

Research on the influence of fineness and content of lithium slag on the performance of cement mortar

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Abstract. Lithium slag (LS) is industrial solid waste during the production of lithium carbonate. LS has pozzolanic effect and replace cement to achieve the purpose of protecting the environment and saving resources. In order to clarify the influence of fineness and content of LS on the performance of cement mortar. The effects of different fineness and content of LS powder on the workability, mechanical properties and microscopic properties of cement mortar were studied. The results shown that the grinding time refined the particle size of LS and increased the particle content in the range of 0.95 μm ~5.68 μm . Fineness of LS had little effect on the workability and mechanical properties of cement mortar. Excessive LS had significant negative impact on workability and mechanical properties of cement mortar. When the content of LS was 10 %, the heat release, the production of $\text{Ca}(\text{OH})_2$ and ettringite of cement paste increased. Early mechanical property of cement mortar was unreduced and effectively improved later mechanical properties under this content. The research can provide data support for the application of LS in practical engineering.

1. Introduction

In recent years, with the acceleration of China's urbanization process, a large number of infrastructure has been built. Concrete, as an easily available and inexpensive inorganic non-metallic material, is widely used in roads, bridges and housing construction. According to the report of Sifang New Materials, the amount of commercial concrete in China will be $558.75 \times 10^4 \text{m}^3$ in 2023. Cement is the main cementitious materials in concrete. National Bureau of Statistics survey that China's cement production is 2.023 billion tons in 2023[1]. Cement, as a major CO_2 emitter in the building materials industry, produces about 2.3~2.5 billion tons of CO_2 per year[2]. In order to achieve the goals of carbon peak and carbon neutrality proposed by the building materials industry, it is urgent to find inorganic non-metallic replaces to cement to reduce CO_2 emissions. At present, a large number of scientific researchers have attempted to apply industrial solid waste with potential activity as substitute material for cement in concrete and have achieved phased results. Wu et al.[3] found that the filling effect of limestone powder and the pozzolanic effect of fly ash and slag improved the frost resistance of composite limestone-fly ash-slag concrete. Wu et al.[4] prepared 108 groups of concrete specimens and

found that large amount of limestone powder inhibited the development of concrete strength, but still met the design requirements and had good economic benefits. Fine limestone powder improved the strength and ductility of concrete. Sahmaran et al[5] found that auxiliary cementitious materials significantly enhanced the self-healing ability of cement-based composites. However, there are few reports on the systematic study of the influence of LS with different fineness and content on the mechanical properties of cement mortar at present.

With China's increasing emphasis on the field of new energy, the lithium battery industry is rapidly developing. LS is an industrial solid waste produced by spodumene treatment of grinding, high temperature calcination, acidification and leaching. Relevant research[6] shown that about 10 tons of LS produced for each ton of lithium carbonate produced. As major lithium resource country, China is mainly distributed in Jiangxi, Sichuan and Xinjiang. Due to the ineffective utilization of LS, it is randomly stacked, which not only occupies a large amount of land resources but also causes serious environmental pollution[7,8]. In recent years, with the deepening of research on LS, many researchers have studied LS as auxiliary cementitious material of cement-based composites[9,10]. Tan et al.[11] studied the effect of LS on the early mechanical properties of sulphate aluminium cement paste. The results shown that

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content of LS less than 10 % accelerated the hydration of slurry and improved the early mechanical properties of slurry. Liu et al.[12]found that the SO_4^{2-} content of LS was high, which made LS unable to replace cement in a high proportion, and small amount of LS reduced the internal pores of concrete and improved the performance of concrete. Zhang et al.[13] studied the corrosion resistance of concrete with LS under acid rain erosion, and found that LS accelerated the hydration of cement and improved the durability of concrete. However, SO_4^{2-} of LS had negative impact on the compressive strength and mass loss of concrete.

In this paper, the fineness and content of LS are used as variables. Through tests of workability and mechanical property, the influence of LS on the performance of cement mortar is explored. The influence mechanism of LS on the mechanical properties of cement mortar was investigated by particle size analyzer, scanning electron microscope and X-ray diffractometer(XRD).

2. Experimental

2.1 Materials

The cement was purchased from Wuhu Conch Cement Co., Ltd. Specific surface area of cement was $361m^2/kg$ and the CaO content was 58.44 % (mass fraction). The LS was collected from lithium industry Co., Ltd in Sichuan province. The SEM of the LS with silicon-aluminum content of 61.11 % (mass fraction) is shown in Figure1. Standard sand was purchased from Shanghai Aisiou Co., Ltd. Table 1 shows the chemical compositions of cement and LS.

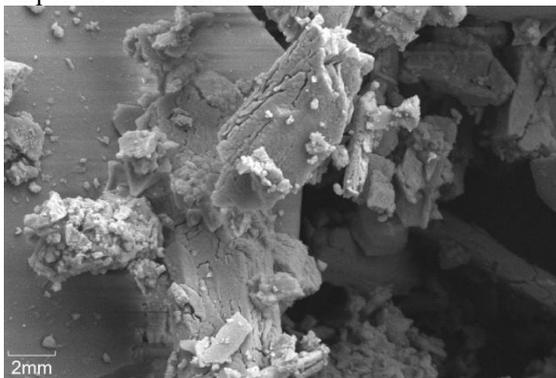


Fig. 1. SEM images of LS

Table 1. Chemical compositions of cement, LS and SF (wt%).

Materials	Cement	LS
SiO ₂	23.33	42.85
SO ₃	3.12	23.85
Al ₂ O ₃	8.55	18.26
CaO	58.44	11.53
Fe ₂ O ₃	2.81	1.89
K ₂ O	1.27	0.64
P ₂ O ₅	-	0.4
TiO ₂	0.39	0.22
MnO	0.04	0.15

2.2 Preparation of cement mortar

Prepared LS with different fineness using SM-500 ball mill, and LS was added to replace cement by weight (10%, 20% and 30% of binder). The w/b and binder to aggregate ratio of two mixtures were kept as constants, 0.50 and 3.00, respectively. The details of the components used in cement mortar are shown in Table 2.

Table 2. Mix proportions of cement mortar containing LS

Tests	Cement /g	LS /g	Sand /g	Water /g	Grinding time/min
0LS	450	-	1350	225	-
4LS10	405	45	1350	225	4
4LS20	360	90	1350	225	4
4LS30	315	135	1350	225	4
8LS10	405	45	1350	225	8
8LS20	360	90	1350	225	8
8LS30	315	135	1350	225	8
12LS10	405	45	1350	225	12
12LS20	360	90	1350	225	12
12LS30	315	135	1350	225	12
16LS10	405	45	1350	225	16
16LS20	360	90	1350	225	16
16LS30	315	135	1350	225	16
20LS10	405	45	1350	225	20
20LS20	360	90	1350	225	20
20LS30	315	135	1350	225	20
24LS10	405	45	1350	225	24
24LS20	360	90	1350	225	24
24LS30	315	135	1350	225	24
28LS10	405	45	1350	225	28
28LS20	360	90	1350	225	28
28LS30	315	135	1350	225	28
32LS10	405	45	1350	225	32
32LS20	360	90	1350	225	32
32LS30	315	135	1350	225	32
36LS10	405	45	1350	225	36

2.3 Experimental methods

2.3.1 Grinding

The moisture content of LS was dried to less than 1.5% by oven, and LS with 5kg was ground by SM-500 ball mill according to the YB/T 4230-2010 standards in China[14]. It was found that the LS was agglomerated when the LS was ground to 40 min. Therefore, the LS was ground to 36 min.

2.3.2 particle size distribution

The particle size distribution of LS was tested by using the Sympatec GmbH particle size analyzer. The dispersion pressure was 1.7 bar, the dispersion vacuum was 80 mbar, and the injection rate was 30 %.

2.3.3 Preparation and curing of Sample

The water and cementing material were placed in the JJ-20H cement mortar mixer, and then the standard sand was placed in the sand adding device to start the automatic mixer. The mixed cement mortar is poured into

the mold. After 24 hours of curing, sample was placed in the standard curing box for curing.

2.3.4 Workability

According to the standard[15], the mixed cement mortar was poured into mold and evenly compacted with ramming rod, and then mold was slowly lifted along the vertical direction, and then the jump table was started. After the jump table stopped, the diameter of the cement mortar in the vertical direction was measured with scale, and the average value was the workability of the cement mortar.

2.3.5 Mechanical property

According to the standard[16], the mechanical properties of the specimens were tested, and the flexural strength and compressive strength of the cured cement mortar were tested by a WANCE testing machine.

2.3.6 Analysis of hydrates

Hydration heat was examined by the isothermal calorimeter (TAM AIR, 605000) and the date was automatically recorded within 70 h. 3.33g binders composed of cement and LS(0%, 10%, 20, 30%) was prepared with W/B of 0.50.

The phase of hydration products in LS-cement was detected by XRD. The XRD measurement was carried out with Cu radiation , at a scanning rate of 10°/min with the 2-theta ranging from 5° to 80°.

The morphology of cement mortar was detected by Zeiss scanning electron microscope. The cement mortar was first broken into small pieces of 3 ~ 5mm, and then the small pieces were immersed in anhydrous ethanol for 3 days.

3. Results and discussions

3.1 Effect of grinding time on fineness

The effect of grinding time on fineness of LS was shown in Fig.2. Fig.2 (a) shown that fineness of LS decreased with the increased of grinding time. The frequency distribution is the density distribution on the distribution coordinates, which can intuitively and quickly observe the degree and center trend of data dispersion. The frequency distribution of LS was divided into three intervals: interval I (0.95~5.68 μm), interval II (5.68~45.83 μm) and interval III (45.83~320.78 μm) were shown Fig.2(b). The frequency distribution of LS in interval I increased with the increased of grinding time. However, the law was completely opposite in interval II. The frequency distribution of LS was unchanged in interval II. Interestingly, there was a turning point (about

5.68 μm) between interval I and II. In interval III, with the increased of grinding time, the frequency distribution of LS decreased sharply.

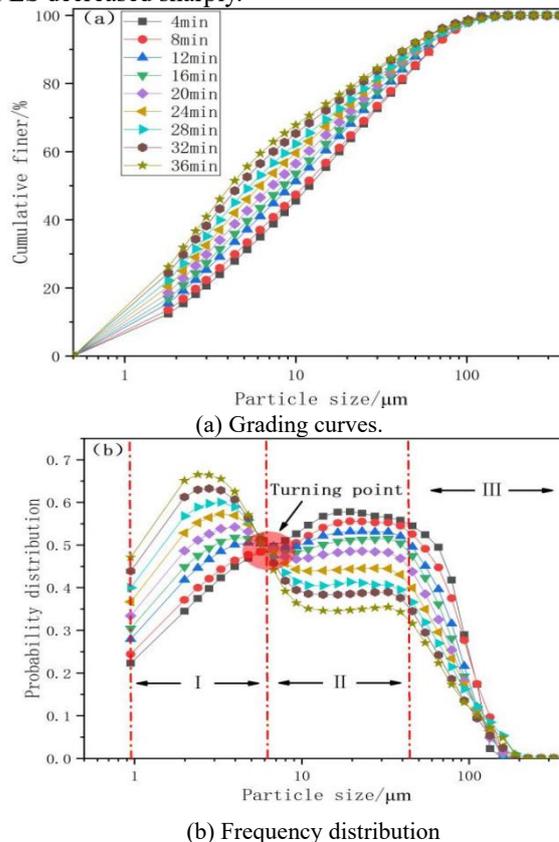


Fig. 2. Relationship between grinding time and fineness

3.2 Influence of fineness and content on the workability

The Fig.3 shown relationship between the workability of cement mortar and the fineness and content of LS. The workability of cement mortar slightly increased and then decreased with the increase of content of LS. The improvement of the workability of the cement mortar was due to LS became spherical during the ball milling. Fig.1 shown that LS was loose and porous particle with large specific surface area, and the density of LS was less than that of cement. Therefore, LS replaces cement with same mass will produce more particles, resulting in the workability of cement mortar decreased. When the content of LS was 10 % and grinding time of LS less 24 min, increased workability. When the content of LS was more than 10 %, grinding time has little effect on the workability. The above research indicated that grinding time increased the content of 0.95~5.68 μm particles, LS with porous also reduced the workability of cement mortar, but the grinding time has little effect on workability of cement mortar. Therefore, porous characteristics of LS are the main factors affecting the workability.

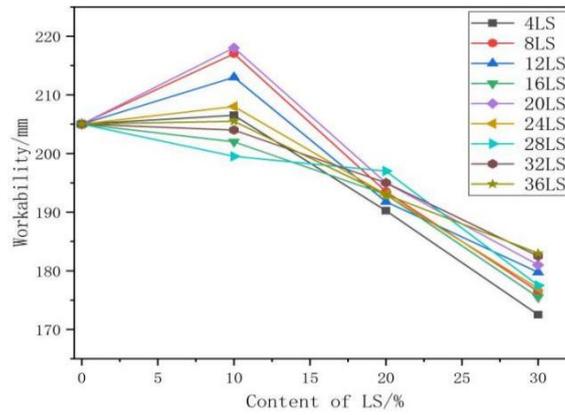


Fig.3. Effect of fineness and content of LS on workability of cement mortar

3.3 Influence of fineness and content on the mechanical property

The influence of LS on the mechanical property of cement mortar were shown Fig.4 and Fig.5. Fig.4 shown that there were no significant negative effect mechanical property of cement mortar at 7d when the content of LS was 10%, while significantly decreased when the content exceeds 10%. With the extension of LS grinding time, the mechanical property of cement mortar has no obvious improvement, but grinding time of LS exceeds 24min, 30% LS had certain degree of improvement on the mechanical property. Fig.5 shown that the content of LS within 20% increased the mechanical property at 28 days. The influence of grinding time on mechanical property at 28d is consistent with that of 7d, but the mechanical property of 30 % LS cement mortar exceeds that of the control group after grinding time exceeds 20min.

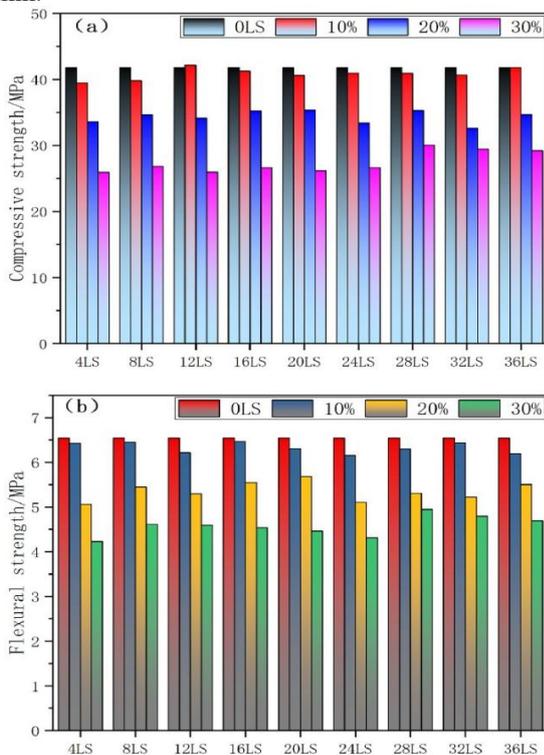


Fig. 4. Effect of LS on compressive strength and flexural strength of cement mortar at 7d

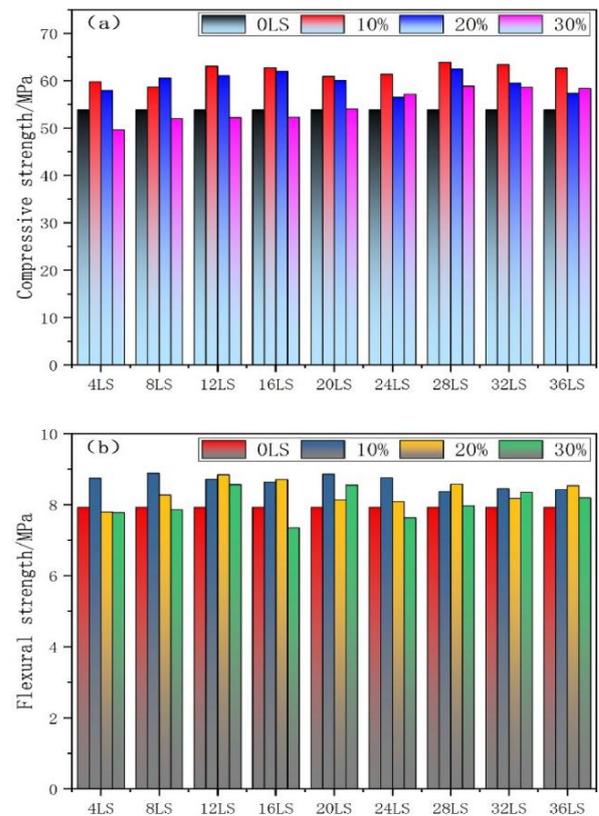


Fig. 5. Effect of LS on compressive strength and flexural strength of cement mortar at 28d

3.4 Hydration heat

Fig.6 shown the hydration heat of cement with LS paste was studied. LS significantly delayed the appearance time of the exothermic peak. The exothermic peak of the control group appeared at 16 hours, while the highest exothermic peak of cement with 30% LS was delayed to 33 hours. LS significantly prolonged the induction period of cement hydration, from 4h to about 18h. The results shown that too much LS is not conducive to cement hydration and reduced the early mechanical properties of cement-based materials. 10% LS increased the hydration heat of cement paste during the hydration deceleration period, while the hydration heat of cement paste significantly decreased when content of LS exceeded 10%. When the content of LS was 10%, the heat release

of the cement slurry was lower than that of the control group at 16h and 24h. While the heat release of the cement slurry was 204.2J/g and 234.4J/g at 48h and 70h, which was 2.6% and 3.7% higher than that of the control group.

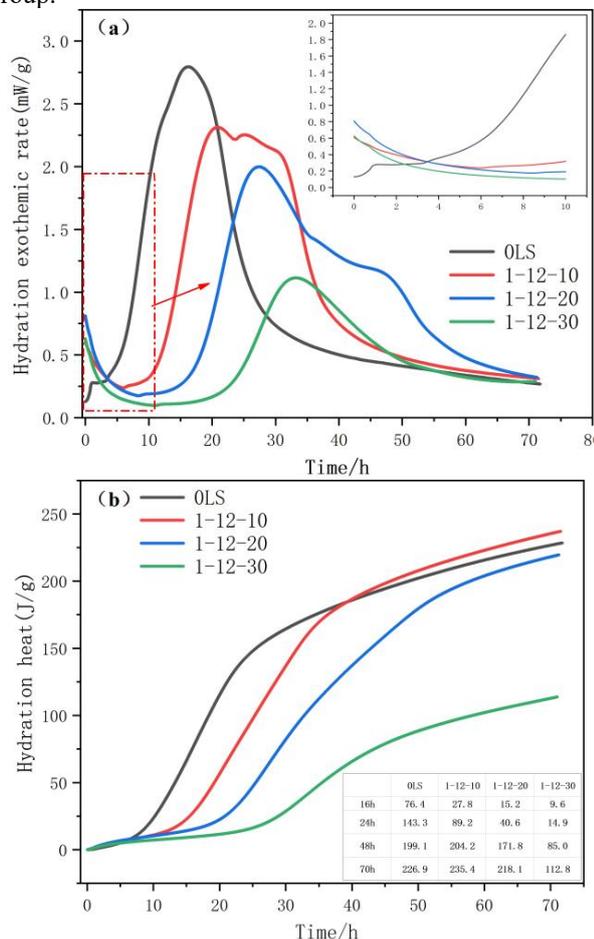


Fig. 6. Hydration heat of cement paste with LS

3.5 XRD analysis

Analysis of hydration products of cement mortar with LS, as shown in Figure 7. Studies have shown that $\text{Ca}(\text{OH})_2$ and ettringite are considered to be characteristic peaks of hydration products. And higher the peak value, the more hydration products are produced[17]. The content of $\text{Ca}(\text{OH})_2$ in LS-cement system was determined by the hydration reaction of cement and the pozzolanic reaction of LS. With the content of LS increased, the diffraction peak of $\text{Ca}(\text{OH})_2$ shown first increasing and then decreasing. When the content of LS was 10 %, the diffraction peak of $\text{Ca}(\text{OH})_2$ was the highest, indicated that the $\text{Ca}(\text{OH})_2$ formed by hydration of 10 % LS was much larger than that consumed by pozzolanic reaction. This was the reason 10% LS did not reduce the mechanical properties of cement mortar at 7 days and improved the mechanical properties at 28 days.

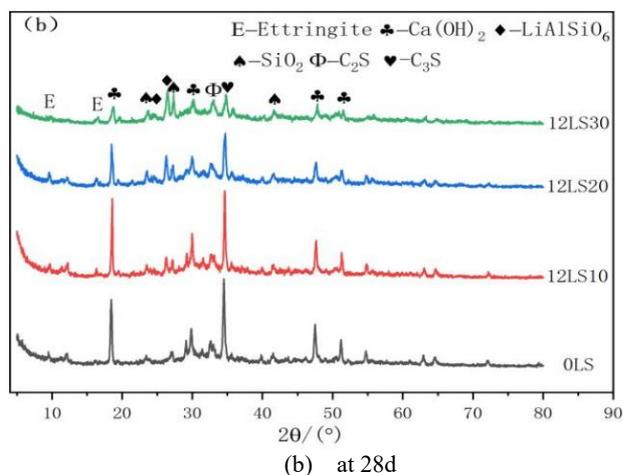
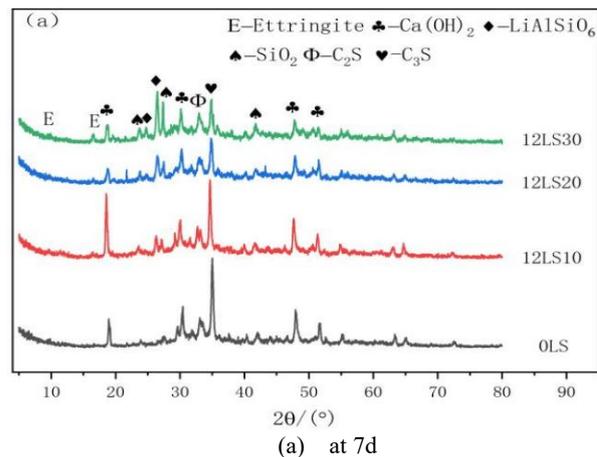


Fig. 7. XRD patterns of paste samples

3.6 SEM analysis

Fig.8 and Fig.9 shown the SEM images of cement mortar with different LS at 7d and 28d, respectively. It can be seen from Fig.8 (a) that internal porosity of control group was small and there was small amount of ettringite; SO_3 (23.85wt% shown table 1) in LS existed in the form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Figure 8 (b)~(d) shown that with the increase of LS content, the ettringite and porosity of cement mortar gradually increased, which leads to the decrease of the mechanical properties of the cement mortar. The cement mortar without LS was not dense and contained small amount of flaky $\text{Ca}(\text{OH})_2$ were shown Fig.9(a). Cement mortar with 10% and 20% LS was denser, while the cement mortar with 30 % LS has more pores and ettringite were shown Fig.9(b) and (c).Therefore, the mechanical properties of cement mortar can be significantly improved when the LS content are 10% and 20%, while mechanical properties of cement mortar reduced when content of LS exceed 30%.

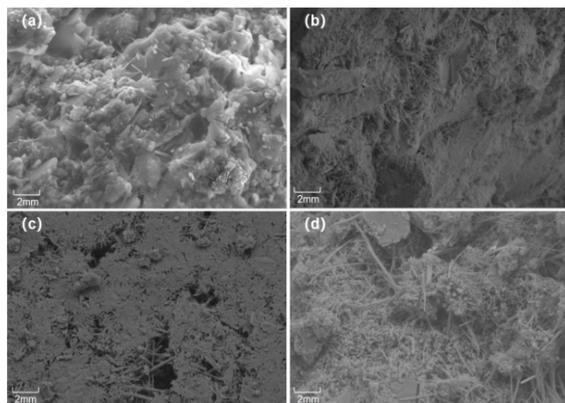


Fig. 8. SEM images of cement mortar at 7d containing LS: (a)0LS;(b)1-12-10;(c)1-12-20;(d)1-12-30(a)

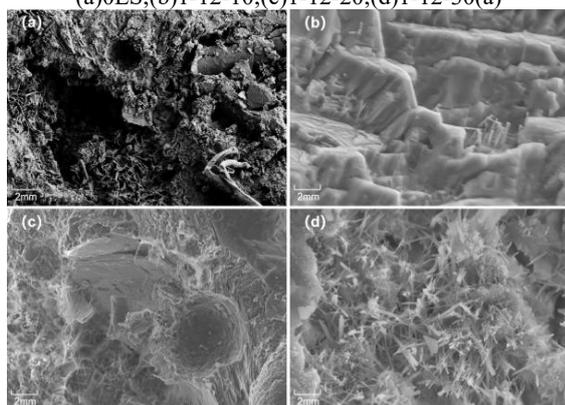


Fig. 9. SEM images of cement mortar at 28d containing LS: (a)0LS;(b)1-12-10;(c)1-12-20;(d)1-12-30

4. Conclusions

In this paper, the effect of fineness and content of LS on mechanical properties and microstructure evolution of cement mortar has experimentally been studied. The following conclusions can be drawn:

The frequency distribution of LS was divided into three intervals. With the extension of grinding time, the particle distribution in the range of interval I (0.95~5.68 μ m) increases, and the particle distribution in the range of interval II(5.68~45.83 μ m) and interval III (45.83~320.78 μ m) decreases. The particle content is almost the same in the range of interval II(5.68 ~ 45.83 μ m).

Ball milling can improve the sphericity of LS. When the content of LS is less than 10 % and the grinding time is less than 24 min, the fluidity of cement mortar can be improved. The influence of porous characteristics of LS on the workability of cement mortar is greater than that of grinding time.

LS has no significant effect on the mechanical properties of cement mortar at 7d, and mechanical properties of cement mortar are significantly improved at 28d when the content of LS is less than 20%. Grinding time of LS are 20min and 24min, the mechanical properties of cement mortar were increased at 7 d and 28 d when content of LS is 30%.

When the content of LS is 10 %, the hydration heat of cement mortar is significantly increased, and a large amount of Ca(OH)₂ and ettringite are generated to

accelerate cement hydration. Therefore, when the content of LS is less than 10 %, the performance of cement-based materials can be effectively guaranteed.

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