Preparation of Molybdenum Powder from Molybdenite Concentrate Through Vacuum Decomposition-Acid Leaching Combination Process

**Chongfang Yang, Yuezhen Zhou, Dachun Liu,
Wenlong Jiang, Fansong Liu and Zewei Liu**

Abstract A novel process that the combination of vacuum decomposition and acid leaching was proposed. The influence of distillation times, diameter and thickness of the feeding material on the mass fraction of Molybdenum (Mo) and sulphur (S) in residual was investigated. The influence of leaching temperature, leaching time, concentration of hydrochloric acid solution, and ratio of liquid to solid on leaching rates of Mo and S in acid leaching process was also investigated. Due to the fact that SO_2 emission happening in the long process of traditional molybdenum metallurgy could be avoided in this novel method, this combination process was environmentally-friendly. Molybdenum powder was obtained through handling molybdenite concentrate under the optimal condition parameters, and the mass fraction of Mo reached 98.29 wt%. So it's feasible to produce molybdenum powder from molybdenite concentrate by using this new method.

Keywords Molybdenite concentrate · Vacuum decomposition · Acid leaching · Molybdenum powder

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C. Yang · Y. Zhou · D. Liu · W. Jiang · F. Liu · Z. Liu
The National Engineering Laboratory for Vacuum Metallurgy, Kunming University of Science and Technology, Kunming 650093, People's Republic of China
e-mail: 476559736@qq.com

C. Yang · Y. Zhou · D. Liu · W. Jiang · F. Liu · Z. Liu
Key Laboratory for Nonferrous Vacuum Metallurgy of Yunnan Province,
Kunming 650093, People's Republic of China

D. Liu · W. Jiang (✉)
State Key Laboratory of Complex Nonferrous Metal Resources Clear Utilization,
Kunming 650093, People's Republic of China
e-mail: 122397715@qq.com

H. Kim et al. (eds.), *Rare Metal Technology 2017*,
The Minerals, Metals & Materials Series,
DOI 10.1007/978-3-319-51085-9_25

Introduction

Molybdenum (Mo) is widely used in special steels, aviation, alloys, chemistry, electronic and medical industries. MoS_2 is the main component of molybdenite which is the raw material to produce molybdenum metal products and chemical products. Molybdenite concentrate treatment can be classified into two major categories, including hydrometallurgy and pyrometallurgy. The common feature of these two methods is that the sulfide ores were converted into oxide or its salts, then the further purification of intermediates was carried out, and finally the Mo metal was obtained by reduction of MoO_2. These methods are widely used by large manufacturers in the world due to low cost and easy operation. But simultaneously there are some problems and the insufficiency, such as long flow sheet, large amount of SO_2 emission and serious environmental pollution [1–5].

To solve the SO_2 pollution problem, the main extraction processes for molybdenite concentrates include lime-roasting and pressure oxidation leaching. The sulfur was converted to calcium sulfate for the lime-roasting, it greatly reduced the emergence of SO_2 gas, but it generated a lot of calcium sulfate slag [6]. The sulfur was converted to sodium sulfate into the solution for the pressure oxidation leaching, this method avoided the problem of SO_2 emission, but led to a high production cost, because of heavy use of sodium hydroxide [7].

Many scholars have made several meaningful researches on vacuum decomposition process of molybdenite concentrate, from economy, working conditions and environmental protection, etc. Chen [8] investigated vacuum decomposition process of analytic grade molybdenum disulfide and molybdenite concentrate respectively, and useful experimental parameters were obtained. Liu et al. [2] simulated the crystal structure of MoS_2 by dynamics simulations, and studied the thermal decomposition of MoS_2, theoretical calculation provided guidance for the experimental results. Wang et al. [9, 10] studied the key steps, morphology and phase evolution of thermal decomposition process of molybdenum concentrate in vacuum, which was verified by vacuum decomposition experiments.

The main purpose of this research is to verify the feasibility of this new method of producing molybdenum powder from molybdenite concentrate, and further investigate the influence of distillation times, material diameter and thickness (in vacuum decomposition process) and leaching temperature, leaching time, concentration of hydrochloric acid, ratio of liquid to solid (in leaching process) on properties of the products.

Theoretical Analysis

Vacuum Decomposition Basis

The possible mechanism of thermal decomposition of MoS_2 was as follows, and the Gibbs free energy for reactions at different pressures were shown in Table 1 [9–11].

$$4MoS_2 = 2Mo_2S_3 + S_2 \tag{1}$$

$$Mo_2S_3 = Mo + 1.5S_2 \tag{2}$$

As can be seen from Table 1 that the initial decomposition temperature decreases monotonously with decreasing pressure. And comparing to reactions happened at atmospheric pressure, whose initial decomposition temperatures at above 2000 K, the temperatures were 1491 and 1575 K when the pressure fell to 10 Pa. In order to investigate the volatilization behaviors of Mo and S during vacuum decomposition process, saturated vapor pressure of Mo, S and MoS_2 were calculated in the Clausius-Clapeyron equation expressed as follows [12]:

$$\lg P^{\theta} = AT^{-1} + B\lg T + CT + D \tag{3}$$

$$\lg P^{\theta} = -AT^{-1} + B \tag{4}$$

where p^{θ} was the saturated vapor pressure, Pa. A, B, C and D were evaporation constants [13]. T was the absolute temperature, K. The melting point and saturated vapor pressure of Mo, S and its compound were shown in Table 2 and Fig. 1.

When the temperature was between melting point (1458 K) and initial decomposition temperature (1491 or 1575 K) of MoS_2 and Mo_2S_3, MoS_2 existed in liquid form in the experimental material. And according to the saturated vapor pressure of MoS_2, it could not evaporate into condensate during the vacuum decomposition process. When the temperature was higher than initial decomposition temperature of MoS_2, it was decomposed into Mo and S_2. Mo could not evaporate into

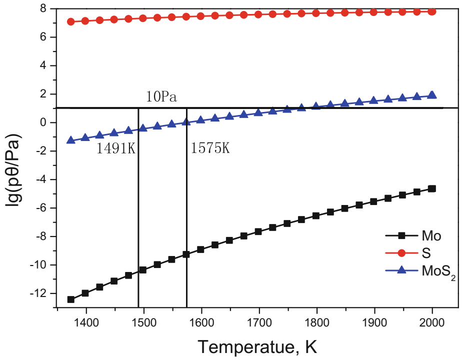
Table 1 Initial decomposition temperature of MoS_2 and Mo_2S_3 at different pressures

Reaction	Initial decomposition temperature/K			
	101,325 Pa	1000 Pa	100 Pa	10 Pa
$4MoS_2 = 2Mo_2S_3 + S_2(g)$	2053	1728	1601	1491
$Mo_2S_3 = 2Mo + 1.5S_2(g)$	2282	2052	1707	1575

Table 2 Melting points of Mo, S and its compound

	Mo	S	MoS_2
T_M/K	2896	388	1458

Fig. 1 Relationship between temperature and saturated vapor pressure



condensate because its melting point was much higher than chamber's temperature, and S could easily evaporate into condensate because its saturated vapor pressure was much higher than chamber pressure (5–35 Pa).

The theoretical research shows that vacuum decomposition is feasible to separate Mo and S in molybdenite concentrate. Mo nearly enriched in the residual, and S could easily evaporate into the condensate.

Acid Leaching Basis

The main impurities in crude molybdenum were mainly divided into three parts: acid oxide (SiO_2), alkaline oxides (Al_2O_3, MgO and CaO) and sulfides (such FeS). So the Gibbs free energy of leaching reactions of the alkaline oxides and sulfides in hydrochloric acid solution was shown in Table 3 [14].

As shown in Table 3, alkaline oxides (Al_2O_3, MgO and CaO) could be easily dissolved with hydrochloric acid, and sulfides (such FeS) could be partly dissolved with hydrochloric acid. Consequently, it was feasible to remove impurities and obtain molybdenum powder from crude molybdenum through acid leaching process.

Table 3 Gibbs free energy of leaching reactions

Leaching reaction	T/K	ΔG/(kJ mol^{-1})
$Al_2O_3 + 6H^+ = 2Al^{3+} + 3H_2O$	293–373	ΔG = 0.3745T − 237.98
$MgO + 2H^+ = Mg^{2+} + H_2O$		ΔG = 0.0477T − 145.51
$CaO + 2H^+ = Ca^{2+} + H_2O$		ΔG = 0.0214T − 184.78
$FeS + 2H^+ = Fe^{2+} + H_2S$		ΔG = −0.2833T + 99.98

Table 4 Chemical composition of molybdenite concentrate

Element	Mo	S	O	C	Al	Si	Mg	Ca	Fe	Cu	Others
wt%	50.73	35.96	5.61	0.32	4.52	1.29	0.12	0.10	0.78	0.40	0.17

Material

The high grade molybdenite concentrate was selected in this experiment. The chemical composition of molybdenite concentrate was got by chemical titration was shown in Table 4, and XRD pattern of molybdenite concentrate which were used in this research was shown in Fig. 2, respectively.

Apparatus and Methods

The vacuum decomposition equipment is developed independently by the National Engineering Laboratory for Vacuum Metallurgy. Major components of the system include vacuum equipment, heating equipment and Evaporator-Condenser set The schematic diagram of the vertical vacuum distillation furnace is shown in Fig. 3. The ohmic heating method was employed, and the heating temperature range is 300–1973 K. The vacuum level for this equipment is 5 Pa.

Fig. 2 XRD pattern of molybdenite concentrate

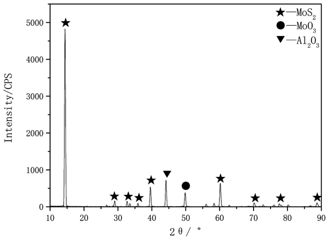


Fig. 3 Schematic diagram of vertical vacuum distillation furnace: *1* Furnace lid; *2* Furnace body; *3* Vacuum pipe; *4* Temperature sensor; *5* Furnace bottom; *6* Crucible holder; *7* Crucible; *8* Heat holding cover; *9* Electrode; *10* Heating unit; *11* Condenser

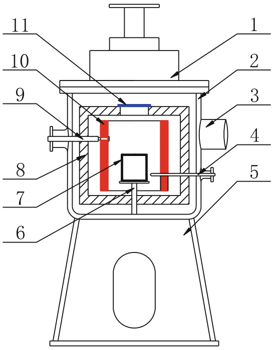
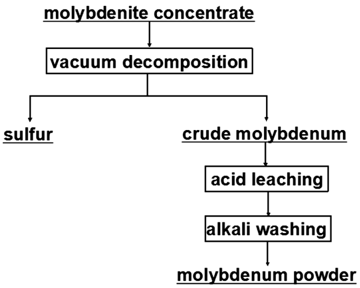


Fig. 4 Main flowsheet of the process



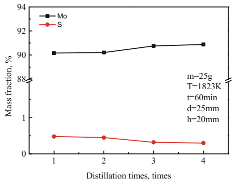
The main flowsheet of the process is shown in Fig. 4. The process mainly includes vacuum decomposition, acid leaching and alkali washing.

Results and Discussion

Effect of Distillation Times

Our previous research work, verified the feasibility of producing crude molybdenum from molybdenite concentrate by vacuum decomposition process. The influence of temperature and heat preservation time on the mass fraction of Mo and S in residual have been obtained [15]. the better condition of temperature and heat preservation time was 60 min and 1823 K, respectively. However, it was only part of the experimental rules with the vacuum decomposition of molybdenite concentrate. So the influence of distillation times on the mass fraction of Mo and S in residual was further investigated, as shown in Fig. 5. As shown in Fig. 5, as the distillation times increased, the mass fraction of Mo in residual increased from 90.17 to 90.88 wt%, while the mass fraction of S decreased from 0.48 to 0.30 wt%, which indicates that the increase of the distillation times was beneficial to decreasing the content of S in the residual, however, the decrease of the mass fraction was too small to be considered. Thus, compared with the influence of temperature and heat preservation time on the mass fraction of Mo and S in residual, the influence of distillation times could be ignored.

Fig. 5 Influence of distillation times on the mass fraction of Mo and S in residual (d is the material diameter, h is the material thickness)



Effect of Material Diameter and Thickness

To investigate the interplay of diameter and thickness in feeding material, the experiments were carried out. The results influence of diameter and material thickness on the mass fraction of Mo and S in residual, as shown in Fig. 6. Figure 6 shows the mass fraction of Mo decreased, while the mass fraction of S increased, with diameter of feeding material distributed in the range of 20–30 mm. Compared with the influence of the diameter of feeding material, the influence of the material thickness was similar.

As mentioned above, optimal condition parameters of vacuum decomposition experiment can be summarized as follows: experiment was carried under the pressure of 5–35 Pa for 60 min at 1823 K, distillation times was once, the sample mass was 25 g, material diameter and thickness was 25 and 20 mm, respectively. The chemical composition of the residual was got by chemical titration, and the removal rate was calculated from Eq. (5), were shown in Table 5. XRD pattern of residual were shown in Fig. 7.

$$r_v = \frac{m_x - m_y}{m_x} \times 100\% \tag{5}$$

where r_V is the removal rate of element in the vacuum decomposition process, %. m_x is the content of element in the molybdenite concentrate, g. m_y is the content of element in residual.

As shown in Table 5 and Fig. 7, residual was obtained after vacuum decomposition was crude molybdenum. The condensate gathered from the condenser was crude sulfur. The direct recovery rate of Mo was 97.28%, which indicated that a very small amount of Mo was lost, and the possible reason accounting for the phenomenon above could be that the mechanical loss was caused by vacuum system. As to the impurity elements, such as O, Al, Si and Cu, their removal rates were relatively large, ranging from 67.8 to 90.15%. However, the mass fraction of

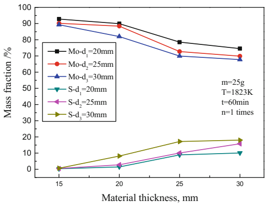
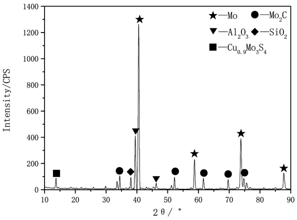


Fig. 6 Influence of material thickness on the mass fraction of Mo and S in residual

Table 5 Chemical composition and removal rate (r_V)

Element	Mo	S	O	C	Al	Si	Mg	Ca	Fe	Cu	Others
wt%	90.17	0.48	3.30	0.90	3.09	0.30	0.21	0.17	0.98	0.07	0.33
r_V.%	2.72	99.27	67.80	−53.94	62.58	87.27	4.22	6.96	31.23	90.15	–

Fig. 7 XRD pattern of residual after vacuum decomposition



C increased from 0.32 to 0.9 wt% in the residual. The reason was the formation of Mo_2C, as shown Fig. 7, because the high-purity graphite crucible used in experiments provided the carbon source and high temperature promoted carbon to participate in the experimental material.

Effect of Temperature

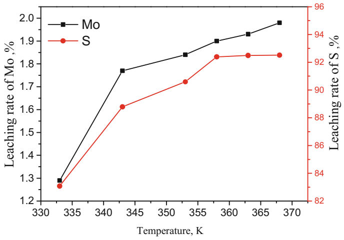
In this work, the crude molybdenum was obtained after vacuum decomposition, the mass fraction of Mo and S was 90.17 and 0.48 wt%, respectively. The crude molybdenum was the experimental materials at the leaching process. Leaching experiments were performed under ordinary pressure, the sample mass was 18.0 g, and the dried powders were smaller than 200 mesh. The influence of leaching temperature on the leaching rate of Mo and S was studied, and the leaching rate of Mo and S in the leaching slag was calculated from Eq. (6) presented in Fig. 8.

$$r_L = \frac{m_i - m_j}{m_i} \times 100\% \tag{6}$$

where r_L is the leaching rate of Mo and S in the leaching process, %. m_i is the content of element in the crude molybdenum, g. m_j is the content of element in leaching slag.

Figure 8 shows when the leaching temperature increased from 333 to 358 K, the leaching rate of S increased from 83.08 to 92.39%, and the leaching rate of Mo ranged from 1.29 to 1.9%. Beyond 358 K, the leaching rate of S increases slowly,

Fig. 8 Influence of temperature on Mo and S leaching (L/S ratio 8 ml/g, 120 min, initial hydrochloric acid concentration 4 mol/L)



but the leaching rate of Mo increases quickly,so a further increase in temperature to 368 K has no significant effect, and further experiments were carried out for 358 K.

Effect of Time

The leaching rate of Mo and S is also influenced by leaching time. The higher leaching rate of S may not be achieved in a short time whilst long time have disadvantages such as higher production cost. So, in this work, an intermediate time range from 15 to 240 min was selected and its influence was studied as shown in Fig. 9. It can be seen the leaching rate of S is increased from 90.48 to 93.59%, and the leaching rate of Mo ranged from 0.78 to 1.93%, when the leaching time increased from 30 to 120 min. Beyond 120 min, the leaching rate of S increases slowly, but the leaching rate of Mo increases quickly, so all further experiments were carried out for 120 min.

Effect of Hydrochloric Acid Concentration

In order to investigate the effect of the hydrochloric acid concentration on the leaching rate of Mo and S, the experiments was carried out at 358 K for 120 min with sample mass was 18.0 g, and the results was shown in Fig. 10. It can be seen from Fig. 10 that the effect of hydrochloric acid concentration under the same

Fig. 9 Influence of time on leaching rate of Mo and S (L/S ratio 8 ml/g, 358 K, initial hydrochloric acid concentration 4 mol/L)

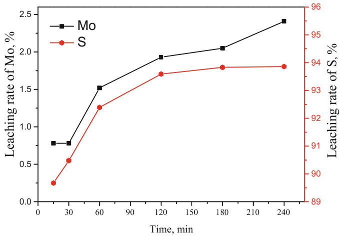
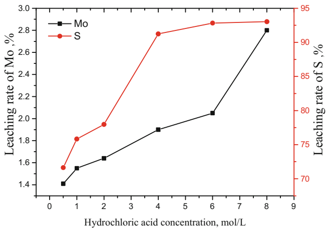


Fig. 10 Influence of hydrochloric acid on leaching rate of Mo and S (L/S ratio 8 ml/g, 120 min, 358 K)



conditions as before. Therefore the optimum hydrochloric acid concentration appears to be 4 mol/L and all further experiments were carried out at this hydrochloric acid concentration.

Effect of Liquid-to-Solid Ratio

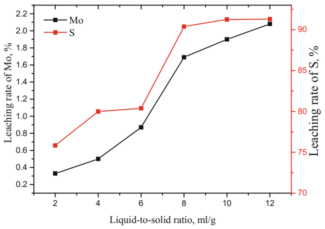


Fig. 11 Influence of liquid-to-solid ratio on leaching rate of Mo and S (initial hydrochloric acid concentration 4 mol/L, 120 min, 358 K)

The ratio of liquid to solid plays an important role in leaching processes. The results of liquid-to-solid ratio shown in Fig. 11 under optimum leaching conditions, indicate that the leaching rate of S increases from 75.83 to 90.38%, the leaching rate of Mo increases from 0.33 to 1.69% as the liquid-to-solid ratio increases from 2 to 8 ml/g. A further increase in liquid-to-solid ratio up to 12 ml/g has not helpful to leaching rate of S, and the S leaching rate can get to 90.38% in 120 min. So 8 ml/g is selected.

Under above optimization experimental conditions, acid leaching slag was obtained. In order to further remove the acid oxides, in this work, the acid leaching slag was handled by alkali washing (1.0 mol/L, NaOH solution). And the slag obtained after alkali washing process was the molybdenum powder. The chemical composition of the leaching slag was got by chemical titration, and the removal rate of element in the molybdenum powder was calculated from Eq. (7) were shown in Table 6.

$$r_R = \frac{m_a - m_b}{m_a} \times 100\% \tag{7}$$

Table 6 Chemical composition and removal rate (r_R) of molybdenum powder

	Mo	S	O	C	Al	Si	Mg	Ca	Fe	Cu	Others
wt%	98.290	<0.005	0.190	0.920	0.180	<0.005	<0.005	0.060	0.240	0.006	0.099
r_R.%	4.86	99.99	98.34	−41.18	98.04	99.81	97.95	70.54	84.89	99.26	–

where r_R is the removal rate of element through vacuum decomposition-acid leaching combination process, %. m_a is the content of element in the molybdenite concentrate, g. m_b is the content of element in the molybdenum powder.

Conclusions

(1) It's feasible to produce molybdenum powder from molybdenite concentrate by using the new method proposed in this research. Above all, this novel process was short flow, environment-friendly compared with the traditional methods.
(2) The crude molybdenum was obtained by vacuum decomposition of molybdenite concentrate. The mass fraction of Mo and S is 90.17 and 0.48 wt%, respectively. The optimal condition parameters are as follows: the pressure of 5–35 Pa for 60 min at 1823 K, distillation times is once, material diameter and thickness is 25 and 20 mm, respectively.
(3) The molybdenum powder was obtained by the acid leaching and alkali washing of the residues of vacuum decomposition. The mass fraction of Mo and S is 98.29 and 0.005 wt% respectively, and removing rate of S reached 99.99%. And the optimal condition parameters are as follows: the leaching temperature, leaching time, concentration of hydrochloric, concentration of NaOH and ratio of liquid to solid is 358 K, 120 min, 4.0, 1.0 mol/L and 8 ml/g, respectively.

Acknowledgements The authors acknowledge the financial support from National Natural Science Foundation of China (NO. U1202271), the Program for Innovative Research Team in University of Ministry of Education of China (NO. IRT1250), and the Program for Innovative Research Team in Nonferrous Metal Vacuum Metallurgy of Ministry of Science and Technology (Grant No. 2014RA4018), and the Cultivating Plan Program for the Technological Leading Talents of Yunnan Province (2014HA003).

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