Effect of limestone on rheological, shrinkage and mechanical properties of alkali–Activated slag/fly ash grouting materials

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HIGHLIGHTS

• The incorporation of fine limestone powder can improve the rheological properties and mechanical properties of alkali-activated slag/fly ash grouting materials.
• The utilization of fine limestone can reduce the cost of alkali-activated slag/fly ash grouting materials.
• The addition of fine limestone can reduce the shrinkage of alkali-activated slag/fly ash grouting materials.
• The limestone powders primarily provided a physical filling effect, but non-negligible chemical nucleation in the solid and liquid waterglass activated the slag-fly-ash paste.

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ABSTRACT

The effect of limestone powder (5%, 10% and 20%) on the rheological properties, drying shrinkage and mechanical properties of alkali-activated slag/fly ash grouting materials (AASFGM) are investigated. The results show that AASFGM with or without limestone powder conforms to the Bingham fluid model. The incorporation of fine limestone powder into AASFGM has a positive effect on rheology, strength and shrinkage properties. The yield stress, plastic viscosity and drying shrinkage properties activated by the solid waterglass are larger than those of the liquid type. However, the paste activated by the solid waterglass with 10% limestone powder exhibited satisfactory compressive strength and drying shrinkage after curing for 28 d. The shrinkage was decreased for finer limestone particle packing and filling to improve the compactness of AASFGM.

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1. Introduction

Alkali-activated grouting materials (AAGM) are a new class of cementitious materials that can be synthesized with metakaolin or fly ash [1,2]. Alkali-activated materials (AAM) have received extensive attention of researchers owing to their higher strength, higher resistance to chemical attack, better thermal properties (e.g., fire resistance and low thermal conductivity), and significantly lower energy and greenhouse gas (e.g., CO₂) emissions [3–8]. In alkali-activated slag mortar or concrete, there are many disadvantages, including high drying shrinkage, fast setting rate, and poor workability [9–11]. The incorporation of fly ash into alkali-activated slag can effectively reduce the shrinkage of alkali-activated slag-fly ash mortar [11,12]. Alkali-activated slag-based materials show good reactivity and high early strength, however it often need to delay curing in engineering applications, which can be achieved by incorporating fly ash into the alkali-activated slag cementitious material [13]. Therefore, the mixture of slag and fly ash is a good choice as the precursor of alkali-activated materials. The production location of slag and fly ash is far from their practical application area, they need to be transported across regions if let them be used nationwide. So this will increase transportation costs [14].
As a cheap inert mineral admixture, limestone has been used in the cement concrete industry. The limestone resources are rich and distributed geographically in China; thus, using limestone to fabricate admixture is feasible and non-expensive [15]. Currently, the blocks of limestone from quarries are cut into smaller suitable sizes to be used as aggregates of cement concrete. The processing limestone which includes crashed limestone production is resulting approximately 20% limestone powder. Large quantities of limestone powder are generated which pollute the environment and made waste of natural resource. In order to expand the full utilization of limestone powder resources, using limestone as mineral admixture in cement has been widely attention. In fact, the positive effect of limestone used as an admixture to improve the rheological properties of ordinary Portland cement has attracted the attention of researchers worldwide [16,17]. Vance et al. [18] claimed that with the use of 15 μm limestone powder replacement of cement in pastes, the yield stress and plastic viscosity decreased. Kunlin et al. [19] found that the yield stress and plastic viscosity improved with the increasing introduction of limestone powder in pastes. Recently, some researchers have begun to explore the role of limestone powder in the AAM. Cwirzen et al. [20] reported the effect of calcite on the alkali-activated metakaolin reaction mechanism and found that the dissolution of aluminum and silicon ions in metakaolin increases when calcite was added to the paste. Yip et al. [21] reported that even with curing under the same conditions, the alkali-activated metakaolin pastes containing calcite or dolomite have a positive effect on strength compared to the samples without admixture. The rheological properties of AAM are relevant to the whole reaction mechanism, from the initial dissolution to the final gradual polymerization. However, there are limited studies on the relationship between the shrinkage, rheological performance, and strength of AASFGM containing limestone powders.

Cement-based grouting materials are widely used in many loose soils to improve or restore their mechanical, anti-seepage property. But a few studies on AASFGM for grouting in the literature, especially alkali-activated slag-fly ash cementitious materials. It is necessary that the grouts easily penetrate into the medium to be strengthened, which requires the grouting materials to have appropriate rheological properties, strength and shrinkage. Rheology is very important for the engineering application of AAM, especially in permeable grouting materials. The rheology of cement paste is effectively improved by introducing organic or inorganic additives. However, the raw materials and reaction mechanisms of AAM are different from those of cement. Therefore, the organic admixtures used in traditional Portland cements in the pastes did not work in the alkali-activated cementing materials, because the organic functional group was destroyed by the high alkali concentration in AAM. Palacios et al. [22] studied the adsorption effect of superplasticizers on alkali-activated slag pastes; the experimental results showed that the adsorption of superplasticizers on alkali-activated slag pastes was significantly different from that on ordinary Portland cement. Criado et al. [23] pointed out that chemical additives produced a limited effect on the plastic viscosity and yield stress of the alkali-activated fly ash system.

Therefore, in order to enlarge the project application of AAM in grouting materials and reduce the amount of slag and fly ash, this study aims to use limestone powder as an admixture and to research the influence of fine limestone powder on the AASFGM properties of rheology, drying shrinkage, and mechanical development. The rheological performance was tested by advanced rheological equipment and the microstructure was analyzed by scanning electron microscopy (SEM) and Energy Dispersive Spectrometer (EDS). Shrinkage and mechanical strength were also investigated.

2. Materials and methods

2.1. Materials

Ground granulated blast furnace slag (SL) and fly ash (FA) were provided by Bei-hai Chengde Group Company and Guodian Nanning Power Generation, respectively, and were used as the raw materials in this study. Limestone powder (LP), purchased from Guangxi Tiandong Longxin Calcite Powder Co., Ltd. China, was used as the admixture. The chemical composition and specific surface area of slag, fly ash and limestone powder were determined by X-ray fluorescence (XRF) and the BET method respectively, and are shown in Table 1. The particle size distribution analyzed by Mastersizer 3000 (Malvern) laser diffraction analyzer is shown in Fig. 1. Two types of waterglass, solid and liquid, were used in the experiment. The solid waterglass (Foshan Zhongfa Waterglass Factory, China) comprises 50.80 wt% SiO2, 26.20 wt% Na2O and 23.00 wt% H2O; molar ratio: SiO2/Na2O = 2.0. The specific surface area of the waterglass was 1.24 m2/g. The liquid waterglass (from Foshan Zhongfa Water Glass Factory, China) had a solid content of 38.7 wt% and a molar ratio of SiO2/Na2O = 3.31, and NaOH (96% pure) was added to yield a molar ratio of SiO2/Na2O = 2.0.

2.2. Mixture proportions

Eight AASFGM paste-mixture proportions are shown in Table 2. The addition of 0 wt%, 5 wt%, 10 wt% and 20 wt% limestone powder, as well as different forms of waterglass, was examined to assess the effect of the powder on the rheological characteristics and shrinkage properties. The water/solid ratio (w/s, water including: water and liquid part of waterglass; solid including: SL, FA, LP and solid part of waterglass) and activator concentration (Na2O by powder mass) were 0.35 and 4%, respectively.

2.3. Testing

2.3.1. Determination of rheological parameters: yield stress and plastic viscosity

The AASFGM pastes were prepared by mixing (based on Table 2) for 3 min: at a speed of 100 rpm for 1 min, followed by 2 min at 1000 rpm. The pastes were immediately added to the Anton Paar MCR rotational rheometer to test the rheological parameters. For this test, the shear rate was 100 s−1, pre-shearing was performed for 2 min, followed by ramping up from 0 to 10 s−1 in 1 min and from 10 to 100 s−1 in 1 min, before ramping down from 100 to 50 s−1 in 1 min and from 50 to 0 s−1 in another 1 min. This cycle was repeated six times, with 5 s pauses between the cycles [22,24]. Fig. 2 shows the test procedure. In order to calculate the yield stress and plastic viscosity values of fresh AAGM, at least three rheological tests on fresh AAGM activated with same waterglass were performed for fluid model function. According to previous studies [24], there are two mathematical model function Bingham (Eq. (1)) and Herschel-Bulkley model (Eq. (2)) can be used to fit the flow curve.

Bingham model: \[ \tau = \tau_0 + \gamma \eta \] (1)

Herschel-Bulkley model: \[ \tau = \tau_0 + K \gamma^n \] (2)

where \( \tau \) is the shear stress (Pa), \( \eta \) is the shear rate (s−1), \( \tau_0 \) is the yield stress (Pa), and \( K \) and \( n \) are the consistency coefficient (Pa s) and the dimensionless fluidity index.

Table 1

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>SiO2</th>
<th>Al2O3</th>
<th>CaO</th>
<th>Fe2O3</th>
<th>K2O</th>
<th>MgO</th>
<th>Na2O</th>
<th>SO3</th>
<th>LOI</th>
<th>BET/m2/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag</td>
<td>19.2</td>
<td>9.5</td>
<td>57.4</td>
<td>2.9</td>
<td>0.5</td>
<td>3.3</td>
<td>0.3</td>
<td>5.0</td>
<td>0.5</td>
<td>0.7888</td>
</tr>
<tr>
<td>Fly ash</td>
<td>66.3</td>
<td>15.8</td>
<td>2.5</td>
<td>2.8</td>
<td>2.4</td>
<td>0.9</td>
<td>0.6</td>
<td>0.3</td>
<td>4.9</td>
<td>2.4277</td>
</tr>
<tr>
<td>Limestone powder</td>
<td>0.04</td>
<td>0.02</td>
<td>55.9</td>
<td>0.01</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>0.01</td>
<td>43.4</td>
<td>1.6018</td>
</tr>
</tbody>
</table>
2.3.2. SEM/EDS analyses
SEM/EDS were performed to analyze the fracture surface of the specimens with an S-3400N device (Japan Hitachi Limited Company) with an acceleration voltage of 20 kV. The specimens were impregnated using absolute ethyl alcohol, polished with SiC paper, and then coated with gold.

2.3.3. Compressive strength and drying shrinkage
The limestone powder was mixed with slag and fly ash for 1 min; the powders, waterglass, and water were mixed for another 3 min; and the homogenous paste was cast into cubic (20 × 20 × 20 mm³) [25,26] and prism (25 × 25 × 280 mm³) molds and vibrated for 1 min to eliminate the voids in the cement-mortar vibration-compaction equipment. The samples were covered with a plastic wrap to avoid moisture loss. After 24 h, the samples were demoulded carefully and the specimens were placed in a temperature humidity chamber at 20 ± 1 °C and relative humidity 90 ± 5%.

Compressive strength testing was performed on the 20 × 20 × 20 mm³ specimens using a DNS100 electronic universal testing machine. The displacement rate used was 0.5 mm/min. The test was performed on specimens cured for 3, 7, and 28 days. Drying shrinkage testing was performed on 25 × 25 × 280 mm³ specimens using a bench comparator with an accuracy of 0.001 mm to determine the linearity of the prism specimen along the longitudinal axis. The first reading was recorded immediately after demolding and the measurement was conducted in triplicate for each mix for up to 28 d.

3. Results and discussion

3.1. Yield stress and plastic viscosity measured by means of rotation measurement

3.1.1. Effect of limestone powder in liquid waterglass-activated slag-fly ash
As an example, Fig. 3 shows the shear-stress-versus-shear-rate curves for the pastes l-LP-5 and s-LP-5. It was found that the ramp down of the two curves are almost a straight line that fit the Bingham fluid model. Hence, Eq. (1) was used to fit the data of the downward arm of every cycle with an excellent R² value, greater than 0.999.

Fig. 4 shows the variation in yield stress (Fig. 4A) and plastic viscosity (Fig. 4B) of the end of every cycle in pastes l-LP with different LP contents (0, 5, 10, and 20 wt% by total powder mass). It is noted that as the amount of slag and fly ash replacement by limestone is increased from 5% to 20%, both the yield stress and plastic viscosity decreased. In Fig. 4A, except the l-LP-0 pastes, the slag and fly ash replacement by limestone is noted to exhibited a similar behavior, but the yield stress at the end of the first and third cycle was greater than that of the l-LP-0 pastes. In the first cycle, a possible reason is that the fine limestone powder filled the micropores, thereby modifying the particle packing. The solid particles accumulated together compactly, which increased the friction between them, so the yield stress increased. When finer limestone particles than slag and fly ash particles are introduced, this results in a decreased in the spacing between the particles, which increases the ability of the pastes with limestone powder to resist shear. So yield stress of pastes with limestone at the end of first cycle is high. The yield stress between 11 and 19 min had a prominent point (see Fig. 4A), which indicated the formation of gel, and the recovery of yield stress of gel breakdown [24].
The plastic viscosity of the pastes with limestone powder was lower than that of the l-C-0 pastes. In general, the larger the particles contained in the suspension, the greater the viscosity. From Fig. 1, we see that the particles of limestone powder are smaller than the slag and fly ash. Therefore, plastic viscosity decreased when fine limestone powder was added to the pastes. Limestone powder exhibits physical filling, which can be assessed from the SEM/EDS analyses. Fine limestone mixed with slag and fly ash decrease the water demand when they fill the micropores. Therefore, more of the available water can be used to lubricate the particles, leading to a lower plastic viscosity.

3.1.2. Effect of limestone powder on solid waterglass-activated slag-fly ash

The change in yield stress and plastic viscosity in pastes s-LP with different limestone content is shown in Fig. 5. Note that the yield stress and plastic viscosity decreased with added limestone in the solid waterglass-activated pastes. In Fig. 5A, the yield stress decreased with the increase in limestone powder content, and the viscosity values for the solid waterglass-activated pastes with added limestone were 15–30% lower than the values for those with no limestone (showed in Fig. 5B). When limestone powder was added to the pastes, the finer limestone particles filled the microvoids instead of water. The particle packing model can then be optimized in the slag-fly ash-limestone ternary system. Therefore, more water can be used to lubricate the raw material, resulting in a decrease in yield stress and viscosity. Some water will be consumed by the dissolution of the solid waterglass. Therefore, a small variation in the amount of water can cause significant changes in the rheological parameters of pastes s-LP.

But in the Fig. 5A, note that yield stress of solid waterglass activated materials with limestone show a different behavior that the lowest yield stress appears at the end of different cycles, as the content of limestone powder increase. The reason is that coarser particles (solid waterglass) were added into the fresh pastes. The different phase activators were compared in respect of the yield stress and plastic viscosity (Figs. 4 and 5). It is clear that both yield stress and plastic viscosity were higher in the single-component pastes. One reason is that the dissolution of the waterglass is an exothermic process, whereas the polymerization of the silicate gel formed by gelation of the waterglass and Ca²⁺ from dissolution of slag is a heat-absorbing process. Therefore,
the dissolution heat of waterglass can improve the formation and size of the C-S-H gel. Another possible explanation for the higher rheological parameters in pastes s-LP is that insufficient water is used to lubricate the material particles compared with pastes l-LP. Because the dissolution of solid waterglass will consume a large amount of water, the water demand for the pastes increases.

3.2. Microstructural characterization (SEM/EDS)

In SEM/EDS images (see Fig. 6A and D), we observed and confirmed there are some solid waterglass particles that were not completely dissolved in the hardened samples. This indicated that water is insufficient in solid waterglass activated materials. For two seasons, the yield stress of pastes s-LP is 2–3 times higher than that of pastes l-LP, and the plastic viscosity is more stable with time. Fig. 6 shows that the typical SEM/EDS images of the sectional AASFGM pastes incorporation 20% limestone powder after 28 days of curing is the same as that of ordinary Portland cement pastes. The two samples consist of a binder matrix with unreacted lime-stone powder and slag particles. In the solid waterglass-activated sample, more cracks are present in the hydration products and around the unreacted particles caused by contraction stress. Solid waterglass particles as the activator were added into the fresh pastes, a greater shrinkage stress is produced due to the faster reaction [27]. And numerous small pores with size ranging from several to approximated ten microns can be seen in the SEM image of solid waterglass-activated pastes, because coarser solid waterglass particles are not good for particle packing. It is noted that the limestone powder is unreacted, but there are some gel phase on the unreacted limestone powder surface. This indicate that limestone powder shows mainly a physical filling effect and a small but nonnegligible chemical nucleation mechanism, forming C-(A)-S-H gels for long time. Previous research found the same results in alkali-activated metakaolin and slag-fly-ash mixtures [20,28].

3.3. Drying shrinkage testing

Fig. 7 shows the time-dependent drying shrinkage of the mixtures containing different amounts of limestone powders. It was found that the limestone powder has a significant effect on the shrinkage of liquid waterglass-activated slag and fly ash (see Fig. 7A), but only has a slight effect on other alkali-activated systems (see Fig. 7B). According to the results displayed in Fig. 7, the data briefly illustrates the correlation of the shrinkage with the variation in limestone content. It can be seen that the shrinkage of liquid waterglass-activated slag-fly ash was at the minimum when mixing 10 wt% limestone powder; however, mixing 5 wt% and 20 wt% limestone resulted in shrinkage that was slightly lower than that of the control group (see Fig. 7A). A tendency was found in solid waterglass-activated material, although the data changes were not obvious. The addition of limestone did not increase the drying shrinkage of AAM, and had a positive effect on the drying shrinkage. The shrinkage of cementation material is controlled by capillary tension, disjointing pressure, surface tension, and the removal of interlayer water [29–32]. AAM is different from ordinary Portland cement, so the shrinkage mechanism is different. Previous research indicated that the capillary tensile forces and the structural incorporation of alkali cations in C-A-S-H are two significant factors for the drying shrinkage of alkali-activated slag [33–35].

Fig. 8 shows the pore size distribution for the AAM paste. The envelopes show that the drying shrinkage of liquid waterglass-activated slag and fly ash decreases with the increase in limestone
powder content. By using fine limestone powder in slag and fly-ash mixes, finer particles will fill the microvoids and a better particle packing will be achieved. Therefore, the number of micropores ranging from 1 to 100 nm is reduced in the l-LP pastes (see Fig. 8A), which resulted in lower drying shrinkage because of the overall reduction in capillary tensile forces. When mixing with 20 wt% limestone powder, the value for the shrinkage was almost the same with another group (mixing 5% limestone) but greater than pastes mixed with 10% limestone powder. A possible explanation for the increased shrinkage of pastes with 20% limestone is that the dissolved Ca from limestone powder was more than pastes mixed with 10% limestone, so the dissolved Ca from limestone

Fig. 7. Drying shrinkage of AASFGM pastes with different doses of limestone powder: (A) liquid waterglass, (B) solid waterglass.

Fig. 8. Pore size ((A) liquid waterglass, (C) solid waterglass) and pore volume distribution ((B) liquid waterglass, (D) solid waterglass) of AASFGM pastes with different dosage of limestone powder.
with the Si and Al resealed by leaching the slag and fly ash formed more of the gel (including C-S-H and C-A-S-H). Previous research found that the slow release of calcium from limestone formed a large amount of geopolymeric gels in blends of metakaolin-limestone [20]. Ye et al. [34] pointed out that the large shrinkage in alkali-activated slags is attributed to C-A-S-H, because the gels can more easily collapse and redistribute upon drying. Dissolved Ca from limestone increases with the increase in mixing limestone powder, so dissolved Ca from limestone will be incorporated in gels, resulting in more shrinkage than pastes mixed with 10% limestone.

However, the pore size distribution of s-LP pastes was much the same (see Fig. 8A). Mixing fine limestone cannot obviously refine the pores or reduce the number of micropores due to the larger particle size of solid waterglass. According to a previous study, the pore size diameter ranging 10 nm–100 nm belongs to capillary pores [36]. When fine limestone powder filled the pores, there are fewer capillary pores above 10 nm compared to that in pastes with 0 wt% limestone powder. The drying shrinkage of c-LP pastes decreased. Because the cumulative pore volume and capillary pores distribution of samples with 5 and 20 wt% limestone are similar, so the shrinkage also is similar.

### 3.4. Compressive strength testing

Fig. 9 shows the compressive strength for the two types of pastes mixed with different amounts of limestone powder. It can be seen that the paste sample shows a different tendency in the strength development at 3, 7, and 28 days. It can be found that the compressive strength will increase with the addition of limestone powder to the AASFGM paste. However, the sample shows a slightly different tendency in terms of strength development. We can see that the strength was increased with the increase in limestone content in I-LP paste, but the strength was increased and then decreased in the s-LP paste.

In the I-LP paste, when the limestone powder content increases from 0% to 20% by mass, the three-day compressive strength increases from 29.4 MPa to 34.7 MPa, and the 7- and 28-day compressive strength also increase from 37.7 MPa and 55.8 MPa to 42.4 MPa and 58.9 MPa, respectively. In the s-LP paste, when the content of limestone increased from 0% to 20%, the compressive strength increased by 4.6 MPa, 3.8 MPa and 1.2 MPa compared to the control sample (no limestone) for 3 days. Similarly, the strength increased 2.5 MPa, 5.2 MPa, and 3.2 MPa at 28 days. These results show that the fine limestone powder has a slight positive effect on the compressive strength. This result can be attributed to the physical filling effect of the limestone powder. Mixing in the limestone powder will increase the content of fine particles within the I-LP pastes (see Fig. 1), which can reduce the cumulative pore volume of I-LP pastes from 0.07419 cm$^3$/g to 0.02223 cm$^3$/g as the limestone content increased (see Fig. 8B) because the fine limestone particles refined particle packing, which leads to an increase in strength. Because of larger particles of solid waterglass, the cumulative pore volume of s-LP-10 paste is minimal of 0.06267 cm$^3$/g (see Fig. 8D). This corresponds to previous research that found the coarser the porosity, the less is the compressive strength of the system [32].

### 4. Conclusions

The effect of fine limestone powder on the performance of an alkali-activated slag-fly ash-limestone cementing system were investigated to assess its application in grouting materials. The following conclusions can be drawn from the experimental results:

The incorporation of fine limestone powder into alkali-activated slag-fly ash materials has a positive effect on rheology, strength and shrinkage properties. The rheological behavior of solid and liquid waterglass-activated slag and fly ash fits the Bingham fluid model, and the addition of limestone powder did not change the rheological behavior.

The rheological characteristics, drying shrinkage, and strength of liquid waterglass-activated slag–fly ash paste are better than those of solid waterglass–activated slag–fly ash paste. However, the paste activated by solid waterglass with 10% limestone powders exhibited preferable performance in terms of compressive strength and drying shrinkage after curing for 28 d.

The SEM results show that the limestone powders primarily provided a physical filling effect, but non-negligible chemical nucleation in the solid and liquid waterglass activated the slag-fly ash paste.

### Conflict of interest

None.
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