



Leaching molybdenum from a low-grade roasted molybdenite concentrate

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Abstract

A technique for leaching molybdenum from low-grade roasted molybdenite concentrate was proposed by the aqueous solution containing sodium chlorate and sodium carbonate. The effect of molar ratio of sodium chlorate to molybdenum, leaching time, liquid–solid ratio, leaching temperature, sodium carbonate concentration and agitating speed on leaching rate of molybdenum was studied. The experimental results showed that the temperature and concentration of sodium carbonate are key factors to influence the leaching efficiency of molybdenum, and leaching rate achieves above 98% when the molar ratio of sodium chlorate to molybdenum is up 13.5, the temperature is 343.15 K, the agitating speed is 500 rpm, the liquid–solid ratio is 10:1 and the concentration of sodium carbonate is above 10 g/L. The leaching process was mainly controlled by chemical reaction and mass transfer. The leaching time is shorter and the heavy metal content in leaching aqueous solution is lower in basicity than those in acid situations.

Keywords Leaching · Sodium chlorate · Sodium carbonate · Molybdenite concentrate

1 Introduction

Molybdenum is a refractory metal with high boiling point and high melting point, mainly used in nonferrous metallurgy, oil and gas industry, and is a strategic metal for industrial, pharmaceutical, human and plant essential elements [1].

Molybdenite is the main raw material for the extraction of molybdenum, and the method of molybdenum ore treatment includes fire and wet two categories [2]. Whether it is a fire or a wet method, the common point is that the sulfide ore is to be oxidized to an oxide or its salt, and then the impure intermediate product is further purified to a pure molybdenum compound.

Molybdenite concentrate roasting process is a complex physical and chemical process, the entire oxidation process can be divided into four categories [1, 3]: the reaction that MoS_2 oxidation to MoO_3 ; the occurrence of redox

reaction among molybdenum sulfide, molybdenum oxide and oxygen; Other metal sulfide oxidation reaction; MoS_2 reacts with other metal oxides, sulfates and carbonates to produce molybdates. The roasting method can probably be divided into three types, such as direct oxidizing roasting, soda roasting and lime roasting, et al. The adopted equipment is mainly reverberatory furnace, fluidized bed, multiple hearth furnace and rotary kiln Li et al. [4].

Oxidation roasting is the dominant method for the treatment of molybdenite concentrate by pyrometallurgy methods. However, the release of sulfur dioxide in the process poses a great threat to the environment. Therefore, it is of great significance to study and develop the desulfurization process or wet treatment process. Since the 1970s, research on Mo wet alkali and acidic leaching has attracted more attention [5, 6], the oxygen pressure process [7], nitric acid decomposition [8], sodium hypochlorite

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[9], electro-oxidation and bio-leaching [10–14] method have been developed one after another.

Oxygen pressure process and nitric acid oxidation consumed cheap oxidants or air. This process not only need high temperature and high pressure but also require high demands for chemical reactor. It's difficult to control this leaching process, and there are certain security risks in the production those technologies are barely applied by small and medium sized manufacturers, so some domestic manufacturers have already discarded it. The sodium hypochlorite method has moderate reacting conditions, low equipment investment, and is easy to control when compared with the above two former processes. But it has a main disadvantage that large reagent consumption, and it is mainly used in low-grade molybdenum, tailings leaching, and molybdenum reclamation from the traditional process [15–19].

The leaching molybdenum from low-grade molybdenite concentrate has been widely investigated, mainly in relation to acidic oxidative leaching for the direct extraction of molybdenum [20–22]. The advantages lie in no SO₂ emission but the impurities such as iron, calcium, magnesium, phosphorus and arsenic et al. are also dissolved in the leaching solutions. In fact, the advantage of leaching molybdenum under basicity and common temperature and pressure conditions from low-grade roasted molybdenite concentrate is in evidence, although the process lets out the harmful gas but it can be deleted through adding Na₂CO₃, NaNO₃ or NaCl in roasting process [23–27], but the main existing methods leaching molybdenum with sodium carbonate or ammonium hydroxide aqueous solution need multi-stage leaching process, following more equipment, longer time and lower leaching efficiency [28, 29].

The purpose of the present work tries to leach molybdenum from low-grade roasted molybdenite concentrate using sodium chlorate as the oxidant in basic condition under common temperature and pressure. Several influential parameters, such as the molar ratio of sodium chlorate to molybdenum, leaching time, liquid–solid ratio, leaching temperature, sodium carbonate concentration, and stirring speed, on leaching rate of molybdenum were investigated.

2 Materials and methods

The roasted concentrate used in this study, belonging to porphyry mineralization, was provided by Liaoning, China. The main chemical composition was shown in Table 1. X-ray diffraction of the roasted ore was as shown in Fig. 1. As can be seen from the figure, MoO₃, MoO₂, MoS₂ and other metal oxide and sulfide were detected. Sodium chlorate was obtained directly from Kai tong Chemical Reagent Co., Ltd. (Tianjin, China). Sodium carbonate was provided by Wind Boat Chemical Reagent Technology Co., Ltd. (Tianjin, China). All reagents were of analytical grade and were directly used. The distilled water was used in all experiments.

Leaching experiments were carried out in a 100 mL beaker. The beaker was heated with a water bath. The mixture was stirred by a rotor and the temperature and agitation speed were set by a constant temperature heated intelligent magnetic stirrer (ZNCL-GS, Yuhua Instrument Company Limited, Gongyi, China).

Typically, a certain amount of sodium chlorate and roasted molybdenite concentrate were mixed with the sodium carbonate in a beaker and then heated. When the water bath was heated to the desired temperature, the slurry was stirred. After leaching the residue was filtered and thoroughly washed. The washing water was mixed with the leach liquor, so called leaching mixture.

The molybdenum concentration in leaching mixture was determined with using thiocyanate photometric

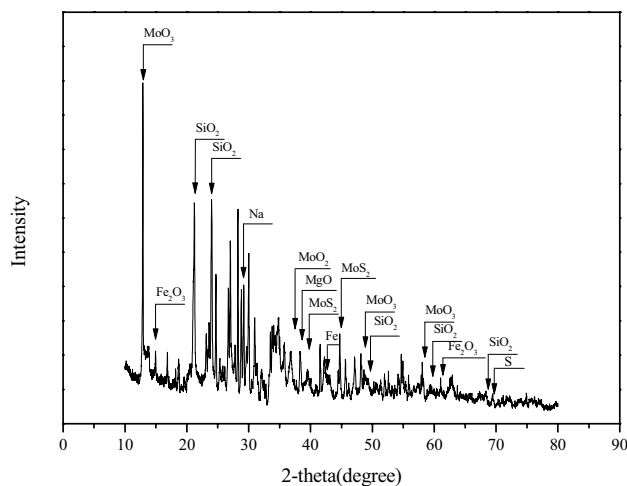


Fig. 1 XRD patterns of the roasted molybdenite concentrate

Table 1 Main chemical composition of roasted molybdenum concentrate

Component	Mo	Fe	Ca	Al	Mg	Zn	O	S	Na	SiO ₂	K	Others
% (w/w)	7.82	2.33	4.01	4.12	0.71	0.47	51.50	2.33	11.38	8.98	0.90	5.45

method by visible spectrophotometer (1800P, Shanghai, China). The other components were analyzed by inductively couple plasma atomic emission spectrometry (ICP-AES 6300 Radial, Thermo Scientific, USA).

3 Results and discussion

3.1 Effect of sodium chlorate concentration

In our present study, we studied the effect of the molar ratio of sodium chlorate to molybdenum (mol/mol) ranging from 0 to 18 on the leaching efficiency of the roasted molybdenum.

The effect of sodium chlorate concentration on leaching rate was shown in Fig. 2. When the molar ratio of sodium chlorate to molybdenum increased from 0 to 13.5, the leaching rate of molybdenum increases from 85.75 to 98.70%, but has no significant effect as a further increase above 13.5 in the molar ratio of sodium chlorate to molybdenum. Therefore the optimum the molar ratio of sodium chlorate to molybdenum appears to be 13.5. The results showed that a small quantity of MoO_2 and MoS_2 oxidized incompletely in roasted ore was oxidized by sodium chlorate to form MoO_4^{2-} into aqueous phase. The main ionic chemical reaction can be described by the Eqs. (1) and (2):

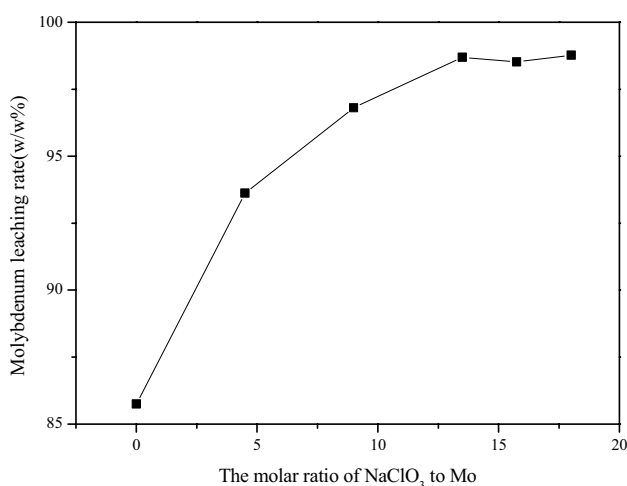
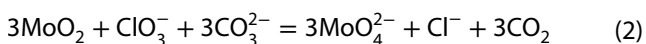
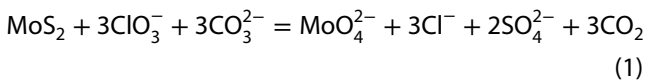


Fig. 2 Effect of molar ratio of sodium chlorate to molybdenum on the molybdenum leaching rate (L:S=10:1, T=343.15 K, r=500 rpm, $c_{\text{Na}_2\text{CO}_3} = 20$ g/L, $\theta = 4$ h)

The oxidizing ability of sodium chlorate is closely related with acidity and basicity in aqueous solution. The standard reduction potential of sodium chlorate is higher under acidic condition than that in alkaline condition, which indicated that the oxidation of sodium chlorate is stronger under acidic condition than that in alkaline condition, so the leaching is more favor under acidic condition than in alkaline condition, but the more impurity was transferred into aqueous phase under acidic condition and the smaller mineral particles were required for nonporous molybdenite concentrate. The leaching roasted molybdenite concentrate in alkaline condition had the advantages on controlling impurity in leaching liquor and adopting the bigger mineral particles for porous roasted ore, although the oxidant dosage is higher than that under acidic condition [5].

3.2 Effect of leaching time

Under the conditions of liquid-to-solid ratio 10:1, temperature 343.15 K, agitation speed 500 r/min, sodium carbonate concentration 20 g/L, and the molar ratio of sodium chlorate to molybdenum is 13.5, we studied the effect of leaching time on molybdenum extraction. It is shown from the Fig. 3 that the leaching rate of molybdenum increases from 87.4 to 98.1% as increasing leaching time from 1 to 2 h and is no significant increase beyond 2 h, so all further experiments were carried out at 2 h. The behavior of molybdenum leaching in these tests was similar to some previous experiments [11, 30, 31]. However, the specific leaching time in this experiment is far shorter than that in acid leaching condition, because the roasted molybdenite

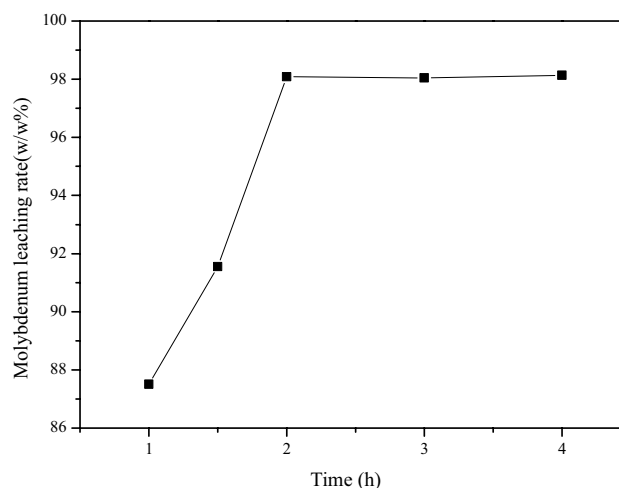


Fig. 3 Effect of leaching time on the molybdenum leaching rate (L:S=10:1, T=343.15 K, r=500 rpm, $c_{\text{Na}_2\text{CO}_3} = 20$ g/L, $n_{\text{NaClO}_3} : n_{\text{Mo}} = 13.5:1$)

concentrate is porous and provides the greater mass transfer area, leading to the higher leaching efficiency.

3.3 Effect of leaching temperature

Leaching temperature also affects the leach of molybdenum. Under the low temperature conditions, it is difficult to achieve high molybdenum leaching rate in a short time, and if choose a high temperature, there is a need for higher energy shortcomings. Therefore, in this study, the medium temperature range from 323.15 to 363.15 K was selected, and its effect on molybdenum leaching rate was shown in Fig. 4 under the conditions of a liquid-to-solid ratio of 10:1, agitation speed of 500 rpm, sodium carbonate concentration of 20 g/L, mixing time of 2 h, molar ratio of sodium chlorate to Molybdenum of 18. It is clear from the figure that the molybdenum leaching rate increases from 44.65 to 98.16% when the temperature increases from 323.15 to 343.15 K, but has no significant effect with a further increase in temperature to 363.15 K. The behavior of molybdenum leaching with the increase in the leaching temperature was similar to some former experiments [32, 33]. Therefore 343.15 K is the optimum temperature and all further experiments were carried out at this temperature.

3.4 Effect of agitating speed

The effect of agitating speed on leaching process was shown in Fig. 5 under the conditions of 323.15 K and 343.15 K. It is can be seen from the figure that the molybdenum leaching rate increases from 85.19 to 98.9% when the agitation speed increases from 300 to 500 rpm, and has no significant effect when agitation speed increase up to 700 rpm at 343.15 K, and increases from 75 to 92%

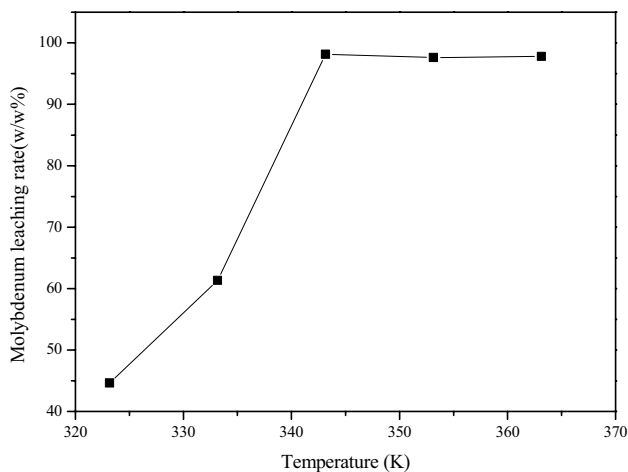


Fig. 4 Effect of temperature on the molybdenum leaching rate (L:S = 10:1, r = 500 rpm, $c_{Na_2CO_3} = 20$ g/L, $\theta = 2$ h, $n_{NaClO_3}:n_{Mo} = 13.5:1$)

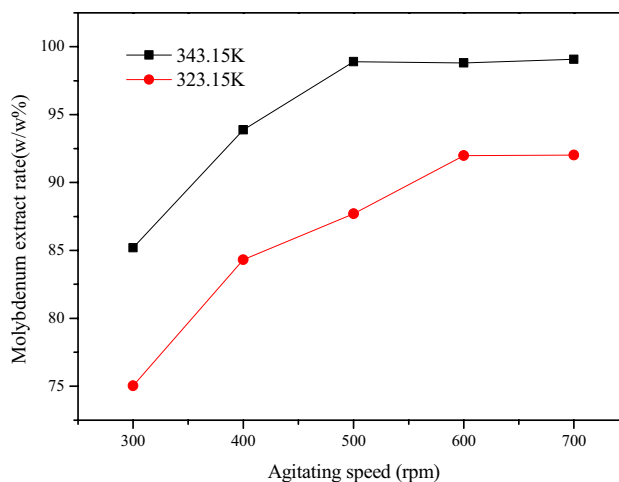


Fig. 5 Effect of agitating speed on the molybdenum leaching rate (L:S = 10:1, T = 343.15 K, $c_{Na_2CO_3} = 20$ g/L, $\theta = 2$ h, $n_{NaClO_3}:n_{Mo} = 13.5:1$)

with increasing the agitation speed from 300 to 600 rpm at 323.15 K. So the influence of the agitation speed on molybdenum leaching rate has relationship with the leaching temperature, indicating that the leaching process was mainly controlled by chemical reaction rate and mass transfer rate. This rule is different from some previous studies, where the leaching process was controlled by diffusion process due to molybdenite concentrate was leached directly without roasting process [5, 34]. The optimization value of agitation speed was maintained at 500 rpm at 343.15 K.

3.5 Effect of liquid-to-solid ratio

When leaching temperature is 343.15 K, agitation speed is 500 rpm, sodium carbonate concentration is 20 g/L, mixing time is 2 h, and the molar ratio of sodium chlorate to molybdenum is 13.5, the effect of liquid-to-solid ratio (volume/mass) from 5:1 to 20:1 on molybdenum leaching rate was shown in Fig. 6, it is clear from the figure that the leaching rate of molybdenum gradually increases with increasing liquid-to-solid ratio, which is beneficial to leaching, because increasing liquid-to-solid ratio can enlarge mass transfer area of solid-liquid two phase, and benefit reactive medium diffusion in the two phase, and then making the reaction more enough [35, 36], but increasing the ratio is not helpful to leaching rate when liquid-to-solid ratio up to 10:1, and the leaching rate of molybdenum can get to 98.85% within 2 h, in addition, a higher liquid-to-solid ratio would decrease molybdenum concentration in leaching liquor and raises the cost for next procedure, so liquid-to-solid ratio of 10:1 was selected.

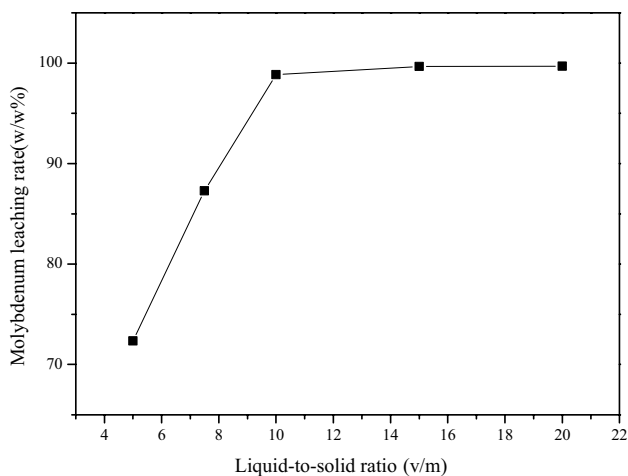


Fig. 6 Effect of liquid-to-solid ratio on the molybdenum leaching rate ($r=500$ rpm, $T=343.15$ K, $c_{Na_2CO_3} = 20$ g/L, $\theta=2$ h, $n_{NaClO_3}:n_{Mo} = 13.5:1$)

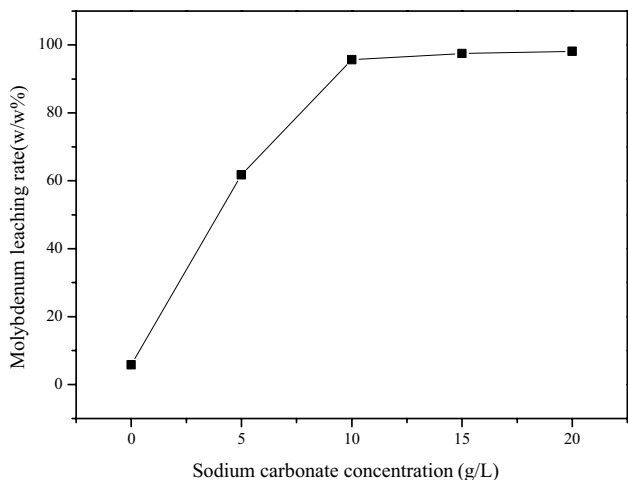


Fig. 7 Effect of sodium carbonate concentration on the molybdenum leaching rate ($L:S=10:1$, $r=500$ rpm, $T=343.15$ K, $\theta=2$ h, $n_{NaClO_3}:n_{Mo} = 13.5:1$)

3.6 Effect of sodium carbonate concentration

When temperature was 343.15 K, agitation speed was 500 rpm, a liquid-to-solid ratio was 10:1, mixing time was 2 h, and the molar ratio of sodium chlorate to molybdenum was 18, the effect of sodium carbonate concentration on leaching rate of molybdenum was shown in Fig. 7, it is obvious from the figure that the leaching rate of molybdenum increases from 6 to 98% as increasing sodium carbonate concentration from 0 to 20 g/L, indicating that the oxidation of sodium chlorate to molybdenum was evidently influenced by basicity in solution, which can be seen from the reaction Formula (1) and (2). This rule is the same as the previous study by Pradhan et al. [11].

Under above optimization experimental conditions, that was a liquid-to-solid ratio 10:1, temperature 343.15 K, agitation speed 500 rpm, sodium carbonate concentration 20 g/L, mixing time was 2 h, and the molar ratio of sodium chlorate to molybdenum was 13.5, the molybdenum leaching rate reached to above 98% for two parallel experiments, which is shown in Table 2.

The main chemical composition of the leaching and washing mixture solution is shown in Table 3. We can see from the table that the leaching solution is essentially free of Fe^{3+} , Mg^{2+} and Zn^{2+} , the reason is that the solution is alkaline by the addition of sodium carbonate and these elements form salt carbonate precipitates, but the content of aluminum and silicon in the mixture solution is higher and removing silicon from leaching solution is necessary before extracting and separating molybdenum.

4 Conclusion

A new method on leaching molybdenum from low-grade roasted molybdenite concentrate was proposed by sodium chlorate and sodium carbonate aqueous solution under the conditions of common temperature and pressure. The experiments proved that sodium chlorate is

Table 2 Molybdenum leaching rate under the optimum conditions

L/S ratio vol/mass	Temperature K	Agitation speed rpm	$c_{Na_2CO_3}$ g/L	Time h	n_{NaClO_3}/n_{Mo} mol/mol	Mo % (w/w)
10:1	343.15	500	20	2	13.5	98.56
10:1	343.15	500	20	2	13.5	98.76

Table 3 Main chemical composition of the leaching solution (including washing liquor)

Component	Mo	Al	Na	Ca	Si	Fe	Mg	Zn
% (w/w)	0.67	0.23	0.63	0.003	0.07	-	-	-

an effective oxidant to a little MoO_2 and MoS_2 in roasted molybdenite concentrate in alkaline condition. The alkaline environment is in favor of oxidation of molybdenum and restrains formation of heavy metal molybdate precipitate by adding sodium carbonate to the slurry, leading to a little heavy metal ions content in the leaching liquor, and increases the leaching rate of molybdenum. The effects of leaching temperature and agitating speed on leaching rate are all outstanding, showing that the leaching process was mainly controlled by chemical reaction rate and mass transfer rate, for the porous roasted minerals provide greater mass transfer area and smaller mass transfer resistance for reaction and diffusion in liquid–solid two phases. The optimum operating parameters were established as follows: leaching time is 2 h; sodium carbonate concentration is 20 g/L; liquid-to-solid ratio is 10:1; leaching temperature is 343.15 K; agitation speed is 500 rpm, the molar ratio of NaClO_3 to Mo is 13.5. Under these experimental conditions, the leaching rate of molybdenum is above 98% in single stage. The leaching efficiency of molybdenum is superior to the traditional methods with sodium carbonate and ammonium hydrate aqueous solution.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Human and animal rights and informed consent The authors declare that the research has no involving on Human Participants and/or Animals Informed consent.

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