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Research on the Influence of Mineral Admixtures on Carbonization of Concrete

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Abstract

By studying single- and double-admixed fly ash on the concrete carbonization performance and the preparation of concrete with different proportions of fly ash. It shows that: with the increase of fly ash content, the content of $Ca(OH)_2$ in concrete decreases with the increase of fly ash content, which leads to the increase of carbonization depth of concrete; after adding mineral powder in different proportion, the shape effect and micro aggregate effect of mineral powder and fly ash make the internal structure of concrete become more dense, and the carbonization resistance performance plays a positive role. The results show that the carbonization resistance of concrete with double mineral admixtures is better than that of concrete with single mineral admixtures in a certain range.

Keywords

Fly Ash, Mineral Powder, Concrete, Carbonization.

1. Introduction

Carbonization of concrete is one of the hot issues in the durability research of reinforced concrete. It refers to the reaction of acid gases such as CO_2 in the air and water with $Ca(OH)_2$ produced by hydration of concrete to form carbonate and other substances, which reduces the alkalinity of concrete. For reinforced concrete, the steel bar can form a passive film in the alkaline environment of concrete to avoid corrosion. When the alkalinity of concrete continues to decrease, the passive film will be destroyed, and the reinforcement will lose its protection and rust, which will lead to the decline of structural bearing capacity. Nowadays, with the rapid development of China's industry, cars increase rapidly, the exhaust emissions of vehicles are increasing day by day, too. And the concentration of CO_2 in the environment is increasing, which makes the carbonization of concrete more and more concerned. It is of great significance to study the influence of carbonization on the performance of concrete to accurately predict the service life of reinforced concrete structures. With the development of high performance and green concrete materials, fly ash and other mineral admixtures are widely used in engineering structures as an important part of concrete. But it also brings some harm. Concrete with mineral admixtures, especially concrete with large amount of mineral admixtures, is easier to be carbonized because of its little internal alkali reserve. Therefore, the selection of appropriate mineral admixtures can not only improve the workability of concrete, but also ensure the durability of concrete.

In this thesis, by changing the proportion of mineral admixtures to replace cement and the ratio between fly ash and mineral powder, the influence of single and double mineral admixtures on the carbonization performance of concrete is studied.

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2. Test Overview

2.1. Test Raw Materials

2.1.1. Cement

The Portland cement used in this test was produced by a cement company in Dazhou, Sichuan, the type is P·O42.5. The cement performance is illustrated in Table 1.

Table 1. Basic Performance Indicators of Cement

Cement Fineness/% (80μm sieved)	Stability	Setting Time/min		Bending Strength /MPa		Compression Strength /MPa	
		Initial	Finally	3d	28d	3d	28d
1.7	Qualified	115	370	4.3	8.6	27.2	43.1

2.1.2. Fine Aggregate

The fine aggregate used in this test is from river sand in Sichuan. After screening, it is confirmed that the sand is medium sand, belonging to Level II sand with good gradation. Its basic physical properties are shown in Table 2.

Table 2. Basic Physical Properties of the Fine Aggregate

Items	Apparent Density/(g/cm3)	Mud Content /%	Mud Lump Content/%	Fineness Modulus
Fine Aggregate	2.62	1.9	0.3	2.5

2.1.3. Coarse Aggregate

In this test, continuous graded crushed stone is selected as the coarse aggregate for preparing concrete specimens. Its particle size is 5mm - 31.5mm, and its basic physical properties are shown in Table 3.

Table 3. Basic Physical Properties of the Coarse Aggregate

Items	Apparent Density/(g/cm^3)	Mud Content /%	Irregular Mud Content/%	Crush index/%
Coarse Aggregate	2.65	0.4	5.8	11.2

2.1.4. Fly Ash

The fly ash used in this test was produced by a power plant in Sichuan, which is black powder and well packaged. The basic properties are illustrated in the Table 4.

Table 4. Basic Properties of Fly Ash

Density/(g/cm^3)	Fineness/% (80μm sieved)	Water Demand Ratio /%	Water Content/%	28d Activity Index/%
2.42	3.5	99	0.82	89.0

2.1.5. Mineral Powder

Types and related properties of mineral powder are shown in the Table 5.

Table 5. Types and related properties of mineral powder

Origion	Density (g/cm^3)	SSA (m^2/kg)	Water Content (%)	Activity Index(28d) (%)
Qingdao Alkali	2.83	404	0.14	89.0

2.1.6. Additive

Water reducing agent comes from polycarboxylic acid water reducing agent produced by a company in Sichuan.

2.2. Test Methods

C40 concrete is prepared by replacing equivalent cement with fly ash and mineral powder. Concrete without mineral admixtures is defined as blank group, numbered K0. The concrete with mineral admixtures equivalently replacing a certain amount of cement is defined as the experimental group, and the proportion of grade II fly ash added by equivalent replacement method is 20%, 30%, 40% and 50% of the cement quality respectively; after confirming the content of fly ash, mineral powder is added according to the ratio of fly ash to mineral powder of 4:1 and 3:1, with a total of 12 groups, numbered D1-D4, F1-F4, H1-H4. In the test, the size of all concrete specimens is 100mm × 100mm × 100mm. The concrete specimens of all proportions are cured to 28 d under standard conditions, and then placed in the carbonization box to carbonize for 7 d, 14 d, 21 d and 28 d for comparison.

2.3. Test Plans

In this test, the rapid carbonization test method is used to compare the carbonization test of ordinary concrete and concrete with mineral admixture.

(1) In this test, 100 mm × 100 mm × 100 mm cube concrete blocks with standard curing time of 28 days were selected. Three blocks were taken out of the standard curing room two days before the test, and were dried at 58 °C – 62 °C for 48 hours. Then, except one or two opposite sides, other surfaces were sealed with melted paraffin and placed on the side draw parallel lines along the length direction with a pencil at a distance of 10 mm to determine the measurement point of carbonization depth.

(2) Put the test block prepared according to the first step into the carbonization box. Pay attention to that the distance between carbonization surfaces of each test block shall not be less than 50 mm.

(3) Seal the carbonization box with mechanical method or oil seal, and pay attention not to use water to seal. Then open the gas convection regulating device of the carbonization box, and slowly fill the carbon dioxide gas into the box. In this process, the carbon dioxide concentration in the box should be measured, and it should be adjusted within the range of 20% ± 3%. In addition, to ensure that the relative humidity in the carbonization box is in the range of 65% - 75% and the test temperature is in the range of 15 °C - 25 °C, the moisture preservation measures can adopt the dehumidification device or the method of putting silica gel, and the temperature can be adjusted according to the temperature regulator.

(4) Since the temperature, humidity and CO_2 concentration in the carbonization box are variable, it is necessary to measure the temperature, humidity and CO_2 concentration at a certain time. Generally, it is measured every 2 hours on the first day and the second day of the carbonization test, and then every 4 hours after the carbonization test. Then, the corresponding adjustment should be made according to the measured data, and the silica gel should be replaced frequently.

(5) After carbonization to 7d, 14d, 21d and 28d, take out three specimens and split them from the middle on the cutting machine.

(6) Remove the powder on the cutting surface of the test block, and spray (drop) 1% phenolphthalein ethanol solution (containing 20% distilled water) on the cutting surface. After 30s, measure the carbonization depth (the depth of the non-discoloration zone) of the predicted points marked according to the first step with a steel ruler. If coarse aggregate particles are embedded on the carbonization boundary at the measuring point, the carbonization depth of the measuring point can be the average value of the carbonization depth at both sides of the particle, and the carbonization depth measurement is accurate to 1 mm.

(7) The average carbonization depth of concrete at each test age shall be calculated according to Formula 1, accurate to 0.1 mm.

$$\overline{d_t} = \frac{\sum_{i=1}^{n} d_i}{n} \tag{1}$$

In Formula 1, d_t —— The average carbonization depth of the test block after carbonization T, mm;

d_i——Carbonization depth of each measuring point on two sides, mm;

n——Total number of measuring points on two sides.

The measured value of the average carbonization depth of concrete at each test age is the average value obtained by dividing the carbonization depth of three test blocks under corresponding conditions by 3, which is used to compare and evaluate the carbonization resistance of various concrete and the protection effect on reinforcement. The law of concrete carbonization development is based on the carbonization depth calculated at each age, and the curve of carbonization time t and carbonization depth d under this condition is drawn.

2.4. Admixture Ratio

According to JGJ55-2011 Process for Mix Proportion Design of Ordinary Concrete [1], the mixture Ratio of blank group C40 ordinary concrete is obtained through calculation. On this basis, the equivalent replacement method is used to replace 20%, 30%, 40% and 50% of cement to obtain the mixture ratio of D1 - D4 group concrete admixed with fly ash. In order to carry out test comparison, according to the ratio of mineral powder to fly ash of 1:4 and 1:3 respectively, the mixture ratio of F1 - F4 and H1 - H4 is obtained. See Table 6 for all mix proportions.

Table 6. Mixture Ratio of Each Concrete Group/(g/cm^3)

Number	Water Gel Ratio	Cement	Fly Ash	Mineral Powder	Sand Ratio/%	Fine Aggregate	Coarse Aggregate	Water	Water Reducer/%
K0	0.46	377	0	0	47	851	960	175	1.2
D1	0.46	302	75	0	47	851	960	175	1.2
D2	0.46	264	113	0	47	851	960	175	1.3
D3	0.46	226	151	0	47	851	960	175	1.4
D4	0.46	189	188	0	47	851	960	175	1.4
F1	0.44	302	75	18	47	831	960	175	1.1
F2	0.43	264	113	28	46	820	960	175	1.3
F3	0.42	226	151	37	46	810	960	175	1.3
F4	0.41	189	188	47	45	800	960	175	1.5
H1	0.44	302	75	25	46	831	960	175	1.1
H2	0.42	264	113	37	46	820	960	175	1.3
H3	0.41	226	151	50	46	810	960	175	1.3
H4	0.40	189	188	62	45	800	960	175	1.4

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3. Test Results and Analysis

3.1. Influence of Fly Ash Content on Concrete Carbonization Performance

As an important component of concrete, mineral admixtures play an important role in the carbonization resistance of concrete. The influence of different fly ash content on concrete carbonization performance is studied. The test results are shown in Figure 1. It can be seen from Figure 1 that with the extension of carbonization time, the carbonization depth is deepened, and with the increase of fly ash content, the carbonization depth also increases again. This is because the content of $Ca(OH)_2$ in ordinary concrete specimens were kept at a high level, which hinders the penetration of carbon dioxide, and the degree of carbonization is not serious. The addition of fly ash reduces the cement clinker content in concrete. At the same time, the "pozzolanic effect" of fly ash will further reduce the content of $Ca(OH)_2$, which is not conducive to the carbonization resistance of concrete [2]. From the analysis of Figure 1, when the content of fly ash is less than 30%, the growth rate of concrete carbonization depth is relatively slow, but it is still larger than that of ordinary concrete. This is because after adding fly ash, the internal pore structure and compactness of concrete of concrete is improved [3]. At the same time, the morphological effect and micro aggregate effect of fly ash strengthen this phenomenon and promote carbonization resistance performance. It plays a positive role, but due to the insufficient early hydration degree, large voids are not easy to fill. Under the condition of high concentration of CO_2, the carbonization degree of the concrete is still relatively high, and the carbonization resistance performance is relatively poor.

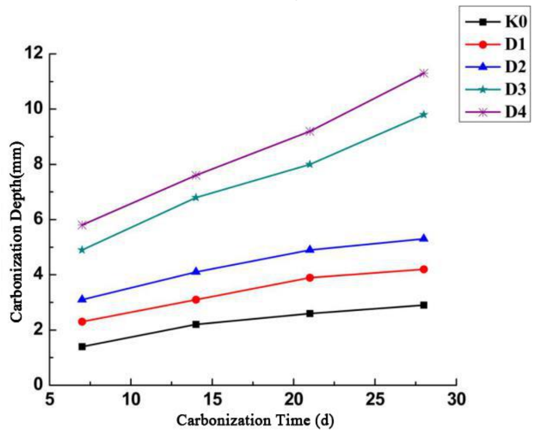

Figure 1. Influence of Fly Ash Content on Concrete Carbonization

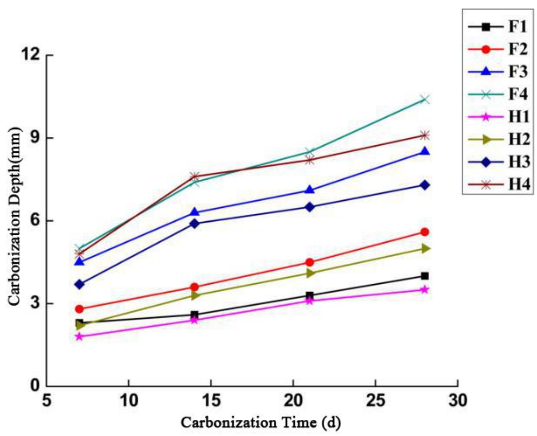

Figure 2. Influence of Different Double Admixtures Ratio on Concrete Carbonization

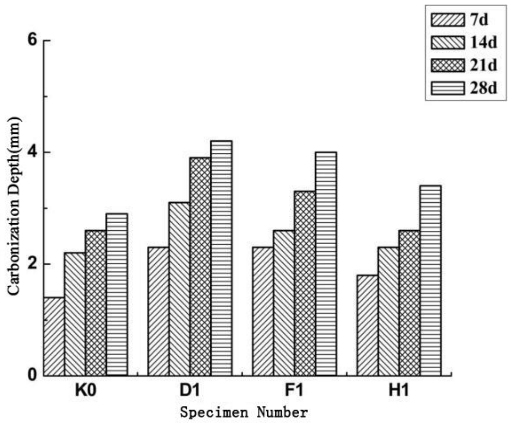

Figure 3. Comparison of the Influence of 20% Single and Double Admixtures on Concrete Carbonization

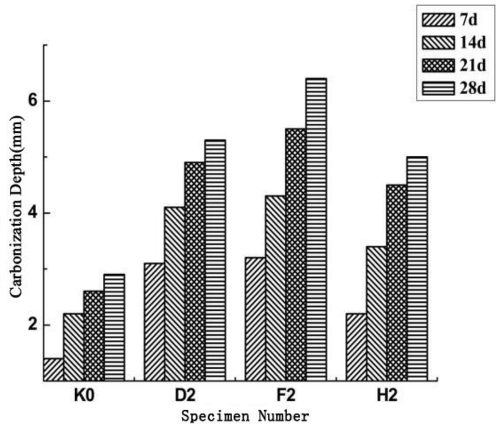

Figure 4. Comparison of the Influence of 30% Single Admixture and Double Admixtures on Concrete Carbonization

3.2. Influence of Two Admixtures-- Fly Ash and Mineral Powder on Carbonization Performance of Concrete

Fine slag and fly ash are two kinds of mineral admixtures commonly used in the process of concrete preparation. Generally speaking, they have micro aggregate effect, morphological effect and pozzolanic effect in concrete. In this test, the influence of the two on the carbonization performance of concrete is studied by changing the proportion relationship between the two in the concrete production process (the ratio of group F fly ash to mineral powder is 4:1, and the ratio of group H fly ash to mineral powder is 3:1). The test results are shown in Figure 2, 3 and 4. It can be seen from the three groups of Figures that the carbonization performance of concrete is improved to a certain extent after the concrete is admixed with mineral powder. When the content of fly ash is less than 30%, the carbonization resistance of double-admixed concrete is better than that of single fly ash concrete, and the ratio of mineral powder to fly ash is 1:3, which is because the activity of mineral powder is higher than that of fly ash, the content of calcium oxide in mineral powder is much higher than that of fly ash, and the reaction with water generates more $Ca(OH)_2$, which improves its pozzolanic effect and enhances hydration After hardening, the internal structure of concrete is more dense. This shows that though replace cement with equivalent admixture in concrete will reduce the concrete carbonization resistance, the composite technology of fly ash and slag powder can significantly alleviate the decline of carbonization resistance ability of concrete admixed with single fly ash, and can increase the total amount of admixtures in concrete, reducing the amount of cement and save the engineering cost [4]. Only from the perspective of carbonization resistance, it is concluded that the best ratio of concrete admixed with mineral admixtures is H1 group.

3.3. Relation between Carbonization Depth and Time

According to Fick's first diffusion law, the mathematical model of concrete carbonization is established [5], and the theoretical calculation formula of concrete carbonization depth is as follows:

$$x = \sqrt{\frac{2D_{CO_2} \cdot C_{CO_2}}{M_{CO_2}}} \cdot \sqrt{t} = K \cdot \sqrt{t} \quad (2)$$

In the formula, x ——carbonization depth from the surface of the specimen to its interior, mm;

D_{co_2}——effective diffusion coefficient of CO_2 in concrete;

C_{co_2}——the CO_2 concentration on the concrete surface which is the CO_2 concentration in the air;

M_{co_2}——amount of external CO_2 absorbed by unit volume concrete;

t ——corresponding carbonization years, S;

K ——carbonization coefficient, $mm \cdot S^{-0.5}$.

Because carbonization is a liquid phase reaction, if in a very dry environment, the carbonization of concrete is very difficult; in the air humidity of 60% - 80%, and because the dense concrete surface pore is very small, it is easy to absorb water from the moist air, so the whole gap is full of moisture, at this time, the concrete is not easy to carbonize; in the non-dense concrete surface layer, the pore is very small macro pores are dry, and the carbonization process of concrete is completed by diffusion of gaseous carbon dioxide into water filled capillary pores. From Formula 2, it can be seen that the carbonization rate of concrete is directly proportional to the square root of the carbon dioxide concentration on the concrete surface. Therefore, the surface carbonization speed of concrete structure depends not only on the environmental conditions, that is, the concentration of CO_2 in the atmosphere, humidity, temperature, etc., but also the density of concrete. Because the durability and compactness of concrete are affected by the variety of cement, aggregate gradation, water cement ratio, vibration degree, pouring method and wet curing time, it is very difficult to measure the influence of these factors, and can't be quantitatively related to the safe use years of concrete. Therefore, these factors and environmental conditions are integrated into the carbonization coefficient K of concrete [6].

The relation between carbonization depth and time is analyzed by comparing the double-admixed mineral content concrete and ordinary concrete with the optimal carbonization resistance ratio obtained in the previous section. Taking carbonization time as variable, the relationship between carbonization depth and carbonization time was analyzed by fitting curve. In the process of analysis, the curve power function $x=at^b$ is used for analysis, and the results are as follows:

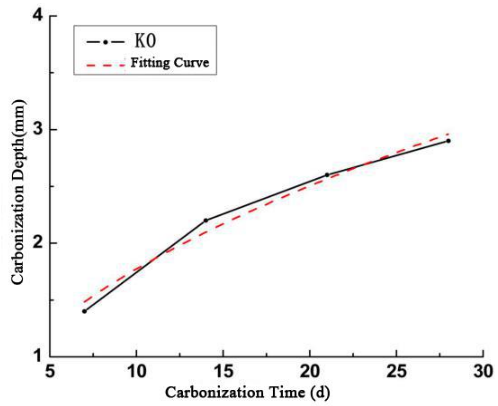

Figure 5. Regression Analysis of the Relation between Carbonization Depth and Time in K0 Group

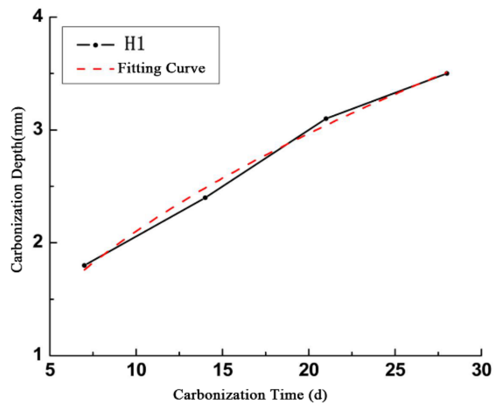

Figure 6. Regression Analysis of the Relationship between Carbonization Depth and Time in Group H1

Table 7. Regression Analysis of the Relation between Carbonization Depth and Time of Concrete

Number	$x=at^b$	a	b	R2
K0	$x=0.56407t^{0.49752}$	0.56407	0.49752	0.9731
H1	$x=0.66834t^{0.49772}$	0.66834	0.49772	0.98904

According to the above Table 7, the carbonization coefficient of K0 group concrete is 0.56407mm $S^{-0.5}$, and that of H1 group is 0.84332mm $\cdot S^{-0.5}$. The safe service year t of concrete can be defined as the time when the carbonization depth reaches the surface of the reinforcement, that is, the thickness of the protective layer

$$t=\left(y^{'}/K\right)^{2} \tag{3}$$

In the formula, y'——Net cover thickness of reinforcement for engineering components, mm

The rapid carbonization method reflects the carbonization results under laboratory conditions. In practical engineering, the safe service life of the specimens made under the same environmental category is shown in Table 8. In concrete, after adding mineral admixtures, due to the serious carbonization degree of concrete with mineral admixtures, in addition to the safe service life of structure and environmental category, the thickness of protective layer of reinforcement can be calculated according to Formula 3.

Table 8. Safe Service Life of Concrete

Number	Carbonization Coefficient K(mm·S-0.5)	Safe Service Life (Years)
K0	0.56407	26
H1	0.84332	27

4. Conclusion

(1) The carbonization depth of concrete is larger than that of blank concrete, and the carbonization resistance of concrete decreases after adding only fly ash into concrete. With the increase of concrete content, the carbonization depth of concrete is gradually increasing, and the carbonization resistance is weaker.

(2) When the fly ash content is 20%, the carbonization resistance of the concrete with different amount of mineral powder is better than that of the concrete with single-admixed concrete, but the carbonization depth of the concrete is larger than that of the blank group concrete under the same conditions.

(3) The variation of carbonization depth of concrete with time is fitted by power function x=atb. The results show that the safe service life of concrete is 1 year longer than that of ordinary concrete when 20% fly ash and 1/3 fly ash are admixed into concrete.

(4) Adding fly ash and mineral powder into concrete can save a certain amount of cement, reduce the cost of concrete, and cut lots of energy consumption and greenhouse gas CO_2, which is conducive to environmental protection and has certain economic and social benefits.

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