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 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 $CaSO_4$ slag. In this work, a novel process, in which the molybdenite was roasted with $CaCO_3$ followed by $(NH_4)_2CO_3$ solution leaching, was proposed to improve the art of lime roasting−sulfuric acid leaching. Oxidizing roasting of molybdenite with $CaCO_3$ was investigated through thermodynamic calculation, thermogravimetric analysis and roasting experiments. The results show that the products of the oxidizing reaction of MoS_2 in the presence of $CaCO_3$ and O_2 are $CaSO_4$, $CaMoO_4$ and CO_2 at 573−1000 K. The MoS_2 conversion rate achieves approximately 99% and the sulfur-retained rate attains approximately 95% with a $CaCO_3$-to-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 $(NH_4)_2CO_3$ 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 This process presents many drawbacks because of its outdated technology as well as small production scale [2].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 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 $CaMoO_4$ and $Ca(ReO_4)_2$, respectively, whereas sulfur turns to $CaSO_4$ when lime is added in the oxidizing roasting process. $Ca(ReO_4)_2$ in the calcine can be leached out immediately by water. $CaMoO_4$ can transform to H_2MoO_4 and $CaSO_4$ 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 $CaSO_4$ 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.

$CaCO_3$ 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, $(NH_4)_2CO_3$ can react with $CaMoO_4$, forming $CaCO_3$ and $(NH_4)_2MoO_4$. Additionally, adding some $(NH_4)_2CO_3$ in the traditional aqueous ammonia leaching process can increase Mo recovery from 83%−85% to 93%−96% by preventing the generation of $CaMoO_4$ and $FeMoO_4$ and inhibiting the coverage of $Fe(OH)_2$ up to the Mo-bearing ore particles [16]. Thus, if $CaCO_3$ is employed to replace CaO during the oxidizing process of molybdenite, and $(NH_4)_2CO_3$ solution as leaching agent to replace sulfuric acid in the leaching process, we will obtain leaching residue mainly consisting of $CaCO_3$ which could be conveniently reused in the raw meal preparation for roasting, and the remaining $(NH_4)_2SO_4$ 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 $CaCO_3$ and the resultant calcine was leached by $(NH_4)_2CO_3$ solution.

In this work, oxidizing roasting process in the presence of $CaCO_3$ and 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 $(NH_4)_2CO_3$ 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 $CaCO_3$ mainly involve the oxidation of MoS_2 [17,18] and the reactions between MoS_2 and $CaCO_3$ in the presence of 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 $CaCO_3$ 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 $CaCO_3$ and 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	$\Delta G/(kJ \cdot mol^{-1})$				ΔG equation
		298 K	600 K	800 K	1000 K	
1	$MoS_2+7/2O_2=MoO_3+2SO_2$	−1000.128	−937.412	−895.787	−854.744	$\Delta G=0.2007T−1058.6398$
2	$MoS_2+3O_2=MoO_2+2SO_2$	−864.855	−823.244	−795.328	−767.724	$\Delta G=0.1380T−905.9915$
3	$6MoO_3+MoS_2=7MoO_2+2SO_2$	−53.219	−138.033	−192.575	−245.600	$\Delta G=−0.2718T+27.2933$
4	$MoO_2+0.5O_2=MoO_3$	−156.692	−144.201	−100.459	−87.021	$\Delta G=0.0046T−158.3734$
5	$2MoS_2+O_2=Mo_2S_3+SO_2$	−161.487	−170.347	−175.775	−181.224	$\Delta G=−0.0282T−153.0845$
6	$Mo_2S_3+5O_2=2MoO_2+3SO_2$	−1568.223	−1476.075	−1414.881	−1354.224	$\Delta G=0.3043T−1658.8985$
7	$2SO_2+O_2=2SO_3$	−141.490	−84.754	−47.193	−10.011	$\Delta G=0.1869T−197.1901$
8	$3CaCO_3+MoS_2+4.5O_2=2CaSO_4+CaMoO_4+3CO_2$	−1616.971	−1530.604	−1473.008	−1415.990	$\Delta G=0.2857T−1702.1338$
9	$2CaCO_3+MoS_2+4O_2=CaSO_4+CaMoO_4+2CO_2+SO_2$	−1325.869	−1275.996	−1242.408	−1209.067	$\Delta G=0.1662T−1375.5504$
10	$CaCO_3+MoS_2+3.5O_2=CaMoO_4+2SO_2+CO_2$	−1034.767	−1021.388	−1011.809	−1002.144	$\Delta G=0.0468T−1048.9670$
11	$CaCO_3+MoO_3=CaMoO_4+CO_2$	−34.640	−83.976	−116.022	−147.399	$\Delta G=−0.1539T+9.6728$
12	$2CaCO_3+2SO_2+O_2=2CaSO_4+2CO_2$	−582.203	−509.216	−461.199	−413.846	$\Delta G=0.2388T−653.1667$
13	$CaCO_3+MoO_2+0.5O_2=CaMoO_4+CO_2$	−169.912	−198.177	−216.481	−234.420	$\Delta G=−0.0912T−142.9755$
14	$CaCO_3=CaO+CO_2$	130.127	82.987	52.608	23.017	$\Delta G=−0.1511T+174.6393$