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The Study on Alkali Fusion-water Leaching of Silicon From Molybdenum Tailings

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ABSTRACT

Taking the molybdenum tailings produced after beneficiation of the Luanchuan molybdenum mine in Henan Province as the research object, the effects of alkali ore ratio, calcination time and calcination temperature on the activation effect of molybdenum tailings, and the effects of leaching time, leaching temperature and leaching liquid-solid ratio on the silicon leaching rate were investigated by using sodium hydroxide alkali melting-water leaching process. The results show that the optimal conditions for activation are as follows: alkali-ore ratio 1.2:1, calcination time 1 h, calcination temperature 700°C. Under these conditions, the concentration of alkali fusion leaching (Si+Al) of molybdenum tailings is 1.396 mg/L. The optimum conditions for leaching are as follows: leaching time 7 h, leaching temperature 45°C, leaching liquid-solid ratio 6: 1. Under these conditions, the leaching rate of silicon can reach 26.88%. During the calcination process, the crystal structure of quartz is destroyed, and sodium hydroxide reacts with quartz at high temperature to form soluble silicate, which improves the activity of molybdenum tailings and increases the dissolution of silicon.

KEYWORDS

Molybdenum tailings; Alkali melting and calcination; Water immersion.

1. INTRODUCTION

Molybdenum tailings (MT) are fine-grained tailings produced during the flotation of molybdenum ore. China is the world 's largest molybdenum resource country[1]. Molybdenum is often used as a refractory metal alloy to improve the corrosion resistance and strength of metals due to its high melting point, high strength, good abrasion resistance and corrosion resistance[2]. With the continuous expansion and development of the use of molybdenum resources in high-tech and other fields, the demand for molybdenum and its metal products is also increasing. In this case, a large number of MT will inevitably be produced. According to the data released by the Ministry of Natural Resources in 2022, China 's molybdenum resource reserves reached 5.905 million tons, and the accumulation of MT was about 30 million tons, ranking first in the world[3]. The accumulation of tailings not only occupies land, pollutes water and soil, increases the construction and maintenance costs of tailings reservoirs, but also causes great safety hazards to the surrounding ecology[4]. Therefore, the research on the comprehensive utilization of MT resources has become a key research topic in the fields of mine management and environmental protection[5].

The main chemical composition of MT is iron and silicon, both of which are more than 30%. The iron content can be increased by selective dissolution of silicon, and the dissolution of silicon can provide silicon source for the preparation of silicon products. At present, the methods of extracting silicon from silicon-containing minerals mainly include sodium carbonate alkali fusion method, sodium hydroxide alkali fusion method and alkali leaching method[6]. Studies have shown that molybdenum tailings are a kind of aluminosilicate minerals with high crystallinity, which are difficult

to react with alkali solution, so it is difficult to effectively dissolve silicon in tailings directly by alkali leaching process. In this paper, the molybdenum tailings were activated by sodium hydroxide alkali fusion-water leaching process and the dissolution of active silicon was carried out. The phase composition and microstructure of the activated tailings were characterized by X-ray diffraction(XRD), X-ray fluorescence spectroscopy(XRF) and scanning electron microscopy(SEM).

2. EXPERIMENTAL

2.1. Materials

The experimental raw materials were taken from the molybdenum tailings produced after the beneficiation of the Luanchuan molybdenum mine in Henan. The tailings were analyzed by X-ray fluorescence spectroscopy (XRF), and the results are shown in Table 1. The XRD spectrum is shown in Fig.1. According to Table 1 and Fig.1, it can be seen that the Fe_2O_3 and SiO_2 contents are both above 30%, indicating high iron and high silicon molybdenum tailings. The main mineral composition is quartz (crystalline SiO_2) and hematite.

Table 1. Main chemical composition of molybdenum tailings

Constituent	Fe_2O_3	SiO_2	Al_2O_3	SO_3	Na_2O	K_2O	CaO
Mass fraction /%	39.53	33.13	7.5	7.6	4.85	2.72	1.54

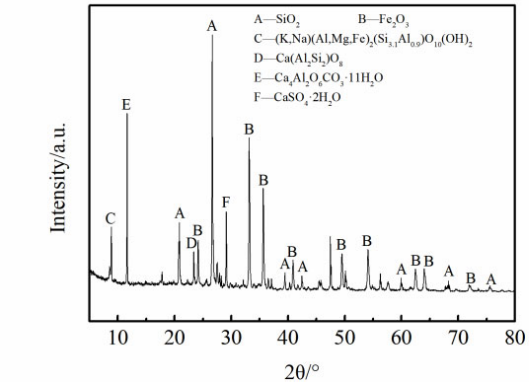

Figure 1. XRD pattern of molybdenum tailings

2.2. Experimental Methods

2.2.1. Calcination experiment

Sodium hydroxide was dissolved in a small amount of water and mixed with molybdenum tailings (10g) at a certain mass ratio. After mixing completely, it was placed in an oven at 80℃ for 12 h. The dried mixed tailings were placed in a resistance furnace for calcination. After cooling, the calcined clinker was ground and sieved to obtain alkali fusion activated tailings.

2.2.2. Characterization of tailings activity

The sample obtained by alkali melting is mixed with deionized water in a liquid-solid ratio of 10:1 and stirred at 80℃ for 30 minutes to dissolve. After dissolution, it is filtered while hot and diluted 2000 times. The content of (Si+Al) in the diluted filtrate is determined by ICP. By characterizing the activity of tailings, the optimal calcination mass ratio and calcination temperature can be obtained.

2.2.3. Water immersion silicon experiment

Take 5g activated molybdenum tailings in a conical flask, add deionized water according to a certain liquid-solid ratio, and place it on a constant temperature oscillator for heating and shaking, and the stirring intensity is 200 r/min. When the temperature rises to a predetermined value, it is recorded as the start time. After a certain time of heating shock, the heating is stopped, the cooling dilution is 1000 times filtered, and the concentration of silicon in the leaching solution is measured by ICP-OES. Through the concentration of silicon in the leaching solution, the optimum leaching time, leaching liquid-solid ratio and leaching temperature were obtained.

3. RESULTS AND DISCUSSION

3.1. Molybdenum tailings alkali fusion activation

The factors affecting the activation of molybdenum tailings mainly include alkali-ore ratio, calcination temperature, etc., and single factor experiments were carried out to determine the optimal activation conditions.

3.1.1. Effect of alkali-mineral ratio on activation

Under the condition of calcination temperature of 700°C and calcination time of 1 h, the effect of alkali ore ratio on (Si+Al) content is shown in Fig.2. When the alkali-ore ratio is less than 1.2, the (Si+Al) content gradually increases with the increase of alkali-ore ratio. When the alkali-ore ratio is higher than 1.2, the (Si+Al) content has a downward trend. Therefore, when the alkali-ore ratio is 1.2, the content of (Si+Al) is the highest, which is 2.437 mg/L, and the activation effect is the best. This shows that the increase of alkali ore ratio is conducive to the contact between alkali and tailings, so that the reaction is more thorough, but when the alkali content is excessive, the excess alkali will continue to react with the reaction products to produce less active minerals, so that the (Si+Al) content of tailings is reduced. All things considered, the calcined caustic soda ore ratio is 1.2:1.

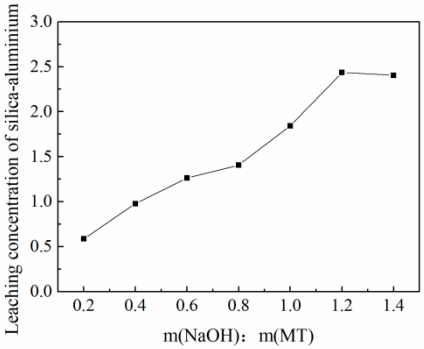

Figure 2. Effect of m(NaOH):m(MT) on the leaching content of silica-aluminium

3.1.2. The effect of calcination temperature on activation

The effect of calcination temperature on the content of (Si+Al) is shown in Fig.3 under the condition of alkali ore ratio of 1.2 and calcination time of 1 h. With the increase of temperature, the content of (Si+Al) increases first and then decreases, and the content of (Si+Al) is the highest at 700 °C, which is 1.396 mg/L. As the calcination temperature increases, the sodium hydroxide melts into a liquid phase, and the calcination reaction changes from a solid-solid reaction to a liquid-solid reaction, which promotes molecular activation and thermal mass transfer, and the chemical reaction rate is accelerated. Therefore, the concentration of silicon and aluminum produced by the reaction will also increase. As the temperature continues to increase, the reaction products continue to react at high

temperatures to form insoluble substances, resulting in a decrease in (Si+Al) content. Considering comprehensively, the calcination temperature was selected as 700°C.

3.2. Leaching test

The water leaching experiment was carried out on the calcined clinker of molybdenum tailings after calcination at 700°C for 60 min with alkali-ore ratio of 1.2:1. The effects of leaching time, leaching temperature and liquid-solid ratio on silicon leaching rate were investigated.

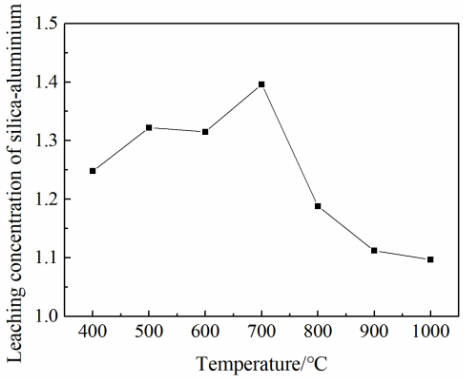

Figure 3. Effect of calcination temperature on the leaching content of silica-aluminium

3.2.1. The influence of leaching time

The leaching rate of silicon is shown in the Fig.4, under the condition of liquid-solid ratio of 10:1 and leaching temperature of 75°C for different time. When the leaching time is less than 7h, the leaching rate of silicon shows an obvious upward trend with the increase of leaching time. When the leaching time is more than 7 h, the upward trend of silicon leaching rate is stable. Therefore, in order to maintain low energy consumption and improve work efficiency, the leaching time is determined to be 7h, and the silicon leaching rate is 22.89%.

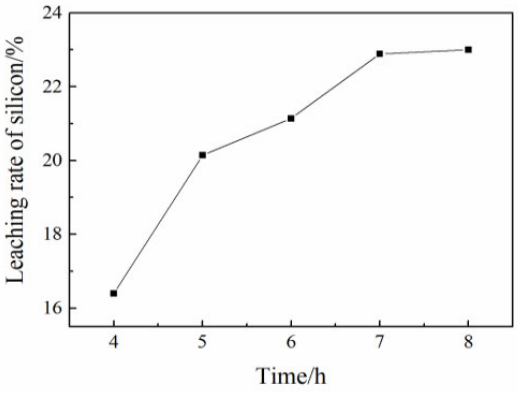

Figure 4. Effect of leaching time on silicon leaching rate

3.2.2. Effect of leaching temperature

Under the conditions of liquid-solid ratio of 10:1 and leaching time of 7 h, the effects of different leaching temperatures on the leaching rate of silicon were investigated, and the results are shown in the Fig.5. The leaching rate of silicon increases with the increase of leaching temperature, but when the leaching temperature is greater than 45°C, the leaching rate of silicon decreases. This is because

silicon mainly exists in the form of sodium silicate in the solution. The increase of temperature can increase the solubility of sodium silicate in the solution, which is beneficial to the dissolution of silicon. Continue to increase the temperature will increase the ionic strength in the leaching solution, which will have a negative impact on the solubility of sodium silicate and inhibit the dissolution of silicon. Therefore, the leaching temperature was determined to be 45°C, and the leaching rate of silicon was 23.49%.

3.2.3. The effect of leaching liquid-solid ratio

The effects of different liquid-solid ratios on the leaching rate of silicon were investigated under the conditions of leaching time of 7 h and leaching temperature of 45°C. The results are shown in the Fig.6. It can be seen from the figure that when the liquid-solid ratio is less than 6:1,

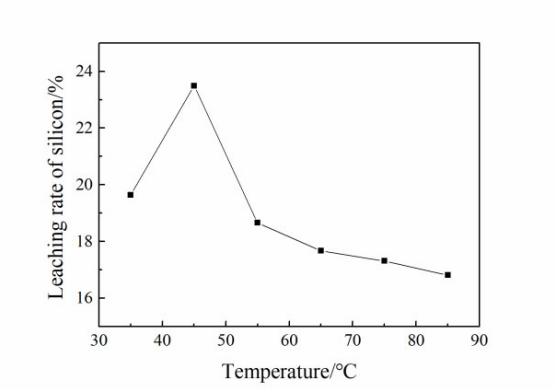

Figure 5. Effect of leaching temperature on silicon leaching rate

the leaching rate of silicon shows an increasing trend, and when it is greater than 6:1, the leaching amount of silicon is basically unchanged and tends to be stable, indicating that when the liquid-solid ratio is 6:1, the sodium silicate in the sample can be completely dissolved, and the leaching rate of silicon in the leaching solution is 26.88%.

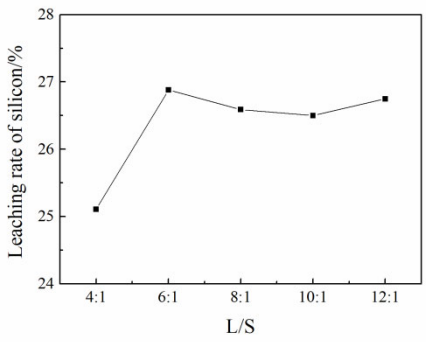

Figure 6. Effect of L/S on silicon leaching rate

3.3. Mechanism analysis of sodium hydroxide alkali fusion-water leaching

3.3.1. Phase analysis

The blank calcined sample, 700°C alkali fusion calcined sample and 900°C alkali fusion calcined sample were analyzed by X-ray diffraction (XRD). The results are shown in Fig.7. It can be seen from Fig.1 that there are mainly minerals such as quartz, hematite and mica in the raw ore, while the blank calcined samples in Fig.7 are mainly quartz and hematite, which indicates that direct calcination will decompose mica, while quartz and hematite do not change. Compared with the blank calcined sample, the quartz diffraction peak and hematite diffraction peak in the alkali fusion calcined sample

basically disappeared, and the Na_4SiO_4, $NaAlSiO_4$ and $NaFeO_2$ diffraction peaks appeared at the same time. This indicates that under the calcination conditions, sodium hydroxide will react with quartz and hematite to form Na_4SiO_4, NaAlSiO4 and $NaFeO_2$ mineral phases. When calcined at 700°C, the diffraction peaks of Na4SiO4 and $NaFeO_2$ are mainly generated in the calcined sample. Na_4SiO_4 is dissolved in water or dilute alkali solution, so Na_4SiO_4 can be leached by water leaching, while $NaFeO_2$ remains in the leaching residue. When the calcination temperature rises to 900°C, the $NaAlSiO_4$ diffraction peak appears in the XRD pattern. This is due to the fact that the aluminum-containing minerals in the tailings will react with the silicate minerals when the temperature continues to rise.

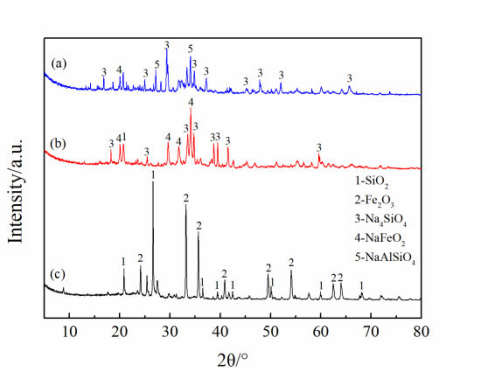

Figure 7. XRD pattern of calcined. (a) alkali fusion calcined sample in 900°C; (b) alkali fusion calcined sample in 700°C; (c) blank calcined sample

3.3.2. Micromorphology analysis

The microstructure of raw ore, blank calcined sample and alkali fusion calcined sample is shown in the Fig.8. The raw ore is mainly composed of massive particles, with obvious crystal characteristics, smooth surface and dense structure. After calcination, the block particles of the blank calcined sample become smaller, which increases the specific surface area of the reaction. After calcination by sodium hydroxide alkali fusion, the surface of the tailings particles is uneven, the crystal characteristics are weakened, and many pore structures appear. This shows that at high temperature, molybdenum tailings react with sodium hydroxide, which destroys the structure of crystalline SiO_2 in molybdenum tailings and achieves activation effect.

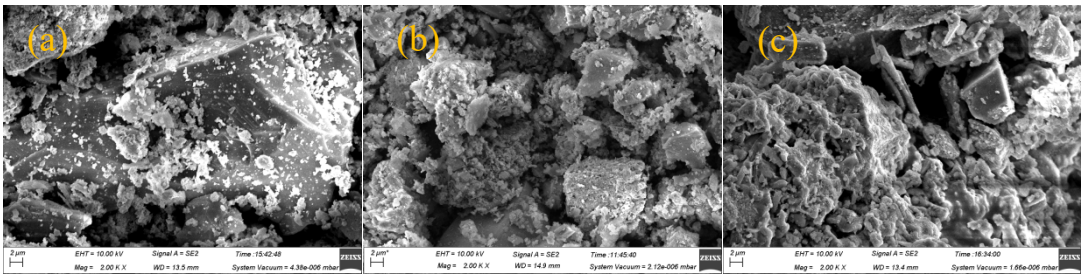

Figure 7. Micro-morphology before and after calcination. (a) MT; (b) blank calcined sample; (c) alkali fusion calcined sample in 700°C

4. CONCLUSIONS

(1) The main mineral phases of molybdenum tailings are quartz and hematite. The crystal structure of quartz phase is stable and the activity is low.

(2) Sodium hydroxide alkali fusion calcination was used to improve the activity of molybdenum tailings. The optimum calcination process was as follows: alkali ore ratio 1.2:1 (g/g), calcination temperature 700°C, calcination time 1h. Under this condition, the concentration of alkali leaching (Si+Al) of molybdenum tailings is 1.396 mg/L.

(3) Water leaching was used to dissolve the silicon in the alkali fusion calcined clinker. The optimum leaching conditions were as follows: leaching time 7 h, leaching temperature 45°C, leaching liquid-solid ratio 6:1. Under this condition, the leaching rate of silicon can reach 26.88%.

(4) The activation modification mechanism of molybdenum tailings was explored by XRD and SEM. Under the condition of alkali fusion calcination at 700°C, the mica stone in molybdenum tailings is decomposed, sodium hydroxide destroys the crystal structure of quartz, increases the roughness of its microscopic surface, and reacts to form Na_4SiO_4, thereby improving the activity of molybdenum tailings.

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