Effect of Alkaline-Earth Metal Oxide on Compressive Strength and Flexural Strength of Alkali-Activated Slag Cement Mortar

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Abstract. The effect of CaO and MgO content on the compressive strength (CS) and flexural strength (FS) of alkali-activated slag mortar (ASM), which was activated by NaOH (Na₂O% = 4%), was investigated. The pore structure of alkali-activated slag paste was investigated via mercury intrusion porosimetry (MIP). The morphology of ASM was observed by field emission scanning electron microscope (FSEM). The study shows that the CS and FS of ASM, which was activated by NaOH, increase first and then decrease with the improvement of CaO and MgO content. The optimal CaO and MgO content for CS are both 9% of the slag mass. The CS of ASM with optimal CaO and MgO content can achieve 46.54MPa and 47.79MPa, respectively. The optimal CaO and MgO content for FS are 6% and 3% of the slag mass, respectively. The FS of ASM with optimal CaO and MgO content can achieve 11.23MPa and 11.11MPa, respectively. The comprehensive mechanics performance of ASM are the best, when the CaO content is 6%.

Keywords. CaO; MgO; alkali-activated slag mortar; compressive strength; flexural strength.

1. Introduction

Alkali-activated slag (AAS) cement not only can make full use of slag, reduce energy consumption and greenhouse gas CO₂ emission, but also has high strength and corrosion resistance. Its frost resistance, impermeability and fire resistance are all superior to those of traditional Portland cement [1-3]. The 2014 Environmental Life Cycle Assessment [3] indicated that compared with ordinary Portland cement concrete with similar compressive strength (CS), AAS concrete reduced 73% of greenhouse gas emission, 43% of energy consumption and 25% of water consumption. Therefore, AAS cement is regarded as the most potential cementitious material in the 21st century [4].

CaO and MgO can improve the mechanical properties of alkali-activated slag cement mortar (ASM). Chen et al. [5] added 2-6% CaO into ASM and found that the 28d CS of ASM increased with the improvement of CaO content. Based on experimental results, Jin et al. [6] concluded that when 0-7.5% MgO was added into the AAS paste, the 1-90d CS of this paste generally increased with the improvement of MgO content. Further, Gawwad et al. [7] showed that when 5% MgO was added, the 1-90d CS of the AAS paste increased, but when the added content exceeded 10%, its 1-90d CS decreased with the improvement of MgO content.

Different expansion characteristics of CaO and MgO and their different hydration products generated when added into AAS cement have different effects on the CS and flexural strength (FS) of ASM. Currently, however, there are no comparative studies on the effects of CaO and MgO content on...
the FS of ASM, nor is a study on the effects of the same content of CaO and MgO on the CS and FS of ASM. In this paper, NaOH was used as an activator (Na$_2$O$\% = 4\%$); CaO and MgO of 3\%, 6\%, 9\% and 12\% were added into ASM, respectively. The influence of each content of CaO and MgO on the CS and FS of ASM was studied, and the optimal content of CaO and MgO was obtained, respectively.

2. Experiment

2.1. Experimental Materials

2.1.1. Slag. The slag used is provided by Fujian Minhong Building Materials Industrial Co., Ltd. Its performance indices are shown in table 1, and its main chemical components are shown in table 2.

Table 1. Property of slag.

| Density (g/cm$^3$) | Specific surface area (m$^2$/kg) | LOI (%) |
|-------------------|----------------------------------|---------|
| 2.92              | 423                              | 1.7     |

Table 2. Main chemical compositions of slag (%).

| CaO     | SiO$_2$ | Al$_2$O$_3$ | MgO | SO$_3$ | TiO$_2$ | MnO | Fe$_2$O$_3$ | Na$_2$O | K$_2$O |
|---------|---------|-------------|-----|--------|---------|-----|-------------|---------|-------|
| 41.84   | 29.49   | 17.52       | 5.48| 1.83   | 0.68    | 0.43| 0.31        | 0.27    | 0.21  |

2.1.2. Fine Aggregate. Minjiang River sand is used in the experiments. According to the standard “Construction Sand” (GB/T 14684-2011) [8], the technical indices of the fine aggregate are shown in table 3, and its grain size gradation is shown in table 4.

Table 3. Property of the fine aggregate.

| Fineness modulus | Bulk density (kg/m$^3$) | Performance density (kg/m$^3$) | Particle size (mm) |
|------------------|-------------------------|-------------------------------|-------------------|
| 2.5              | 1,481                   | 2,590                         | < 5               |

Table 4. Gradation of the fine aggregate (residue on each sieve) (%)  .

| Mesh aperture | < 0.15 mm | 0.15 mm | 0.30 mm | 0.60 mm | 1.18 mm | 2.36 mm | 4.75 mm |
|---------------|-----------|---------|---------|---------|---------|---------|---------|
| Residue on each sieve | 0.5       | 5.1     | 45.1    | 46      | 2.8     | 0.5     | 0.0     |

2.1.3. Alkali Activator. NaOH used is produced by Beijing Kangpu Huiwei Technology Co., Ltd., with an analytical purity of 99\%. CaO and MgO are both produced by Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd., with an analytical purity of 98\%. The specific surface area of CaO is 25.32 m$^2$/g, and the specific surface area of MgO is 42.58 m$^2$/g.

2.1.4 Mixing Water. The water used in the experiments is tap water from the Fuzhou area.

2.2. Mix Proportion

The mix proportion of AAS cement is shown in table 5. The water-binder ratio of the paste and the mortar specimen is both 0.4, where the binder-sand ratio of the mortar specimen is 1: 2. In table 5, $m_{MaO}$, $m_{CaO}$ and $m_{slag}$ are the mass of MaO, CaO and slag, respectively.
Table 5. Mix proportion of AAS cement.

| Group | No. | Activator type | Na$_2$O (%) | $m_{\text{Na}_2\text{O}}/m_{\text{slag}}$ (%) | $m_{\text{CaO}}/m_{\text{slag}}$ (%) |
|-------|-----|----------------|-------------|--------------------------------|--------------------------------|
| N     | N4  |                | 4           |                                |                                |
|       | M3  |                | 4           | 3                              |                                |
|       | M6  |                | 4           | 6                              |                                |
|       | M9  |                | 4           | 9                              |                                |
|       | M12 | NaOH           | 4           | 12                             |                                |
| M     |     |                |             |                                |                                |
|       | C3  |                | 4           |                                | 3                              |
|       | C6  |                | 4           |                                | 6                              |
|       | C9  |                | 4           |                                | 9                              |
|       | C12 |                | 4           |                                | 12                             |

2.3. Experimental Methods

The CS and FS of mortar specimens at curing ages of 3d, 7d, 28d and 90d were measured, respectively, according to the specification GB/T17671-1999 [9]. The PoreMaster-60 automatic mercury injection apparatus (Canta company, USA) was used to test the pore structure of the paste specimen. The microstructure of mortar specimens was observed by a Nova NanoSEM type 230 field emission scanning electron microscope (FSEM) produced by Czech FEI Company.

3. Experimental Results

3.1. CS and FS of ASM after Addition of CaO

Figures 1 and 2 show the CS and FS of ASM after addition of CaO. In figure 1, except for C12, the CS of ASM at each age increased with the improvement of CaO content. At 28d, the CS of C9 (42.36 MPa) exceeded that of C12 (41.53 MPa). At 90d, the CS of C3 (43.01 MPa) and C6 (45.13 MPa) also exceeded that of C12 (41.53 MPa). In terms of the CS of ASM, the optimal content of CaO is 9% of the slag mass.

In figure 2, the 3d FS of ASM increased with the improvement of CaO content. In 7d, the FS of C9 (10.03 MPa) exceeded that of C12 (9.66 MPa). At 28d, the FS of C6 (11.59 MPa) exceeded that of C9 (11.11 MPa), and that of C3 (10.70 MPa) and C6 (11.59 MPa) exceeded that of C12 (10.41 MPa). At 90d, the FS of C3 (10.76 MPa) exceeded that of C9 (10.41 MPa), and the FS of N4 (9.33 MPa) exceeded that of C12 (9.02 MPa). In terms of the FS of ASM, the optimal content of CaO is 6% of the slag mass.

![Figure 1](image1.jpg)  
**Figure 1.** Effect of CaO content on the CS of ASM.

![Figure 2](image2.jpg)  
**Figure 2.** Effect of CaO content on the FS of ASM.
3.2. CS and FS of ASM after Addition of MgO
Figures 3 and 4 show the CS and FS of ASM after addition of MgO. In figure 3, the 3d CS of ASM increased with the improvement of MgO content. At 7d, the CS of M9 (37.32 MPa) exceeded that of M12 (36.76 MPa). At 90d, the CS of M12 (44.82 MPa) was lower than that of M6 (46.77 MPa) and close to that of M3 (44.08 MPa). Therefore, adding MgO into ASM is beneficial to improve its early CS. In terms of the CS of ASM, the optimal content of MgO is 9% of the slag mass.

In figure 4, the 3d FS of ASM increased with the improvement of MgO content. At 7d, the FS of M9 (9.93 MPa) and M6 (9.75 MPa) exceeded that of M12 (9.38 MPa). At 28d, the FS of M12 (9.94 MPa) was lower than that of N4 (10.09 MPa), and that of M9 (11.05 MPa) was lower than that of M3 (11.28 MPa). Therefore, adding MgO into ASM is beneficial to improve its early FS. In terms of the FS of ASM, the optimal content of MgO is 3% of the slag mass.

3.3. Effect of Types of Alkaline-Earth Metal Oxides on the CS and FS of ASM
With the same content of alkaline-earth metal oxides (CaO and MgO), ASM CS test results of group C and group M are shown in figure 5, and their ASM FS test results are shown in figure 6.
In figure 5, when CaO and MgO had the same content, the CS of ASM with MgO was higher than that with CaO. Figure 6 shows that, in 90d, when the alkaline-earth metal oxide content was 3%, the ASM FS of group M was 3.25% higher than that of group C; when the content was 6%, the ASM FS of group M was 2.14% lower than that of group C; when the content was 9%, the ASM FS of group M was 3.75% lower than that of group C; when the content was 12%, the ASM FS of group M was 4.88% lower than that of group C.

3.4. Pore Structure

Table 6 shows the total porosity, average pore diameter and pore size distribution of AAS paste in groups N4, C12 and M12. Academician Wu [10] divided the pores of cementitious materials into four
categories according to their diameter ranges: harmless pores (< 20 nm), less harm pores (20-50 nm), harmful pores (50-200 nm) and multi-harm pores (> 200 nm). Table 6 shows that, in 28d, compared with group N4, the total porosity of the paste in group C12 decreased by 6.46%, the average pore diameter decreased by 29.62%, and the porosity of the pore > 50 nm (harmful pores and multi-harm pores) decreased by 58.83%. Compared with group N4, the total porosity of the paste in group M12 decreased by 9.07%, the average pore diameter decreased by 40.10%, and the porosity of the pore > 50 nm (harmful pores and multi-harm pores) decreased by 79.20%. Compared with group C12, the total porosity of the paste in group M12 decreased by 2.78%, the average pore diameter decreased by 14.90%, and the porosity of the pore > 50 nm (harmful pores and multi-harm pores) decreased by 49.47%.

**Table 6.** Total porosity, pore size distribution and average pore diameter of AAS paste.

| Group    | Total porosity (%) | Average pore diameter (nm) | Pore size distribution (%) |
|----------|--------------------|-----------------------------|----------------------------|
|          |                    |                             | < 20 nm | 20-50 nm | 50-200 nm | > 200 nm |
| N4-28d   | 29.11              | 22.89                       | 9.41    | 8.26     | 9.41      | 2.03     |
| C12-28d  | 27.23              | 16.11                       | 8.18    | 14.34    | 2.70      | 2.01     |
| M12-28d  | 26.47              | 13.71                       | 13.32   | 10.68    | 0.45      | 1.93     |

3.5. Micromorphology

The 28d micromorphology of ASM in groups C9, C12, M9 and M12 is shown in figure 7.

![Images of group C9 at 28d.](image)

![Images of group C12 at 28d.](image)

![Images of group M9 at 28d.](image)

![Images of group M12 at 28d.](image)

**Figure 7.** Images of group C9, C12, M9 and M12 at 28d.

In figures 7a-7d, the width of three cracks was randomly measured and the mean value was calculated, respectively. Figure 7 shows that, at 28d, the mean width of ASM microcracks in group
C12 (2.45 μm) was greater than that in group C9 (0.48 μm). The mean width of ASM microcracks in group M12 (5.53 μm) was greater than that in group M9 (1.10 μm). It indicates that ASM microcracks increase when the content of CaO and MgO increases from 9% to 12%. The ASM microcracks in group M9 (M12) were greater than those in group C9 (C12), suggesting that the ASM microcracks at 28d formed when added with 9% and 12% MgO were greater than those generated with the same content of CaO, respectively.

4. Analysis and Discussion

4.1. Influence Mechanism of the Content of Alkaline-Earth Metal Oxides on the CS and FS of ASM

Before Ca\(^{2+}\) in the solution reaches saturation and achieves dynamic equilibrium with C-(A-)S-H, the added CaO enters into C-(A-)S-H in the form of Ca\(^{2+}\) to increase the Ca/Si of C-(A-)S-H without precipitating Ca(OH)\(_2\) crystals [11-13]. When Ca\(^{2+}\) in the solution reaches saturation and achieves dynamic equilibrium with C-(A-)S-H, adding more CaO will precipitate Ca(OH)\(_2\) crystals and lead to volume expansion. When the number of Ca(OH)\(_2\) crystals is small, its main function is to fill the pores, reduce the total porosity, refine the pore structure, decrease the average pore diameter, reduce harmful and multi-harm pores (table 6), and improve the CS and FS of ASM (figures 1 and 2). However, when there are excessive Ca(OH)\(_2\) crystals, the hardened cement paste limiting its expansion will crack (figure 7), thereby reducing the CS and FS of ASM (figures 1 and 2). At curing ages of 28-90d, the CS of ASM increases while its FS decreases (figures 1 and 2), because the latter is more sensitive to microcracks [14].

When the MgO content is low, the production of hydrotalcite-like compounds (HTLCs) increases with the improvement of MgO content, and the filling of pores in the paste with HTLCs makes the paste denser (table 6), thus improving the CS and FS of ASM (figures 3 and 4). When Al in the solution is exhausted and MgO continues to increase, Mg(OH)\(_2\) is generated and volume expansion occurs to fill the pores of the paste, further improving the compaction of the paste (table 6) and increasing the CS and FS of ASM (figures 3 and 4). However, when there are excessive Mg(OH)\(_2\) crystals, the hardened cement paste limiting its expansion will crack (figure 7), thereby reducing the CS and FS of ASM (figures 3 and 4).

The CaO content in the study of Chen et al. [5] ranges from 2% to 6%, and Jin et al. [6] found that highly active MgO content ranges from 0% to 7.5%. In their experiments, the CS of the specimens increased with the improvement of the content of alkaline-earth metal oxides. This is because the content of these metal oxides in their test group did not reach the optimal content. The experimental results of Gawwad et al. [7] are similar to those in figure 3, that is, there exists an optimal MgO content (5%). The optimal content of alkaline-earth metal oxides is related to the activator type, the activator content and the water-binder ratio.

4.2. Influence Mechanism of the Types of Alkaline-Earth Metal Oxides on the CS and FS of ASM

On the one hand, MgO has a larger specific surface area than CaO, making its contact area with water larger than CaO. This leads to the early generation of more Mg(OH)\(_2\) crystals, expansion, and filling of pores, and the reduction of multi-harm and less harm pores (table 6). Thus, MgO improves the CS and FS of ASM more effectively than CaO, especially before 7d (figures 5 and 6). On the other hand, the addition of CaO makes the Ca\(^{2+}\) in the solution reach saturation and achieve dynamic equilibrium with C-(A-)S-H before the precipitation of Ca(OH)\(_2\) crystals, that is, C-(A-)S-H will consume part of Ca\(^{2+}\). While the addition of MgO directly generates HTLCs and Mg(OH)\(_2\) crystals to fill the pores. Therefore, compared with CaO, MgO can more effectively reduce the total porosity, refine the pore structure, decrease the average pore diameter, and reduce harmful and multi-harm pores (table 6). Meanwhile, it can also make the expansion fissure of ASM develop faster (figure 7). Since the FS is more sensitive to microcracks than the CS [14], when the content of alkaline-earth metal oxides reaches more than 6%, the 90d FS of ASM in group M is lower than that in group C (figure 6).
4.3. Optimal Content
Through the above analysis and discussion, it can be obtained that in ASM with NaOH (Na$_2$O% = 4%) as the activator, in terms of the CS of ASM, the optimal content of CaO and MgO is 9% of the slag mass. The 90d CS reached 46.54 MPa (group C9) and 47.79 MPa (group M9), respectively. In terms of the FS of ASM, the optimal content of CaO is 6% of the slag mass, and its 90d FS reached 11.23 MPa (group C6). The optimal MgO content is 3% of the slag mass, and its 90d FS reached 11.11 MPa (group M3).

When the CaO content is optimal (6%), its CS of ASM is 14.89% higher than that of group N4, and its FS is 20.36% higher than that of group N4. When the MgO content is the optimal content (3%), its CS of ASM is 12.22% higher than that of group N4, and its FS is merely 19.08% higher than that of group N4. Therefore, in ASM with NaOH (Na$_2$O% = 4%) as the activator, when the CaO content is 6%, its comprehensive mechanical properties are optimal.

5. Conclusions
In ASM with NaOH (Na$_2$O% = 4%) as the activator, the 28d CS and FS first increased then decreased with the improvement of alkaline-earth metal oxides.

In ASM with NaOH (Na$_2$O% = 4%) as the activator, in terms of the CS of ASM, the optimal content of CaO and MgO is 9% of the slag mass. The 90d CS reached 46.54 MPa and 47.79 MPa, respectively. In terms of the FS of ASM, the optimal content of CaO is 6% of the slag mass, and its 90d FS reached 11.23 MPa. The optimal MgO content is 3% of the slag mass, and its 90d FS reached 11.11 MPa. When CaO content is 6%, its comprehensive mechanical properties are optimal. When the CaO content is 6%, its comprehensive mechanical properties are optimal.

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