



Experimental Study on Preparation of Cementing Material by Mechanical Activation of Molybdenum Tailings

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Abstract. Molybdenum tailings are the waste of molybdenum extracted from refined molybdenum ore. Because of its potential gelling, it can be prepared as a cementing material instead of cement. In order to improve the pozzolanic activity of molybdenum tailings, mechanical activation method was used to discuss the effect of activation time on its activity, and the activation effect was judged by particle size analysis and other tests. Using calcium oxide and sodium carbonate as composite activator, molybdenum tailings were used to prepare composite cementing material. The effects of activator content, tailing dosage and activation time on mechanical properties and hydration mechanism of the material were evaluated. The results show that mechanical activation can improve the activity of molybdenum tailings, which proves that it can be used as a cementing material instead of cement, which is conducive to the utilization of tailings waste.

Keywords: Molybdenum tailings; Mechanical activation; Volcanic activity

1 Introduction

China is rich in mineral resources, which strongly promotes economic development. However, with the rapid growth of the national economy, the solid waste generated by the mining of mineral resources has risen sharply^[1], among which the tailings deposit is large and the utilization rate is low, especially molybdenum tailings, which not only occupies a large amount of land, but also causes environmental pollution, such as Henan Luanchuan molybdenum mine tailings deposit 120 million tons, covering an area of 800 hectares (12,000 acres), and the surrounding soil cadmium content exceeds the national standard 3 times. Under the national "double carbon" goal, the comprehensive treatment of tailings is imminent.^[2] The annual discharge of molybdenum tailings in China is 36 million tons, and it continues to rise with the increase of metal molybdenum demand. Exploring its resource utilization is the key to the sustainable development of mining industry. In the field of building materials, many scholars have conducted research on molybdenum tailings. On the one hand, some studies use molybdenum tailings as a concrete aggregate substitute. Luo et al.^[3] Replacing cement mortar in concrete

with molybdenum tailings with different replacement rates found that slump and compressive and tensile strength of concrete could be reduced, but internal porosity could be improved. Gao et al.^[4] used molybdenum tailings as aggregate to prepare thixotropic cement slurry, and obtained the best ratio through orthogonal test, with good economic benefits. Quan et al.^[5] showed that molybdenum tailings had the potential to replace natural river sand, but the corrosion resistance decreased significantly when the replacement rate was 60%.

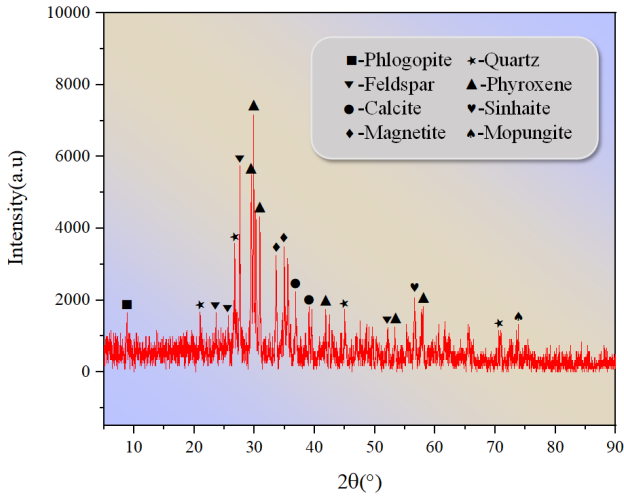
On the other hand, with the wide application of supplementary gelling materials, the potential gelling activity of molybdenum tailings has been concerned. Han et al.^[6] used molybdenum tailings modified fly ash to prepare geopolymer, and found that 20% content could improve the strength and fracture resistance of geopolymer. Luo et al.^[7] combined molybdenum tailings with other cementing substances to prepare concrete, and found that the content of tailings affected the slump and other properties of concrete. Yang et al.^[8] determined the optimum preparation conditions for the preparation of geopolymer by alkaline hydrothermal activation of molybdenum tailings. Liu et al.^[9] used molybdenum tailings instead of fly ash to prepare modified concrete, and found that the compressive strength and freezing resistance were ideal when the content was 20%. In addition, Li Y et al.^[10] analyzed the characteristics and mechanism of molybdenum tailings under various activation modes. Ahmed M et al.^[11] studied the performance of low-carbon self-compacting concrete with molybdenum tailings; Wang A^[12] discussed the high temperature mechanical behavior of geopolymers modified by molybdenum tailings. Domestic scholars such as Shi Zitong and Zhang Xiaohan^[13-14] have made in-depth exploration from the directions of ceramisite technology and cement matrix insulation materials. Liu Xuan, Zhan Jiayu et al.^[15-16] studied the effect of mechanical activation on the gelling properties of molybdenum tailings and related products, providing theoretical and practical support for its application in the field of gelling materials. Molybdenum tailings are similar in composition to Portland cement, which has potential gelling, stability, good mechanical properties, low energy consumption and pollution, and is a good material to replace cement. However, due to the characteristics of its crystalline phase, the reactivity is low and requires mechanical or chemical activation. Aiming at the status quo of molybdenum tailings replacing cement at home and abroad with few studies and unclear activation mechanism, this study explored the activity of molybdenum tailings after physical and chemical activation, determined the best mechanical activation time, adopted composite activators, identified the best ratio of clinker-free molybdenum tailings cementing material, revealed the reaction mechanism, and helped its engineering application.

2 Materials and Tests

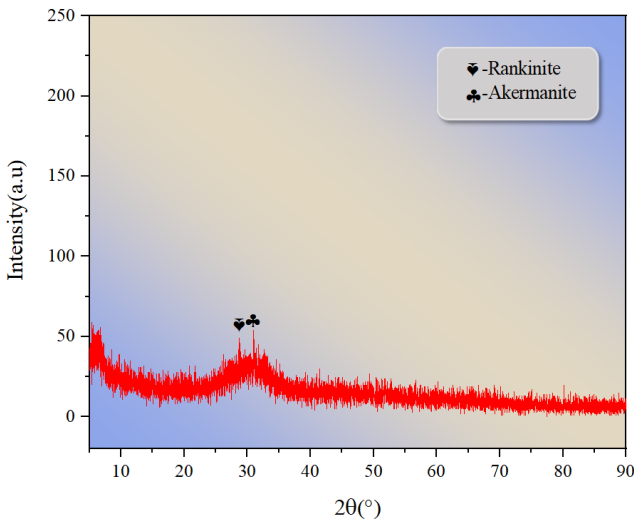
2.1 Raw Materials

Molybdenum tailings are supplied by Zhaogou Mining Co., LTD., Lianshan Molybdenum Industry, Huludao, Liaoning, China. In order to facilitate the development of the test, the original tailings are first put into the drying box, and the temperature is set to dry at 105°C. The mineral composition of the original tailings was analyzed by XRD,

the results of which are shown in Figure 1. It can be seen from Figure 1 that the molybdenum tailings mainly consist of quartz, feldspar, diopside, calcite and magnetite, while the contents of phlogopite, boromagnesite and hornblende are not significant. The analysis results of XRF are shown in Figure 2. It can be seen from Fig.2 that the main chemical components of molybdenum tailings include SiO_2 , CaO , SiO_2 , Al_2O_3 , MgO and Fe_2O_3 , of which SiO_2 has a higher content, followed by CaO , which is similar to the composition of cementing materials and has potential pozzolanic activity. This provides a material basis for the strength development of cementitious materials prepared from tailings.



(a)



(b)

Fig. 1. XRD analysis of molybdenum tailings and slag

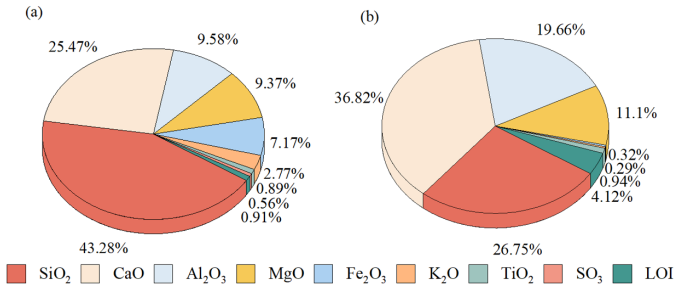


Fig. 2. Chemical composition of raw materials

2.2 Experimental Design

Based on RSM experimental design principle, Box-behnken experimental design method was adopted, taking activation time, Na₂O mass fraction and molybdenum tailings content as variables, and 28d compressive strength, flow and setting time as response values, a three-factor and three-level design scheme was developed in this experiment. Through experimental testing, an interval response surface for each parameter was obtained. The test factors and horizontal parameters are shown in Table 1.

Table 1. Level and factors of experimental design

Factor	Code	Level		
		Low	median	High
Activation time of molybdenum tailings (min)	A	20	60	100
Na ₂ O Mass fraction (%)	B	4.5	6.5	8.5
Molybdenum tailings content (%)	C	40	60	80

3 Preparation of Gelling Materials

Molybdenum tailings and slag were mixed in different proportions, and after being mixed evenly, CaO and Na₂CO₃ were used as composite activators to add to the system according to the mass fraction of Na₂O (the mass ratio of Na₂O generated by the reaction of CaO and Na₂CO₃ to the mass of the cementation material). Based on previous studies, the water-cement ratio was set at 0.45 and the mass fraction of Na₂O was set at 4.5%, 6.5% and 8.5% respectively. The test mix ratio of activator, molybdenum tailings and slag content was shown in Table 2.

Table 2. Test mix ratio of gelled material

Na ₂ O Mass fraction (%)	Molybdenum tailings content (%)	Slag content (%)
4.5	40	40

6.5	50	60
8.5	60	80

The paste was poured into a cubic mold with a size of 40mm×40mm×40mm to form, and the excess paste was removed from the surface of the test mold with a scraper. After the excess gas in the paste was vibrated out with a shaking table, the paste was put into a curing box with a temperature of (20±2) °C and relative humidity greater than 95% for 24h. Then the mold was removed and the curing was continued until the specified age for relevant tests. Three parallel samples were prepared for each group of experiments, and the average value of the three samples was taken as the test result to reduce the influence of other factors. All specimens are covered with a layer of plastic wrap during curing to prevent test errors.

3.1 Test Method

According to the Chinese standard GB/T 1346-2011, the coagulation time of the composite cementing material was determined at (20±2)°C. According to the Chinese standard GB/T 8077-2000, the fluidity of the prepared composite cementified material was tested. According to GB/T 17671-2021 "Cement mortar Strength Test Method (ISO Method)", WAW-300E type constant load cement pressure testing machine (Figure 3) was used, and the compression rate was maintained at 0.5MPa /s to test the compressive strength of specimens at various ages solidified at (20±2)°C and RH > 95%. The test results are calculated according to the following formula(1).

$$R = \frac{F}{A} \quad (1)$$

Where: R is compressive strength, MPa; F is the maximum bearing stress, N; A is the bearing pressure area (mm²).

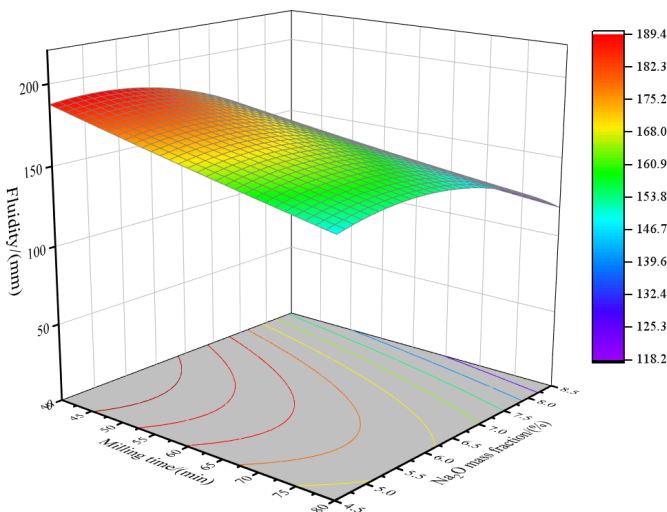


Fig. 3. WAW-300 type constant load cement pressure testing machine

4 Results and Discussion

4.1 Mobility

The interactive effects of different factors on the fluidity of gelled materials can be analyzed through Figure 4(a-c). Fig. 4 (a) shows the interaction between grinding time of molybdenum tailings and Na_2O mass fraction. When the grinding time was fixed and the Na_2O mass fraction was increased, the fluidity of the gelling material decreased significantly, with a maximum decrease of 41.04%. If the Na_2O mass fraction is unchanged, the fluidity increases with the increase of grinding time, and the maximum increase is 23.53%. Figure 4 (b) shows the interaction between the grinding time of molybdenum tailings and the content of molybdenum tailings. When the grinding time remained the same, the content of molybdenum tailings increased and the fluidity continued to increase, from the minimum value increased by 36.54%. When the content of molybdenum tailings is fixed, the grinding time increases and the fluidity decreases gradually, with the maximum decrease of 27.87%. In Figure 4 (c), for the interaction between the Na_2O mass fraction of molybdenum tailings and the content of molybdenum tailings, when the Na_2O mass fraction is unchanged, the content of molybdenum tailings increases, and the liquidity increases significantly, by as much as 76.86%. If the content of molybdenum tailings remains unchanged, the mass fraction of Na_2O increases and the fluidity decreases, with a maximum decrease of 19.80%. In summary, the fluidity of the gelled material decreases with the increase of alkali concentration, due to the reaction water consumption, the influence of ions and the change of slurry structure. The increase of molybdenum tailings content improves fluidity, its particle properties improve slurry and delay reaction. Increased grinding time reduces fluidity due to particle refinement, shape change and accelerated polymerization.



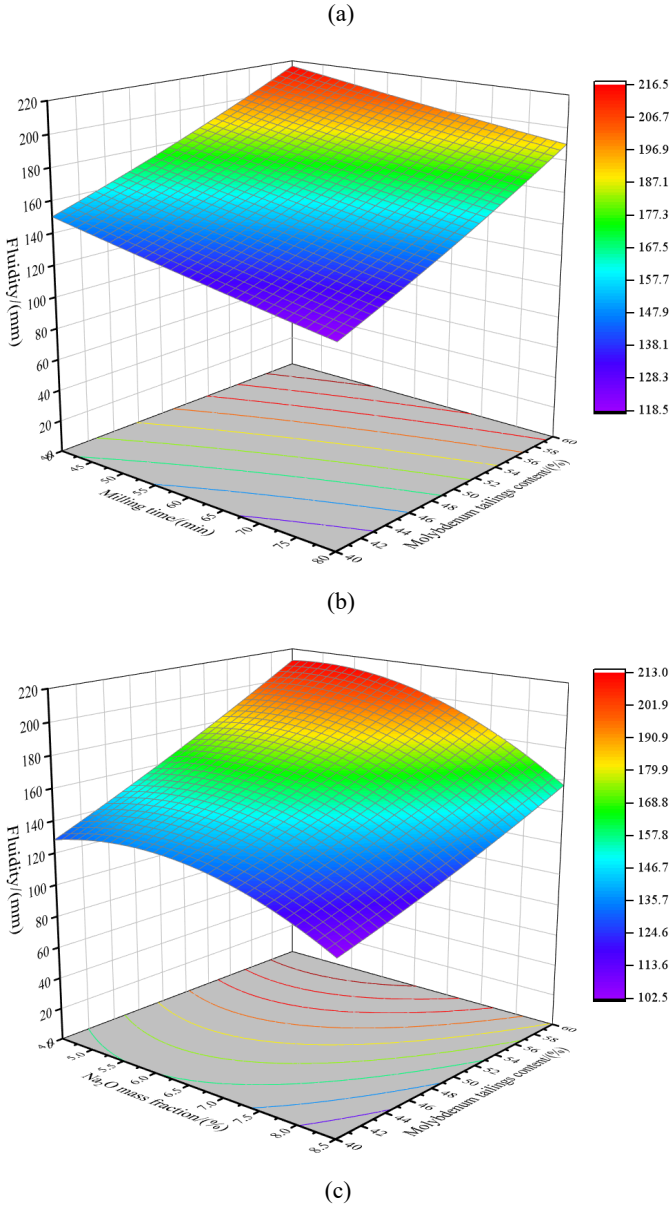


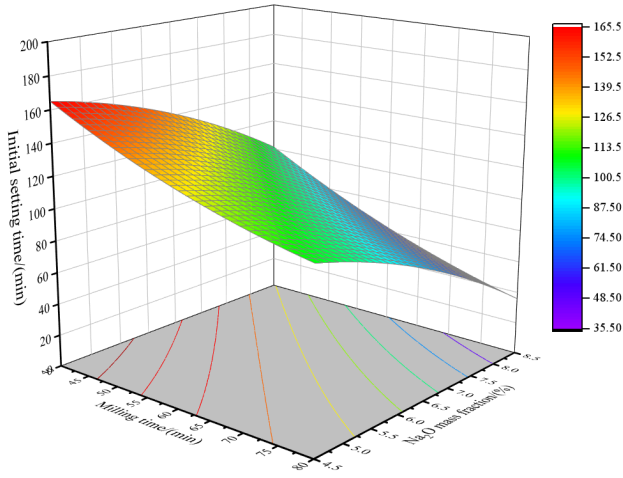
Fig. 4. Influence of interaction of various factors on fluidity of gelled materials

4.2 Time of Coagulation

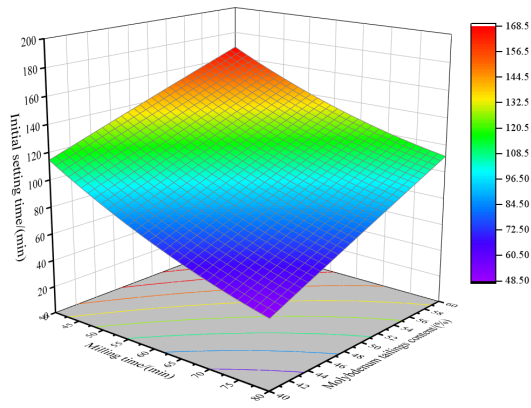
Fig. 5 and Fig. 6 show the influence of interaction of different factors on setting time of cementitious materials. First look at the interaction between grinding time of molybdenum tailings and Na_2O mass fraction (Figures 5 (a) and 6 (a)). When the grinding

time is fixed, with the increase of Na₂O mass fraction, the coagulation time is significantly shortened, the initial coagulation time is reduced by 202.70%, and the final coagulation time is reduced by 76.52%. If the Na₂O mass fraction is unchanged, the grinding time is increased, the coagulation time is also shortened, the initial coagulation time is reduced by 46.43%, and the final coagulation time is reduced by 86.32%. Then look at the interaction between the grinding time of molybdenum tailings and the content of molybdenum tailings (Figure 5(b) and Figure 6(b)). When the grinding time remained unchanged, the content of molybdenum tailings increased, the setting time became longer, the initial setting time increased by 118.36%, and the final setting time increased by 47.21%. When the content of molybdenum tailings is fixed, the grinding time is increased, the setting time is shortened, the initial setting time is reduced by 142.86%, and the final setting time is reduced by 174.89%. Finally, the interaction of Na₂O mass fraction with molybdenum tailings content (Figures 5(c) and 6(c)). The mass fraction of Na₂O is unchanged, the content of molybdenum tailings increases, the coagulation time becomes longer, the initial coagulation time increases by 62.5%, and the final coagulation time increases by 61.83%. If the content of molybdenum tailings is unchanged, the Na₂O mass fraction is increased, the coagulation time is shortened, the initial coagulation time is reduced by 68.75%, and the final coagulation time is reduced by 107.76%.

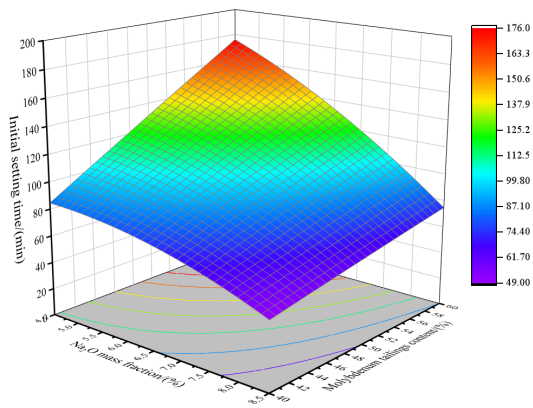
As can be seen from Figure 5(a-c) and Figure 6(a-c), with the increase of alkali concentration, the initial and final coagulation time of the cementing material decreases. Due to the increased Na₂O concentration, the polymerization reaction was [SiO₄]²⁻ and AlO₂⁻ concentrations increased in the solution. More active Si/Al participated in the reaction. The alkali metal ions accelerated the reaction kinetics and the C-S-H gel formation rate increased. With the increase of molybdenum tailings, the coagulation time of geopolymer is prolonged, because its low active minerals slow down the reaction, dilute the active components, and affect the pH value of the system. With the increase of grinding time, the condensation time of geopolymer is shortened, the particle size is reduced, the reaction surface area is increased, the reactivity is improved, the hydration product formation is accelerated, and the pore structure is improved.



(a)

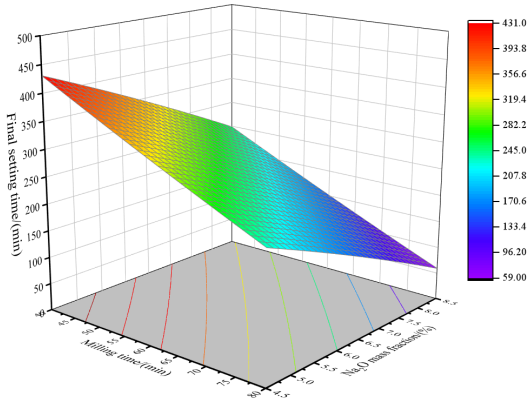


(b)

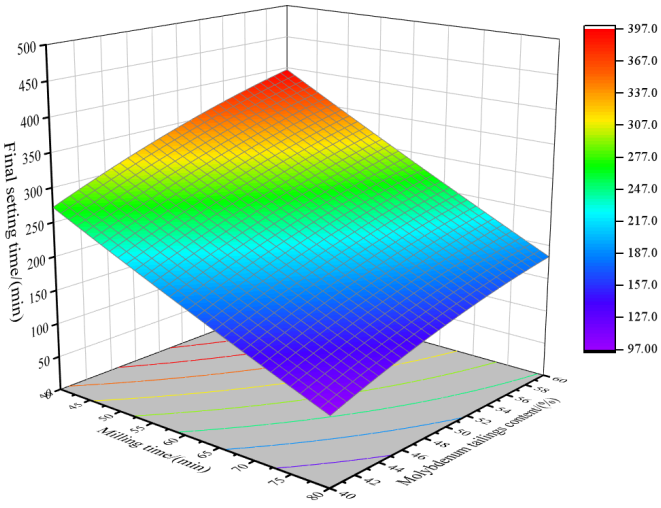


(c)

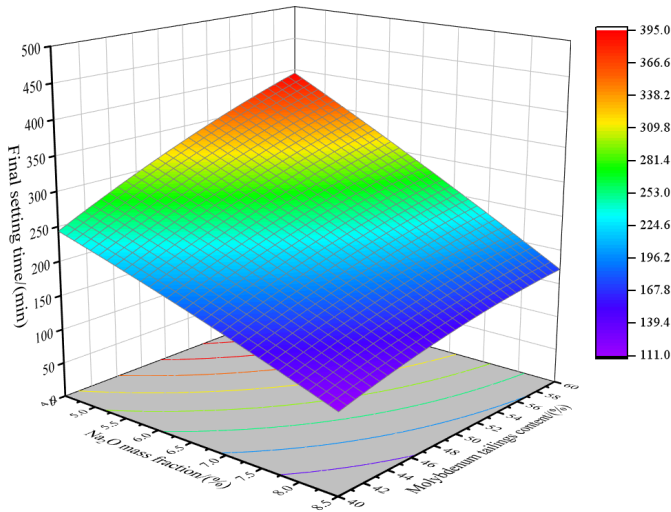
Fig. 5. Influence of interaction of various factors on the initial setting time of gelled materials



(a)



(b)



(c)

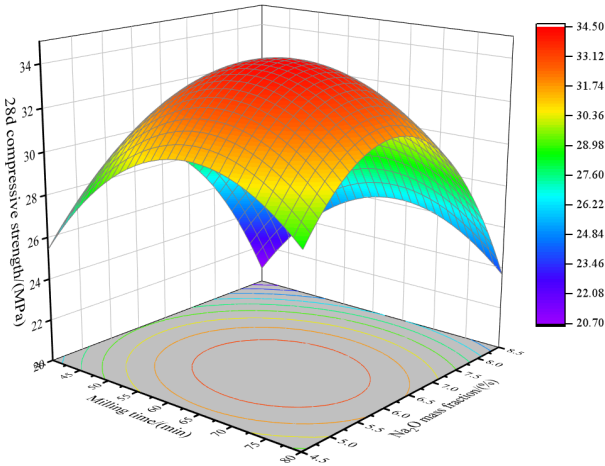
Fig. 6. Influence of interaction of various factors on final setting time of gelled materials

4.3 Compressive Strength

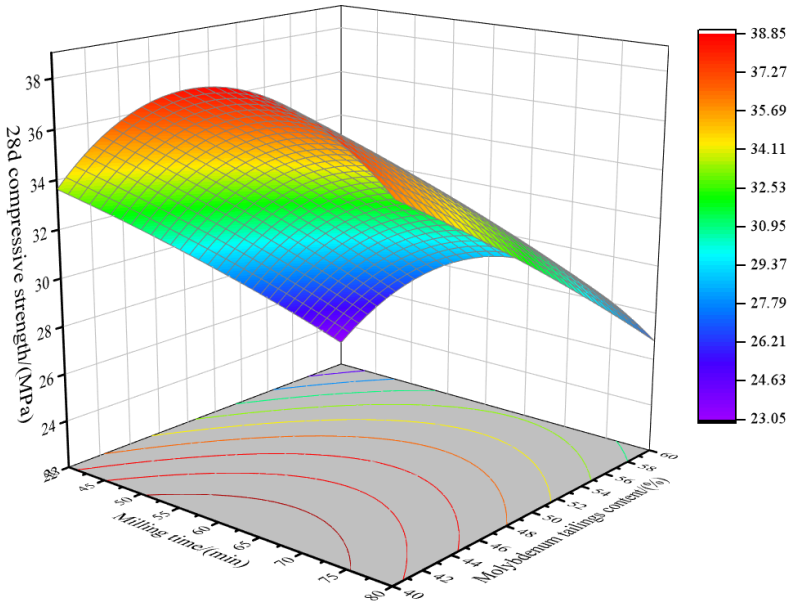
Figure 7 shows the influence of interaction of molybdenum tailings related factors on the compressive strength of MPCM. In Figure 7 (a), when the mass fraction of Na₂O is constant, the compressive strength changes parabola with the increase of grinding time of molybdenum tailings, rising first and then decreasing, and the optimal grinding time can be determined. At this time, the maximum compressive strength increases by 17.64%, and the interaction is most prominent when the mass fraction of Na₂O is 6.5%. If the grinding time is constant, with the increase of Na₂O mass fraction, the compressive strength also rises first and then falls, the best amount of alkali can be determined, the maximum compressive strength is increased by 32.33%, and the interaction is most obvious when the grinding time is 60min. Figure 7(b) shows that when the content of molybdenum tailings is constant, the grinding time increases and the compressive strength increases first and then decreases. With constant grinding time, the content of molybdenum tailings increased, and the compressive strength decreased diagonally and linearly, with a maximum decrease of 35.38%. Figure 7(c) shows that the compressive strength of constant molybdenum tailings increases first and then decreases with the increase of Na₂O mass fraction. With constant Na₂O mass fraction, the compressive strength decreases with the increase of molybdenum tailing content.

Overall, the effect of Na₂O mass fraction and molybdenum tailings content on compressive strength is significant, but the effect of grinding time is relatively small. Na₂O mass fraction increased, the system became more alkaline, the silicic acid material dissolved quickly, the polymerization reaction was intense, the hydration products increased, and CaCO₃ filled the pores, and the strength increased. However, too high concentration will cause excessive alkali activation, resulting in gel phase

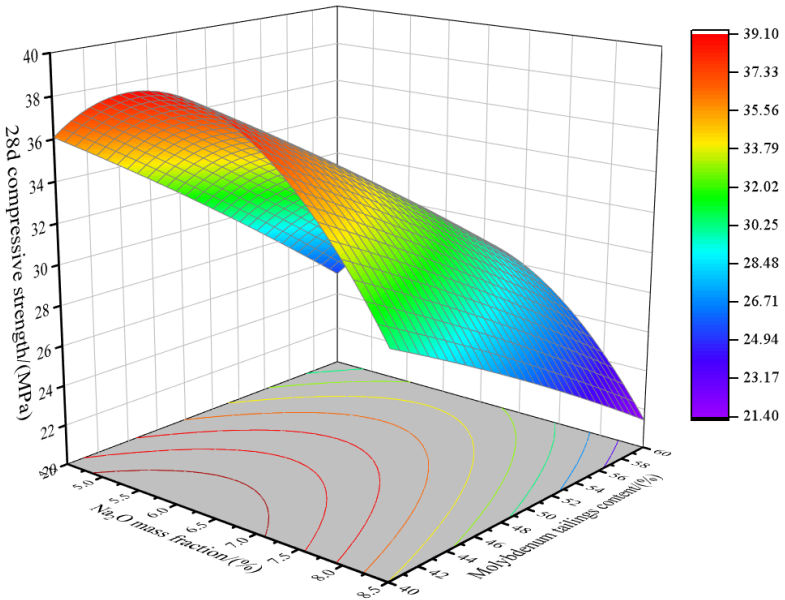
accumulation, loose structure, self-shrinkage, porosity increase, metal cations will also passivate the surface of the raw material, hinder the reaction, reduce strength. The content of molybdenum tailings increases, because the activated components are difficult to participate in the reaction, the overall strength decreases, but the unreacted part can fill the pores and nucleate. The increase of grinding time, the refinement of particles and the increase of reaction sites can improve the strength, but excessive grinding will destroy the microstructure and reduce the strength. In short, an appropriate amount of Na_2O mass fraction, molybdenum tailings content and grinding time can promote gel formation and improve the compressive strength of MPCM.



(a)



(b)



(c)

Fig. 7. Influence of interaction of various factors on compressive strength of cementitious materials

4.4 SEM Test Result

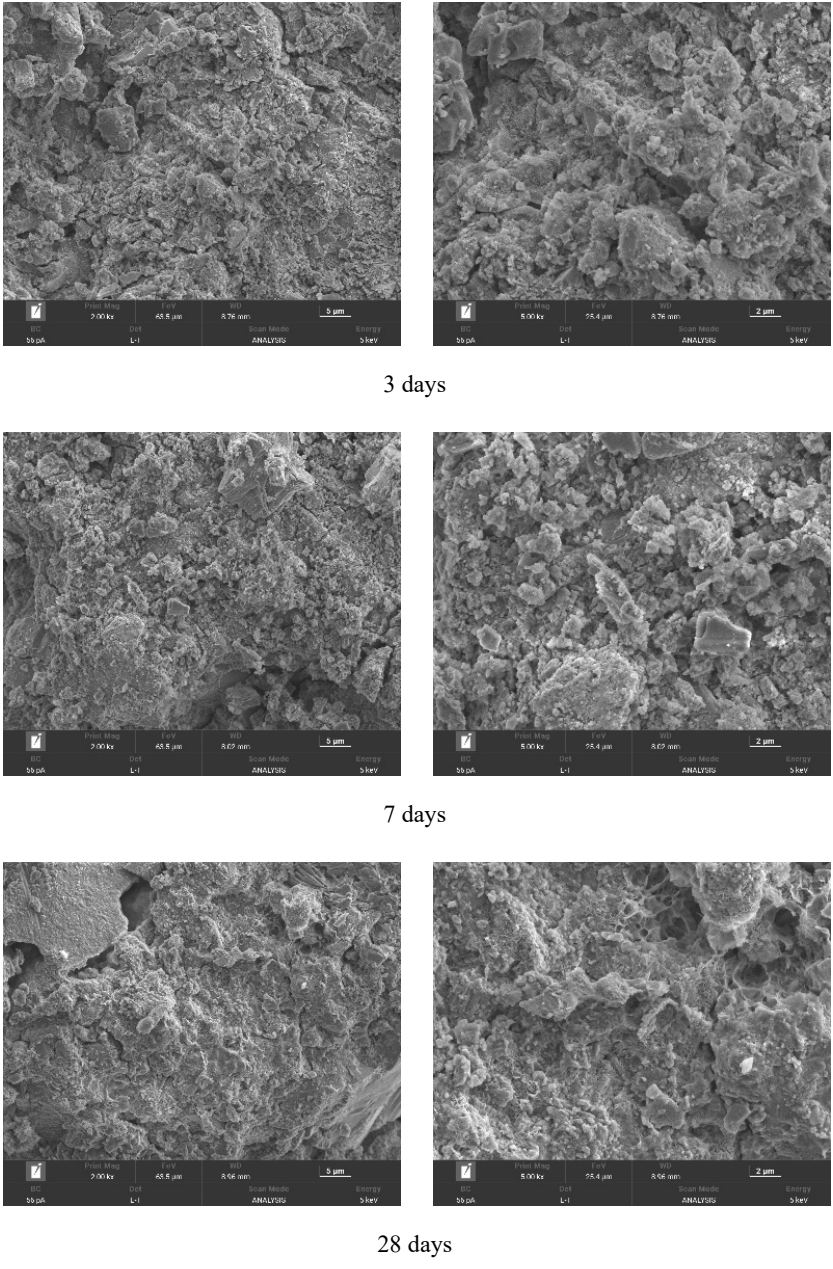


Fig. 8. Microstructure and element analysis

Figure 8 shows the microstructure of the sample at different ages of the optimal mix ratio. It can be seen from the figure that the microstructure of the sample in the early stage of maintenance is loose, with a large number of micro cracks and a small number of coarse cracks. With the increase of curing age, the polymerization products in the system gradually increase, C-S-H and C-A-S-H are the main polymerization products of the gelling material, interweaving in the system to form a spatial network structure to make the internal system more dense. After reaching 28d, the densification of the cementing material reaches the best effect.

5 Conclusions

(1) The fluidity of the cementing material gradually decreases with the increase of mass fraction, the fluidity gradually increases with the increase of molybdenum tailings content, and the fluidity gradually increases with the increase of grinding time.

(2) With the increase of mass fraction, the setting time of the cementing material is gradually smaller, the setting time is gradually longer with the increase of molybdenum tailings content, and the setting time is gradually reduced with the increase of grinding time.

(3) With the increase of mass fraction, the compressive strength of the cementing material first increases and then decreases; with the increase of molybdenum tailings, the compressive strength gradually decreases; with the increase of grinding time, the compressive strength first increases and then decreases.

(4) The optimal mix ratio of cementing material is: mass fraction 6.5%, molybdenum tailings content 50%, molybdenum tailings grinding time 60min. Microscopic tests show that with the increase of curing age, the polymerization products in the system gradually increase, C-S-H and C-A-S-H are the main polymerization products of cementing material. Interweaving in the system to form a spatial network structure makes the system more dense inside.

Proper noun abbreviation

RSM: Response Surface Methodology

MPCM: Micro - encapsulated Phase - Change Materials

SEM: Scanning Electron Microscope

XRD: X-ray diffraction

XRF: X-ray fluorescence

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