

Effects of supplementary cementitious material(SCM) on carbonation resistance of concrete

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Abstract. Using fly ash (FA) and ground granulated blast furnace slag (GGBS) as representatives of supplementary cementitious material (SCM), the effects of the amount and combination of SCM addition on the carbonation resistance of concrete were systematically analyzed through rapid carbonation tests. Combined with XRD chemical analysis and DSC-TG thermogravimetric analysis, the influence mechanism of SCM on the carbonation resistance of concrete was discussed. The research results indicate that the addition of SCM increases the carbonation depth of concrete. When the single addition of FA exceeds 40%, the carbonation depth of concrete increases very quickly. Under the premise of the same total addition amount, the carbonation resistance performance of the composite FA and GGBS groups of concrete is better than that of the single FA group. Among the different combinations of FA and GGBS, the concrete with S95 grade GGBS+ grade I FA has the best carbonation resistance. The impact of FA on the carbonation resistance of concrete is manifested as a positive and negative effect.

Keywords: concrete; supplementary cementitious material; FA; GGBS; carbonation resistance; Ca(OH)₂ content.

1. Introduction

Concrete is a multiphase composite material composed of cement, coarse and fine aggregates, among which the production of cement is often accompanied by high energy consumption and high pollution[1]. In recent years, supplementary cementitious materials(SCM) with good Volcanic ash activity, such as fly ash (FA), ground granulated blast furnace slag (GGBS), have been used to partially replace cement and are increasingly widely used in concrete production, reducing production costs and bringing good environmental benefits[2-4]. Durability is the primary factor for the sustainable development of concrete engineering, and one of the main reasons for the durability failure of reinforced concrete is the corrosion of steel bars. Carbonation reaction is the main factor leading to corrosion of steel bars, deterioration of reinforced concrete materials, and structural durability failure[5-6].

When FA and GGBS are incorporated into concrete, the active ingredients SiO₂ and Al₂O₃ in them will consume alkaline substances in the pore liquid during hydration, which will lead to the deterioration of concrete's ability to resist CO₂ corrosion[7]. Gao et al. [8] found that as the total amount of FA and GGBS increases, the carbonation resistance of concrete decreases. When the total content is constant, the carbonation resistance of concrete increases with the increase of GGBS proportion. Luo et al. [9] found that the carbonation depth of concrete mixed with SCM had a great correlation with standard curing time and humidity. Zhao et al. [10] showed that 90-day wet curing made the transition zone of concrete interface more dense, which had a positive impact on the carbonation resistance of concrete, while the hydration of fly ash had a negative impact on the consumption of Ca(OH)₂.

At present, researches on concrete carbonation resistance mostly focus on the influence analysis and model establishment of preparation parameters and curing conditions [11], and there are few researches on the synergistic influence of SCM on concrete carbonation performance. In view of this, this study systematically analyzed the effect of the amount of FA and GGBS and the combination of incorporation methods on the carbonation depth of concrete through the rapid

carbonation test. The mechanism of the influence of SCM on the carbonation resistance of concrete was revealed by XRD chemical analysis and DSC-TG thermogravimetric analysis. The research can provide theoretical and technical support for carbonation durability prediction of concrete structure with SCM.

2. Materials and methods

2.1. Raw material

Cementing material: P·II 42.5 Portland cement (code C), Grade I, Grade II FA (code F.I, F.I), Grade S95, Grade S105 GGBS (code S95, S105). The coarse aggregate is natural crushed stone with continuous grading of 5-16 mm. The fine aggregate is machine-made sand with a fineness modulus of 2.3.

The particle size distribution of the gelled material was tested by laser particle size analyzer, as shown in Figure 1. It can be seen from Figure 1 that the small and medium particle size (below 20 μm) of Grade I FA and Grade S105 GGBS are relatively large, and the overall particles are relatively fine.

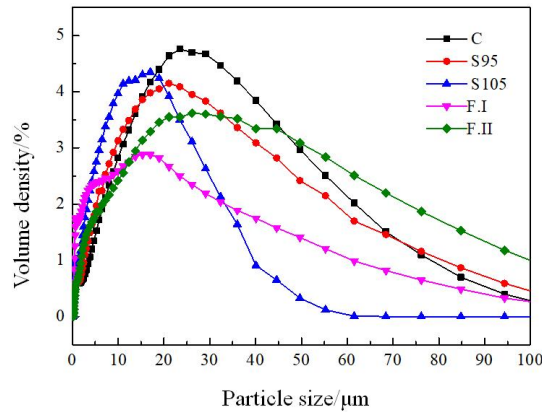


Fig.1 Size distributions of cementitious mate

2.2. Mix proportions design

The cross design method was used to design 10 groups of concrete mix ratio, the total amount of cementing material was fixed at 450 kg/m³, the total amount of aggregate was 1822 kg/m³, the water binder ratio was 0.35, and the sand rate was 38%.

The influencing factors are as follows: Single-doping grade I FA content (0, 20%, 40%, 60%), multi-doping grade S95 slag + total amount of grade I FA (40%, 60%, 80%) and combination mode (S95+F.I, S95+F.I, S105+F.I, S105+F.I). The specific mix design is shown in Table 1.

Table 1 Mix proportion design kg/m³

Group	C	F.I	F.II	S95	S105	mixing amount
A	450	0	0	0	0	0
B	360	90	0	0	0	F20%
C	270	180	0	0	0	F20%
D	180	270	0	0	0	F60%
E	270	90	0	90	0	F20%+S20%
F	90	180	0	180	0	F40%+S40%
G	180	135	0	135	0	F30%+S30%
H	180	0	135	135	0	F30%+S30%
I	180	135	0	0	135	F30%+S30%
J	180	0	135	0	135	F30%+S30%

2.3. Experimental method

HTX-12X microcomputer concrete carbonation test chamber was used to carry out carbonation test, the test conditions were: CO₂ concentration of $20 \pm 3\%$, humidity of $70 \pm 5\%$, temperature of $20 \pm 2^\circ\text{C}$.

The samples were tested by XRD with D/MAX-2500/PC X-ray diffractometer. The prepared sample was dried in an oven at 60°C for 24 h, and ground through a 0.16mm square sieve. The operating voltage of the test instrument is 40 kV, the scanning interval is $5^\circ - 90^\circ$, and the scanning speed is $2^\circ/\text{min}$.

3. Results and discussion

3.1. Effect of single FA addition amount

Figure 2 shows the development of carbonation depth of concrete with different FA content. It can be seen from Figure 2 that the addition of FA increases the carbonation depth of concrete at each carbonation age compared with that of the unadded group, that is, the carbonation resistance decreases. The higher the FA content, the more obvious the reduction of carbonation resistance. When the FA content exceeds 40%, the carbonation depth of concrete increases rapidly with the extension of carbonation age, and the carbonation depth of 60%FA concrete has reached 18.5 mm at 56 d, indicating that the carbonation resistance has deteriorated significantly.

SiO₂ and Al₂O₃ in FA will consume alkaline substances in the gelling system, weakening the ability of concrete to resist CO₂ erosion. However, when the dosage is small, the micro-aggregate effect and the activity effect exerted by it can produce a dense effect on concrete. Therefore, when the dosage of Grade I FA is less than 40%, the carbonation resistance of concrete is slightly decreased, but the reduction range is small. When the amount of incorporation is too large, it will directly cause the initial pH value of the concrete hole solution to decrease, the effect of resisting CO₂ diffusion is weakened, and the anti-carbonation performance of concrete is weakened.

3.2. Effect of total amount of FA and GGBS mixed

Figure 3 shows the development of concrete carbonation depth with age for different S95 GGBS+Grade I FA totals. It can be seen from the analysis of Fig. 3 that the greater the total amount of compound FA and GGBS, the greater the carbonation depth, which is consistent with the influence of the single-doped FA content on the carbonation depth. When mixed with 80%S95 GGBS+I FA, the 56d carbonation depth reached 19.3mm. According to the comprehensive comparative analysis of FIG. 2 and FIG. 3, it can also be seen that under the condition of the same total dosage, the anti-carbonation performance of the compound mixture concrete is better than that of the single FA. Especially when the content is 60%, the 56d carbonation depth of Group D concrete with single FA is 18.5mm, which is almost the same as the carbonation depth of group F with double 80%. The 56d carbonation depth of the 60% group G is only 6.5mm, which is much lower than that of the single group.

This is because the simultaneous incorporation of FA and GGBS into concrete can effectively exert the micro-aggregate effect and increase the density of the slurry. Moreover, since the pozzolanic activity of GGBS is higher than that of FA, the pozzolanic superposition effect generated by the two mixtures can make the secondary hydration reaction more adequate and improve the concrete compactness and strength. Therefore, the carbonation resistance of concrete mixed with GGBS and FA is better than that of single FA.

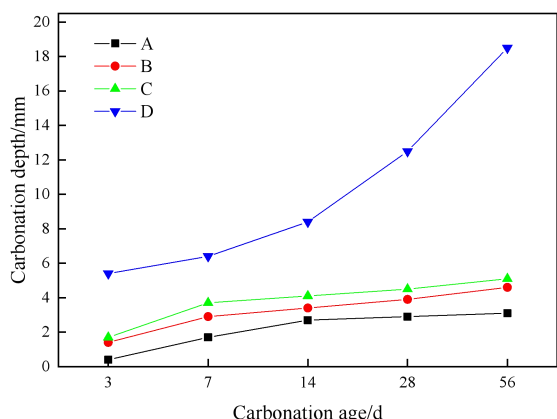


Fig.2 Effect of single addition of Grade I FA on the carbonation depth of concrete

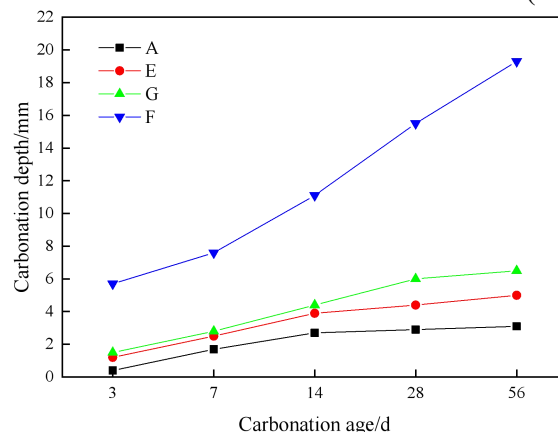


Fig.3 Effect of total amount of mixed FA and GGBS

3.3. Effect of the combination of FA and GGBS

The effect of the combination method of GA and GGBS on the carbonation depth of concrete is shown in Figure 4. It can be seen that different combination methods also have certain differences in the carbonation depth of concrete at different ages. Among them, the carbonation depth of S95 grade GGBS+II grade FA composite concrete (Group H) is the highest, reaching 9 mm at 56 days of age. The combination of S95 grade GGBS+I grade FA has the smallest carbonation depth in concrete (Group G), while the difference in carbonation depth between the other two combination methods is relatively small.

According to the principle of tight packing and combined with Figure 1 for analysis, only when the coarse and fine particles of FA and GGBS complement each other reasonably and fill each other can the performance of concrete be improved. Therefore, there is an optimal combination of FA and GGBS for the improvement effect of concrete. The proportion of fine particles in Grade I FA is relatively large, which can compensate for the lack of other cementitious materials in the small particle size range. Therefore, Group G can form an ideal continuous grading. However, the particles of Grade II FA and S95 GGBS are relatively large and have similar particle sizes, so the group H cementitious material failed to play an effective complementary role, resulting in poor compactness. This precisely confirms the results of the carbonation depth test.

4. Microscopic mechanism analysis

4.1 XRD analysis of hydration products

In order to analyze the effects of FA and GGBS on the hydration products inside the concrete, X-ray diffraction technology was used to conduct XRD chemical analysis on the hardened clean paste samples after curing for 28 days. To save space, Fig.5 only shows the XRD patterns of the samples of groups A, B, C and D.

It can be seen from Fig. 5 that the types of hydration products of the clean pulp samples with different FA content are basically the same, and the crystals with obvious diffraction peaks in the products are $\text{Ca}(\text{OH})_2$, CaCO_3 and C_3AH_6 . By comparing the four groups of curves, it can be seen that with the increase of FA content, the diffraction peak height of $\text{Ca}(\text{OH})_2$ gradually decreases, indicating that the content of $\text{Ca}(\text{OH})_2$ is decreasing. This is because the $\text{Ca}(\text{OH})_2$ in the hydration products is consumed by the volcanic ash reaction generated by the hydration of FA, which leads to the gradual deterioration of the carbonation resistance of concrete.

SEM-EDS test and XRD analysis confirm the test results of concrete carbonation resistance.

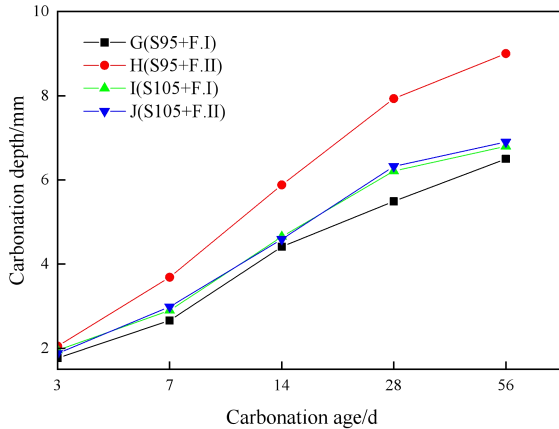


Fig. 4 Effect of combination of GGBS and FA on carbonation depth of concrete

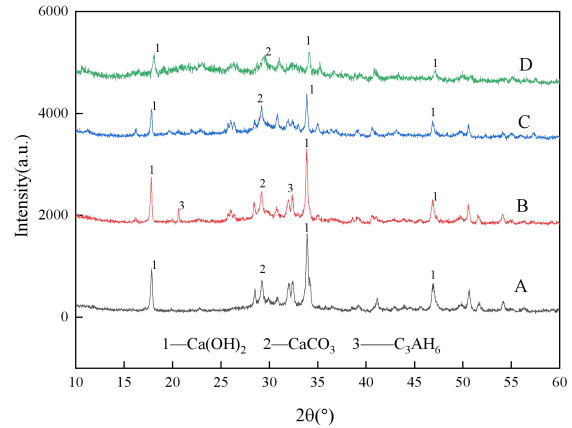


Fig.5 XRD pattern of the clean paste sample after curing for 28 days

4.2 DSC-TG analysis

The DSC-TG curves of the samples of group A, B, C and D are shown in Figure 6. According to the study of NHDA et al.[13], C-S-H gel and ettringite crystal (AFt) are decomposed by heat when the temperature rises to 100 °C, and the amount of dehydration increases with the increase of temperature, thus producing a heat absorption peak at about 100 °C. When the temperature rises to 400~500 °C, Ca(OH)₂ is decomposed into CaO and H₂O by heat, and water evaporation results in mass loss, so an endothermic peak is generated in this temperature range, and the mass is also reduced.

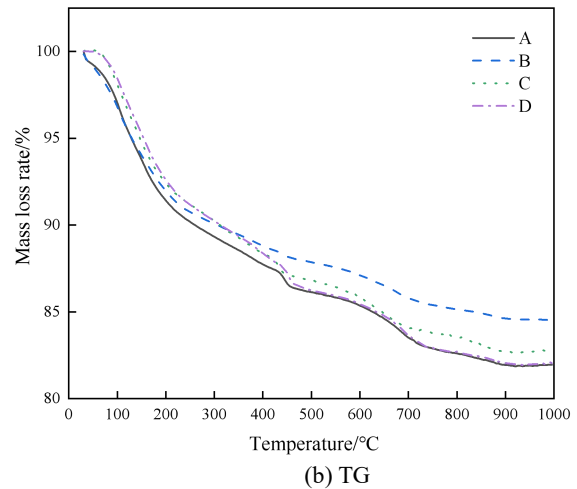
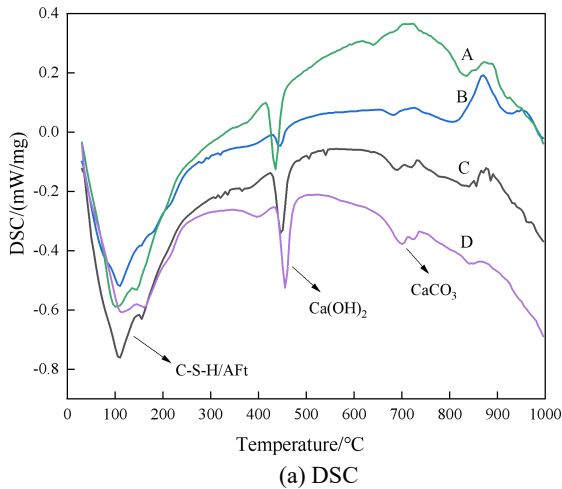


Fig.6 TG-DSC curves of composite paste samples

Since the Ca(OH)₂ crystal will release H₂O and CO₂ after thermal decomposition, resulting in a reduction in sample mass, the crystal content can be quantitatively analyzed through mass loss, and the calculation formula is as follows:

$$W_C = WL_C \frac{M_C}{M_H} \quad (1)$$

Where: W_C is the percentage content of Ca(OH)₂, %; WL_C is the mass loss rate in Ca(OH)₂ decomposition process, %; M_C and M_H are the relative molecular weights of Ca(OH)₂ and H₂O, respectively.

The content of Ca(OH)₂ in samples of group A, B, C and D was obtained by Proteus thermal analysis software, as shown in Table 2. It can be seen from Table 2 that with the increase of FA content, the content of Ca(OH)₂ in the sample gradually decreases, which exactly supports the XRD test results.

Based on the above carbonation depth test data and microscopic analysis results, the influence of FA on concrete carbonation resistance can be attributed to positive and negative aspects: First,

the micro-aggregate effect exerted by FA fine particles can reduce the pores in concrete, thus preventing the diffusion of CO₂ gas and enhancing the carbonation resistance, which is a positive effect; Secondly, the addition of FA reduces the generation of Ca(OH)₂ from the perspective of raw materials, and consumes a large amount of Ca(OH)₂ during secondary hydration reaction, resulting in the reduction of concrete alkalinity and the weakening of carbonation resistance, which is a negative effect.

Table 2 Calculation results of Ca (OH)₂ content

Group	A	B	C	D
Ca(OH) ₂ content	12.79	9.76	5.98	3.65

%

5. Conclusion

(1) The addition of SCM increases the carbonation depth of concrete. Under the premise of the same total dosage, the carbonation resistance of concrete mixed with GGBS and FA is better than that of single FA.

(2) Among the different combinations of auxiliary SCM, the concrete of grade S95 GGBS+ Grade I FA combination has the best carbonization resistance, while that of grade S95 GGBS+ Grade II FA combination has the worst carbonization resistance.

(3) The XRD and DSC TG analysis results indicate that the influence of FA on the carbonation resistance of concrete is manifested in two aspects: enhancing and weakening.

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