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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 $CaSO_4$ and $CaMoO_4$. The initial oxidation temperature of MoS_2 is 450 °C, while the formation of $CaMoO_4$ and $CaSO_4$ 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 $CaMoO_4$ but is disadvantageous to sulfur fixing rate and molybdenum retention rate. Calcification efficiency of Ca-based additives follows the order: $Ca(OH)_2$>CaO>$CaCO_3$. With increasing the dosage of $Ca(OH)_2$, the molybdenum retention rate and sulfur-fixing rate rise, but excessive dosages would consume more acid during leaching process. The appropriate mass ratio of $Ca(OH)_2$ 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 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 MoS_2. Meanwhile, molybdates that are indissolvable in ammonia and further impede the recovery of molybdenum are easy to form. In addition, the low 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 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 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 MoO_3 together with SO_2, and the generated $CaMoO_4$ 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 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 SiO_2, CaO, 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	SiO_2	MgO
39.27	29.73	5.23	9.77	4.29
TFe	Cu	Al_2O_3	K_2O	Na_2O
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.

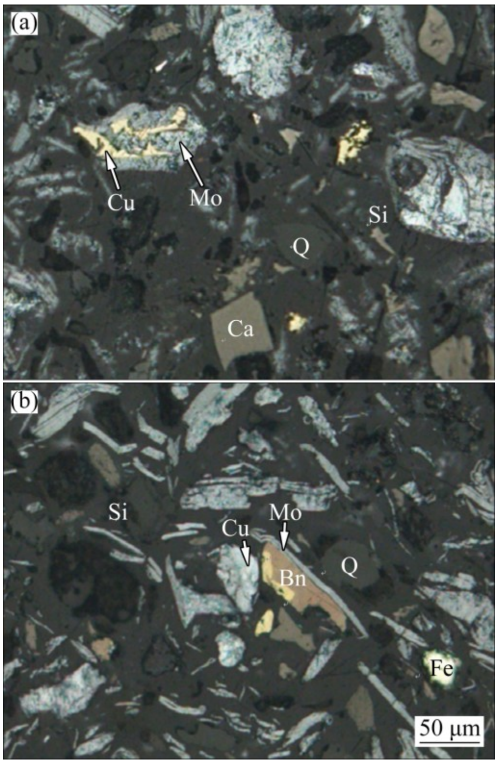


Fig. 1 Dissemination characteristics of main minerals in molybdenum concentrate (Mo—Molybdenite; Cu—Copper pyrite; Bn—Bornite; Ca—Calcite; Q—Quartz; Fe—Pyrite; Si—Silicate): (a) Molybdenite coated by copper pyrites; (b) Molybdenite dissociated from quartz and silicate

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 $CaCO_3$, CaO and $Ca(OH)_2$, 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 equipments such as X-ray diffraction (XRD) and scanning electronic microscope (SEM). XRD measurements were performed on the samples with a powder diffractometer(Rigaku D/M4X 2500) using a Cu K_α radiation. The range of scanning angle (2θ) was from 5° to 100° and the scanning speed was 0.2156 (°)/s. SEM (JEOL JSM−5600) with energy dispersive X-ray (EDX) was used to analyze particle morphology and major chemical distribution in typical minerals.

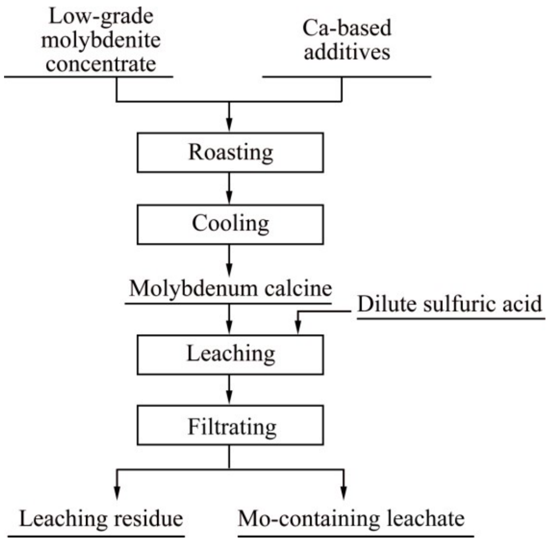


Fig. 2 Flow diagram of calcification roasting−acid leaching

Roasted products were ground into 0.074 mm with mass fraction above 80%, and then samples were obtained for examining the contents of molybdenum and sulfur. Another 5 g calcine was added into flasks containing dilute sulfuric acid for leaching molybdenum. The acid leaching conditions were set up as follows: sulfuric acid concentration of 70 g/L, temperature of 90 °C, time of 2 h, and liquid−solid ratio of 5:1. After leaching, the suspended solution was filtrated using a vacuum filter, and then the content of molybdenum in the residue was analyzed.

The evaluation indicators of roasting−acid leaching process mainly contain the leaching rate of molybdenum (α_{Mo}), the retention rate of molybdenum (η_{Mo}) and the sulfur-fixing rate β_{S}, which can be calculated as follows:

$$\alpha_{\mathrm{Mo}}=\frac{m_2w_2-m_3w_3}{m_2w_2}\times100\% \tag{1}$$

$$\eta_{\mathrm{Mo}}=\frac{m_2w_2}{m_1w_1}\times100\% \tag{2}$$

$$\beta_{\mathrm{S}}=\frac{m_2w_5}{m_1w_4}\times100\% \tag{3}$$

where m_1, m_2 and m_3 stand for the mass of molybenite concentrate, molybdenum calcine and leaching residue, respectively, g; w_1, w_2 and w_3 stand for the mass fractions of molybdenum in molybenite concentrate, molybdenum calcine and leaching residue, respectively, %; w_4 and w_5 stand for the mass fractions of sulfur in molybenite concentrate and molybdenum calcine, respectively, %.

3 Results and discussion

3.1 Thermodynamics of calcification roasting process

During the roasting process of molybdenum concentrate, the reactions of MoS_2 oxidation, calcium molybdate generation and sulfur-fixing reaction occur potentially. And the oxidation of MoS_2 is shown as: $(2/7)MoS_2+O_2(g)=(2/7)MoO_3+(4/7)SO_2(g)$, $\Delta G_T^\Theta=-300.83+0.05T$ (kJ/mol). When the temperature is lower than 6000 K, MoS_2 oxidation reaction is spontaneous because of $\Delta G_T^\Theta<0$. As calcium-based additives were mixed with molybdenum concentrate, calcium-based additives can react with the oxidative products of MoS_2 like MoO_3 and SO_2. The thermodynamic conditions of the formation reactions of molybdate and the sulfation reactions are shown in Fig. 3. If the temperature is below 798 K, the easy tendencies of different calcium-based additives reacting with MoO_3 and SO_2 to generate $CaMoO_4$ and $CaSO_4$ can be ranked as CaO>$Ca(OH)_2$> $CaCO_3$. While at the temperature of

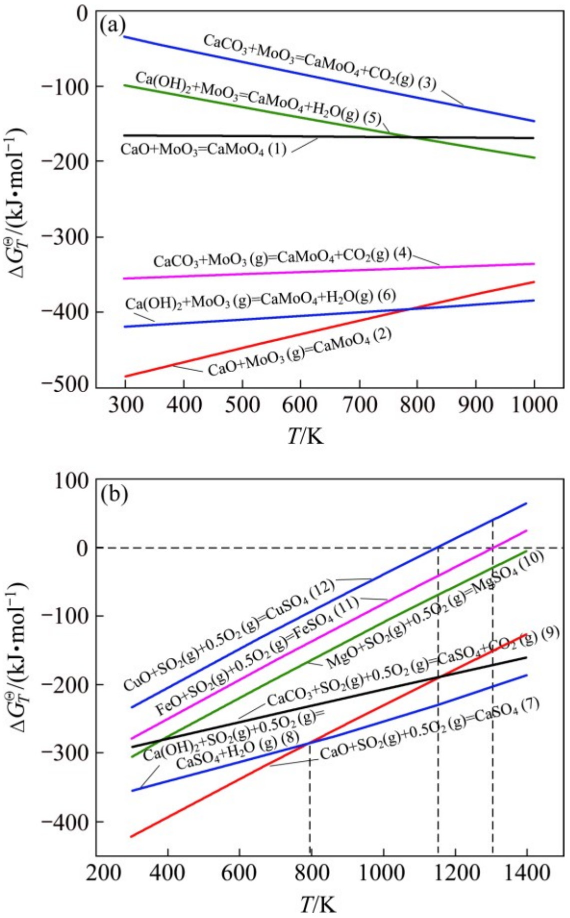


Fig. 3 Relationship between $\Delta G_T^\Theta-T$ for formation of molybdate and sulfate

above 798 K, the order changes to be $Ca(OH)_2$>CaO>$CaCO_3$. As can be observed from the thermodynamic curves, CaO, MgO, FeO and CuO react with SO_2 below 1150 K, and the products are $CaSO_4$, $MgSO_4$, $FeSO_4$ and $CuSO_4$, respectively. However, the reaction tendency decreases successively. $CuSO_4$ is resolved into CuO and SO_2 above 1150 K, and $FeSO_4$ will be decomposed above 1300 K. But $CaSO_4$ and $MgSO_4$ are only decomposed at high temperatures, which proves that sulfur-fixing reactions are qualified to proceed during the calcification roasting process.

Although there are differences in reactive ability of three calcium-based additives, the formation of molybdate and the sulfation reaction occur spontaneously in the temperature range of 400−1300 K. Therefore, the oxidation and calcification reactions are carried out simultaneously according to thermodynamic analysis.

3.2 Effects of calcium-based additives on roasting

As adding calcium-based additives with their theoretical quantities (theoretical amount means that molybdenum and sulfur convert to $CaMoO_4$ and $CaSO_4$ completely, and theoretical amounts of CaO, $Ca(OH)_2$ and $CaCO_3$ are the mass ratios of 0.64:1, 0.84:1 and 1.13:1 compared with molybdenum concentrate), the effects of roasting temperature on the roasting−leaching process of molybdenum concentrate at the roasting time of 90 min are given in Fig. 4. With temperature rising, the retention rate of molybdenum decreases gradually. Especially when the temperature increases to above 750 °C, the retention rate of molybdenum is observed to decrease apparently. The reason is that MoS_2 is oxidized to MoO_3 rapidly and part of MoO_3 volatilized before reacting with calcium-based additives at high temperatures. The loss of molybdenum is relatively small below 700 °C. Using $Ca(OH)_2$ achieves the highest retention rate of molybdenum, which nearly reaches 100% at 650 °C. Differences in the sulfur-fixing rate of these additives are studied, adsorption efficiency firstly increases and then decreases with the temperature rising. According to its effects, the sulfur-fixing rate of different additives can be ranked as $Ca(OH)_2$>CaO>$CaCO_3$, and the sulfur-fixing rate achieves the maximum at 650−700 °C. However, the sulfur-fixing rate is lower when using theoretic dosage of additives. During the experiments of leaching molybdenite by acid, the leaching rate increases with the rise of roasting temperature, but then the leaching rate increases at a slower pace above 700 °C. Taking the effects of three additives on retention rate of molybdenum, sulfur-fixing rate and leaching rate of molybdenum into consideration, 650 °C is suitable for roasting.

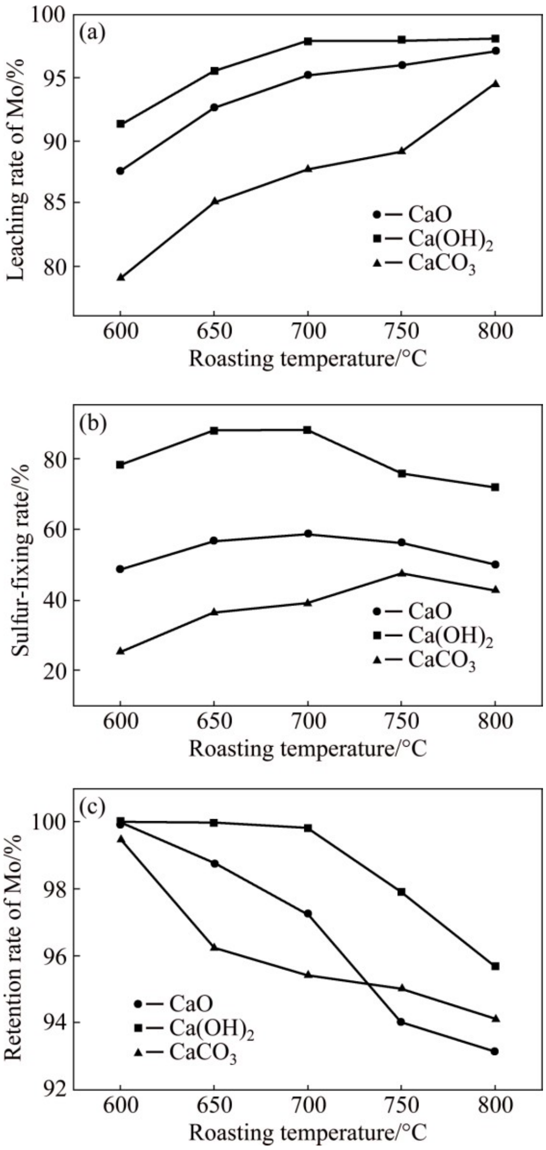


Fig. 4 Effects of roasting temperature on calcification roasting and acid leaching

Figure 4 shows that the sulfur-fixing rate stays at a low level when using the theoretic dosage of additives, thus it is necessary to add more additives. When roasting molybdenum concentrate at 650 °C for 90 min, the effects of different additives on roasting−leaching rate are studied, and the results are shown in Table 3. On one hand, with increasing the dosage of $Ca(OH)_2$ or CaO, the retention rate and the leaching rate of molybdenum and the sulfur-fixing rate tend to increase; on the other hand, increasing the dosage of $CaCO_3$ improves both the retention rate of molybdenum and the sulfur-fixing rate, while the leaching rate of molybdenum increases firstly and then decreases for the reason that excessive $CaCO_3$ consumes more acid, which leads to lower leaching rate of molybdenum.

According to the retention rates and the leaching rates of molybdenum, it can be concluded that all of the calcium-based additives can react with MoO_3 to generate $CaMoO_4$, and the reaction ability can be ranked as $Ca(OH)_2$>CaO>$CaCO_3$. From the sulfur-fixing rate, it is believed that the sulfur-fixing efficiencies of $Ca(OH)_2$ and CaO are better than that of $CaCO_3$, and the sulfur-fixing efficiencies of $Ca(OH)_2$ are better than that of CaO. The sulfur-fixing rate with the addition of $CaCO_3$ is only 41.67% even though the dosage of $CaCO_3$ is 1.4 times of molybdenum concentrate, which indicates that the sulfur-fixing efficiency of $CaCO_3$ is inferior to that of other additives. When the mass ratio of $Ca(OH)_2$ to MoO_3 is 1:1, the retention rate of molybdenum reaches 100%, the sulfur-fixing rate attains 92.92%, and the leaching rate of molybdenum is 99.12%.

Table 3 Effects of dosages of calcium-based additives on calcification roasting and acid leaching

Additive	Mass ratio of additive to molybdenum concentrate	Retention rate of molybdenum/%	Sulfur-fixing rate/%	Leaching rate of molybdenum/%
CaO	0.60:1	98.61	54.73	89.09
	0.64:1*	98.76	56.67	92.63
	0.80:1	99.89	68.15	93.54
	1.00:1	100.00	88.48	95.53
$Ca(OH)_2$	0.80:1	98.97	86.17	89.32
	0.84:1*	99.99	87.90	95.58
	1.00:1	100.00	91.49	99.12
	1.20:1	100.00	93.57	99.18
$CaCO_3$	1.00:1	96.09	34.89	80.98
	1.13:1*	96.25	36.50	85.11
	1.20:1	97.14	37.99	71.20
	1.40:1	97.38	41.67	52.16

* Theoretical values for molybdenum transforming to calcium molybdate

3.3 Phase evolution during calcification roasting process

In order to study the effects of additives on the particle morphology of calcine and the formation of products, energy dispersive X-ray spectrometric microanalyzer (EDS) with SEM is employed and the scanning pictures are shown in Fig. 5. In this study, the roasting process of molybdenum concentrate is performed under conditions of adding additives at theoretic ratios and roasting at 650 °C for 90 min. With the addition of $CaCO_3$, the original particle morphology is not changed after roasting, but some new phases appear on the surface and a few particles bond mildly. With the addition of CaO, crystalline transformation is observed mainly to be needle-like and granular, and other morphology of the complex interwoven structure is formed after sintering. With the addition of $Ca(OH)_2$, two kinds of particles with different crystalline forms appear, one is developed from aggregated particles, and the other is small monomer bean shaped particles.

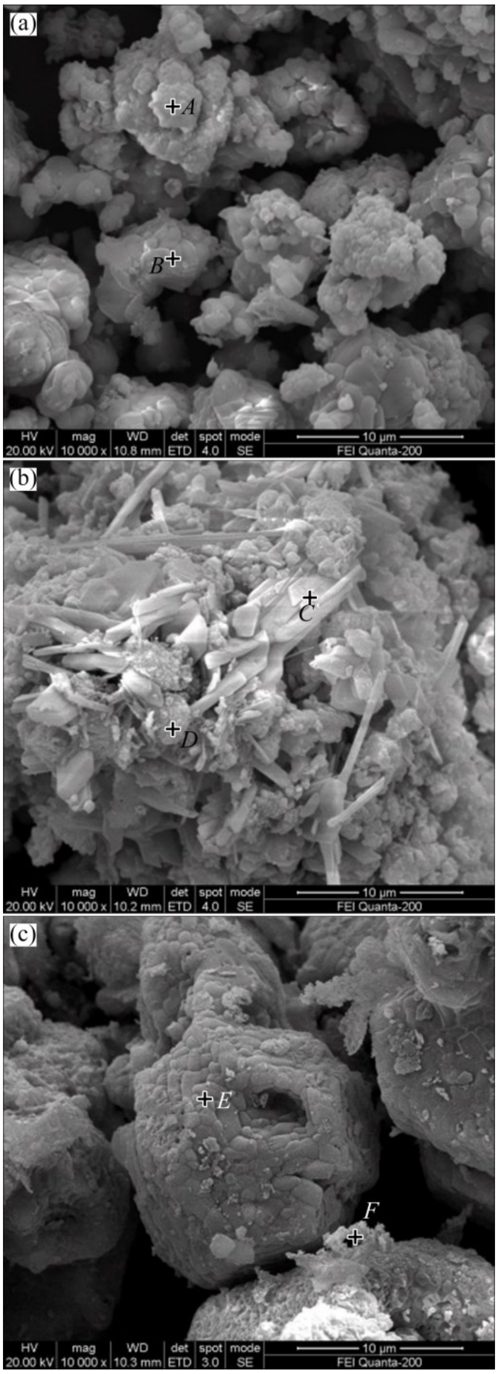
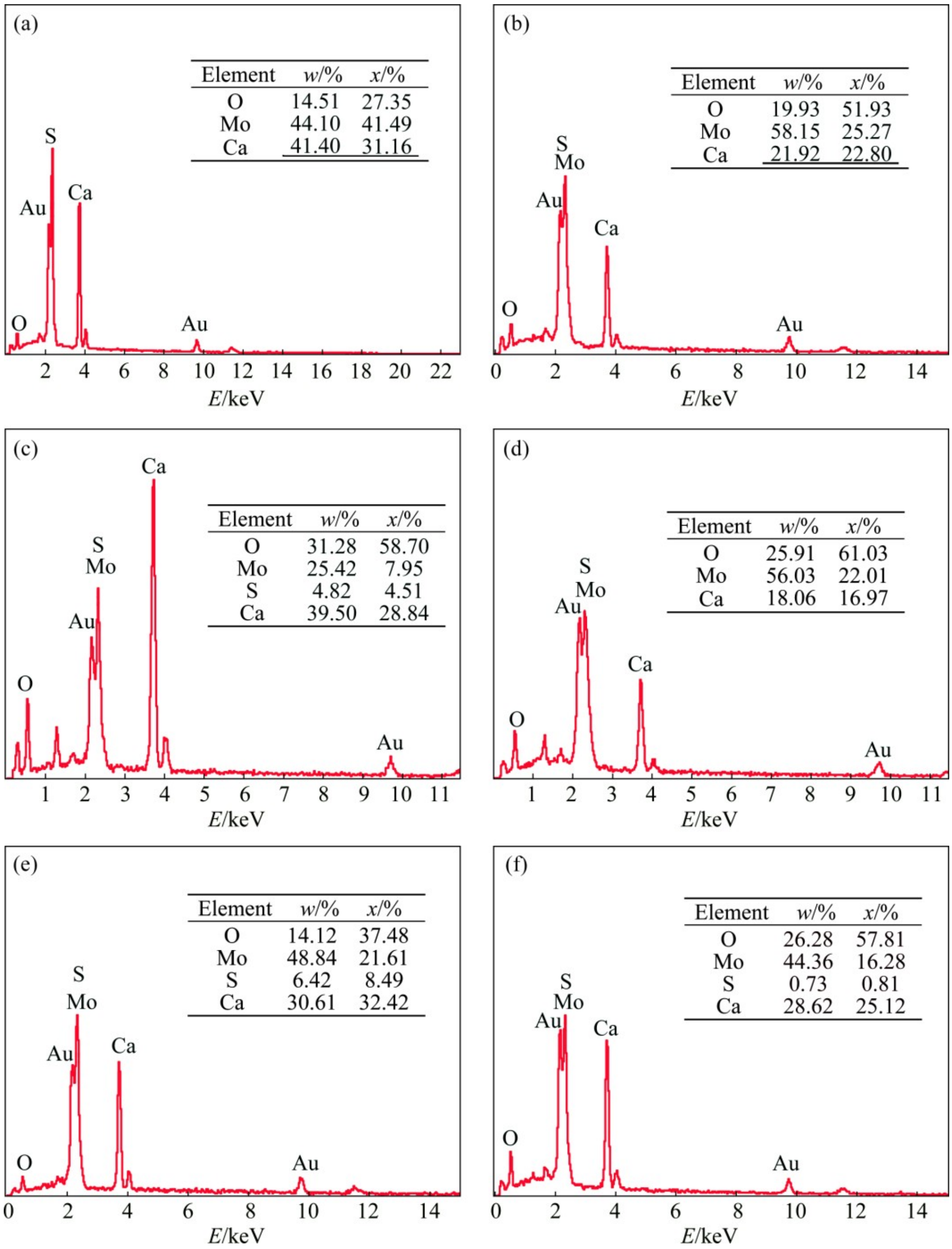


Fig. 5 SEM images of roasted products with different calcium-based additives: (a) $Ca(OH)_2$; (b) CaO; (c) $CaCO_3$

For revealing the types of products after roasting, the energy spectrum analyses of different zones in the calcine are applied, and the results are shown in Fig. 6. With the addition of $Ca(OH)_2$, well-crystallized $CaSO_4$ and $CaMoO_4$ appear in Zones *A* and *B* in (Fig. 6(a)). With the addition of CaO, the sulfur-fixing rate is evaluated to be lower. According to the analyses of



(a)

Element	*w*/%	*x*/%
O	14.51	27.35
Mo	44.10	41.49
Ca	41.40	31.16

(b)

Element	*w*/%	*x*/%
O	19.93	51.93
Mo	58.15	25.27
Ca	21.92	22.80

(c)

Element	*w*/%	*x*/%
O	31.28	58.70
Mo	25.42	7.95
S	4.82	4.51
Ca	39.50	28.84

(d)

Element	*w*/%	*x*/%
O	25.91	61.03
Mo	56.03	22.01
Ca	18.06	16.97

(e)

Element	*w*/%	*x*/%
O	14.12	37.48
Mo	48.84	21.61
S	6.42	8.49
Ca	30.61	32.42

(f)

Element	*w*/%	*x*/%
O	26.28	57.81
Mo	44.36	16.28
S	0.73	0.81
Ca	28.62	25.12

Fig. 6 SEM−EDAX patterns of different zones in Fig. 5 in calcine: (a) Zone *A*; (b) Zone *B*; (c) Zone *C*; (d) Zone *D*; (e) Zone *E*; (f) Zone *F*

Zones *C* and *D* in Fig. 5(b), the main component is $CaMoO_4$ and there are still a few of $CaSO_4$ and CaO. With the addition of $CaCO_3$, $CaSO_4$ and $CaMoO_4$ in roasted product are detected in Zones *E* and *F*, whose content of $CaSO_4$ is less than that with the addition of CaO. Illustrated by the results of SEM, reactions run smoothly and well-crystallized particles of $CaMoO_4$ and $CaSO_4$ are formed with the addition of $Ca(OH)_2$. In addition, the generation of $CaMoO_4$ becomes relatively difficult and the sulfur-fixing rate decreases obviously during the roasting process with the addition of $CaCO_3$ or CaO.

The roasted products, which come from the molybdenum concentrate that is roasted at 650 °C for 90 min with theoretic quantities of additives, are investigated by means of XRD and the patterns are shown in Fig. 7, from which it can be seen that the common phases of the calcines are $CaMoO_4$, $CaSO_4$ and $Mg_3(Si_4O_{10})(OH)_2$. The intensities of the $CaSO_4$ diffraction peaks with different additives can be ranked as $Ca(OH)_2$>CaO>$CaCO_3$, which indicates that calcium-based additives are convinced to have the function on sulfur fixation. This agrees with the thermodynamic results.

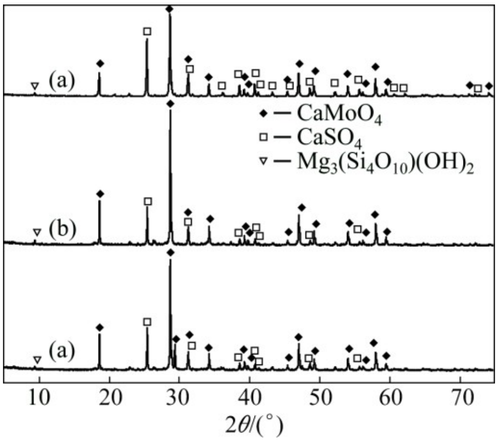


Fig. 7 XRD patterns of roasted products with different additives: (a) $CaCO_3$; (b) CaO; (c) $Ca(OH)_2$

The retention rates of molybdenum are 98.76%, 99.99% and 96.25% with the addition of CaO, $Ca(OH)_2$ and $CaCO_3$, respectively (Table 3). High retention rate of molybdenum indicates that the solid−solid reactions or gas−solid reactions between MoO_3 or MoO_3 (g) and additives can run smoothly. The sulfur-fixing rates being 56.67%, 87.90% and 36.50% respectively indicate that reactions between $Ca(OH)_2$ and SO_2 are able to proceed more sufficiently. The leaching rates of Mo in calcine are 92.63%, 95.58% and 85.11%, respectively. The phase analyses also sustain the fact that a large amount of calcium molybdate, which can be dissolved in acid, generates under the roasting temperature. Therefore, the most suitable calcium-based additive is $Ca(OH)_2$.

$Ca(OH)_2$ is the product of CaO hydration. $Ca(OH)_2$ colloid particles are formed in the process of hydration, which makes larger specific surface area of $Ca(OH)_2$ than that of CaO. Therefore, reactions are easily to proceed on the kinetics because of the larger contact area with molybdenum concentrate. Whereas, compared with $CaCO_3$, thermodynamics trend of reaction between $Ca(OH)_2$ and MoO_3, SO_2 is larger. Moreover, the decomposition temperature of $CaCO_3$ is high, it starts to decompose at 530 °C and decompose acutely at 900 °C to form CaO. As a consequence, the calcification efficiency of adding $Ca(OH)_2$ to roast molybdenum concentrate is the best.

Molybdenum concentrates with equivalent mass of $Ca(OH)_2$ are roasted for 90 min at different temperatures, the phase compositions of the products are analyzed, and the patterns are shown in Fig. 8.

The molybdenum phase is mainly composed of MoS_2 at about 400 °C, where the oxidation reaction does not start yet. When the temperature increases to 450 °C, the product of MoO_3 appears through the oxidization of MoS_2, and $Ca(OH)_2$ begins to decompose where the diffraction peak of CaO appears. The height diffraction peaks of MoS_2 and MoO_3 drop significantly while the diffraction peaks of $CaMoO_4$ and $CaSO_4$ appear at 500 °C. It can be known that MoO_3 and SO_2, which derive from the oxidization of MoS_2, begin to react with CaO. When the temperature is above 600 °C, the main diffraction peaks are those of $CaMoO_4$ and $CaSO_4$, and MoS_2 is completely transformed into $CaMoO_4$.

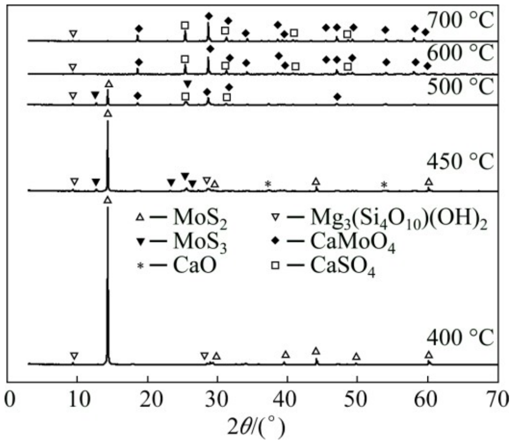


Fig. 8 XRD patterns of roasted products at different temperatures

The reaction process between molybdenum concentrate and $Ca(OH)_2$ is further proved by thermal gravity analysis. According to the TG−DSC curves (Fig. 9), the evaporation of moisture and the volatilization of something volatile go on before 400 °C. When the temperature ranges from 400 to 470 °C, the oxidization of sulfide and the decomposition of $Ca(OH)_2$ occur. When the temperature surpasses 470 °C, three exothermic peaks appear at 530.5, 574.4 and 640.9 °C, respectively, where the reaction speed of MoO_3

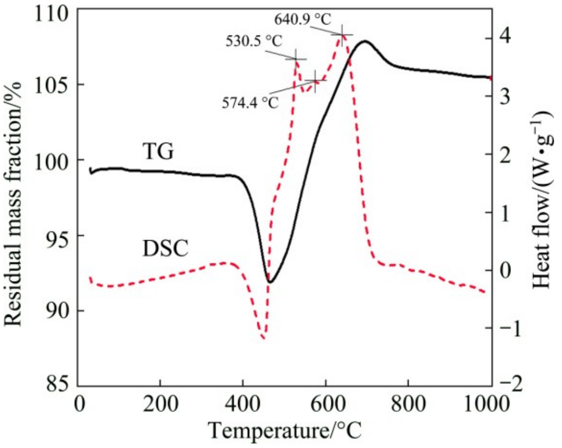


Fig. 9 Thermogravimetric curves of molybdenite concentrate and $Ca(OH)_2$ in air

oxidation and the generation speed of $CaMoO_4$ and $CaSO_4$ are the fastest. As it has been introduced in Figs. 8 and 9, the transformation process is as follows: $Ca(OH)_2$ decomposition→MoS_2 oxidation→molybdate and sulfate generation.

3.4 Calcification roasting−acid leaching process

The quality flow chart of calcium-based roasting and acid-leaching process is shown in Fig. 10. According to the analysis of the calcine and the leaching residue, which is roasted from the molybdenum concentrates with addition of equivalent mass of $Ca(OH)_2$ at the roasting temperature of 650 °C for 90 min, the leaching conditions are set up as follows: concentration of sulfuric acid of 70 g/L, leaching at 90 °C for 120 min, ratio of liquid to solid 5:1. It can be concluded that molybdenum is hard to be lost or volatilized during the roasting process. The sulfur-fixing rate is 91.49%, which indicates that little sulfur is volatilized into the smoke as SO_2, and it can be absorbed by alkali. After acid leaching, the surplus grade of molybdenum attains 0.2%, the leaching rate of molybdenum reaches 99.12%, and the total loss is only 0.88% in the whole process.

The phase compositions of calcine and the leaching residue are studied by XRD analysis as shown in Fig. 11.

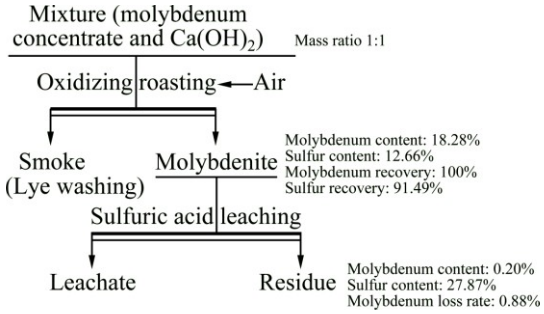


Fig. 10 Quality flow chart of of calcium-based roasting and acid leaching process

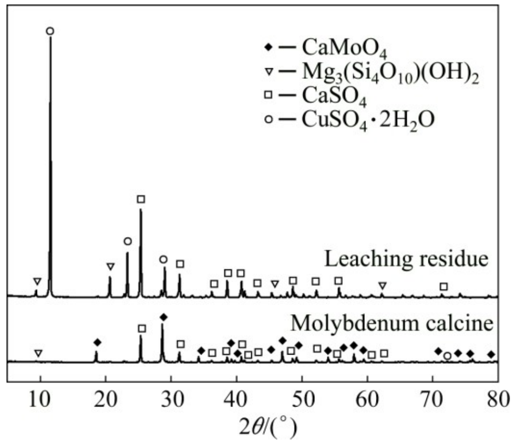


Fig. 11 XRD patterns of leaching residue obtained with acid leaching

MoS_2 disappears after roasting, and the main phases of calcine are $CaMoO_4$ and $CaSO_4$. The characteristic peaks of $CaMoO_4$ disappear, and the peaks of $CaSO_4$ are markedly strengthened after acid leaching, indicating that calcium molybdate is completely dissolved. The main components of the leaching residue are $CaSO_4$, gypsum ($CaSO_4 \cdot 2H_2O$) and talc ($Mg_3(Si_4O_{10})(OH)_2$). As a conclusion, molybdenum in low-grade molybdenum concentrate can be recycled completely by calcification roasting−acid leaching process.

4 Conclusions

1) During the roasting process of molybdenum concentrate with calcium-based additives, additives are able to react with MoO_3 and SO_2 to form $CaMoO_4$ and $CaSO_4$. Adding $Ca(OH)_2$ can achieve the best roasting effects and sulfur-fixing rate, which is followed by CaO, and then $CaCO_3$. The microstructure of calcine shows that the intact grains of $CaMoO_4$ and $CaSO_4$ are formed with the addition of $Ca(OH)_2$, while adding CaO or $CaCO_3$ is unable to achieve the above effect.

2) Higher roasting temperature contributes to the formation of $CaMoO_4$ while it causes the decrease of both sulfur-fixing rate and retention rate of molybdenum. The phase evolution indicates that MoS_2 starts to be oxidized at 450 °C, while $CaMoO_4$ and $CaSO_4$ start to form at 500 °C, and the main phase compositions of calcine are $CaMoO_4$ and $CaSO_4$ at temperatures of 600−650 °C, at which the calcification reaction is nearly completed.

3) With increasing the dosage of $Ca(OH)_2$, the retention rate of molybdenum and the sulfur-fixing rate tend to grow with more acid consumed. The appropriate mass ratio of $Ca(OH)_2$ to molybdenum concentrate is 1:1. By roasting the molybdenum concentrate at 650 °C for 90 min with appropriate dosage of $Ca(OH)_2$, the retention rate of molybdenum during the roasting process achieves 100%, the sulfur-fixing rate attains 92.92%, and the leaching rate of molybdenum achieves 99.12%.

References

[1] GUPTA C K. Extractive metallurgy of molybdenum [M]. London: CRC Press, 1992: 15−30.

[2] JENNINGS P H, STANLEY R W, AMES H L. Development of a process for purifying molybdenum concentrate [C]//Proceedings of the second International Symposium on Hydrometallurgy. New York: AIME, 1974: 868−883.

[3] XIANG Tie-gen. Molybdenum metallurgy [M]. Changsha: Central South University Press, 2002: 1−20. (in Chinese)

[4] GAN Min, FAN Xiao-hui, ZHANG Lin. Reaction behavior of low grade molybdenum concentrates in oxidation roasting process [J]. The Chinese Journal of Nonferrous Metals, 2014, 24(12): 3315−3322. (in Chinese)

[5] PENG Jian-rong, YANG Da-jin, CHEN Jia-xi, YAN Jiang-feng. Experimental study on alkaline leaching of crude molybdenite under pressure of oxygen [J]. Chinese Journal of Rare Metals, 2007, 31(6): 110−113. (in Chinese)

[6] WANG Si-fu, WEI Chang, DENG Zhi-gan, LI Cun-xiong, LI Xin-bing, WU Jun, WANG Ming-shang, ZHANG Fan. Extraction of molybdenum and nickel from Ni−Mo ore by pressure acid leaching [J]. Transactions of Nonferrous Metals Society of China, 2013, 23(10): 3083−3088.

[7] KETCHAM J. Pressure oxidation process for the production of molybdenum trioxide from molybdenite: United States, US6149883 [P]. 2000−11−21.

[8] ZHANG Qi-xiu, ZHAO Qin-sheng. Molybdenum tungsten metallurgy [M]. Beijing: Metallurgical Industry Press, 2005: 26−32. (in Chinese)

[9] MANOJ K, MANKHAND T R, MURTHY D S R, MUKHOPADHYAY R, PRASAD P M. Refining of a low-grade molybdenum concentrate [J]. Hydrometallurgy, 2007, 86(3): 56−62.

[10] WARREN I H, MOUNSEY D M. Factors influencing the selective leaching of molybdenum with sodium hypochlorite from copper/molybdenum sulphide minerals [J]. Hydrometallurgy, 1983, 10(3): 343−357.

[11] ANTONIJEYIC M M, PACOVIC N V. Investigation of molybdenite oxidation by sodium dichromate [J]. Minerals Engineering, 1992, 5(2): 223−233.

[12] CAO Zhan-fang, ZHONG Hong, JIANG Tao, LIU Guang-yi, WANG Shuai. Selective electric-oxidation leaching and separation of Dexing molybdenum concentrates [J]. The Chinese Journal of Nonferrous Metals, 2013, 23(8): 2290−2295. (in Chinese)

[13] FU Jian-gang, ZHONG Hong, HUANG Yong-ping, PU Xiang-ming. Indirect electro-oxidation of molybdenite by Mn^{3+}/Mn^{2+} [J]. Journal of Central South University (Science and Technology), 2004, 35(5): 797−801. (in Chinese)

[14] ROMANO P, BLAZQUEZ M L, ALGUACIL F J, MUNOZ J A, BALLESTER A, GONZALEZ F. Comparative study on the chalcopyrite bioleaching of a molybdenum concentrate with mesophilic and thermophilic bacteria [J]. FEMS Microbilology Letters, 2001, 196(1): 71−75.

[15] GREGORY J O, THOMAS R C. Bioleaching of molybdenite [J]. Hydrometallurgy, 2006, 82(3): 133−136.

[16] LI Hong-gui, HUO Guang-sheng, SUN Pei-mei, ZHAO Zhong-wei, LI Yun-jiao, SU Peng-tuan. Developing new reagent for selectively precipitation of molybdenum from tungstate solution [J]. Transactions of Nonferrous Metals Society of China, 2003, 13(1): 184−187.

[17] CAO Zhan-fang, ZHONG Hong, LIU Guang-yi. Electric-oxidation kinetics of molybdenum concentrate in acidic NaCl solution [J]. The Canadian Journal of Chemical Engineering, 2009, 87(6): 939−944.

低品位钼精矿钙化焙烧的反应机理

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摘　要：研究了钙基添加剂对低品位钼精矿焙烧性能的影响。结果表明，钙基添加剂可与钼精矿反应生成 $CaSO_4$ 和 $CaMoO_4$。450 °C 时 MoS_2 开始氧化，500 °C 以上生成 $CaMoO_4$ 和 $CaSO_4$，600~650 °C 时钙化反应基本完成；进一步提高焙烧温度有利于 $CaMoO_4$ 的生成，但会降低焙烧过程固硫率和钼保留率。钙基添加剂焙烧效果依次为 $Ca(OH)_2$>CaO>$CaCO_3$。随着 $Ca(OH)_2$ 用量的增加，钼保留率和固硫率均呈上升趋势，但过多的钙基添加剂会使酸浸过程硫酸的消耗增加，$Ca(OH)_2$ 与钼精矿适宜的质量比为 1:1。在 650 °C 下焙烧 90 min 时，低品位钼精矿钙化焙烧过程中钼保留率为 100%、固硫率为 92.92%，经硫酸浸出后钼的浸出率达到 99.12%。

关键词：钼精矿；钙化焙烧；反应机理；热力学研究；相变

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