiO_2	Al_2O_3
48.1	0.7	2.3	1.8	34	0.7	0.2

Table 2 : Sieve analysis of Rakha molybdenite concentrate

Tylor Screen Size	Wt.% retained on each screen	Wt.% passed through each screen
- 45 + 60	0.35	100.00
- 60 + 100	1.42	99.65
- 100 + 170	9.35	98.23
- 170 + 200	28.86	88.88
- 200 + 270	16.22	60.02
- 270 + 325	4.02	43.08
- 325	39.78	39.78

Procedure

The investigations on soda ash roasting and lime enhanced carbothermic reduction were carried out on a 0.25 kg scale of the concentrate. In soda ash roasting the charge mixture, containing the concentrate and soda ash in different mole ratios, was roasted up to a temperature of 650°C in an electric resistance furnace. The roasted mass was twice leached with water to recover molybdenum as Na_2MoO_4. To the molybdate solution, NH_4OH was added slowly and the pH of the resulting solution was adjusted to 2 for precipitating out ammonium molybdate. NH_4MoO_4, so formed, was calcined to MoO_3.

In the lime enhanced carbothermic reduction, investigations were carried out using stoichiometric amounts of carbon and different mole ratios of $CaCO_3$. The pelletized charge mixture was reduced in an induction furnace at a temperature range of 1000°-1200°C and under reduced pressure (<0.1 Pa). The reduced mass, after cooling, was powdered and the slag, CaS, was separated from the metal by elutriation. The metal powder was again compacted and sintered up to a temperature of 1500°C under reduced pressure (0.01 Pa) for subsequent evaluations.

RESULTS AND DISCUSSION

The soda ash roasting and the lime enhanced carbothermic reduction reactions of molybdenite can be represented as follows:

$$MoS_2^{(s)} + 3Na_2CO_3^{(s)} + 9/2\ O_2^{(g)} \rightarrow Na_2MoO_4^{(s)} + 2Na_2SO_4^{(s)} + 3CO_2^{(g)}$$

$$MoS_2^{(s)} + 2CaO^{(s)} + 2C^{(s)} \rightarrow Mo^{(s)} + 2CaS^{(s)} + 2CO^{(g)}$$

The experimental parameters which influenced molybdenum recovery and purity were reaction temperature, soaking time and charge composition. The optimum operating conditions are shown in Table 3. The chemical analyses of products, obtained under these conditions, are given in Table 4. From this table, it can be inferred that the products were not sufficiently pure and hence required further treatment to prepare high purity metal.

Table 3 : Optimum condition for soda ash roasting and lime enhanced carbothermic reductions of the molybdenite

	Soda ash roasting	Lime enhanced carbothermic reduction
Temperature (°C)	600	1150
Soaking Period (h)	0.75	2
Lime to concentrate mole ratio	–	2.5
Molybdenum recovery (%)	99.5	96
Elutriation Efficiency (%)	–	90
Molybdenum purity (%)	99.9	98.7

Table 4 : Chemical analyses of molybdenium products before purification

Metallic impurities	MoO_3 (wt%) (by soda ash roasting)	Mo (wt%) (by lime enhanced carbothermic reduction)
Cu	0.003	0.36
Ni	0.0056	0.03
Fe	0.058	0.34
Si	0.7	—
S	—	>0.1
Ca	—	0.16
Mo	99.0	98.7

Purification

In soda ash roasting process, purification of sodium molybdate was carried out by carbon adsorption/desorption technique before converting it to ammonium molybdate [12]. Activated charcoal was used as the adsorbent on which MoO_4^{2-} got selectively adsorbed, leaving the impurities in solution. Molybdenum impregnated charcoal was treated with NH_4OH to release molybdenum as NH_4MoO_4. The ammonium molybdate was converted to ammonium polymolybdate at 90°C after adjusting the pH to 2. Ammonium polymolybdate was calcined to MoO_3 at 500°C. The analysis of MoO_3, produced after purification, is given in Table 5.

Table 5 : Chemical analysis of molybdenum products after purification

Metallic impurities	MoO_3 (wt%) (soda ash roasting)	Mo (wt%) (lime enhanced carbothermy)
Cu	< 0.0005	< 0.0015
Ni	0.002	< 0.0125
Fe	0.003	< 0.1
Si	0.02	—
Al	0.01	—
Ca	—	< 0.003
Oxygen	—	< 0.01
Nitrogen	—	< 0.01
Carbon	—	0.002

In the lime enhanced carbothermic process, the sintered metal was refined by fused salt electrolysis. The electrolytic cell, used in the present study is shown in Fig. 1. The electrorefined bath (KCl-K_3MoCl_6) was prepared by *in-situ* chlorination of Mo metal in molten KCl to form K_3MoCl_6[13]. The sintered metal was placed at the bottom of a graphite crucible, containing the electrolyte. Pure meal was electrodeposited by optimising various process parameters such as electrolysis temperature, soluble Mo in the bath and cathode current density. The operating data are given in Table 6 and chemical analysis of pure metal is given in Table 5. The flow sheet, developed for these processes, is shown in Fig. 2.

Table 6 : Optimum parameters for fused salt electrolysis

Electrolyte	:	KCl – K_3MoCl_6
Soluble molybdenum content	:	7.5 wt%
Temperature	:	900°C
Cathode current density	:	450 A/ft²
Cathode current efficiency	:	85%

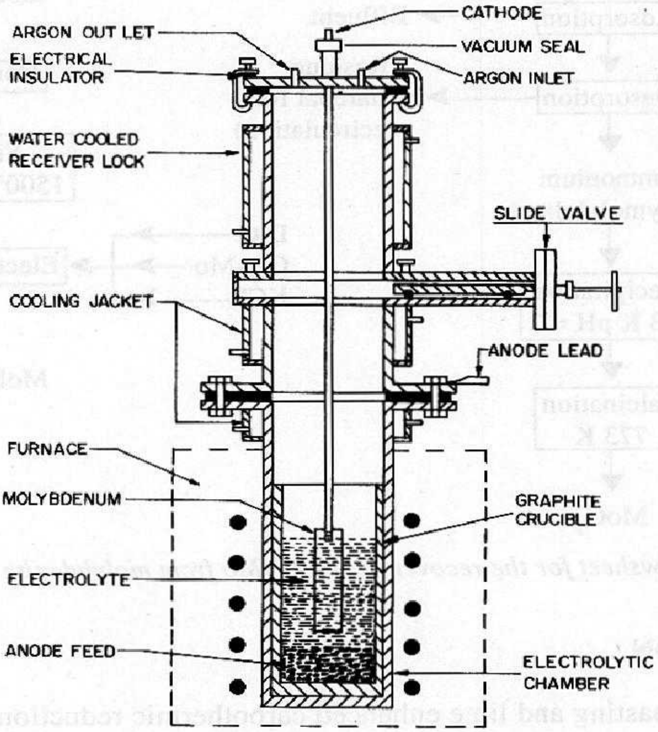

Fig. 1 : Electrorefining cell

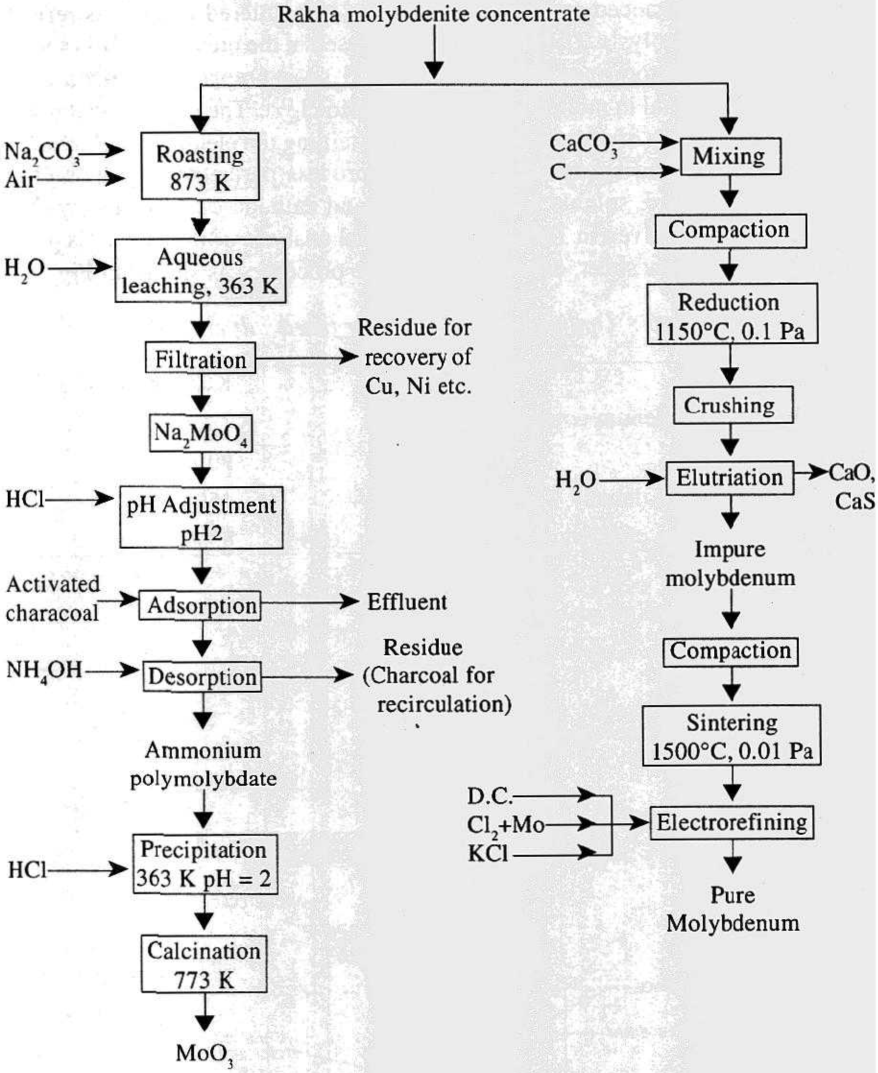

Fig. 2 : Flowsheet for the recovery of MoO_3/Mo from molybdenite concentrate

CONCLUSION

Soda ash roasting and lime enhanced carbothermic reduction processes, developed for the extraction of molybdenum from low grade concentrate, produce no air pollutants. In soda ash roasting process, sulphur of the molybdenite is converted to sulphate whereas in lime enhanced carbothermic reduction, it is converted to CaS, which can further be converted to $CaSO_4$. Both Na_2SO_4 and $CaSO_4$ are useful products. High purity MoO_3 and Mo have thus been prepared which meet the specifications for industrial consumption.

ACKNOWLEDGEMENT

The authors wish to express their sincere thanks to Dr. A.K. Suri, Head, Materials Processing Division, Bhabha Atomic Research Centre, Trombay, Mumbai for his constant encouragement during the course of the present investigation.

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