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UP-GRADATION OF MoO_3 AND SEPARATION OF COPPER, IRON, ZINC FROM ROASTED MOLYBDENUM ORE BY A LEACHING PROCESS

Jin-Young Lee, Jyothi Rajesh Kumar*, Ho-Seok Jeon and Joon-Soo Kim

Extractive Metallurgy Department, Mineral Resources Research Division,
Korea Institute of Geoscience and Mineral Resources (KIGAM),
124 Gwahang-no, Yuseong-gu, Daejeon 305-350, Republic of Korea.
Phone: + 82-42-868-3313, Fax: + 82-42-868-3418,
E-mail: rajeshkumarphd@rediffmail.com; rkumarphd@kigam.re.kr

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Abstract - The present research paper deals with the oxidation process of molybdenum ore. The main target of the present study is the up-gradation of MoO_3 from roasted molybdenum ore by a leaching process without waste generation. The most important application of hydrometallurgical processing is the leaching process of the ore and it is the primary process to make pure metal from ore. The present investigations optimize the following experimental parameters to improve the concentration of MoO_3 as well as the separation of copper, iron and zinc in roasted molybdenum ore: effect of acid concentration, temperature, pulp density and leaching time were studied systematically. The temperature study was carried out at 550-595 °C for the oxidation process. The XRD result shows that oxidation process of molybdenum ore and SEM pictures were taken for particles before and after the oxidation process at 585 °C for 360 min.

Keywords: Molybdenum; Up-gradation; Leaching process; Separation.

INTRODUCTION

Molybdenum is the most important metal in human life. In recent years, the world molybdenum demand has been increasing. The world's largest producers of molybdenum materials are the United States, Canada, Chile, Russia, and China. Though molybdenum is found in minerals like wulfenite ($PbMoO_4$) and powellite ($CaMoO_4$), the main commercial source of molybdenum is molybdenite (MoS_2). Molybdenum is mined as a principal ore and is also recovered as a byproduct of copper and tungsten mining (Guptha, 2000). Processing of molybdenum from natural resources yields molybdenite concentrate, which is the first commercial product. To generate MoS_2 from the ore, physical treatments like crushing, pulping, grinding and flotation are the essential steps. The primary molybdnum ores will give as final product 90-95% MoS_2, whereas the complex ores of copper molybdenum will give 90% MoS_2 as final product (Gupta, 2000).

Within the field of metals science and technology, the leaching process is the most important technique for recovery and extraction of precious metal ions from natural and other sources. The leaching process is the one of the key steps in hydrometallurgical processes and the new millennium spurred interest in leaching processes to produce high purity rare and precious metals. Many of the new developments involve leaching processes at elevated temperatures and pressures. The advantages in operating under these conditions are greatly increased rates of reaction, favorable displacement of thermodynamic equilibria and the possibility of using certain gaseous or highly volatile reagents (Pehlke, 1975).

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*To whom correspondence should be addressed

Recently the two review articles were reported in the literature on extraction and recovery of molybdenum from spent catalysts by metallurgical processing (Zeng and Cheng, 2009a, 2009b). The first review concluded that, among all the metallurgical processes for spent catalysts, a process consisting of roasting and sulphuric acid leaching seems to be the best option since all of the valuable metals dissolve. In all the leaching routes, the metals in the solution have to be separated and purified by conventional separation techniques such as precipitation, solvent extraction, ion-exchange and adsorption methods. The second review article focused on the separation and purification of the molybdenum via hydrometallurgical concepts like precipitation, carbon adsorption, ion exchange and solvent extraction.

The process developed consisted of roasting at 750 °C followed by water leaching at 80 to 90 °C of the residue of the spent catalyst materials, and finally calcinations at 500 °C to prepare MoO_3 (Chen *et al.*, 2006). The soda ash roasting process is another methodology developed and reported for a secondary source of molybdenum (Kar *et al.*, 2004). At low temperatures (200-450 °C), the method established for the leaching process for spent $Co\text{-}Mo/Al_2O_3$ catalyst was sulfuric acid baking (Kim *et al.*, 2009). Thiophosphinic acid was proposed as a promising and selective extractants for recovery of the molybdenum from low grade ores (Archana *et al.*, 1996). For environmental protection, a less polluting process was proposed and established by a roasting operation at low temperatures for facilitating solubilising molybdenum of a low grade molybdenite concentrate (Singh *et al.*, 1998; van den Berg *et al.*, 2002).

80% of the molybdenum is used as an alloy element in steelmaking by the oxidized (MoO_3) powder form or Fe-Mo alloy form. The content of copper is restricted to less than ~ 0.5 % of the molybdenum oxide for steelmaking raw material. In steelmaking manufacturing process, copper was used for the surface of the end product. Therefore, an oxidation process of molybdenum ore was carried out for selective production of molybdenum oxide (Luo *et al.*, 2006; Dolati *et al.*, 2003; Ling *et al.*, 2003). Nickel laterite ores kinetic studies were reported, recently (Sahu *et al.*, 2011), and statistical examinations on gold-copper acid leaching studies were also reported (Mendes *et al.*, 2003). Mathematical models developed on heap and column leaching studies developed and reported (de Andrade Lima 2004).

Improvement and up-grading of the molybdenum content from ores or any other resources to meet the world-wide demand for molybdenum metal is an important task these days. We propose a leaching process to control and separate the other elements like copper, iron and zinc from molybdenum oxide, as well as improve the molybdenum metal content. This study focused on the acid concentration influence in the leaching process, the leaching time, temperature and pulp density. The thermodynamic potential at constant volume of the reaction points to a very irreversible and exothermic reaction. The oxidation process of MoO_3 is the main phenomenon in the present proposed process and temperature plays a main role in controlling the molybdenum loss rate. Therefore, an oxidation process of molybdenite was carried out at 550-595 °C in the present study.

MATERIALS AND METHODS

Apparatus and Reagents

Analysis of the metals such as Mo, Cu, Fe and Zn was performed using an inductively coupled plasma optimal emission spectrometer (ICP-OES) Perkin Elmer Model Optima 2000 Dr. An advanced pH/mV/RmV/ORP meter was used for pH measurements (Model: Orion 520A+, Thermo Electron Corporation). All the solid products were characterized by X-ray diffraction (XRD), model MAX 2500h, Rigaku and scanning electron microscopy (SEM) on a model JSM-6380LA, JEOL. The magnetic stirrer used for the leaching process was a MSH-20D Wise Stir model supplied by Daihan Scientific Company. All reagents used were analytical reagent grade.

Leaching Procedure

The experimental set up for the leaching process was made of Pyrex because of sudden temperature changes with sulfuric acid. A reflux condenser was employed to prevent a change in the density due to water evaporation during the reaction process (temperature is more than 45 °C). A thermocouple measured the temperature of the reaction water and maintained the temperature of the reaction water ±3 °C inside and outside of the reaction apparatus. After reaching the optimum temperature condition the molybdenum oxide ore sample was added to the sulphuric acid solution. A cross-shaped magnetic stirring bar was used for proper mixing of the sample with acid solution. Analysis of the metals such as copper, iron and zinc was recorded by ICP-OES and the leach rate was calculated. Finally, molybdenum oxide with improved content was obtained by a washing and drying process after the leaching process and copper impurities were removed from the sample as confirmed by XRD analysis. The general agreement between the percent leaching obtained was within ± 2 to 3%.

RESULTS AND DISCUSSIONS

The raw material contains 52.5% of molybdenum (Table 1, oxide standard 78.7%) in the molybdenum oxidation state. Figure 1 shows the oxidation process of molybdenum ore, as confirmed by XRD analysis of raw material. But the content of the copper impurities included in the process product is 0.92% and the present raw material not useful for making Fe-Mo alloy products. Therefore, the main objective of the present scientific study main objective is to produce molybdenum oxide with a copper content that is practicable for a Fe-Mo alloy product.

Figure 2 ((a) and (b)) shows a SEM picture of the sample before oxidative roasting and after oxidative roasting of the molybdenite ore. From the SEM picture we note that the size of the particles decreased when they convert from MoS_2 to MoO_3. The picture shows that before the oxidation process the surface of the mineral was very fine. On the other hand, the surface of the sintered ores after the process becomes very rough. This is because MoO_3 with a small volume is formed in the oxidative reaction of molybdenite, represented by reaction Equations (1) to (3). Therefore, an oxidation process reaction mechanism for a molybdenite ore shows that the size of the particle will gradually decrease (Figure 3).

General oxidation reaction equations for MoS_2:

$$MoS_2 + 3O_2 = MoO_2 + 2SO_2 \qquad (1)$$

$$MoO_2 + ½\, O_2(g) = MoO_3 \qquad (2)$$

$$MoS_2 + 3.5\, O_2 = MoO_3 + 2SO_2(g) \qquad (3)$$

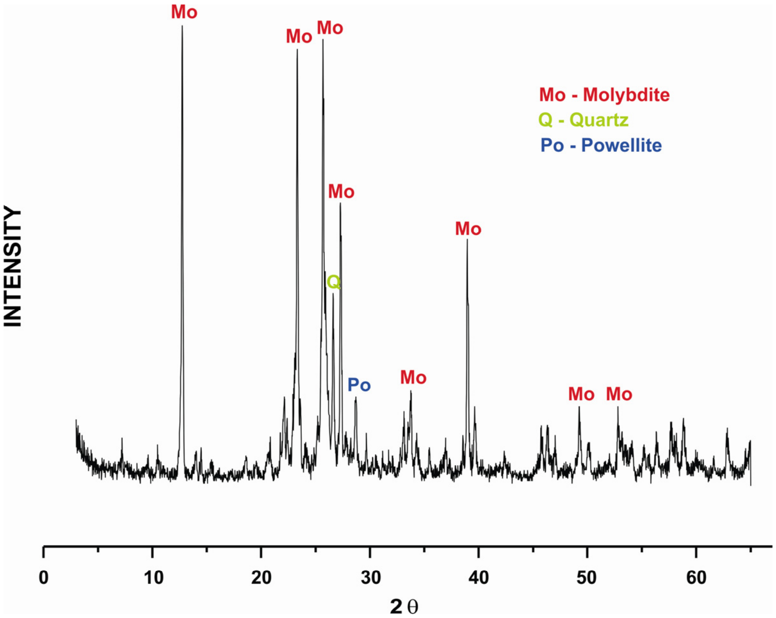
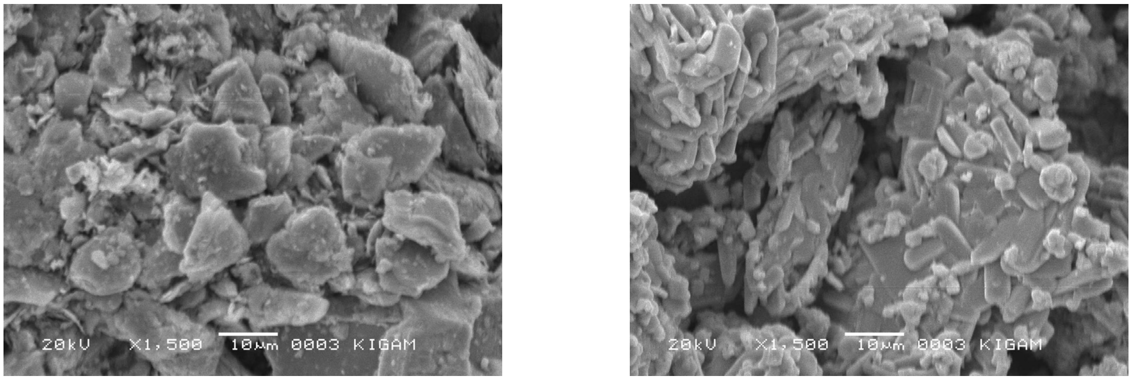


Figure 1: XRD patterns of molybdenum oxide used in the study.

Table 1: Chemical composition of molybdenum oxide before and after oxidative roasting

Name of the metal	Before oxidative roasting, amount (%)	After oxidative roasting, amount (%)	% Removal
Molybdenum	52.5	53.9	--
Copper	0.92	0.083	~91%
Iron	2.85	0.92	~67%
Zinc	0.29	0.016	~94.5%



(a) Before oxidative roasting (b) after oxidatve roasting

Figure 2: SEM pictures for particles before/after oxidative roasting at 585 °C for 360 min.

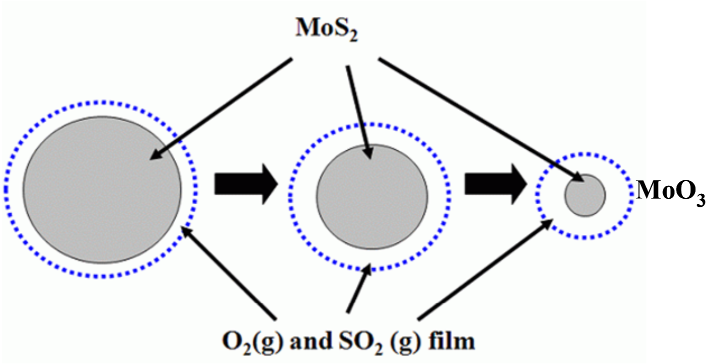


Figure 3: Schematic representation of a molybdenite particle.

Effect of Acid Concentration

The effect of sulphuric acid concentration was carried out between 1.0 to 10.0 wt% and the other experimental conditions were fixed such as temperature, 20 °C, pulp density, 10% and leaching time, 60 min. The experimental results clearly demonstrate that, the leaching rate of copper is very high and leached fast compared to other metals; it reached 90% with 1 wt% of acid concentration. On the other hand, the remaining metals like Zn leached ~72% and Fe leached ~46%. At high acid concentrations (5 wt% sulfuric acid), the leach rate of Fe and Zn increased. Copper oxide leaching kinetics are different and very fast compared with Zn and Fe. Literature on copper leaching with H_2SO_4 demonstrates that, the reaction process follows a second order reaction (Vracar *et al.* 2003). The leaching kinetics and rate constants for these metals were reported recently (Tshiongo *et al.*, 2011). For the removal of copper as target impurity, 2.5 wt% sulfuric acid (Figure 4) is more than enough for 100% leaching.

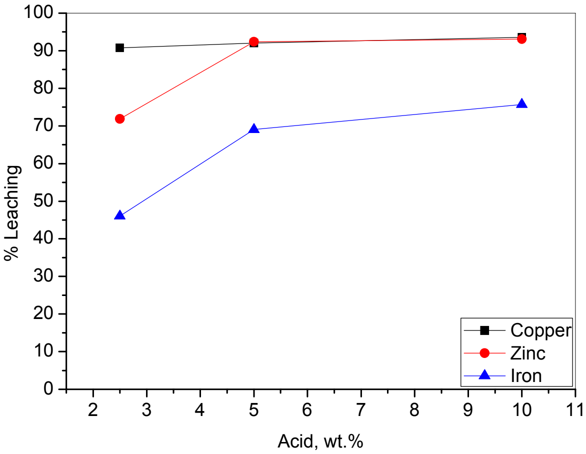


Figure 4: Effect of acid concentration on the leaching of impurity in molybdenum oxide (Temp.: 20 °C, pulp density: 10%, leaching time: 60min)

Effect of Temperature

The main aim of this experiment is the influence of temperature on the leaching process. The temperature was changed from 20 °C to 65 °C and other experimental conditions were: H_2SO_4, 2.5%, pulp density, 10%, leaching time, 60 min. Even at low temperatures copper was more influenced compared to other metals like zinc and iron. Finally, copper and zinc were quantitatively leached (~100%) at above 65 °C, but in the case of iron even at 70 °C it was ~ 96% (Figure 5). The leach rate of impurities increases upon increasing the reaction temperature, but in the case of copper at room temperature, the leach rate is ~90 %.

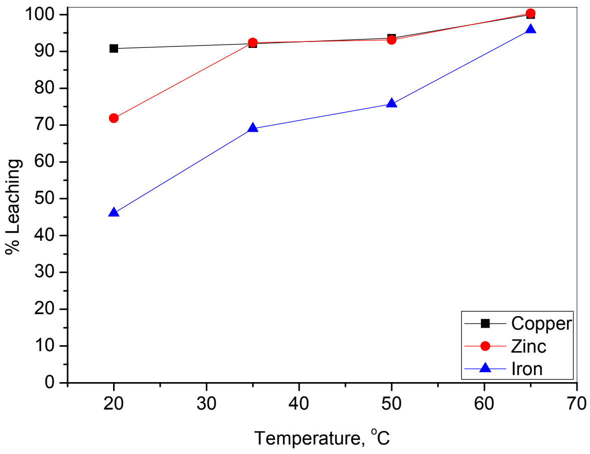


Figure 5: Effect of temperature on the leaching of impurity in molybdenum oxide (H_2SO_4: 2.5%, pulp density: 10%, leaching time: 60min)

Effect of Pulp Density

The density is generally connected with the productivity of the leaching process, so it is necessary to examine the density influence on the operational condition of the leach rate. Experimental conditions were 20 °C, a sulfuric acid density of 2.5 wt% and a leaching time of 60 minutes. The results are presented in Figure 6. From the figure, the leach rate decreases upon increasing pulp density. For the three metals copper, iron and zinc, the pulp density influence follows the order: copper > zinc > iron. Especially in the case of copper the pulp density reached 20% and even though the leaching rate is more than 90%. In the case of iron even with 5% pulp density only a leach rate below ~65% is possible.

Effect of Leaching Time

Influence of time in the present leaching process was studied in the range 1 to 60 min. The other experimental conditions were 10 wt% pulp density, 2.5 wt% sulfuric acid density and 20 °C reaction temperature. Figure 7 presents experimental results, which shows the influence of time on the leaching process. Copper and zinc were quickly influenced by the time, whereas iron was slowly influenced by the time. This is because the leaching kinetics of copper are fast relative to the other metals. Therefore, when considering only the copper leach rate (because only copper is a restriction target), 10 minutes is more than enough to leach ~80 to 83% (Fig. 7).

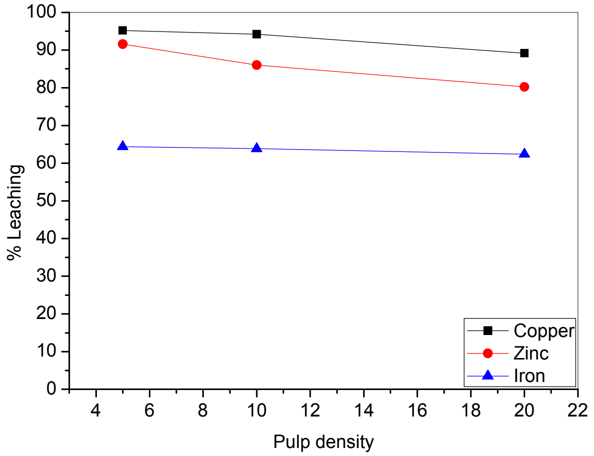


Figure 6: Effect of pulp density on the leaching of impurity in molybdenum oxide (H_2SO_4: 2.5 wt%, Temp.: 20 °C, leaching time: 60 min)

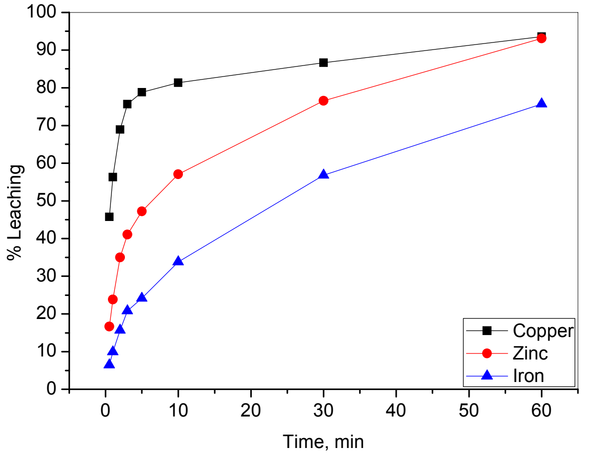


Figure 7: Effect of leaching time on the leaching of impurity in molybdenum oxide (H_2SO_4: 2.5%, Temp.: 20 °C, pulp density: 10%)

Based on the above scientific investigations, we propose optimum leaching conditions for the molybdenum ore oxidation process: H_2SO_4, 2.5%, temperature, 20 °C and leaching time, 30 minutes. After establishing the proper conditions for the leaching process, we achieved the main target of the present study. By reducing the other metal ions concentrations in the raw material, the molybdenum content was automatically improved in the oxide form. These results are presented as Table 1. The content of the molybdenum was increased by the present leaching methodology to ~53.9% and the content of copper was decreased to 0.083% from 0.92% (~91 % removal).

CONCLUSIONS

The following conclusions can be drawn from the present investigations on up-grading of the molybdenum oxide content in roasted molybdenum ore by the leaching process:

1. For the improvement of the molybdenum oxide concentration in roasted molybdenum ore: we are able to apply a sulphuric acid leaching process for up-grading molybdenum oxide as well as reducing the copper content of the raw material.
2. Even the low sulphuric acid density (2.5 wt%) removed the iron impurities; leaching kinetics of copper were quite fast compared with Zn and, showed more than 90 % copper leach.
3. The target metal copper was leached above 90% at room temperature whereas other metals like zinc and iron did not reach 90%.
4. The pulp density also influenced the other metals like zinc and iron and their rate of leaching drastically decreased, where-as copper was much less influenced by the pulp density with only a 5% leach rate change.
5. The leaching kinetics of copper is very fast when compared with other metals like zinc and iron. Within ten minutes, the copper leach reached ~80%
6. The present investigations gave the optimum conditions for copper removal from molybdenum ore: sulphuric acid density, 2.5 wt%, temperature, 20 °C (room temperature), time, 30 minutes, and pulp density, 20%. These conditions apply for leaching of copper and up-grade of molybdenum oxide with a removal rate of ~ 91%.
7. Finally, the present research concludes that, the proper leaching conditions (above) full fill the present demand for Ferro-molybdenum oxide

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