



## Reaction mechanisms of low-grade molybdenum concentrate during calcification roasting process



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**Abstract:** The effects of Ca-based additives on roasting properties of low-grade molybdenum concentrate were studied. The results show that calcium-based additives can react with molybdenum concentrate to form  $\text{CaSO}_4$  and  $\text{CaMoO}_4$ . The initial oxidation temperature of  $\text{MoS}_2$  is 450 °C, while the formation of  $\text{CaMoO}_4$  and  $\text{CaSO}_4$  occurs above 500 °C. The whole calcification reactions are nearly completed between 600 and 650 °C. However, raising the temperature further helps for the formation of  $\text{CaMoO}_4$  but is disadvantageous to sulfur fixing rate and molybdenum retention rate. Calcification efficiency of Ca-based additives follows the order:  $\text{Ca}(\text{OH})_2 > \text{CaO} > \text{CaCO}_3$ . With increasing the dosage of  $\text{Ca}(\text{OH})_2$ , the molybdenum retention rate and sulfur-fixing rate rise, but excessive dosages would consume more acid during leaching process. The appropriate mass ratio of  $\text{Ca}(\text{OH})_2$  to molybdenum concentrate is 1:1. When roasted at 650 °C for 90 min, the molybdenum retention rate and the sulfur-fixing rate of low-grade molybdenum concentrate reach 100% and 92.92%, respectively, and the dissolution rate of molybdenum achieves 99.12% with calcines being leached by sulphuric acid.

**Key words:** molybdenum concentrate; calcification roasting; reaction mechanism; thermodynamic analysis; phase transformation

### 1 Introduction

Molybdenum concentrate is commonly extracted after  $\text{MoS}_2$  is oxidized to high-valence molybdenum [1]. Two kinds of oxygenolysis processes for molybdenum concentrates are usually applied. One is pyrometallurgy, the other refers to hydrometallurgy which has been developed since 1970s [2]. Pyrometallurgy includes the process of oxidizing roasting, alkali fusing method and additive roasting [3]. In China, oxidizing roasting process is the most widely applied process, which commonly roasts molybdenum concentrates in rotary kiln, multiple hearth furnace, flash furnace etc. However, for low-grade molybdenum concentrate with abundant impurities such as calcium, magnesium, copper, iron and lead, low-melting-point compounds can easily be generated during oxidization roasting, which will lead to agglomeration and even restrict the thorough oxidization of  $\text{MoS}_2$ . Meanwhile, molybdates that are indissolvable in ammonia and further impede the recovery of

molybdenum are easy to form. In addition, the low  $\text{SO}_2$  concentration in roasting flue gas makes its recovery costly and causes environmental pollution [4]. Hydrometallurgical processing refers to oxygen pressure process [5–7], nitric acid decomposition [8,9], sodium hypochlorite oxidation [10,11], electro-oxidation [12,13] and bioleaching method [14,15]. Although hydrometallurgy has the advantage of solving  $\text{SO}_2$  emission problem, lacking low-cost oxidant makes it difficult to solve the problem thoroughly. Meanwhile, some impurities like metal compounds are easy to dissolve, which increases the difficulties of the follow-up purification. As a result, the high cost of leaching and purification restricts the development of hydrometallurgy to process low-grade molybdenum concentrates mostly [16,17].

Consequently, the key point of low-grade molybdenum concentrate utilization lies in improving the oxidation efficiency of molybdenum and resolving  $\text{SO}_2$  pollution problem. Benefiting from the effects of calcium-based additives during roasting, calcification

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roasting is able to fix sulfur and inhibit the volatilization of  $\text{MoO}_3$  together with  $\text{SO}_2$ , and the generated  $\text{CaMoO}_4$  can be fully dissolved in acid. This method is prospective to solve current problems in oxidizing roasting and hydrometallurgical processing. So, the selection of additives for calcification roasting was investigated in this work, and the mechanisms of sulfur fixing and  $\text{MoS}_2$  oxidization during calcification roasting were revealed, based on which a novel method for effectively handling low-grade molybdenum concentrate was provided.

## 2 Experimental

### 2.1 Materials

The chemical composition of molybdenum concentrate is shown in Table 1. The molybdenum content is 39.27%, which is lower than that of standard-molybdenum concentrate with Mo content above 45%. The impurity substances mainly consist of  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and iron-containing minerals. According to the mineral compositions of molybdenum concentrate (Table 2), the major component is molybdenite, which takes up 65.4%, followed by sulfide ores including copper pyrites, bornite and iron pyrite. There are also iron oxides mainly consisting of limonite and hematite, silicon gangue minerals composed of aluminosilicate, magnesium-silicate and quartz, and carbonates composed of calcite and dolomite.

**Table 1** Chemical composition of molybdenum concentrate (mass fraction, %)

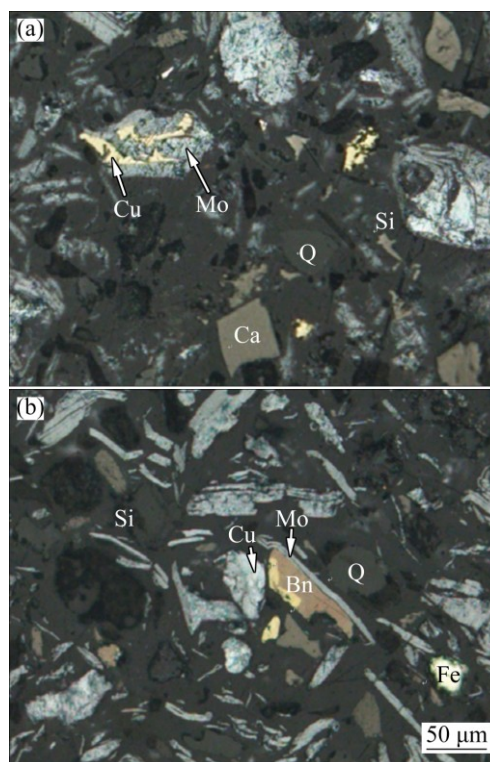
Mo	S	CaO	$\text{SiO}_2$	MgO
39.27	29.73	5.23	9.77	4.29
TFe	Cu	$\text{Al}_2\text{O}_3$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$
3.04	0.66	0.24	0.10	0.47

**Table 2** Mineral compositions of molybdenum concentrate

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

The mineral dissemination characteristics of molybdenum concentrate are investigated by optical microscope, as can be seen in Fig. 1. Molybdenite

mainly appears as monomer particle with sizes of 0.02–0.20 mm, which are scale-like, slab-like, strip and irregular particles. Few molybdenite particles are interlocked by pyrites otherwise coated by large particles of copper pyrites, which indicates that molybdenite and other sulfide ores are embedded closely. Most of calcite, quartz and silicate have been dissociated from molybdenite.



**Fig. 1** Dissemination characteristics of main minerals in molybdenum concentrate (Mo—Molybdenite; Cu—Copper pyrite; Bn—Bornite; Ca—Calcite; Q—Quartz; Fe—Pyrite; Si—Silicate): (a) Molybdenite coated by copper pyrites; (b) Molybdenite dissociated from quartz and silicate

### 2.2 Methods and evaluation indicators

The flow diagram of experiments, which simulated the oxidation process of molybdenum concentrate, is depicted in Fig. 2. The raw material was dried at 70 °C in the oven till its mass remained unchanged. 50 g molybdenum concentrates and moderate quantity of calcium-based additives were weighed to be mixed at a certain proportion. Calcium-based additives applied in the experiments included  $\text{CaCO}_3$ ,  $\text{CaO}$  and  $\text{Ca}(\text{OH})_2$ , which were analytical reagents.

Molybdenum concentrates and calcium-based additives were mixed thoroughly, and then roasted in a muffle furnace. After being roasted for a prescribed time, the molybdenum calcine was cooled in inert atmosphere. The phases and microstructures in roasted products were studied by using the modern microcosmic detecting

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