



CARBOTHERMIC REDUCTION OF MOLYBDENUM FROM MOLYBDENUM OXIDES AND CONCENTRATES

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| Received: 25.12.2023 | Accepted: 06.01.2024 | Published: 11.01.2024

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Abstract

This article presents brief data on molybdenum and its ores and minerals and also molybdenum concentrates processing methods were given in this paper. Importance of carbothermic reduction was explained and effect of lime and carbon content on the reduction process was investigated in this research paper.

Keywords: carbothermic reduction, molybdenum oxide, carbon, molybdenum.

Introduction

Molybdenum is an important non-ferrous metal, which finds widespread applications in many key areas of modern technology. One of the primary ore bodies of this metal has been its sulphide (MoS_2), which is first roasted in the temperature range 873–923 K to form the oxide (MoO_3). The oxide is then reduced with hydrogen to prepare molybdenum metal powder. The desired temperature control, during roasting of the sulphide, is achieved in a Herreshoff type multiple hearth roaster. This process is well suited to those concentrates, which possess at least 90 wt-% MoS_2 . MoO_3 , produced from these sources by conventional roasting process, is usually found to contain sulphur in the range of 0.1–0.5%. The stack gas contains SO_2 in the range of 0.9–1.5% and the concentration of particulates is about 20% of the feed. Despite technical improvements made in the art of roasting of the molybdenite concentrate and by providing an efficient dust catching system, it has been observed that the off gases still carry particulates, to an extent of 10% of the feed material. Moreover, 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 3–5%, which is too low for its subsequent conversion to H_2SO_4 . The emitted particulate and SO_2 are harmful air pollutants that affect human beings, vegetation and materials. When this process is applied to low grade concentrates, the resultant flue gas, besides being low in SO_2 concentration, would contain large quantities of particulates. Therefore, the emission control and cleaning of off gas will be an expensive proposition because of the involvement of high cost and relatively

large load on the equipment. Keeping in view the growing concern for the environmental pollution, new extractive processes should be developed, which may either not release SO_2 or recover sulphur in its elemental form to be converted to H_2SO_4 at a later stage. In recent years, a number of hydro- and pyrometallurgical processes, such as:

1. electro-oxidation
2. nitric acid treatment
3. alkali leaching
4. alkali fusion
5. lime or soda ash roasting
6. chlorination
7. lime enhanced reduction, have been developed for processing low grade molybdenite concentrates/ores.

Among the hydrometallurgical processes, electro-oxidation requires critical control of process parameters such as pH, pulp density, salt concentration and temperature. Moreover, this process requires consumption of reasonably large amount of electrical energy. Nitric acid treatment and alkali leaching processes require complex and costly equipments to dissolve molybdenum from the concentrates and thus are capital intensive. Because of these difficulties, hydrometallurgical processes have not been considered for commercial exploitations.

Among pyrometallurgical processes, chlorination uses either elemental chlorine or a mixture of chlorine and oxygen to convert molybdenum in the concentrate to MoCl_5 and MoO_2Cl_2 respectively. This process releases S_2Cl_2 and SO_2 , which are air

pollutants, hence requiring elaborate off gas treatment measures. Roasting of the concentrate with lime/soda ash produces molybdate sand converts sulphur content of the molybdenite to sulphate. Lime roasting produces water insoluble molybdates and as a result an additional leaching step is required to convert insoluble molybdate to some form of water soluble compounds. Soda ash roasting produces soluble molybdate in a single step operation, thus it can be a preferred process. Lime enhanced reduction process uses hydrogen, carbon monoxide and carbon as reductants to convert molybdenite to molybdenum metal in the reduction step itself.

Ores and minerals

Of the known minerals of molybdenum, the following minerals are most common: molybdenite MoS_2 ; commond CaMoO_4 ; molybdite $x\text{Fe}_2\text{O}_3 \cdot y\text{MoO}_3 \cdot n\text{H}_2\text{O}$ and wulfenite PbMoO_4 . Of major industrial importance are molybdenite and copper-molybdenum ores, from which about 99% of molybdenum is obtained. In ores, molybdenum is often accompanied by tin, tungsten, arsenic, copper, and bismuth. Waste rock of molybdenum ores is represented by quartz, sericite and fluorite.

Molybdenum ores usually contain 0.1-0.2% Mo, and copper-molybdenum - 0.03-0.005% Mo and up to 2% copper. Molybdenite and copper-molybdenum ores are enriched by the flotation method. The extraction of molybdenum from molybdenite ores during enrichment is about 90%, and from copper-molybdenum 50-70%.

The composition of the obtained molybdenum concentrates varies within the following limits, %: Mo-47-50; P-0.07-0.15; As-0.07; Cu- 0.5-2.0; SiO_2 - 5-7. Molybdenum concentrates serve as the starting material for the production of ferromolybdenum, molybdenum anhydride MoO_3 , ammonium paramolybdate, from which molybdenum is obtained.

Reduction of molybdenum from molybdenum concentrates

The general principle of obtaining metals from natural compounds is as follows: the more active a given metal, the more energetic reducing agent must be used to isolate it. Typical reducing agents in metallurgy are hydrogen, carbon, active metals (Al, Zn, Mg, Ca, alkali metals). The choice of a suitable reducing agent is determined not only by the possibility of the redox reaction itself occurring (the value of DO is negative), but also by the occurrence of side reactions of the excess of the reducing agent with the reduced metal. Many transition metals can be reduced from oxides with carbon. However, it forms brittle and refractory interstitial phases with a number of metals. Sometimes this effect is used deliberately, for example, in the carbothermal reduction of iron ore in blast furnaces with the formation of pig iron.

Metallic chromium, molybdenum and tungsten are usually obtained by carbothermal or metallothermic reduction of their oxides or by electrolysis of their salt melt. For the needs of ferrous metallurgy, it is usually not necessary to obtain a very pure alloying metal. Therefore, during carbothermal reduction, together with iron ores, ferro-metals (ferrochromium, ferromolybdenum, ferrotungsten) are usually obtained.

The conventional oxidative roasting process, as applied to high grade molybdenite ores (containing >54% molybdenum), cannot be applied to low grade sulphide ores/concentrates for a variety of

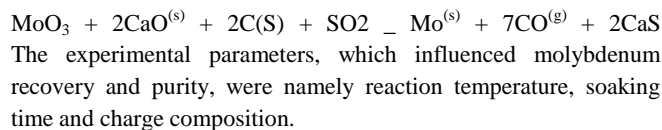
reasons. That is why these ores/concentrates require alternative processing schemes to extract molybdenum metal in a quantitative manner. The present investigation deals with two such processes, namely, soda ash roasting and lime enhanced carbothermic reduction that were successfully applied to extract molybdenum from an indigenous (and low grade) molybdenite concentrate (MoS_2).

These processes yielded molybdenum in the form of molybdenum trioxide (MoO_3) and molybdenum metal respectively. MoO_3 and molybdenum metal, so prepared, were further refined by carbon adsorption desorption and molten salt electrorefining techniques respectively. The final purity of MoO_3 and molybdenum metal were 99.9% and 99.8% respectively. These processes offered effective measures to contain environmental pollution and bypass tedious off gas treatment procedures, which, otherwise, are two major problem areas in the traditional processing of high grade MoS_2 ores/concentrates.

Procedure

During this enhanced carbothermic reduction, investigations are carried out using stoichiometric amounts of carbon and different mole ratios of CaCO_3 . The palletized charge mixture is reduced in a carbolite furnace at a temperature range of 1000–1200 °C and under reduced pressure (< 0.1 Pa). The reduced mass, after cooling, is powdered and the slag, CaS, is separated from the metal by elutriation. The metal powder is again compacted and sintered up to a temperature of 1500 °C under reduced pressure (0.01 Pa) for subsequent evaluations.

The lime-enhanced carbothermic reduction reactions of molybdenum-spent catalyst can be represented as follows:



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 electro-refined bath ($\text{KCl-K}_3\text{MoCl}_6$) was prepared by in situ chlorination of Mo metal in molten KCl to form K_3MoCl_6 . The sintered metal was placed at the bottom of a graphite crucible, containing the electrolyte. Pure metal was electrodeposited by optimizing various process parameters such as electrolysis temperature, soluble Mo in the bath and cathode current density.

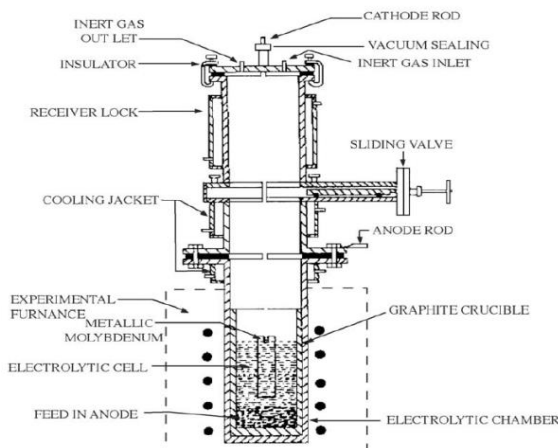


Figure 1. Electrolytic cell for carrying out electro-refining

The flow sheet, developed for these processes, is shown in Fig. 2.

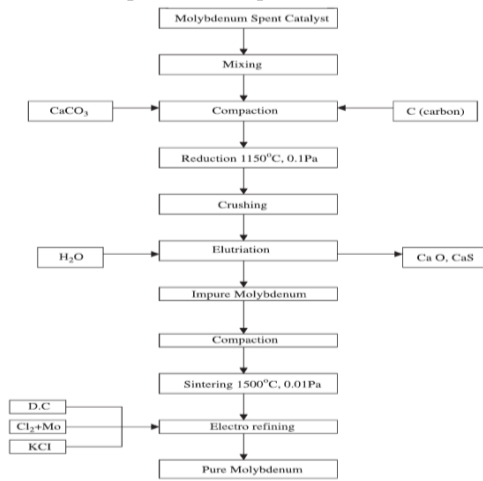


Figure 2. Flow sheet for the recovery of MoO_3/Mo from molybdenum concentrate.

Effect of lime content

Figure 3 describes the effect of the quantity of CaO on the overall reduction process. The extent of reduction increased significantly when the quantity of CaO was increased from 1.0 to 2.5 mol (per mol of MoS_2). At 4.0 mol of CaO (per mol of MoS_2), the reduction reaction was initially faster, but towards the end, the extent of reduction fell below that obtained in the case of 2.5 mol of CaO (per mol of MoS_2). This clearly showed that 2.5 mol of CaO (per mol of MoS_2) was just sufficient for achieving the complete reduction. The slight decrease in reduction rate towards the end was perhaps due to either the decreased contact between MoS_2 and carbon or formation of calcium molybdate.

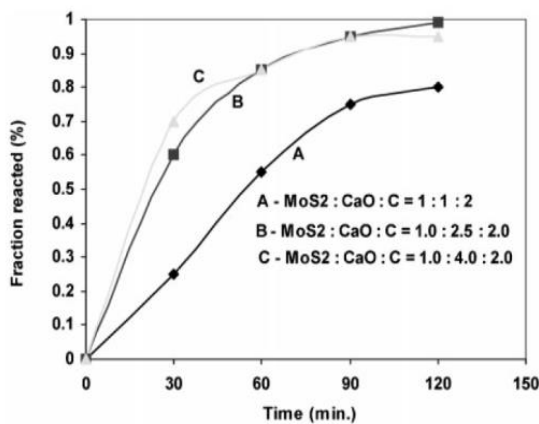


Figure 3. Effect of total lime content on extent of reduction: temperature of reduction was 1423 K

Effect of carbon content

Although addition of excess carbon, over 2.0 mol (per mol of MoS_2), was found to increase the rate of the reduction reaction in the initial stages (Fig. 4), the product, however, was found to contain significant amount of Mo_2C in addition to Mo, when the carbon content was increased from 2.0 to 4.0 mol (per mol of MoS_2). This was evident from the product analysis by XRD. In fact, the major phase was Mo_2C (not Mo) when the initial charge mixture contained 4 mol carbon (per mol of MoS_2). Therefore, the ideal carbon content was found to be 2.0 mol (per mol of MoS_2). The purity of MoO_3 and Mo metal powder, obtained just after the roasting cum leaching and reduction processes respectively, were

99% and 98.7%. Suitable refining techniques were then applied to purify the products further.

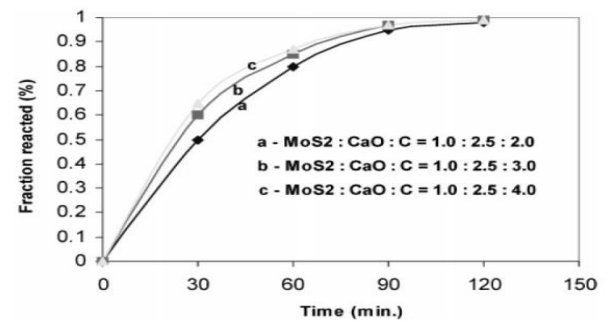


Figure 4. Effect of increasing amount of carbon on reduction rate, temperature of reduction was 1423 K

Conclusion

Molybdenum and molybdenum concentrates processing methods were analyzed and carbothermic reduction was explained and effect of lime and carbon content on the reduction process was investigated. The products, MoO_3 and molybdenum metal, were further refined by carbon adsorption–desorption and molten salt electrorefining processes to a purity of 99.9 and 99.8% respectively. High purity MoO_3 and Mo, thus prepared, could meet the specifications for industrial consumption.

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