



# Roasting oxidation behaviors of $\text{ReS}_2$ and $\text{MoS}_2$ in powdery rhenium-bearing, low-grade molybdenum concentrate

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**Abstract:** The oxidation roasting process of molybdenum concentrate has significant advantages in industrial applications. However, utilization of low-grade mineral has many problems because it is more complex than the standard concentrate. In this study, the oxidation behaviors of powdery rhenium-bearing low-grade molybdenum concentrate were investigated through thermodynamic calculation, roasting experiments, thermogravimetric analysis, and phase analysis. The results obtained show that oxidation of  $\text{MoS}_2$  begins at 450 °C, and  $\text{MoO}_3$  reacts with metal-oxide forming molybdate at 600 °C. Finally,  $\text{MoO}_3$  can be dissolved in ammonia with a maximum content of approximately 80%. The volatile speed of Re was considerably slower than the oxidation speed of  $\text{MoS}_2$  because the nonvolatile products  $\text{ReO}_2$  and  $\text{ReO}_3$  were generated in reactions among  $\text{MoS}_2$ ,  $\text{SO}_2$ , and  $\text{Re}_2\text{O}_7$ . The final volatilization rate of Re was almost 70%. This study determined the problems related to the roasting of low-grade molybdenum concentrate, which lays the scientific foundations for subsequent enhancement of molybdenum and rhenium extraction.

**Key words:** low-grade molybdenum; rhenium; oxidation roasting; thermodynamics; phase evolution

## 1 Introduction

Molybdenum is a rare and refractory metal [1–5] and China's molybdenum reserve ranks second in the world [6]. However, over 64% of the molybdenum deposits in China exist in the form of complex paragenetic mines [7,8] and are characterized as low-grade, which results in processing difficulties. As rhenium is usually associated with molybdenum ore in the form of  $\text{ReS}_2$ , molybdenum and rhenium generally become enriched in the molybdenum concentrate during mineral processing [9]. Rhenium is a rare and precious metal characterized by high temperature resistance, corrosion resistance, a special electronic configuration, and excellent catalytic activity. These characteristics make it efficient for use in spaceflight [10–12], medicine [13], and catalyst [14,15] applications. Because of its widespread commercial value and prospects for development, the recovery of rhenium has attracted substantial research attention. Thus, extracting rhenium during the recovery of molybdenum has great economic value.

The main oxidation methods for rhenium-bearing molybdenum concentrate are hydrometallurgy [16–22] and pyrometallurgy. The hydrometallurgical route can avoid the emission of  $\text{SO}_2$  but requires high-quality facilities, huge investment, and large costs because of the high price of the autoclave (one with a processing capacity of 1000 L costs at least \$150000) and the specific requirements of a waterproof, acid proof, alkaline proof, and anticorrosion workshop.

At present, pyrometallurgy processing is a potentially attractive method of oxidizing molybdenum concentrate that is widely used in China. It includes the oxidizing roasting process, alkali fusing method [23], and lime-roasting process [24,25]. The oxidizing roasting process has greater advantages because it can effectively separate the oxidized products of  $\text{MoO}_3$  and  $\text{Re}_2\text{O}_7$ . In the oxidation process,  $\text{MoS}_2$  and  $\text{ReS}_2$  in the molybdenum concentrate are oxidized to  $\text{MoO}_3$  and  $\text{Re}_2\text{O}_7$ , respectively, and large amounts of  $\text{SO}_2$  are released.  $\text{Re}_2\text{O}_7$  is a volatile compound with a melting point of only 297 °C and vapor pressure that increases rapidly with increasing temperature (0.045 kPa at 200 °C, 22.74 kPa at 300 °C, 1795.84 kPa at 400 °C, and

$1.58 \times 10^6$  kPa at  $650^\circ\text{C}$ ) [26]. Meanwhile, a very small amount of  $\text{MoO}_3$  will volatilize and lead to molybdenum loss at high temperature [27], because its vapor pressure is much lower than that of  $\text{Re}_2\text{O}_7$  (0.0067 kPa at  $650^\circ\text{C}$ , 0.028 kPa at  $670^\circ\text{C}$ , 0.059 kPa at  $700^\circ\text{C}$ ) [26]. However, it must be noted that another rhenium oxide with low valance,  $\text{ReO}_3$ , is nonvolatile as its vapor pressure is extremely low (only 0.013 kPa at  $400^\circ\text{C}$ ) [26]. Thus, sufficient oxidation of  $\text{MoS}_2$  and  $\text{ReS}_2$  is very necessary. In the separation process,  $\text{MoO}_3$  can remain steady in calcine while  $\text{Re}_2\text{O}_7$  evaporates into the flue gas and is enriched in the fume [28]. Moreover, the reaction temperature can be reached by the self-oxidation of molybdenum concentrate, with a massive amount of heat released. Additionally, the method of oxidizing roasting has merits such as being a simple process that requires only basic facilities and has a low cost. These advantages make it a more appropriate method for rhenium-bearing molybdenum concentrate.

Current studies on the oxidation mechanism of  $\text{MoS}_2$ – $\text{ReS}_2$  mainly focus on standard-molybdenum concentrate (Mo content  $>45\%$ ). There have been few reports on the oxidation of low-grade molybdenum–rhenium sulfide concentrate as it is considerably more complex than that of standard-molybdenum concentrate due to, for example, the multiple components and impurities and the low-grade of molybdenum. Thus, the phase evolution and roasting characteristics of low-grade concentrate during the oxidizing process were analyzed in this study. The reaction behaviors of molybdenum, rhenium, and sulfur were also revealed, which could provide the basis for effective molybdenum and rhenium extraction.

## 2 Experimental

### 2.1 Materials

The low-grade rhenium-bearing molybdenum concentrate was collected from separation in a copper mine. The chemical components of the material are shown in Table 1. The molybdenum content is 39.27%, which is lower than the grade of standard-molybdenum concentrate (Mo content above 45%). The content of valuable and usable rhenium is 0.034% (340 g/t). The gangue in the molybdenum concentrate mainly consists of  $\text{SiO}_2$ , CaO, and MgO, which accounts for 9.77%, 5.23%, and 4.29%, respectively. Moreover, some sulfides such as  $\text{CuS}_2$  and  $\text{FeS}_2$  exist in the molybdenum concentrate. The proportion of molybdenum concentrate particles less than 0.074 mm is 65.44%.

The mineral composition of molybdenum concentrate is given in Table 2. The majority of the molybdenum concentrate is molybdenite; approximately 65.4%. Moreover, the sulfides in the concentrate include

copper pyrites, bornite, iron pyrite, arsenopyrite, and sphalerite. The iron-bearing minerals mainly consist of limonite and hematite. Other gangue minerals are composed of aluminosilicate, magnesium silicate, quartz, and carbonate.

**Table 1** Chemical composition of molybdenum concentrate (wt.%)

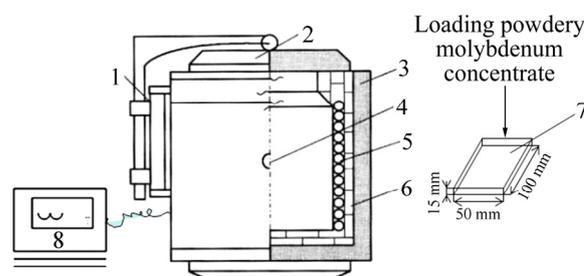
Mo	Re	S	Cu	Fe	$\text{SiO}_2$
39.27	0.034	29.73	0.66	3.04	9.77
$\text{Al}_2\text{O}_3$	CaO	MgO	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	
0.24	5.23	4.29	0.10	0.47	

**Table 2** Mineral compositions of molybdenum concentrate

Mineral	Content/wt.%
Molybdenite	65.4
Copper pyrites and bornite	2.4
Pyrite	8.0
Sphalerite	0.02
Galena	0.02
Arsenopyrite	0.02
Iron oxides (hematite, limonite)	4.2
Aluminosilicate (mica, feldspar)	3.7
Magnesium-silicate (chlorite, talc)	3.1
Carbonate (calcite, dolomite)	8.4
Quartz	3.7
Others	1.04

### 2.2 Methods

The equipment schematically shown in Fig. 1 was used to simulate the oxidation process of multiple hearth furnace using a powdery rhenium-bearing, low-grade molybdenum concentrate. During the process, 20 g of dried molybdenum concentrate was put into an open corundum crucible measuring  $100\text{ mm} \times 50\text{ mm} \times 15\text{ mm}$  and evenly spread onto the crucible. The crucible loaded with molybdenum concentrate was then moved



**Fig. 1** Schematic diagram of oxidizing roasting devices (1—Connecting rod of furnace door; 2—Outer shell of furnace; 3—Inner shell of furnace; 4—Furnace door; 5—Silicon-molybdenum resistance wire; 6—Firebrick; 7—Crucible; 8—Temperature controller)

into a muffle furnace and roasted at a setting temperature (400–700 °C) for a certain period (5–90 min) in air. Eventually, the roasted products were removed and ground to  $-0.074$  mm for subsequent analyses.

The concentration of molybdenum was determined via the lead molybdate weight method, and sulfur was titrated with barium chloride. Rhenium was determined via inductively coupled plasma emission spectroscopy (ICP) with a PS-6 PLASMA SPECTROVAC, BAIRD (USA). The X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer with Cu  $K_{\alpha}$  radiation at 35 kV and 20 mA. TG/DSC curves were obtained on a TG–DSC thermo gravimetric analyzer (Netzsch STA 449 C) in the temperature range of 20–1000 °C at a heating rate of 10 °C/min under air atmosphere. Additionally, all the reagents used in this work, including potassium oxide ( $K_2O$ ), sodium oxide ( $Na_2O$ ), calcium oxide ( $CaO$ ), and magnesia ( $MgO$ ), were of analytical grade.

The key aim of oxidizing roasting is to generate as much  $MoO_3$  and  $Re_2O_7$  as possible because  $MoO_3$  in calcine can dissolve easily in the ammonia and be recycled by ammonia leaching. Meanwhile,  $Re_2O_7$  is easy to volatilize, which results in separation from the molybdenum, and can become enriched and recycled from flue gas as well as smoke dust. The entire flow diagram of oxidation roasting-acid leaching is shown in Fig. 2.

The efficiency of the oxidizing roasting process can be evaluated by the following indexes: the rate of soluble molybdenum in the calcine (the rate of molybdenum dissolved in ammonia to total molybdenum) and the volatilization rate of molybdenum, rhenium, and sulfur. Formulas (1)–(3) show the calculation of the volatilization rate. To achieve desirable indexes, the soluble molybdenum content, as well as the volatilization

rate of rhenium and sulfur, should be kept at a high level, whereas the volatilization rate of molybdenum should be low.

Volatilization rate of molybdenum:

$$\eta_{Mo} = \frac{m_0\pi - m_1\nu}{m_0\pi} \times 100\% \quad (1)$$

Volatilization rate of sulfur:

$$\lambda_S = \frac{m_0\theta - m_1\mu}{m_0\theta} \times 100\% \quad (2)$$

Volatilization rate of rhenium:

$$\xi_{Re} = \frac{m_0\sigma - m_1\tau}{m_0\sigma} \times 100\% \quad (3)$$

where  $\nu$ ,  $\mu$ , and  $\tau$  stand for the molybdenum, sulfur, and rhenium contents in the calcine, respectively (%);  $\pi$ ,  $\theta$ , and  $\sigma$  stand for the molybdenum, sulfur, and rhenium contents in the molybdenum concentrate, respectively (%); and  $m_0$  and  $m_1$  stand for the mass of molybdenum concentrate and calcine, respectively (%).

The rate of soluble molybdenum was detected as follows: 5 g of ground calcine was dissolved in a 100 mL beaker with a liquid/solid ratio of 10:1 and a mass concentration of ammonia of 10%. Calcine was blended with excessive ammonium hydroxide to ensure adequate dissolution. Then, the sealed beaker was placed in a constant temperature oven at 70 °C for 2 h of leaching. Finally, samples were taken out to be filtrated and dried, and the molybdenum content in the leached residue was analyzed.

Rate of soluble molybdenum:

$$\gamma_{Mo} = \frac{m_1\alpha - m_2\beta}{m_1\alpha} \times 100\% \quad (4)$$

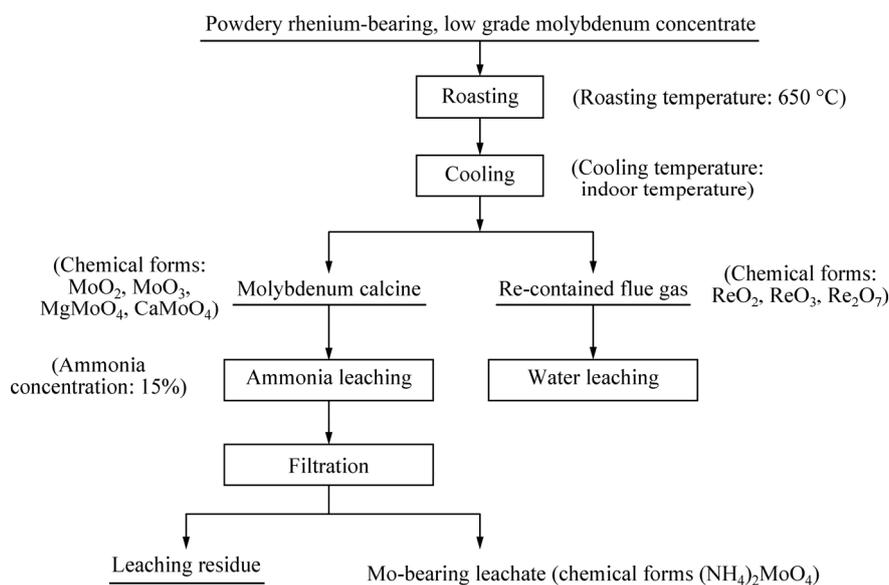


Fig. 2 Flow diagram of oxidation roasting leaching

where  $\alpha$  and  $\beta$  stand for the molybdenum contents in the calcine and in the ammonia leached residue, respectively (%), and  $m_1$  and  $m_2$  stand for the mass of calcine and ammonia leaching residue, respectively (%).

### 3 Results and discussion

#### 3.1 Oxidation behaviors of MoS<sub>2</sub>

##### 3.1.1 XRD and TG–DSC characterization

The phases of roasted products at different roasting temperatures were analyzed by X-ray diffraction (XRD). The results are given in Fig. 3. MoS<sub>2</sub> was not oxidized at 400 °C as molybdenum oxide was not found in the roasted product. When the temperature rose to 450–500 °C, the diffraction peaks of MoS<sub>2</sub> decreased gradually while some diffraction peaks of MoO<sub>3</sub> started to appear. When the temperature increased to above 600 °C, the diffraction peaks of MoS<sub>2</sub> disappeared, and the diffraction peaks of MoO<sub>3</sub> became enhanced. Moreover, diffraction peaks of CaMoO<sub>4</sub> and MgMoO<sub>4</sub> were observed. According to the analyses, the molybdenum phases with sufficient oxidation time were mainly MoO<sub>3</sub>, MgMoO<sub>4</sub>, and CaMoO<sub>4</sub>. These two types of molybdate are considered an obstacle to the leaching of molybdenum because they are difficult to dissolve in the ammonium hydroxide while some types of molybdates easily dissolve in ammonium hydroxide (such as K<sub>2</sub>MoO<sub>4</sub> and Na<sub>2</sub>MoO<sub>4</sub> [18]).

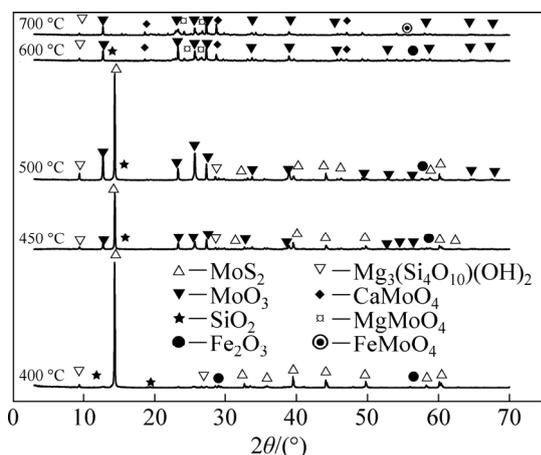


Fig. 3 XRD patterns of products roasted at different temperatures for 90 min

The phases of the roasted products at different roasting time were tested by XRD (Fig. 4). There were several types of Mo-bearing minerals in the roasted product: MoS<sub>2</sub>, MoO<sub>2</sub>, and MoO<sub>3</sub>. The existence of un-oxidized or uncompleted oxidized minerals such as MoS<sub>2</sub> and MoO<sub>2</sub> was the dominant factor leading to low soluble molybdenum content for short roasting time of 5 min. When the roasting time was extended to 10 min, the diffraction peaks of MoS<sub>2</sub> decreased substantially,

while the diffraction peaks of MoO<sub>3</sub> and MoO<sub>2</sub> became somewhat stronger. As the roasting time exceeded 25 min, the diffraction peaks of MoS<sub>2</sub> and MoO<sub>2</sub> disappeared, while the diffraction peaks of MoO<sub>3</sub> became stronger. At the same time, diffraction peaks of MgMoO<sub>4</sub> and CaMoO<sub>4</sub> were observed. These results indicate that metallic oxide could not react with MoO<sub>3</sub> until MoS<sub>2</sub> was completely oxidized, and the products were a large number of molybdates, which could not be dissolved by ammonium hydroxide.

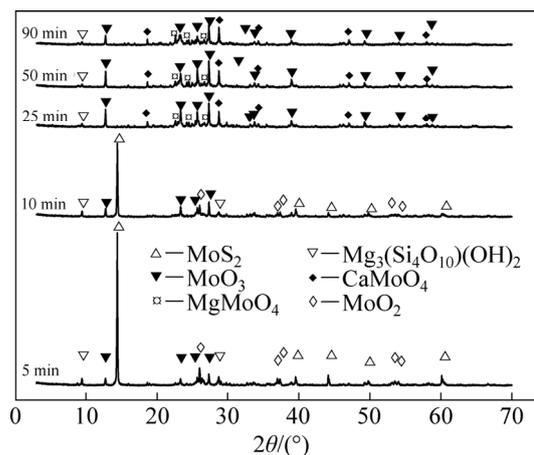


Fig. 4 XRD patterns of roasted products for different time at 650 °C

The oxidation process of MoS<sub>2</sub> was analyzed by thermal gravity analysis in air under a heating rate of 10 °C/min. From the TG–DSC curves (Fig. 5), it was observed that the entire process involved the evaporation of moisture and the volatilization of volatile-like flotation reagents in the molybdenum concentrate below 400 °C. When the temperature increased to 400–625 °C, two exothermic peaks appeared at approximately 548 °C and 619 °C. Correspondingly, the sample continuously lost mass below 625 °C. All these phenomena represented the rapid generation of MoO<sub>2</sub> and MoO<sub>3</sub>. The main reaction from 625–650 °C was the oxidation of remnant MoO<sub>2</sub>. Thus, the transformation process of molybdenite was MoS<sub>2</sub>→MoO<sub>2</sub>→MoO<sub>3</sub>, which

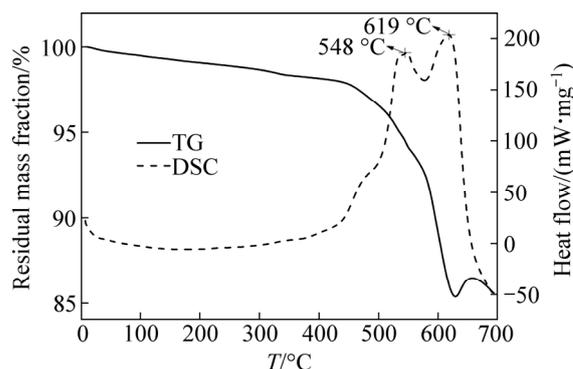


Fig. 5 TG–DSC curves of molybdenum concentrate in air

corresponds to the results shown in Fig. 4. The time interval for the existence of  $\text{MoO}_2$  was relatively short. When the temperature was over  $650^\circ\text{C}$ ,  $\text{MoO}_3$  started to sublime. According to the TGA results, the mass loss indicates that the sublimation of  $\text{MoO}_3$  was the major process after the oxidation of remnant  $\text{MoO}_2$  as the temperature increased above  $650^\circ\text{C}$ .

### 3.1.2 Oxidation process of $\text{MoS}_2$

During the oxidation of low-grade molybdenum concentrate, metallic sulfide ores were oxidized to metallic oxides and  $\text{SO}_2$ . Possible reactions are as follows:

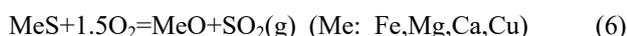
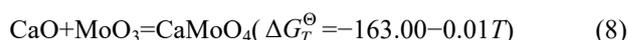


Figure 6 shows the influences of temperature on the oxidation of molybdenum concentrate. Molybdenum could not be oxidized and the rate of soluble molybdenum was below 5% at  $400^\circ\text{C}$  while a portion of  $\text{SO}_2$  volatilized. Analyzing the reactions in thermodynamics [29] showed that the trend of oxidation of  $\text{FeS}_2$  is large under normal pressure. Thus, the reason could be that the oxidation process of  $\text{FeS}_2$  is much easier than that of  $\text{MoS}_2$ . This view is also confirmed in Fig. 3 as the diffraction peaks of  $\text{Fe}_2\text{O}_3$  started to appear at  $400^\circ\text{C}$ . Under the trial conditions, the ores contacted fully with the oxygen and the oxidation desulfurization reactions occurred easily. Corresponding to this, the diffraction peaks of sulfate could not be observed (see Figs. 3 and 4), and the sulfur in metallic sulfide mainly volatilized in the forms of  $\text{SO}_2$ . At a temperature from  $450$  to  $500^\circ\text{C}$ , the oxidation of molybdenum sulfide was reinforced and the volatilization of  $\text{SO}_2$  increased. The rate of soluble molybdenum increased from  $43.14\%$  to  $69.09\%$  as the volatilization rate of sulfur increased from  $47.60\%$  to  $75.57\%$ . The velocity of the oxidizing reaction, especially the oxidation of molybdenum sulfide, increased significantly over  $550^\circ\text{C}$ . Consequently, the rate of soluble molybdenum and the volatilization of sulfur were both above  $80\%$ . However, both indexes increased slowly as the temperature increased from  $600$  to  $700^\circ\text{C}$ . According to the analysis, when the temperature was relatively low at  $450$ – $550^\circ\text{C}$ ,  $\text{MoS}_2$  began to be oxidized and the gas diffused slowly. When the temperature increased to  $600$ – $700^\circ\text{C}$ ,  $\text{MoS}_2$  was almost completely oxidized. The soluble molybdenum approached a peak and the volatilization rate of sulfur was close to  $99\%$  at  $650^\circ\text{C}$ . The analyzing results of the reactions in thermodynamics [29] showed that the generated  $\text{MoO}_3$  could react with some oxides of metallic impurities, forming molybdate and leading to melting and sintering of materials. The main reactions were spontaneous thermodynamics reactions and could be expressed as follows:



This is why the oxidizing process of molybdenum sulfide was restricted at a temperature of  $700^\circ\text{C}$  or above. The occurrence of the molybdate phase confirms this view (Fig. 3).  $\text{MoO}_3$  on the surface became drastically volatilized.

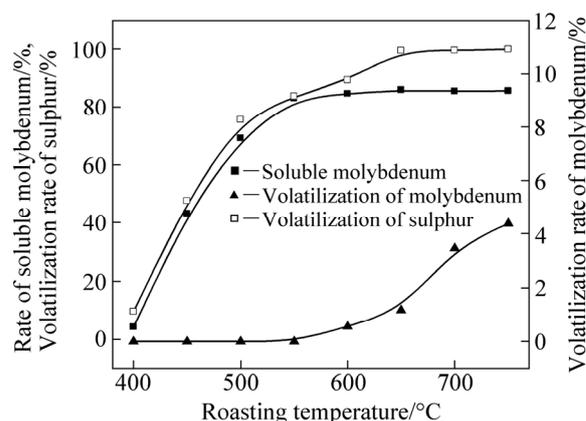


Fig. 6 Effect of roasting temperature on oxidation of molybdenum

The effects of roasting time on the oxidation of molybdenum concentrate are shown in Fig. 7. The molybdenum concentrate was oxidized quickly at  $650^\circ\text{C}$ . When the roasting lasted for 5 min, the rate of soluble molybdenum reached  $25.70\%$  and the volatilization rate of sulfur was  $40.98\%$ . As the roasting continued, sulfur became greatly oxidized and its volatilization rate reached  $96\%$ . The rate of soluble molybdenum was only  $73.76\%$  and the increase was lower than that of sulfur volatilization. In the first 15 min, sulfide minerals were oxidized, and the  $\text{MoO}_3$  product had a disproportionation reaction with  $\text{MoS}_2$ , forming a low valence state of molybdenum such as  $\text{MoO}_2$ , which led to a low content of soluble molybdenum in the early roasted product. After 20 min of roasting, the rate of soluble molybdenum

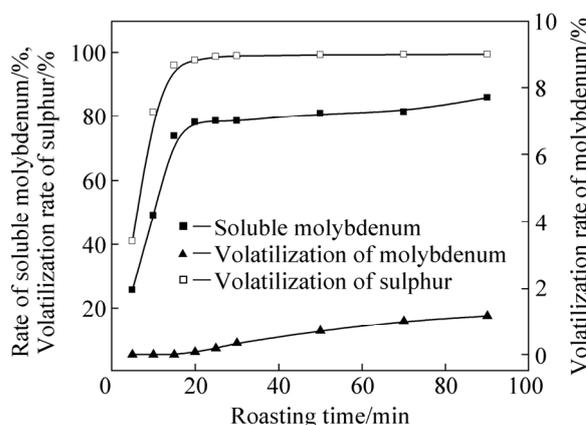


Fig. 7 Effect of roasting time on oxidation of molybdenum at  $650^\circ\text{C}$

changed slightly, which reflected the oxidation of low valence state molybdenum, and the volatilization rate of sulfur increased slightly. As the roasting proceeded, the retention rate of molybdenum decreased due to volatilization of  $\text{MoO}_3$ . When the roasting time exceeded 25 min, the volatilization rate of sulfur increased to 99.70% and the volatilization rate of molybdenum continued to increase, whereas the rate of soluble molybdenum was approximately 80%.

### 3.2 Oxidation behavior of $\text{ReS}_2$

#### 3.2.1 Oxidation process of $\text{ReS}_2$

The oxidizing roasting process of rhenium-bearing molybdenum concentrate is a complicated physico-chemical process. Based on the calculation of thermodynamic data [29], the relationships between  $\Delta G_T^\ominus$  and  $T$  in the reactions were analyzed, and the results are shown in Fig. 8. The main reactions of rhenium include  $\text{ReS}_2$  oxidation, the disproportionation reaction of Mo–Re–S, and the formation of rhenate. Under the standard state,  $\text{ReS}_2$  can be directly oxidized into  $\text{Re}_2\text{O}_7$  (formula (9)). At the beginning of oxidation,  $\text{ReS}_2$  can be easily oxidized. However,  $\text{Re}_2\text{O}_7$  is also easily deoxidized by  $\text{MoS}_2$  that has not been oxidized, forming low valence states of the rhenium oxides like  $\text{ReO}_2$  and  $\text{ReO}_3$  (formulas (14) and (15)).  $\text{Re}_2\text{O}_7$  can also be deoxidized into  $\text{ReO}_3$  by  $\text{SO}_2$  but not  $\text{ReO}_2$ . According to the thermodynamic analysis,  $\text{ReS}_2$  was oxidized along with the molybdenite, and the products were  $\text{ReO}_2$ ,  $\text{ReO}_3$  and  $\text{Re}_2\text{O}_7$ . In the later stage of oxidation,  $\text{ReO}_2$  and  $\text{ReO}_3$  were oxidized into  $\text{Re}_2\text{O}_7$ , which became volatilized,  $\text{MoS}_2$  became completely oxidized, and the concentration of  $\text{SO}_2$  decreased.

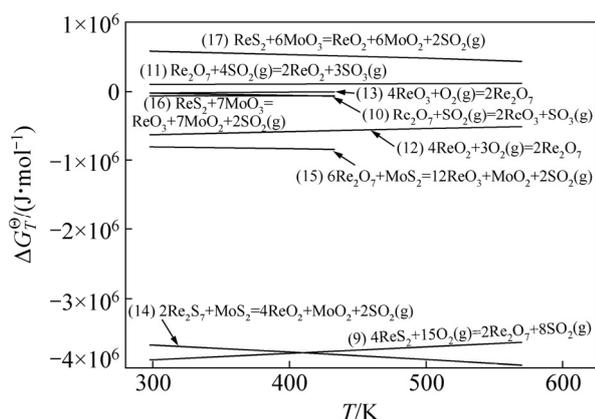


Fig. 8 Relationship between  $\Delta G_T^\ominus$  and  $T$  for rhenium-bearing mineral oxidation reactions

#### 3.2.2 Volatilization of rhenium

The influence of roasting temperature and roasting time on the volatilization of rhenium was also studied (Fig. 9). The volatilization rate of rhenium was very low at 400 °C when  $\text{ReS}_2$  began to be oxidized. After heating

to 450–500 °C, the volatilization rate of rhenium increased but was still below 40%. As the temperature increased to 600–650 °C, rhenium was significantly oxidized and the volatilization rate approached 70%. However, the volatilization rate did not markedly change when the temperature continued to increase. Research on the volatilization of rhenium for different roasting time at 650 °C showed that the volatilization rate of rhenium increased as roasting time proceeded in the early oxidation phase (0–20 min). The volatilization rate rapidly reached 44.38% as the oxidation time increased to 20 min and increased more slowly when the time continued to increase from 20 to 90 min. As the roasting time exceeded 90 min, rhenium could no longer oxidize; the volatilization rate was almost 70% for a roasting time of 90 min.

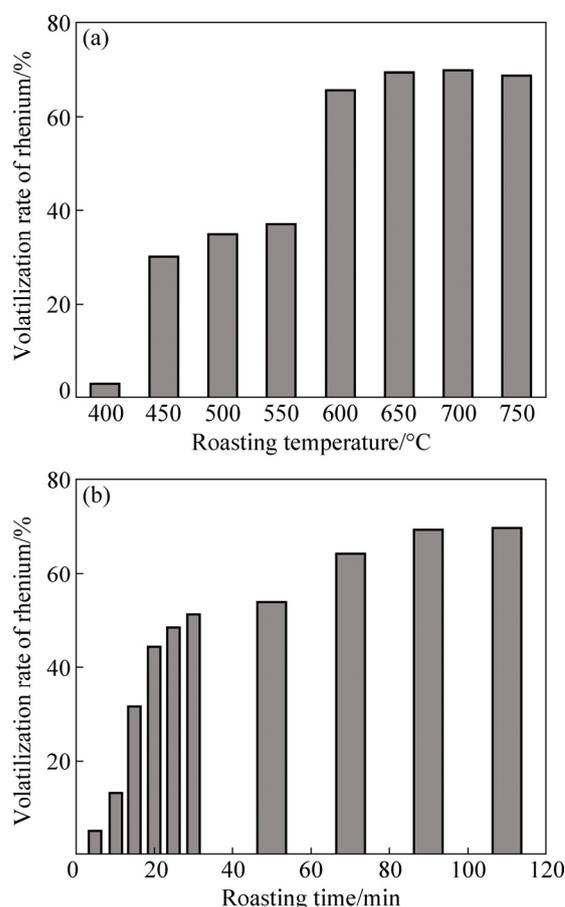


Fig. 9 Effects of roasting temperature on volatilization rate of rhenium with roasting for 90 min (a) and roasting time on volatilization rate at 650 °C (b)

Into the pure substance of  $\text{MoS}_2$ , 0.034% of analytically pure  $\text{ReS}_2$  was added to simulate the Re-bearing molybdenum concentrate. The effects of adding 1% alkali oxides or alkaline earth oxides on the volatilization of rhenium were tested at 650 °C for 90 min, and the results are shown in Fig. 10. Without the addition of alkali oxides or alkaline earth oxides, the

volatilization rate of rhenium was close to 100% during the roasting process, which indicates that almost all the rhenium sulfide can be oxidized to volatile material of  $\text{Re}_2\text{O}_7$ . However, because alkali oxides or alkaline earth oxides exist in sulfide ore, the volatilization of rhenium was very low due to the generation of non-volatile rhenate.  $\text{K}_2\text{O}$  had the greatest effect on the volatilization of rhenium of all the tested metal oxides, followed by  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ , and  $\text{MgO}$ . It was verified that metal oxides in molybdenum concentrate inhibit the volatilization of rhenium.

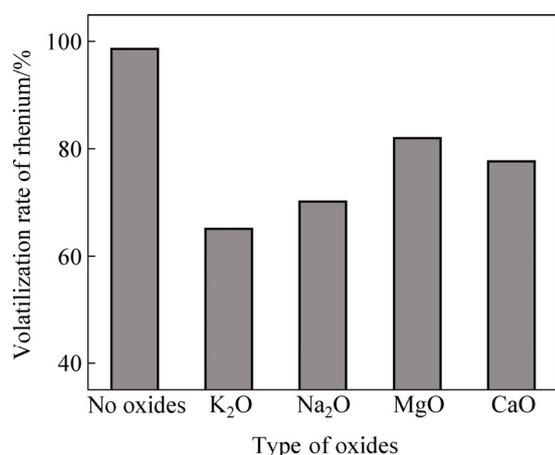


Fig. 10 Effect of metal oxides on rhenium volatilization rate tested at  $650^\circ\text{C}$

### 3.3 Discussion of $\text{MoS}_2$ and $\text{ReS}_2$ oxidation

The relationships among the oxidation of molybdenum, the volatilization of rhenium, and the volatilization of sulfur are shown in Fig. 11. The oxidation of rhenium always lagged behind that of molybdenum and sulfur. The process of rhenium oxidation can be divided into two stages. From 0–20 min, both  $\text{MoS}_2$  and  $\text{ReS}_2$  are oxidized simultaneously. But only a high valence state of rhenium, such as  $\text{Re}_2\text{O}_7$ , can easily volatilize, which reduced the speed of rhenium volatilization compared to that of  $\text{MoS}_2$  oxidation. As the roasting time exceeded 20 min,  $\text{MoS}_2$  became completely oxidized and the removal rate of sulfur

approached 100%. Rhenium continued to oxidize at a relatively low speed between 20 and 90 min. Therefore, the volatilization of rhenium requires its thorough oxidation after complete  $\text{MoS}_2$  oxidation and  $\text{SO}_2$  removal, which explains why the volatilization of rhenium lagged behind the oxidation of molybdenum. Due to the influence of impurities, such as Na, K, Ca, and other alkaline-earth metals in the reaction system, a mass of rhenate formed; the volatilization rate of rhenate only reached 70%. Note that the chemical formulas of the rhenate were  $\text{M}^{\text{I}}\text{ReO}_4$  or  $\text{M}^{\text{II}}(\text{ReO}_4)_2$  because  $\text{M}^{\text{I}}$  and  $\text{M}^{\text{II}}$  were monovalent and divalent cations, respectively.

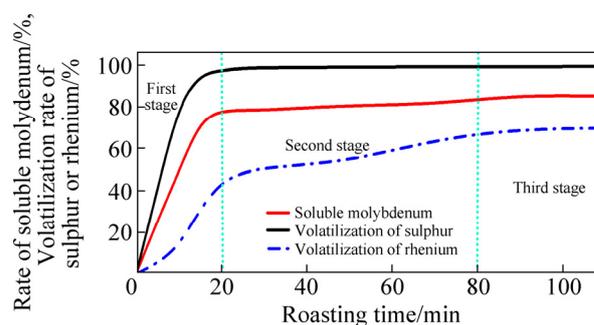


Fig. 11 Effect of roasting time on roasting process of molybdenum concentrate

As stated above, in contrast to standard molybdenum concentrate, more complex physico-chemical reactions occur during the roasting process of low-grade molybdenum–rhenium sulfide concentrate, such as the disproportionation reaction between oxidation products and sulfide, and the formation of molybdate and rhenate. These reactions inhibited the oxidation and separation of molybdenum and rhenium. In the roasting process,  $\text{ReS}_2$  was oxidized along with the molybdenite. The whole oxidation process is shown in Fig. 12.

Step 1: In the early stage of oxidation,  $\text{MoS}_2$  was oxidized to  $\text{MoO}_2$ , and  $\text{ReS}_2$  was simultaneously oxidized to  $\text{Re}_2\text{O}_7$ .

Step 2:  $\text{Re}_2\text{O}_7$  was deoxidized into low valence

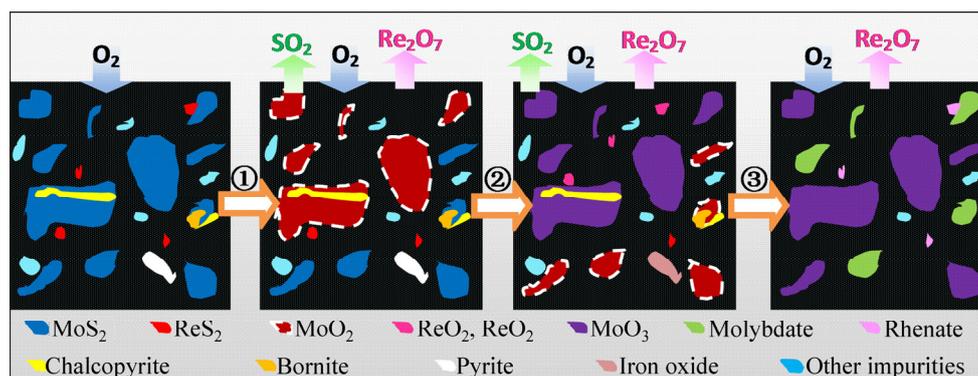


Fig. 12 Roasting process of Mo–Re–S system in molybdenum concentrate

states of rhenium oxides such as  $\text{ReO}_2$  and  $\text{ReO}_3$  by  $\text{MoS}_2$  and  $\text{SO}_2$  because of the disproportionation reaction between oxidation products and sulfide. At the same time,  $\text{MoO}_2$  was continuously oxidized to  $\text{MoO}_3$  with increasing roasting temperature or roasting time.

Step 3: The oxidation of rhenium lagged behind that of molybdenum and sulfur. In the late stage of oxidation,  $\text{MoS}_2$  was completely oxidized and rhenium was continuously volatilized during the formation of  $\text{Re}_2\text{O}_7$ . Finally, due to the influence of impurities,  $\text{MoO}_3$  and  $\text{Re}_2\text{O}_7$  reacted with the metallic oxide, forming a large amount of molybdate and rhenate, and the oxidation process was restricted. Thus, the maximum rate of soluble molybdenum was approximately 80% and the final volatilization rate of rhenium was below 70%. Further research should focus on the inhibition or extraction of molybdate and rhenate.

## 4 Conclusions

(1)  $\text{MoS}_2$  began to be oxidized at 450 °C and achieved complete oxidation over 600 °C.  $\text{MoO}_3$  started to volatilize when the temperature exceeded 650 °C and violently volatilized at 700 °C. The oxidative products of  $\text{MoS}_2$  were mainly  $\text{MoO}_2$ ,  $\text{MoO}_3$ , and molybdate. The maximum rate of soluble molybdenum was approximately 80% due to insoluble molybdate caused by the high impurity content in molybdenum concentrate.

(2) With increasing roasting temperature and roasting time, the volatilization rate of rhenium increased but still lagged behind the oxidation efficiency of molybdenum. When molybdenum was completely oxidized, the volatilization rate of rhenium improved significantly. The formation of rhenate and the difficulty in oxidizing the encapsulated low valence state of rhenium resulted in a final volatilization rate below 70%.

(3) The oxidizing roasting process of rhenium-bearing molybdenum concentrate involved oxidization of the low valence states of molybdenum and rhenium, disproportionation of the Mo–Re–S system, and the formation of molybdate and rhenate. The main products of rhenium sulfide were  $\text{ReO}_2$ ,  $\text{ReO}_3$ , and  $\text{Re}_2\text{O}_7$ .  $\text{Re}_2\text{O}_7$  can react with  $\text{MoS}_2$  and  $\text{SO}_2$  spontaneously, and rhenium can volatilize adequately after the thorough oxidation of  $\text{MoS}_2$  and the complete release of  $\text{SO}_2$ .

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## 粉状含铼低品位钼精矿焙烧过程中 $\text{ReS}_2$ 和 $\text{MoS}_2$ 的氧化行为

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**摘要:** 钼精矿氧化焙烧工艺在工业应用中具有显著的优势。然而, 低品位钼精矿因其比标准钼精矿复杂得多而在应用过程中存在许多问题。通过热力学计算、焙烧实验、热重分析和物相分析等, 研究粉状含铼低品位钼精矿的氧化行为。结果表明,  $\text{MoS}_2$  从 450 °C 氧化, 当温度达到 600 °C 时,  $\text{MoO}_3$  与金属氧化物反应并形成钼酸盐。最终, 由于不可溶的钼酸盐生成, 约 80% 的  $\text{MoO}_3$  溶解氨水中。由于  $\text{Re}_2\text{O}_7$ 、 $\text{MoS}_2$  和  $\text{SO}_2$  之间互相反应生成低价铼氧化物  $\text{ReO}_2$  和  $\text{ReO}_3$ , 铼的挥发速度远落后于钼的氧化速度。当  $\text{MoS}_2$  氧化完全后, 铼的挥发加强, 最终铼挥发率接近 70%。查明了低品位钼精矿在焙烧过程中钼、铼氧化效率低的主要原因, 为后续强化钼、铼的提取奠定了基础。

**关键词:** 低品位钼精矿; 铼; 氧化焙烧; 热力学; 物相演变

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