



## Molybdenite–limestone oxidizing roasting followed by calcine leaching with ammonium carbonate solution

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**Abstract:** Oxidizing roasting of molybdenite with lime can significantly reduce  $\text{SO}_2$  pollution compared with the traditional roasting without lime. However, the calcine is subsequently leached by sulfuric acid, resulting in serious equipment corrosion and abundant non-recyclable  $\text{CaSO}_4$  slag. In this work, a novel process, in which the molybdenite was roasted with  $\text{CaCO}_3$  followed by  $(\text{NH}_4)_2\text{CO}_3$  solution leaching, was proposed to improve the art of lime roasting–sulfuric acid leaching. Oxidizing roasting of molybdenite with  $\text{CaCO}_3$  was investigated through thermodynamic calculation, thermogravimetric analysis and roasting experiments. The results show that the products of the oxidizing reaction of  $\text{MoS}_2$  in the presence of  $\text{CaCO}_3$  and  $\text{O}_2$  are  $\text{CaSO}_4$ ,  $\text{CaMoO}_4$  and  $\text{CO}_2$  at 573–1000 K. The  $\text{MoS}_2$  conversion rate achieves approximately 99% and the sulfur-retained rate attains approximately 95% with a  $\text{CaCO}_3$ -to- $\text{MoS}_2$  molar ratio of 3.6 at 500 °C for 1 h by adding 5% mineralizer A (mass fraction). The leaching results show that the leaching rate of Mo reaches 98.2% at 85 °C for 7 h with a  $(\text{NH}_4)_2\text{CO}_3$  concentration of 600 g/L and a liquid–solid ratio of 10 mL/g. The results presented are potential to develop a novel cleaner technique for ammonium molybdate production.

**Key words:** molybdenite; limestone; ammonium carbonate; oxidizing roasting; leaching

### 1 Introduction

China is rich in molybdenum resource and contributes more than 40% of the global molybdenum production. However, molybdenite concentrate is still primarily processed using the traditional route, in which the concentrate is oxidizing roasted followed by ammonium hydroxide leaching [1]. This process presents many drawbacks because of its outdated technology as well as small production scale [2]. Firstly, the traditional technique exhausts a large amount of low concentration sulfur exhaust gases [3] during oxidizing roasting, exacerbating environmental pollution and limiting sustainable development. Secondly, the resultant  $\text{MoO}_3$  can volatilize at high roasting temperatures. Thirdly, the calcine may block as the molybdenite contains low melting point metal impurities, such as Cu, Pb and Bi [4]. In addition, the overall recovery is not high, and Re in molybdenite is mostly lost with the exhaust gases [5,6], resulting in a large waste of resources. Finally, the traditional technique is not applicable for complex and low grade ores [7–9]. Molybdenum

oxidizing–chlorinating roasting [10] can decrease the oxidizing temperature of molybdenite from 550–600 to 450 °C; however, it needs high requirement for the equipment because of generating chlorine gases.

DAUGHERTY [11] suggested the use of lime-roasting to reduce the exhaust gases and recover Re. Mo and Re in the molybdenite transform to  $\text{CaMoO}_4$  and  $\text{Ca}(\text{ReO}_4)_2$ , respectively, whereas sulfur turns to  $\text{CaSO}_4$  when lime is added in the oxidizing roasting process.  $\text{Ca}(\text{ReO}_4)_2$  in the calcine can be leached out immediately by water.  $\text{CaMoO}_4$  can transform to  $\text{H}_2\text{MoO}_4$  and  $\text{CaSO}_4$  when the calcine is leached by sulfuric acid. Then, Mo can be recovered by ion exchange or solvent extraction. CHEN [12] and ZHOU et al [13] conducted further studies on the lime-roasting process and increased the recovery of Mo to 95% and Re to more than 86%. CHEN et al [14] obtained the sulfur-retained rate up to 91.5% and the leaching rate of molybdenum up to 99.1% through investigating calcium-based roasting of low grade molybdenum concentrates and acid leaching process. However, some deficiencies remain in practical application. This process generates a high amount of non-recyclable residue mainly containing  $\text{CaSO}_4$  because

of the lime addition in the roasting process. Moreover, lime-roasting results in serious equipment corrosion and produces much acid-bearing wastewater because a high amount of non-recyclable sulfuric acid is used to leach the calcine. Ion exchange and solvent extraction for recovering Mo and Re further increase the complexity of the suggested process and discharge a large quantity of wastewater, resulting in a high production cost.

$\text{CaCO}_3$  is more frequently used as a sulfur-fixing agent in industrial production [15] as it is more convenient to store, more stable, and more economical compared with lime. Moreover,  $(\text{NH}_4)_2\text{CO}_3$  can react with  $\text{CaMoO}_4$ , forming  $\text{CaCO}_3$  and  $(\text{NH}_4)_2\text{MoO}_4$ . Additionally, adding some  $(\text{NH}_4)_2\text{CO}_3$  in the traditional aqueous ammonia leaching process can increase Mo recovery from 83%–85% to 93%–96% by preventing the generation of  $\text{CaMoO}_4$  and  $\text{FeMoO}_4$  and inhibiting the coverage of  $\text{Fe}(\text{OH})_2$  up to the Mo-bearing ore particles [16]. Thus, if  $\text{CaCO}_3$  is employed to replace  $\text{CaO}$  during the oxidizing process of molybdenite, and  $(\text{NH}_4)_2\text{CO}_3$  solution as leaching agent to replace sulfuric acid in the leaching process, we will obtain leaching residue mainly consisting of  $\text{CaCO}_3$  which could be conveniently reused in the raw meal preparation for roasting, and the remaining  $(\text{NH}_4)_2\text{SO}_4$  solution after extracting Mo could be used as chemicals. Under these considerations, a novel cleaner process for extracting Mo from molybdenite concentrate was proposed, where the oxidizing roasting of molybdenite was conducted in the presence of  $\text{CaCO}_3$  and the resultant calcine was leached by  $(\text{NH}_4)_2\text{CO}_3$  solution.

In this work, oxidizing roasting process in the presence of  $\text{CaCO}_3$  and  $\text{O}_2$  was thoroughly studied by thermodynamic calculation, thermogravimetric analysis (TGA) and roasting experiments, and then the leaching

process of the calcine obtained under the optimal roasting conditions was preliminarily tested using  $(\text{NH}_4)_2\text{CO}_3$  solution as the leaching agent. Finally, we attempted to propose a cleaner schematic technological process for producing ammonium molybdate.

## 2 Thermodynamic calculation and thermogravimetric analysis

### 2.1 Thermodynamic calculation

The possible reactions during molybdenite oxidizing roasting in the presence of  $\text{CaCO}_3$  mainly involve the oxidation of  $\text{MoS}_2$  [17,18] and the reactions between  $\text{MoS}_2$  and  $\text{CaCO}_3$  in the presence of  $\text{O}_2$ . The reactions were conducted at constant temperature. Thus, the changes in standard Gibbs free energies of the reactions can be calculated in accordance with the classical thermodynamic theory [19]. Most of the thermodynamic data required for the calculation are drawn from Refs. [20–22]. The reactions and thermodynamic calculation are shown in Table 1.

Table 1 indicates that the changes in the Gibbs free energies of Reactions (1) – (13) are all negative at 298–1000 K. This finding suggests that all possible reactions, except for Reaction (14), could occur spontaneously, and that  $\text{CaCO}_3$  would not decompose below 1000 K. The results also show that changes in the Gibbs free energies of some reactions, i.e., Reactions (1), (2), (4), (6)–(10), and (12) increase with increasing temperature, whereas those of the other reactions decrease. However, the change in the Gibbs free energy of Reaction (8) always presents the lowest value at 298–1000 K, suggesting that Reaction (8) is most likely to occur during molybdenite oxidizing roasting process in the presence of  $\text{CaCO}_3$  and  $\text{O}_2$ .

**Table 1** Possible reactions involved in oxidizing roasting process of molybdenite concentrate and changes in Gibbs free energies at different temperatures

| No. | Reaction equation                                                                                           | $\Delta G/(\text{kJ} \cdot \text{mol}^{-1})$ |           |           |           | $\Delta G$ equation              |
|-----|-------------------------------------------------------------------------------------------------------------|----------------------------------------------|-----------|-----------|-----------|----------------------------------|
|     |                                                                                                             | 298 K                                        | 600 K     | 800 K     | 1000 K    |                                  |
| 1   | $\text{MoS}_2 + 7/2\text{O}_2 = \text{MoO}_3 + 2\text{SO}_2$                                                | −1000.128                                    | −937.412  | −895.787  | −854.744  | $\Delta G = 0.2007T - 1058.6398$ |
| 2   | $\text{MoS}_2 + 3\text{O}_2 = \text{MoO}_2 + 2\text{SO}_2$                                                  | −864.855                                     | −823.244  | −795.328  | −767.724  | $\Delta G = 0.1380T - 905.9915$  |
| 3   | $6\text{MoO}_3 + \text{MoS}_2 = 7\text{MoO}_2 + 2\text{SO}_2$                                               | −53.219                                      | −138.033  | −192.575  | −245.600  | $\Delta G = -0.2718T + 27.2933$  |
| 4   | $\text{MoO}_2 + 0.5\text{O}_2 = \text{MoO}_3$                                                               | −156.692                                     | −144.201  | −100.459  | −87.021   | $\Delta G = 0.0046T - 158.3734$  |
| 5   | $2\text{MoS}_2 + \text{O}_2 = \text{Mo}_2\text{S}_3 + \text{SO}_2$                                          | −161.487                                     | −170.347  | −175.775  | −181.224  | $\Delta G = -0.0282T - 153.0845$ |
| 6   | $\text{Mo}_2\text{S}_3 + \text{SO}_2 = 2\text{MoO}_2 + 3\text{SO}_2$                                        | −1568.223                                    | −1476.075 | −1414.881 | −1354.224 | $\Delta G = 0.3043T - 1658.8985$ |
| 7   | $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$                                                                  | −141.490                                     | −84.754   | −47.193   | −10.011   | $\Delta G = 0.1869T - 197.1901$  |
| 8   | $3\text{CaCO}_3 + \text{MoS}_2 + 4.5\text{O}_2 = 2\text{CaSO}_4 + \text{CaMoO}_4 + 3\text{CO}_2$            | −1616.971                                    | −1530.604 | −1473.008 | −1415.990 | $\Delta G = 0.2857T - 1702.1338$ |
| 9   | $2\text{CaCO}_3 + \text{MoS}_2 + 4\text{O}_2 = \text{CaSO}_4 + \text{CaMoO}_4 + 2\text{CO}_2 + \text{SO}_2$ | −1325.869                                    | −1275.996 | −1242.408 | −1209.067 | $\Delta G = 0.1662T - 1375.5504$ |
| 10  | $\text{CaCO}_3 + \text{MoS}_2 + 3.5\text{O}_2 = \text{CaMoO}_4 + 2\text{SO}_2 + \text{CO}_2$                | −1034.767                                    | −1021.388 | −1011.809 | −1002.144 | $\Delta G = 0.0468T - 1048.9670$ |
| 11  | $\text{CaCO}_3 + \text{MoO}_3 = \text{CaMoO}_4 + \text{CO}_2$                                               | −34.640                                      | −83.976   | −116.022  | −147.399  | $\Delta G = -0.1539T + 9.6728$   |
| 12  | $2\text{CaCO}_3 + 2\text{SO}_2 + \text{O}_2 = 2\text{CaSO}_4 + 2\text{CO}_2$                                | −582.203                                     | −509.216  | −461.199  | −413.846  | $\Delta G = 0.2388T - 653.1667$  |
| 13  | $\text{CaCO}_3 + \text{MoO}_2 + 0.5\text{O}_2 = \text{CaMoO}_4 + \text{CO}_2$                               | −169.912                                     | −198.177  | −216.481  | −234.420  | $\Delta G = -0.0912T - 142.9755$ |
| 14  | $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$                                                                  | 130.127                                      | 82.987    | 52.608    | 23.017    | $\Delta G = -0.1511T + 174.6393$ |

## 2.2 Thermogravimetric analysis (TGA)

Analytically pure  $\text{MoS}_2$ , analytically pure mixture of  $\text{MoS}_2$  and  $\text{CaCO}_3$  with a  $\text{CaCO}_3$  to  $\text{MoS}_2$  molar ratio of 3.6, and analytically pure  $\text{CaCO}_3$  were subjected to TGA at a heating rate of 10 K/min from 20 to 1000 °C in an oxidizing atmosphere by using a thermogravimetric analyzer (STA2409PC, NETZSCH Company, Germany).

Figure 1 illustrates the results from the TGA and differential thermal analysis (DTA) of  $\text{MoS}_2$ . An exothermic peak is found in the approximate range from 360 to 580 °C, during which  $\text{MoS}_2$  is oxidized. The oxidation of  $\text{MoS}_2$  begins at approximately 360 °C, accelerates at 400 °C and then terminates at approximately 580 °C. Correspondingly, the sample continuously loses mass below 580 °C, generating  $\text{SO}_2$ . Then, the sample does not sharply lose mass until about 780 °C because of the evaporation of the generated  $\text{MoO}_3$ , which is consistent with the endothermic peak at approximately 800 °C in the DTA curve. Figure 2 shows the TGA and DTA curves of the analytically pure mixture of  $\text{MoS}_2$  and  $\text{CaCO}_3$  with a  $\text{CaCO}_3$  to  $\text{MoS}_2$  molar ratio of 3.6. This result indicates an exothermic

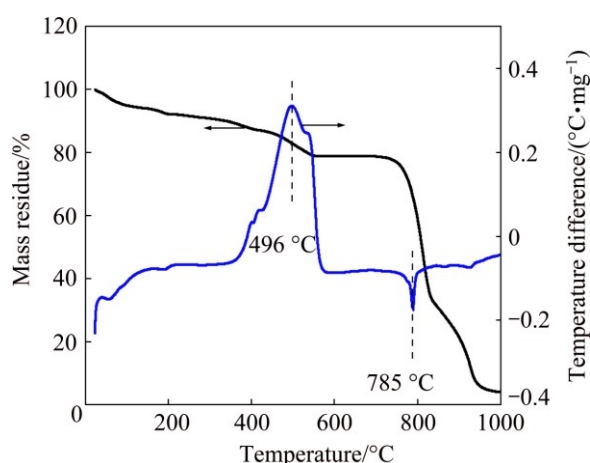


Fig. 1 Thermogravimetric and differential thermal curves of analytically pure  $\text{MoS}_2$

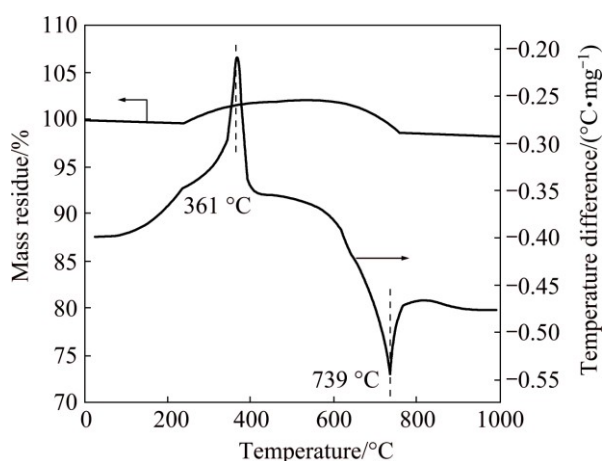


Fig. 2 Thermogravimetric and differential thermal curves of mixture of  $\text{MoS}_2$  and  $\text{CaCO}_3$  at  $n(\text{CaCO}_3):n(\text{MoS}_2)=3.6$

peak at 250–400 °C, in which the sample slightly gains mass as the sulfur in the molybdenite is fixed by  $\text{CaCO}_3$ . That is, the oxidizing roasting of molybdenite may be performed as Reaction (8). The sample then slightly loses mass at 600–800 °C, which corresponds to the endothermic peak at approximately 740 °C in the DTA curve. Compared with the TGA and DTA curves of analytically pure  $\text{CaCO}_3$  in Fig. 3, the slight mass loss at 600–800 °C for the TGA curve in Fig. 2 should be caused by the decomposition of spare  $\text{CaCO}_3$ .

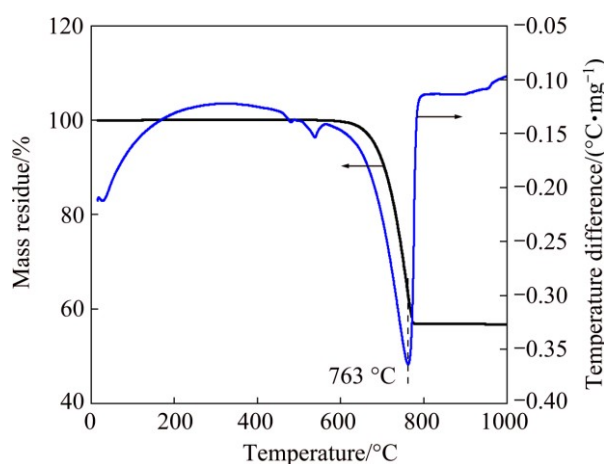


Fig. 3 Thermogravimetric curve of  $\text{CaCO}_3$

The oxidizing roasting temperature of  $\text{MoS}_2$  is reduced to 300–500 °C (Fig. 2) from 400–600 °C (Fig. 1) by adding  $\text{CaCO}_3$ , suggesting that adding  $\text{CaCO}_3$  in the oxidizing process of  $\text{MoS}_2$  can not only fix the sulfur to reduce  $\text{SO}_2$  emission but also apparently promote the oxidizing process of  $\text{MoS}_2$  and consequently reduce the oxidizing roasting temperature. This result agrees with the thermodynamic calculation in Section 2.1.

## 3 Experimental

### 3.1 Raw materials

Molybdenite concentrate used in the experiments was provided by a molybdenum refinery in Jiangxi Province, China. The chemical compositions and the X-ray diffraction (XRD) pattern of the concentrate are shown in Table 2 and Fig. 4, respectively, indicating that the  $\text{MoS}_2$  is the main essential component and the content of Mo is 40.33%. Additionally,  $\text{CaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , mineralizer and  $(\text{NH}_4)_2\text{CO}_3$  used in this work are analytical grade.

Table 2 Chemical composition of molybdenite concentrate (mass fraction, %)

| Mo    | K    | Na   | Cu   | W    | Si   | S     | Others |
|-------|------|------|------|------|------|-------|--------|
| 40.33 | 0.31 | 0.11 | 0.24 | 0.01 | 2.06 | 27.33 | 29.39  |

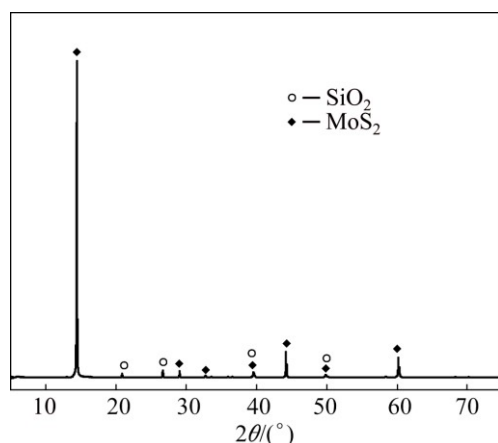


Fig. 4 XRD pattern of molybdenite concentrate

### 3.2 Experimental procedure

#### 3.2.1 Raw meal preparation

The concentrate was firstly mixed with  $\text{CaCO}_3$  at a certain ratio. The mixture was then milled in a low-scale vibration mills thrice for 120 s each instance to ensure that the samples were well mixed and to control the particle size of the mixture to 50–70  $\mu\text{m}$ .

#### 3.2.2 Oxidizing roasting

The raw meal prepared was put in a corundum crucible (100 mm  $\times$  30 mm  $\times$  20 mm) with a meal thickness of 8–10 mm and then roasted under an oxidizing airflow in a muffle furnace at preset temperatures for certain duration. The calcine obtained was subsequently taken out from the furnace and naturally cooled in air to room temperature.

#### 3.2.3 Calcine leaching

The cooled calcine was accurately weighed and then leached by 100 mL  $(\text{NH}_4)_2\text{CO}_3$  solution in a 150 mL sealed rotating steel reactor. The reactor was immersed in a glycerol cell at a preset temperature with temperature precision of 1  $^\circ\text{C}$ . Two 15 mm-diameter and two 5 mm-diameter steel balls were put into the steel reactor to strengthen stirring.

### 3.3 Analysis methods

#### 3.3.1 Phase analysis

Phase analysis was performed for calcines and leaching residue through a Bruker X-ray diffractometer (D8-Advance, Bruker corporation) with  $\text{Cu K}_\alpha$  radiation.

#### 3.3.2 Mo and S contents

The Mo(VI) contents in the calcine and leaching residue were measured by the gravimetric method [23]. The  $\text{CaMoO}_4$  in the calcine was leached by  $\text{Na}_2\text{CO}_3$  leaching [24] at 90  $^\circ\text{C}$  for 2 h with a  $\text{Na}_2\text{CO}_3$  concentration of 120 g/L and a liquid–solid ratio of 25 mL/g, which was employed to determine the conversion rate of  $\text{MoS}_2$ . The sulfur contents were

determined by a sulfur analyzer (HDS3000, Huade Company, China).

The conversion rate of  $\text{MoS}_2$ , the leaching rate of Mo, and the sulfur-retained rate were calculated through Eqs. (1), (2), and (3), respectively as follows:

$$\eta_1 = \left( 1 - \frac{m_2 w_2}{m_1 w_1} \right) \times 100\% \quad (1)$$

where  $\eta_1$  is the conversion rate of  $\text{MoS}_2$ ;  $m_1$  and  $m_2$  are the masses of raw meal and leaching residue by sodium carbonate solution, respectively;  $w_1$  and  $w_2$  are the Mo mass fractions of raw meal and leaching residue by sodium carbonate solution, respectively.

$$\eta_2 = \left( 1 - \frac{m_3 w_3}{m_1 w_1} \right) \times 100\% \quad (2)$$

where  $\eta_2$  is the leaching rate of Mo;  $m_3$  is the mass of leaching residue by ammonium carbonate solution;  $w_3$  is the Mo mass fraction of leaching residue by ammonium carbonate solution.

$$\eta_3 = \left( \frac{m_4 w_4}{m_1 w_1} \right) \times 100\% \quad (3)$$

where  $\eta_3$  is the sulfur-retained rate;  $m_4$  is the mass of calcine;  $w_4$  is the S mass fraction of calcine.

#### 3.3.3 Morphology analysis

The analysis of morphology of the calcine was conducted by scanning electron microscopy (JSM–6360LV, JEOL Company, Japan).

## 4 Results and discussion

### 4.1 Oxidizing roasting of molybdenite in the presence of calcium carbonate

#### 4.1.1 Influence of roasting temperature

Temperature is a momentous parameter for both kinetics and thermodynamics. Thus, roasting temperature is the key influencing factor for calcine quality.  $\text{MoS}_2$  in the molybdenite concentrate is oxidized to  $\text{MoO}_3$  during 400–600  $^\circ\text{C}$  in the traditional oxidizing roasting process [25]. However, based on the thermodynamic and TGA analyses above,  $\text{MoS}_2$  in molybdenite can be oxidized into  $\text{CaMoO}_4$  at above 300  $^\circ\text{C}$  in the presence of  $\text{CaCO}_3$ . Consequently, subsequent experiments were performed at 400–550  $^\circ\text{C}$  to investigate the influence of roasting temperature.

Figure 5 shows the XRD patterns of roasted products at 400, 450, 500 and 550  $^\circ\text{C}$  for 2 h with a molar ratio of  $\text{CaCO}_3$  to  $\text{MoS}_2$  of 3.6. The characteristic peaks of  $\text{MoS}_2$  are evidently receding with increasing roasting temperature, and disappear at above 500  $^\circ\text{C}$ . By contrast, the characteristic peaks of  $\text{CaSO}_4$  and  $\text{CaMoO}_4$  become stronger. Moreover, the molar ratio of  $\text{CaMoO}_4$

and  $\text{CaSO}_4$  in the calcine is approximately 1:2, corresponding to Reaction (8). Reaction (8) is also a typical gas–solid and solid–solid reaction [26]. Thus, elevating temperature can increase the conversion rate of  $\text{MoS}_2$  because it improves mass and heat transfer. This result is consistent with the result in Fig. 6 which shows the conversion rate of  $\text{MoS}_2$  at different roasting temperatures. The conversion rate of  $\text{MoS}_2$  is about 95% when the temperature is only 450 °C (Fig. 6), suggesting that adding  $\text{CaCO}_3$  in the oxidizing process of  $\text{MoS}_2$  can remarkably reduce the oxidizing roasting temperature compared with the temperature of 600 °C for the traditional oxidizing roasting process. This coincides with the previous thermodynamic and TGA analyses.

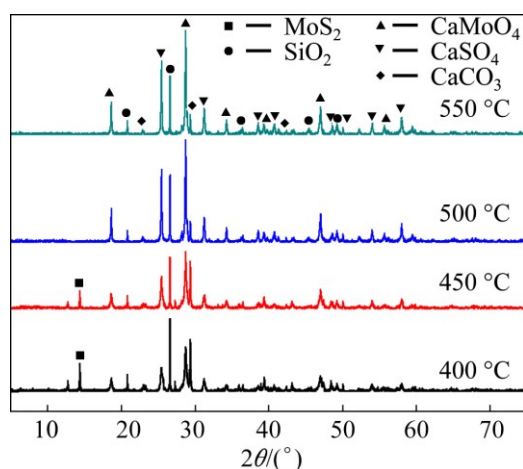


Fig. 5 XRD patterns of roasted products at different temperatures,  $n(\text{CaCO}_3):n(\text{MoS}_2)=3.6$  and  $t=2$  h

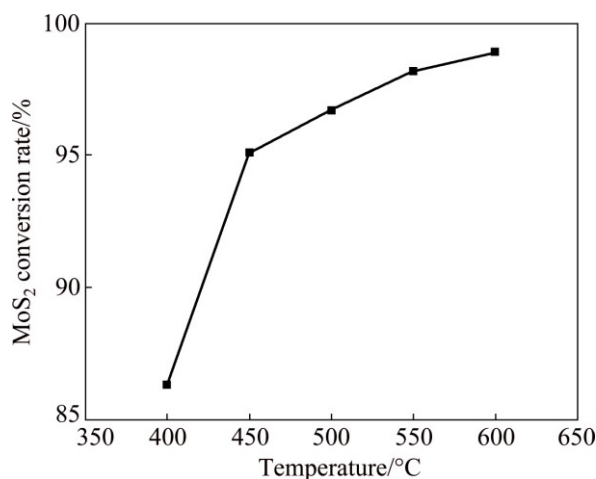


Fig. 6 Influence of roasting temperature on conversion rate of  $\text{MoS}_2$  at  $n(\text{CaCO}_3):n(\text{MoS}_2)=3.6$  and  $t=2$  h

#### 4.1.2 Influence of roasting duration

Duration is another important kinetic factor for chemical reactions. The longer the duration is, the closer the reaction reaches balance. Conceivably, the conversion rate of  $\text{MoS}_2$  is affected not only by the

roasting temperature but also by roasting duration. Thus, the relationship between  $\text{MoS}_2$  conversion rate and roasting duration was studied by roasting the milled samples with a  $\text{CaCO}_3$  to  $\text{MoS}_2$  molar ratio of 3.6 at 500 and 550 °C for different roasting durations, and the results are presented in Fig. 7.

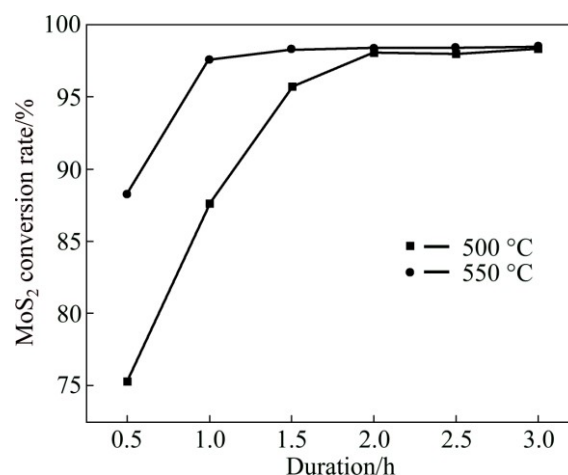


Fig. 7 Influence of roasting duration on conversion rate of  $\text{MoS}_2$  at  $n(\text{CaCO}_3):n(\text{MoS}_2)=3.6$

As shown in Fig. 7, prolonging the roasting duration obviously results in higher conversion rate of  $\text{MoS}_2$  and the  $\text{MoS}_2$  conversion rate approaches the maximum after roasting for a period of time. This shows that extending the roasting time facilitates the conversion of  $\text{MoS}_2$  to  $\text{CaMoO}_4$  and  $\text{CaSO}_4$ . On the other hand, the  $\text{MoS}_2$  conversion rate is up to 98% when roasting at 550 °C for 1 h while at 500 °C for 2 h, illustrating that the duration acquired for reaching the maximum is shorter at elevated temperature than that at low temperature. This suggests that roasting temperature is the decisive factor for the phase transformation rate.

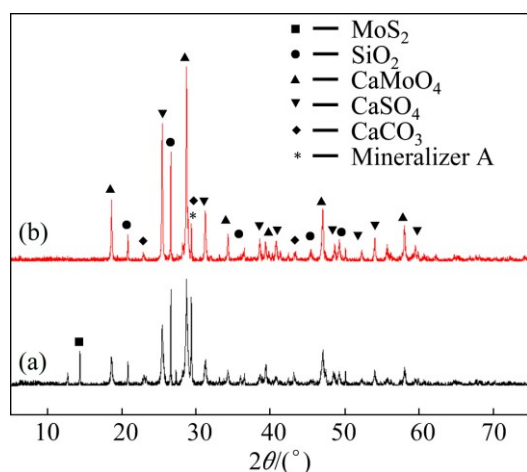
#### 4.1.3 Influence of mineralizer

In view of the problems such as elevated roasting temperature and long roasting duration, mineralizer A, always being used as an additive in roasting process to decrease the roasting temperature [27,28], was added into the oxidizing roasting process of molybdenite to reduce the roasting temperature or shorten the duration.

The XRD patterns of samples roasted at 500 °C for 1 h with 5% (mass fraction) mineralizer A and without mineralizer A are shown in Fig. 8. The characteristic peaks of  $\text{MoS}_2$  for the sample without mineralizer A still exist whereas those for the sample with 5% mineralizer A disappear. Furthermore, stronger characteristic peaks of  $\text{CaMoO}_4$  and  $\text{CaSO}_4$  for the sample with 5% mineralizer A are found compared with those for the sample without mineralizer A. This indicates that the  $\text{MoS}_2$  can convert into  $\text{CaMoO}_4$  and  $\text{CaSO}_4$  more completely by adding 5%



mineralizer A. The reason may be that the incorporation of  $F^-$  in the  $O^{2-}$  lattice sites intensifies the mass transfer or heat transfer of the roasting reaction. In addition, characteristic peaks of mineralizer A still exist in the XRD patterns of samples roasted with 5% mineralizer A, implying that mineralizer A may be reused.



**Fig. 8** XRD patterns of samples roasted without (a) and with (b) 5% mineralizer A at  $n(\text{CaCO}_3):n(\text{MoS}_2)=3.6$ ,  $T=500\text{ }^\circ\text{C}$  and  $t=1\text{ h}$

#### 4.1.4 Influence of $\text{CaCO}_3$ dosage

Based on the study mentioned above, we can make a conclusion that the oxidizing roasting of molybdenite is mainly performed as Reaction (8) when the  $\text{CaCO}_3$  is plenty. As  $\text{CaCO}_3$  dosage can affect both the  $\text{MoS}_2$  conversion rate and the sulfur-retained rate, further experiments were carried out to examine the influence of  $\text{CaCO}_3$  dosage by roasting molybdenite concentrate mixed with different dosages of  $\text{CaCO}_3$  and 5% mineralizer A at  $500\text{ }^\circ\text{C}$  for 1 h. The results are listed in Table 3.

**Table 3** Influence of  $\text{CaCO}_3$  dosage on  $\text{MoS}_2$  conversion rate and sulfur-retained rate

| No. | $n(\text{CaCO}_3):n(\text{MoS}_2)$ | sulfur-retained rate/% | $\text{MoS}_2$ conversion rate/% |
|-----|------------------------------------|------------------------|----------------------------------|
| 1   | 2.0                                | 45                     | 81                               |
| 2   | 2.4                                | 63                     | 90                               |
| 3   | 3.0                                | 76                     | 98                               |
| 4   | 3.3                                | 88                     | 99                               |
| 5   | 3.6                                | 95                     | 99                               |

From Table 3, we can see that both the  $\text{MoS}_2$  conversion rate and sulfur-retained rate increase with the increase of  $\text{CaCO}_3$  dosage, and the conversion rate of  $\text{MoS}_2$  can achieve 98% when roasting with a theoretical amount of  $\text{CaCO}_3$ , almost being in agreement with

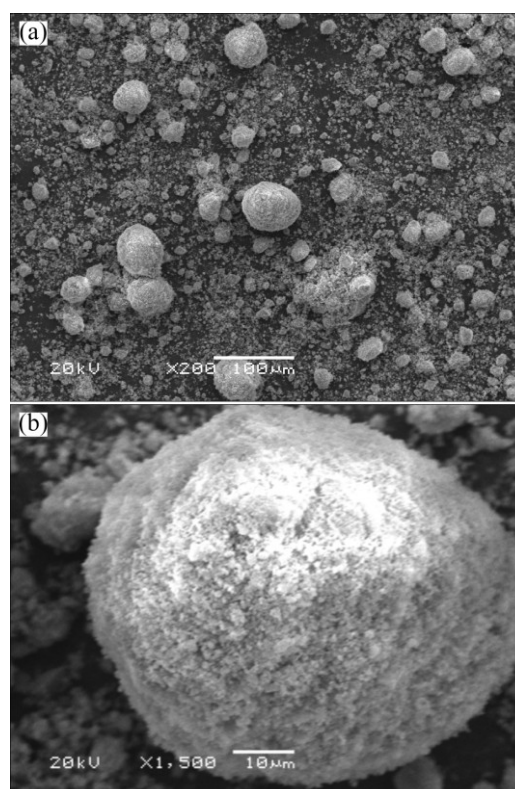
Reaction (8). This validates the thermodynamic result that adding  $\text{CaCO}_3$  can reduce the roasting temperature and intensify the roasting reaction. In addition, the sulfur-retained rate can reach 95% when roasting with 1.2 times that of the theoretical amount of  $\text{CaCO}_3$ , disclosing that  $\text{CaCO}_3$  is a good sulfur-retained agent and that oxidizing roasting of molybdenite in the presence of limestone can significantly reduce  $\text{SO}_2$  pollution.

#### 4.2 Preliminary leaching results of calcine in $(\text{NH}_4)_2\text{CO}_3$ solution

$\text{CaMoO}_4$  is ready to decompose with higher  $\text{CO}_3^{2-}$  concentration through thermodynamics analysis and practical work on  $\text{Ca-Mo-CO}_3\text{-H}_2\text{O}$  system [29]. The leaching reaction of calcine by the  $(\text{NH}_4)_2\text{CO}_3$  solution is a typical liquid–solid reaction. Thus, leaching conditions, such as solution concentration, liquid–solid ratio, temperature, duration, stirring intensity, and particle size, are all important factors of leaching efficiency.

From the SEM images of the calcine as shown in Fig. 9, we can see that the calcine particles are less than  $80\text{ }\mu\text{m}$  and take on spheroid in shape with loose surface, facilitating gas diffusion and thus improving the roasting effect. It is also beneficial to diffusion transport of the reactants and products in the leaching process. The preliminary experiments of the calcine leached by  $(\text{NH}_4)_2\text{CO}_3$  solution were conducted and the results are shown in Table 4.

It is indicated in Table 4 that elevating leaching temperature, extending leaching time, increasing liquid–



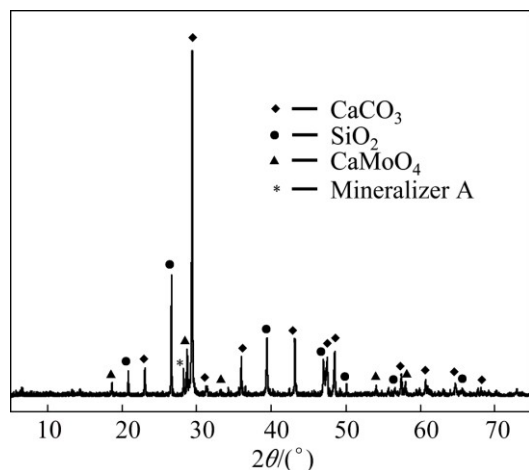
**Fig. 9** SEM images of calcine under different magnification

**Table 4** Preliminary leaching experimental results of calcine in  $(\text{NH}_4)_2\text{CO}_3$  solution

| Temperature/<br>°C | Liquid–<br>solid ratio/<br>( $\text{mL}\cdot\text{g}^{-1}$ ) | Leaching<br>duration/<br>h | $(\text{NH}_4)_2\text{CO}_3$<br>concentration/<br>( $\text{g}\cdot\text{L}^{-1}$ ) | Leaching<br>rate of<br>Mo/% |
|--------------------|--------------------------------------------------------------|----------------------------|------------------------------------------------------------------------------------|-----------------------------|
| 70                 | 5                                                            | 4                          | 400                                                                                | 61.4                        |
| 70                 | 10                                                           | 4                          | 400                                                                                | 68.9                        |
| 80                 | 10                                                           | 4                          | 600                                                                                | 95.4                        |
| 80                 | 10                                                           | 6                          | 600                                                                                | 97.6                        |
| 85                 | 10                                                           | 7                          | 600                                                                                | 98.2                        |

solid ratio and the concentration of  $(\text{NH}_4)_2\text{CO}_3$  solution all can intensify the leaching process. The leaching rate of Mo in the calcine can achieve 98.2% at a leaching temperature of 85 °C for 7 h with a  $(\text{NH}_4)_2\text{CO}_3$  concentration of 600 g/L and a liquid–solid ratio of 10 mL/g.

The XRD pattern of the leaching residue by the  $(\text{NH}_4)_2\text{CO}_3$  solution is shown in Fig. 10, indicating that the strong diffraction peaks of the residue are the diffraction lines of  $\text{CaCO}_3$  and unreacted  $\text{SiO}_2$ . Moreover, some weak diffraction peaks of  $\text{CaMoO}_4$  and mineralizer A are observed. This implies that most of the Mo in the calcine enters the leaching solution, and the  $\text{SiO}_2$  in the  $\text{MoS}_2$  concentrate seems not to participate in reactions in the oxidizing roasting or leaching process by  $(\text{NH}_4)_2\text{CO}_3$  solution.

**Fig. 10** XRD pattern of leaching residue

#### 4.3 Schematic technological process for producing ammonium molybdenate

Based on the results mentioned above, a novel technique for preparing ammonium paramolybdate from molybdenite concentrate was proposed in this work and the schematic technological process is presented in Fig. 11. In this process, molybdenite is roasted in the presence of oxygen and  $\text{CaCO}_3$ , converting Mo and Re in the concentrate to  $\text{CaMoO}_4$  and  $\text{Ca}(\text{ReO}_4)_2$

respectively and sulfur to  $\text{CaSO}_4$ . The resultant calcine is leached by water to recover Re and then leached by  $(\text{NH}_4)_2\text{CO}_3$  solution to form  $(\text{NH}_4)_2\text{MoO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ , and  $\text{CaCO}_3$ . Thus, the lixivium consists of  $(\text{NH}_4)_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{MoO}_4$ , and excessive  $(\text{NH}_4)_2\text{CO}_3$ .  $(\text{NH}_4)_2\text{CO}_3$  is ready to decompose at above 70 °C. Thus, this compound can be isolated from the lixivium by evaporation [30] and recycled conveniently. The remaining  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{MoO}_4$  in the lixivium can be separated by the traditional precipitation of Mo by adding acid, and the  $(\text{NH}_4)_2\text{MoO}_4$  precipitates can be transformed to  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  by dissolution and evaporative crystallization. Mo and Re in the lixivium can also be collected directly by ion exchange or solvent extraction [31–33]. The  $(\text{NH}_4)_2\text{SO}_4$  solution left in the spent liquor may be used as a chemical fertilizer after evaporative crystallization. In addition, the leaching residue, mainly containing  $\text{CaCO}_3$ , can be reused in the raw meal preparation.

Compared with the process of lime-roasting followed by sulfuric acid leaching [11–14], substituting lime with  $\text{CaCO}_3$  in the oxidizing roasting process of molybdenite concentrate is cost effective and allows recycling. Employing  $(\text{NH}_4)_2\text{CO}_3$  solution as a leaching agent not only directly produces  $(\text{NH}_4)_2\text{MoO}_4$  but also eliminates equipment corrosion caused by sulfuric acid leaching of calcine. Furthermore,  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{CaCO}_3$  are both recyclable, and the sulfur in the molybdenite is finally converted to  $(\text{NH}_4)_2\text{SO}_4$ , which is used as a chemical fertilizer [34]. Thus, further improvement of the process of limestone-roasting followed by  $(\text{NH}_4)_2\text{CO}_3$  leaching is potential to establish a recyclable, efficient, and clean process for treating molybdenite concentrate.

## 5 Conclusions

Thermodynamic calculation and experimental results show that  $\text{MoS}_2$  is converted to  $\text{CaSO}_4$  and  $\text{CaMoO}_4$  in the oxidizing roasting process with addition of  $\text{CaCO}_3$ . The oxidizing roasting reaction can occur at relatively low temperatures of 300–500 °C. The reaction rate is mainly influenced by mass transfer and heat transfer. Increasing temperature, extending duration, and adding mineralizer A are all beneficial to the improvement of the conversion rate. The sulfur-retained rate in the roasting process increases with the increase of  $\text{CaCO}_3$  dosage and can achieve approximately 95% with a  $\text{CaCO}_3$  to  $\text{MoS}_2$  mole ratio of 3.6.  $\text{CaCO}_3$  and unreacted  $\text{SiO}_2$  are the main phases in the residue obtained by leaching the calcine with  $(\text{NH}_4)_2\text{CO}_3$  solution. The leaching rate of Mo in the calcine can reach 98.2% at 85 °C for 7 h with a  $(\text{NH}_4)_2\text{CO}_3$  concentration of 600 g/L and a liquid–solid ratio of 10 mL/g.

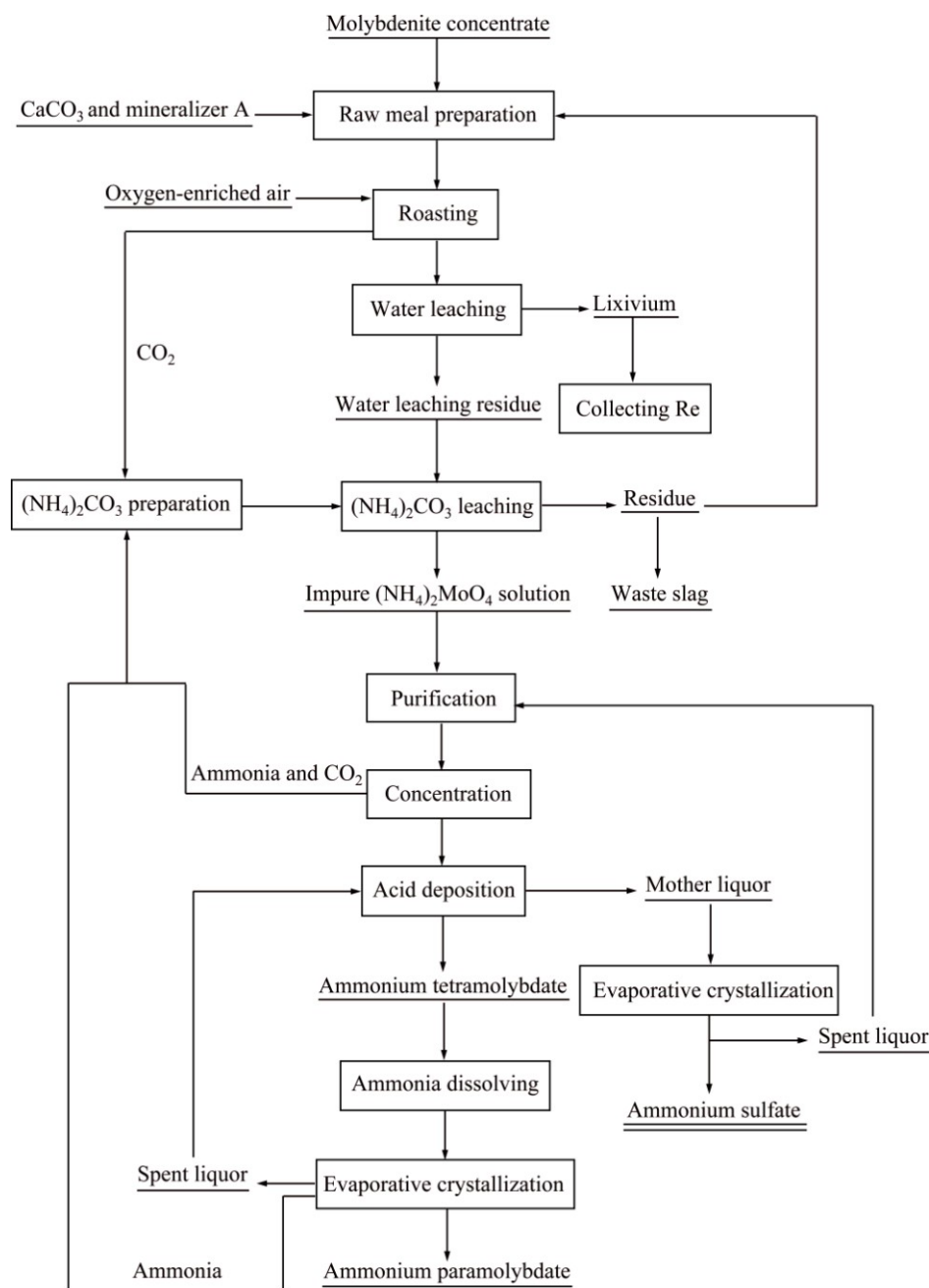


Fig. 11 Schematic technological process for preparing ammonium paramolybdate from molybdenite concentrate

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## 辉钼矿—碳酸钙氧化焙烧及熟料在碳酸铵溶液中的浸出

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**摘 要:** 石灰焙烧—硫酸浸出法可大大降低传统氧化焙烧—氨浸工艺处理辉钼矿的含硫烟气污染, 但存在设备腐蚀严重、渣量大等缺点。基于石灰焙烧工艺研究, 本文作者提出“碳酸钙氧化焙烧—碳酸铵浸出”新工艺来处理辉钼矿。通过热力学计算、热重分析以及焙烧试验等对辉钼矿—碳酸钙氧化焙烧过程进行详细研究。结果表明, MoS<sub>2</sub>与CaCO<sub>3</sub>和O<sub>2</sub>在573~1000 K下反应的主要产物是CaSO<sub>4</sub>、CaMoO<sub>4</sub>和CO<sub>2</sub>; 当CaCO<sub>3</sub>和MoS<sub>2</sub>的摩尔比为3.6并加入5%矿化剂A在500 °C下焙烧1 h时, 钼精矿中的MoS<sub>2</sub>的分解率达到约99%, 固硫率达到约95%。用碳酸铵溶液浸出焙烧后熟料, 控制碳酸铵浓度为600 g/L、液固比为10 mL/g, 在85 °C下浸出7 h, Mo浸出率可达98.2%。该研究结果将有助于钼酸铵清洁生产新技术的开发。

**关键词:** 辉钼矿; 碳酸钙; 碳酸铵; 氧化焙烧; 浸出

(Edited by Wei-ping CHEN)