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Study on mechanical properties and air-void structure characteristics of hybrid fiber fly ash concrete under sulfate attack

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Abstract
Sulfate attack is one of the common durability problems of concrete. The concrete structure in saline soil is particularly susceptible to sulfate attack. The aim of this paper was to investigate the effect of fly ash on the mechanical properties and pore structure of fiber reinforced concrete under sulfate attack. The sulfate resistance of different content of fly ash (0%, 10%, 20%) at different sulfate attack ages (0 d, 30 d, 60 d, 90 d, 120 d, 150 d) was presented. By analyzing the variation of mass loss rate, ultrasonic wave velocity, relative compressive strength and relative splitting tensile strength, the mechanical properties of concrete under sulfate attack were studied. In addition, the air-void structure test was carried out to explore the pore structure characteristics of concrete. The test results suggested that the contribution of fly ash could improve the sulfate resistance of concrete. At the same sulfate attack age, compared with other contents, the hybrid fiber fly ash concrete with 10% fly ash could strongly resist sulfate attack. At the later stage of sulfate attack, the corrosion resistance of concrete weakened, the mass loss rate, wave velocity, relative compressive strength and relative splitting tensile strength were reduced, while the pore structure parameters showed that fly ash could fill large pores for reducing corrosion damage. Adding 10% fly ash refined pores and enhanced the strength of concrete. The generation of pores is a major factor for the deterioration of concrete structure. The fractal dimension well expressed the changes of pores in concrete. Based on fractal dimension and fly ash content, the damage model was established, which could predict the damage deterioration of hybrid fiber fly ash concrete under sulfate attack.

1. Introduction
Concrete is one of the most widely used building materials in the field of civil engineering, with the characteristics of low price and excellent performance, the durability of concrete plays an important role in engineering construction [1]. Concrete has been seriously sulfate attack in salt lake, industrial wastewater, heavy saline soil, groundwater, sea water and other environmental conditions [2], which costs a lot of money and energy to maintain the structural performance of concrete every year. Therefore, the research on the damage deterioration process of concrete and the damage model under sulfate attack is beneficial to delay the attack damage of concrete structure and evaluate its service state. At present, many researchers have carried out a lot of studies on the sulfate resistance of concrete, the results showed that the addition of appropriate amount of fly ash can improve the sulfate resistance of concrete [3–5]. Fly ash showed better performance than Portland cement because of its stronger cross-linked structure [6]. As the main waste of coal burning, replacing part of cement with fly ash can reduce energy loss and environmental pollution [7–9].

Many scholars continue to explore various measures to improve the anti-cracking behavior of concrete, reduce the generation of shrinkage cracks and enhance the mechanical properties of concrete. Adding fibers into...
Concrete is considered to be one of the effective measures to improve the above defects [10–12]. In the past, the durability of single fiber reinforced concrete was mostly discussed. Elango et al [13] found that the ultimate load of basalt fiber reinforced beams increased by 1.5 times compared to conventional steel reinforced beam, which can be attributed to the improvement of tensile strength carrying capacity of basalt fiber rebars. Niu et al [14] studied the effect of basalt fiber (BF) on the mechanical properties, chloride ion content and sorptivity of coral aggregate concrete (CAC) at different curing ages. The test results had been noticed that CAC with 0.05% BF showed 9.87% and 1.36% at 28 days increase in compressive strength and splitting tensile strength compared to control concrete. The chloride ion content in coral aggregate concrete with 0.05% BF was the highest at 28 and 90 days, whereas sorptivity of specimen showed the lowest. Wei et al [15] simulated the corrosion activities of carbon fiber reinforced concrete structures in harsh environment. Specifically, reinforced concrete beams were exposed to 3.5% (mass fraction) Sodium Chloride marine wet-dry cycle and high temperature (50 °C) environment, and sustained point loading for 360 days. By describing the steel corrosion characteristics of reinforced concrete structures with different cut carbon fiber content (0%, 2.5%, 5%), it is concluded that the reinforced concrete beam with 2.5% chopped carbon fiber content showed the strongest corrosion resistance and the highest ultimate strength. Behfarnia et al [16] investigated the effect of various pozzolanic binders and polypropylene fibers on the durability of self compacting concrete in sulfate environment. The results revealed that the compressive strength of 10% silica fume and 10% metakaolin mixtures reached the highest after 9 months. All specimens immersed in 10% magnesium sulfate solution became lighter after 9 months. The mass of specimens containing polypropylene fibers lost less than those without fibers. Wang et al [17] evaluated the mechanical properties, microstructure and durability of polypropylene fiber reinforced rubber concrete. The mechanical property test results showed that the compressive strength at 28 days exceeded 40 MPa. However, compared with control samples, the addition of polypropylene fiber has little contribution to the compressive strength and splitting tensile strength. The mixtures of 0.5% macro PP fiber and 10% rubber aggregates showed the best freeze-thaw resistance due to the lowest transport property obtained in the bulk electrical resistivity test. And SEM image of the fracture surface showed that the crack width on the rubber surface was small.

In addition to adding single type of fiber to concrete, fiber admixture can significantly improve the working performance of concrete. In addition to adding single type of fiber to concrete, fiber admixture can significantly improve the working performance of concrete. Bankir and sevim [18] measured the strength and mass loss of thirty different Hybrid Fiber Concrete (HFC) samples in 5% H$_2$SO$_4$ and Na$_2$SO$_4$ solutions after 400 days. To ensure the better acid and sulfate resistance of HFC, the optimal contribution ratio of different types of fibers, aggregates and binders was proposed. It is found that the compressive strength loss of HFC designed with the optimization will reach 25% after 400 days. Ranjith et al [19] investigated the durability of different volume fraction of both polypropylene fibers and glass fibers (0.5%, 1%, 1.5%, 2%) in Engineered Cementitious Composites (ECC), and pointed out that the compressive strength of ECC containing 1.5% glass fiber was 34% higher than that of cement mortar specimens after 90 days in the sulphate attack test. Compared with other mixes, ECC with 1.5% glass fiber performed less mass loss and lower chloride permeability.

Currently, researchers mainly explored the damage model of concrete in sulfate attack environment to describe the deterioration of macro mechanical properties, but failed to present the damage inside concrete at the mesoscopic level [20–22]. However, concrete is a heterogeneous material, and there are a lot of micro cracks, micro voids and other defects in it. Under the effect of external environment, these defects are the main causes of concrete damage. Under the sulfate attack, a series of physical and chemical reactions occur in concrete, resulting in large crystallization pressures and expansion stress, leading to internal damage of concrete structure [23]. The damage of concrete materials is the macro reflection of meso structure, so some researchers described the macro damage behavior of concrete materials by studying the changes of meso structure. Zhang et al [24] studied the evolution characteristics of mesoscopic pore structure of concrete with three water-to-binder (w/b) ratios (0.38, 0.45, 0.52) under chemical and physical conditions in different sulfate attack periods. From the experimental results, in the early stage of sulfate attack period, the reaction products were mostly accumulated in the macropores under chemical sulfate attack, resulting in the reduction of pore volume. In the middle and late stage of period, the increase of micropore volume under physical sulfate attack led to the expansion of concrete cracks. In addition, the lower w/b ratio will enhance the sulfate resistance of concrete. Nehdi et al [25] explored the surface degradation and pore structure performance of concrete specimens under sulfate attack. And the specimens with different w/b ratio (0.30, 0.45, 0.60) were placed in the cycling environment of temperature and relative humidity. It is concluded that low water-binder ratio and moist-curing reduced the surface degradation of concrete due to the decreasing of pore volume, further improved the resistance of concrete to physical sulfate attack. Wang et al [26] proposed that, when the dry wet ratio was 3:1, concrete exposed to sulfate attack has the most serious deterioration. At the same time, it is found that the smaller the dry-wet ratio, the more obviously the decrease of concrete porosity. Due to the reduction of harmful pores (50 nm ≤ d < 200 nm), the pore diameter becomes finer. Kearsley et al [27] showed that the compressive strength of foam concrete has a good functional relationship with porosity. According to the equations derived by Hoff, the compressive strength of
foamed concrete with high content of ash can be predicted by calculating theoretical porosity. Neithalath et al. [28] predicted the permeability of pervious concrete mixtures through pore structure characteristics. It is found that the increase of permeability by increasing pore sizes or porosity, but led to the degradation of mechanical properties of concrete. Appropriate aggregate gradations can enhance the connectivity of pores for improving permeability. Nakamura et al. [29] studied the effect of moisture content on the pore distribution and strength development of fly ash concrete with different curing ages (7 d, 28 d, 120 d). It can be found that the concrete of 120 d curing ages showed the highest strength with the decrease in moisture content and low porosity. Because the difference of moisture content in the specimens affected the pore size distribution, the porosity of the specimens with higher moisture content was 100%, and the porosity increased with the increase of age. This implied that the pore structure produced by the moisture content is an important factor for the strength development of fly ash concrete during 120 days curing period.

Adding fiber and fly ash effectively improved the corrosion resistance of concrete under sulfate conditions. However, most of the previous research works studied single type of fiber or adding fly ash in concrete to improve the durability of concrete, and there were few studies focused on the durability of hybrid fiber fly ash concrete. Therefore, it is imperative to analyze the mechanical properties and pore structure of hybrid fiber fly ash concrete. In this paper, hybrid fiber concrete was selected to study the effect of fly ash content and sulfate attack age on the basic mechanical properties and pore structure of concrete. The corrosion failure state under different fly ash content and different sulfate attack age was observed, the changes of macro mechanical properties (compressive strength, splitting tensile strength, wave velocity, mass loss) of concrete were analyzed, the pore distribution in concrete was measured by air-void structure tester, and the sulfate attack damage model was established based on each evaluation index, it provides theoretical and experimental research basis for the studies of sulfate resistance of hybrid fiber fly ash concrete in saline area.

2. Experimental program

2.1. Raw materials and mix proportion

The ordinary Portland cement (P.O. 42.5) and Fly ash (0%, 10%, 20% replacement) were used in this study. The loss on ignition of cement is 2.53%. The chemical compositions are shown in table 1. Crushed stone was used as a coarse aggregate and a continuous gradation of 5–15 mm. Natural medium sand with fineness modulus of 2.3 was selected as fine aggregate. The Basalt fiber with the length of 6 mm was added by volume ratios of 0.1%, the Polypropylene fiber with the length of 12 mm was added by volume ratios of 0.2%. The size of basalt fiber and polypropylene fiber are shown in figure 1. The laboratory tap water was used as test water. Sodium sulfate is a white crystal with density of 2.68 g cm$^{-3}$. According to the Chinese code (JG) 55–2011 [30], after considering

![Figure 1. Size of basalt fiber and polypropylene fiber.](image)

| Compositions | Al$_2$O$_3$ | SiO$_2$ | CaO | Fe$_2$O$_3$ | SO$_3$ | MgO | Na$_2$O | K$_2$O |
|--------------|------------|--------|-----|-----------|-------|-----|--------|-------|
| Cement       | 6.5        | 19.6   | 66.3| 3.5       | 2.5   | 0.7 | 0.6    | 0.3   |
| Fly ash      | 33.51      | 45.40  | 3.15| 5.28      | 0.45  | 0.06| 2.62   | 3.88  |
the strength, workability and other factors, the final mix proportion of concrete was determined as 350:1196:644:210, the water binder ratio is 0.6. The size of specimens was designed to be 100 mm × 100 mm × 100 mm.

2.2. Method of making concrete specimens

(1) Clean molds were chosen, engine oil was evenly brushed with in the mold for later demoulding, and small pieces of paper were placed at the bottom hole of the mold to prevent slurry leakage.

(2) The forced mixer was used for mixing to ensure uniformity. First, the sand and crushed stones were evenly mixed in the mixer for 30 s, and then the weighed fly ash, cement and fiber were evenly scattered into the mixer for 30 s. Finally, the weighed water was added and stirred for 60 s before discharging.

(3) The concrete was poured into the mold after discharging, the shovel was used to move evenly around the mold to ensure the compactness, finally, the specimens were put on the shaking table to vibrate. When there are no bubbles on the surface, the vibration ends.

(4) The completed specimens were cured for 24 h, then the specimens were demoulded and numbered, those were put into the saturated Ca(OH)₂ solution at 20 ± 2 °C for curing.

2.3. Test methods

2.3.1. Sulfate attack test

The test method for resistance of concrete to sulfate attack was followed the Chinese GB/T50082–2009. [31]. Currently, researchers mostly have used temperature-rising methods for drying to accelerate dry-wet cycle tests, but high-temperature drying has a greater impact on the deterioration of concrete and corrosion products. Therefore, a natural soaking method was used at room temperature in this study. Sulfate attack test was carried out with 5% sodium sulfate solution, investigating the differences of sulfate attack resistance of hybrid fiber fly ash concrete with different fly ash content and attack ages, so as to obtain better applications in the practical engineering. Because the control test was required, both specimens for the sulfate attack test and specimens for comparison in the same period soaked in clean water should be considered during the production of the specimens.

2.3.2. Ultrasonic test

After the age of sulfate attack was reached, the specimens were taken out, and the NM-4A non-metallic acoustic detector was used to measure the ultrasonic wave velocity. The ultrasonic frequency was 50 kHz, the emission voltage was 500 V, and the sampling period was 0.4 μs.

Test methods: Interface of the detector was connected in sequence, then Vaseline was smeared evenly on the test points, three concrete specimens in each group, three pairs of test points were taken in each specimen, and \( t_i \) represents test time. As there are three groups of aspecimens, three pairs of test points in each group, and there are nine groups of data in total, the average value method was used as the time of wave passing through the specimen, and the calculation of this equation can be expressed as equation (1).

\[
\bar{t} = \frac{1}{9} \sum_{i=1}^{9} t_i
\]

(1)

Where \( \bar{t} \) is the average time, s, \( t_i \) is the time measured at each measuring point, s.

2.3.3. Strength test

When the age of sulfate attack was reached, the concrete specimens were taken out from the solution and dried at room temperature. According to the Chinese GB/T50081-2019. [32], the compressive strength and splitting tensile strength tests of concrete were carried out with CSS-YAN3000 press, and the loading rate are 3 mm min⁻¹ and 1 mm min⁻¹ respectively. Each group has three specimens for strength tests, and the average value of the results was taken.

2.3.4. Air-void structure test

The experimental processes of air-void structure of hybrid fiber fly ash concrete are as follows:

(1) The concrete cube specimens of 100 mm × 100 mm × 100 mm were cut into pieces with 20 mm thick. In order to avoid cutting surface smooth, the specimens should be fixed with fixed facilities when cutting, and the cutting speed should be controlled.
After cutting, the concrete pieces were put on the grinding and polishing machine, then coarse grinding, fine grinding and polishing were carried out by using diamond grinding discs with various precisions respectively. Each step lasted for about 30 min until the surface of the pieces could achieve the effect of mirror.

After grinding, the specimens should be clean and dry, the surface of concrete pieces was blackened evenly with black ink, then the pieces were dried in the oven for 24 h, the temperature of the oven was set at 105 °C. Afterwards, the voids were filled with barium sulfate powder, the excess powder was removed before measuring.

The TR-AHS type hardened concrete air-void structure tester was used to measure the specimens, the test results should be recorded and saved.

The specific test procedures are as follows, as shown in figure 2.

3. Results and discussion

3.1. Morphological changes under sulfate attack

The damage morphology can directly analyze the performance changes of concrete under sulfate attack. Figure 3 shows the top view of cube specimens with 0%, 10% and 20% fly ash respectively after 90, 120 and 150 days of submersion in sodium sulfate solution.

In the first 90 days under sulfate attack, the concrete specimens with 0% and 20% fly ash began to appear pores, the edges and corners began to peel off, and micro cracks appeared. However, the surface scaling of specimens with 10% fly ash was little serious. At 120 d, the pores of the concrete specimens with 0% and 20% fly ash content increased, and the corners and edges obviously delaminated, accompanied by extensive cracks. The internal aggregates of the specimens were exposed, the concrete specimens with 10% fly ash content began to peel off, and micro cracks appeared. After 150 days of sulfate attack, the damage continued to increase in severity, all corners and edges were clearly visible. The deterioration was observed on the exterior surface of the specimens, exterior surfaces started to appear frost phenomenon. The reason for this phenomenon is that under sulfate attack, the corrosive products produced by the hydration reaction of sulfate ions and cement made the surface scaling, and a large amount of sulfate accumulated in the concrete, the sulfate crystals precipitated after water evaporating [33–35].

3.2. Physical and mechanical properties under sulfate attack

In order to directly reflect the mass loss, strength changes and internal structure damage of hybrid fiber fly ash concrete specimens under sulfate attack, the physical and mechanical properties such as mass loss rate, relative wave velocity, relative compressive strength and relative splitting tensile strength are introduced as evaluation indexes. The test data is shown in table 2. The equation can be calculated as (2), (3), (4) and (5).

\[ \omega = \frac{(m_0 - m_t)}{m_0} \]  \hspace{1cm} (2)

\[ v_t = \frac{v_t}{v_0} \]  \hspace{1cm} (3)
Where $\omega$ is the mass loss rate (\%), $m_0$ and $m_n$ are the initial mass and the mass of the specimens after $n$ days under sulfate attack respectively (g). $v_r$, $v_0$, $v_n$ are the relative wave velocity, initial wave velocity and wave velocity after $n$ days under sulfate attack respectively (m/s). $f_{cr}$, $f_{c0}$, $f_{cn}$ are the relative compressive strength, the compressive strength before and after $n$ days under sulfate attack respectively (MPa). $f_{st}$, $f_{sto}$, $f_{stn}$ are the relative splitting tensile strength, the splitting tensile strength before and after $n$ days under sulfate attack respectively (MPa).

The relationships among the mass loss rate, relative wave velocity, relative compressive strength, relative splitting tensile strength of hybrid fiber fly ash concrete specimens after sulfate attack and the ages under sulfate attack are obtained according to equations (2)–(5), as shown in figures 4–7.

According to figures 4–7, The mass loss rate, relative wave velocity, relative compressive strength and relative splitting tensile strength under different sulfate attack ages accord with the following rules:

- The mass loss rate increased first and then decreased with the increase of sulfate attack age. Under different fly ash content, the...
change law of mass loss rate is similar with the increase of sulfate attack ages. Under the same sulfate attack age, the mass loss rate is relatively small with 10% fly ash. (2) The relative wave velocity increased first and then decreased with the increase of sulfate attack ages. Under the same sulfate attack age, the relative wave velocity is the largest with 10% fly ash. (3) With different content of fly ash, the relative compressive strength and relative splitting tensile strength increased first and then they began to decline with the increase of sulfate attack ages. Under the same sulfate attack age, the declining speed of relative compressive strength and relative tensile strength is the slowest with 10% fly ash. This is because a large amount of sulfate ions in the solution slowly intruded into the concrete and reacted with the concrete composition materials to form such as gypsum and ettringite, which are adhered to the interior of concrete specimen, resulting in the increase of the mass of the concrete specimens [36]. At the same time, because of the filling effect of fly ash, C-S-H gel and other products can be generated by physical and chemical reactions, which can enhance the internal cohesive force of concrete, reduce the porosity of concrete, increase the compactness and the corrosion resistance to sulfate attack [37]. However, with the continuous attack, sulfate ions continue to invade into the concrete, the growth of crystals, causing the ultimate tensile stress of concrete materials being smaller than the internal crystallization pressures.

![Figure 4. Variation trends of mass loss rate under different sulfate attack ages.](image)

### Table 2. Test data under different sulfate attack ages.

| Specimen number | Mass before sulfate attack (g) | Mass after sulfate attack (g) | Wave velocity before sulfate attack (m s⁻¹) | Wave velocity after sulfate attack (m s⁻¹) | Compressive strength (MPa) | Splitting strength (MPa) |
|-----------------|-------------------------------|-------------------------------|--------------------------------------------|------------------------------------------|---------------------------|--------------------------|
| FA0-D0          | 2381                          | 2381                          | 4526.9                                     | 4526.9                                   | 32.1                      | 4.60                     |
| FA0-D30         | 2362                          | 2404                          | 4705.9                                     | 4891.4                                   | 33.5                      | 4.73                     |
| FA0-D60         | 2356                          | 2390                          | 4657.7                                     | 4369.3                                   | 29.6                      | 4.45                     |
| FA0-D90         | 2372                          | 2396                          | 4500.5                                     | 4070.0                                   | 24.8                      | 4.41                     |
| FA0-D120        | 2391                          | 2400                          | 4748.3                                     | 4184.1                                   | 21.4                      | 4.38                     |
| FA0-D150        | 2354                          | 2360                          | 4970.2                                     | 4291.8                                   | 20.3                      | 4.21                     |
| FA10-D0         | 2368                          | 2368                          | 4728.1                                     | 4728.1                                   | 39.2                      | 4.88                     |
| FA10-D30        | 2377                          | 2412                          | 4777.8                                     | 5232.9                                   | 41.1                      | 5.25                     |
| FA10-D60        | 2394                          | 2417                          | 4576.7                                     | 4870.9                                   | 36.5                      | 4.76                     |
| FA10-D90        | 2364                          | 2384                          | 4438.5                                     | 4492.4                                   | 35.2                      | 4.58                     |
| FA10-D120       | 2422                          | 2428                          | 4666.4                                     | 4357.3                                   | 34.7                      | 4.44                     |
| FA10-D150       | 2376                          | 2379                          | 4629.6                                     | 4196.4                                   | 30.4                      | 4.28                     |
| FA20-D0         | 2433                          | 2433                          | 4668.5                                     | 4668.5                                   | 34.7                      | 4.82                     |
| FA20-D30        | 2340                          | 2378                          | 4717.0                                     | 5089.1                                   | 38.8                      | 5.16                     |
| FA20-D60        | 2378                          | 2403                          | 4955.4                                     | 5010.0                                   | 33.1                      | 4.63                     |
| FA20-D90        | 2369                          | 2390                          | 4849.7                                     | 4490.3                                   | 30.0                      | 4.52                     |
| FA20-D120       | 2409                          | 2316                          | 4730.4                                     | 4194.6                                   | 26.7                      | 4.40                     |
| FA20-D150       | 2412                          | 2417                          | 4935.8                                     | 4364.9                                   | 22.3                      | 4.26                     |
the internal structure of concrete being destroyed [38], and the mass, the relative wave velocity, the relative compressive strength and relative splitting tensile strength all decreasing.

### 3.3. Changes of air-void structure under sulfate attack

The air-void structure of hybrid fiber fly ash concrete specimens with different sulfate attack ages was scanned and analyzed by using the hardened concrete air-void structure tester. The trend of air content and chord length frequency at different sulfate attack ages is shown in figure 8.

It can be seen from figure 8 that with the same fly ash content, the air content at 0.50 ~ 1.0 mm chord length first decreased and then increased with the sulfate attack ages. When the attack age is 30 days, the air content of fly ash content of 0%, 10%, and 20% are all reduced to the minimum. Without sulfate attack, the air content of concrete without fly ash is more than 40% at 0.50 ~ 1.0 mm chord length compared to the air content of concrete with fly ash. After 150 days under sulfate attack, the air content of concrete without fly ash is more than 90% at 0.50 ~ 1.0 mm chord length, while the air content of concrete with fly ash is less than 70% at 0.50 ~ 1.0 mm chord length.

With the same content of fly ash, the number of pores at 0 ~ 0.01 mm chord length increased first and then decreased with the sulfate attack. After 30 days under sulfate attack, the number of pores at 0 ~ 0.01 mm chord length

![Figure 5. Variation trends of relative wave velocity under different sulfate attack ages.](image)

![Figure 6. Variation trends of relative compressive strength under different sulfate attack ages.](image)
When sulfate attack exceeds 60 days, the number of pores in concrete decreased at 0 \sim 0.01 mm chord length, and increased at 0.50 \sim 1.0 mm chord length. That is to say, the number of pores with smaller chord length decreased, and the growing number of pores with longer chord length led to the increasing air content. Without sulfate attack, when the fly ash content is 0%, the air-void frequency at 0 \sim 0.01 mm chord length is less than 0.5, the air-void frequency at 0.5 \sim 1.0 mm chord length is more than 0.1. Compared to the fly ash with 0% content, the air-void frequency at 0 \sim 0.01 mm chord length of fly ash with 10% content is higher, and exceeds 0.5, while the air-void frequency at 0.5 \sim 1.0 mm chord length is smaller and less than 0.1. This is because there are certain cracks and damage in the mixing process of concrete specimens. With the increasing of attack time, the cracks and damage further expanded, and the air content gradually increased. The addition of fly ash can fill the large voids, compact the internal structure of concrete, delay the damage, and improve the sulfate attack resistance of concrete specimens [37, 39].

According to the air-void structure tests, four air-void structure parameters of hybrid fiber fly ash concrete were measured, which are air content, air-void spacing factor, air-void average chord length and air-void specific surface area. The air content is the percentage of pore volume in the whole specimen volume. The spacing factor is the farthest distance between any selected point in the specimens and any pore spherical surface adjacent to it [40]. The average chord length is the ratio of the total chord length to the total number of pores in the specimen [41]. Specific surface area is the surface area of per unit volume pores of concrete specimen [42].

The air-void structure parameters under different sulfate attack ages are shown in figure 9. It can be seen from figure 9 that with the increase of sulfate attack ages, the air content, spacing factor and air-void average chord length of hybrid fiber fly ash concrete first decreased and then increased, while the specific surface area of pores performed opposite trend. Compared with no fly ash, the replacement of 10% or 20% fly ash content could refine the pore structure and reduce porosity [43]. Adding suitable fly ash could make the internal structure of concrete more compact, reduce the internal crystallization pressure caused by sulfate attack, further reduce the attack damage. When fly ash is excessive, the internal cement of concrete decreased, the adding of fly ash is not enough to make up for the strength loss caused by the lack of cement. At this time, the resistance to sulfate attack was weakened [44].

With the increase of attack time, the air content, average chord length and spacing factor of the pores increased in varying degrees, and the correlation is significant, but the specific surface area decreased continuously. This is because with the progress of sulfate attack, a large number of sulfate ions in the solution invaded into the concrete structure, resulting in the crystallization phenomenon and the formation of sulfate with crystal water, large crystallization pressures and expansion stress were generated, the internal pore diameter of concrete became larger, the number of harmful and more harmful pores increased, the number of harmless and less harmful pores decreased, and the internal structure of concrete was damaged [45].

3.4. Fractal dimension
Fractal dimension is an important mean to quantitatively describe the complexity of air-void structure in concrete. In order to study the air-void structure characteristics of concrete, it is necessary to establish an appropriate fractal model and obtain the corresponding fractal dimension by calculating the fractal model. Li

![Figure 7. Variation trends of relative splitting tensile strength under different sulfate attack ages.](image-url)
et al [46] studied the pore structure characteristics of hybrid fiber concrete by fractal theory, and confirmed that its pore structure surface has obvious fractal characteristics. TR-AHS type hardened concrete air-void structure tester was used to establish a more accurate fractal model of pore diameter distribution by box-counting dimension [47–49]. The box counting dimension \( d \) can be calculated by equation (6)

\[
d = -\lim_{r \to 0} \frac{\log N_r(A)}{\log r}
\]

(6)

The number of boxes \( (N_r(A)) \) covering \( A \) with different \( r \) values can be calculated, and then the slope of the fitting curve in the double logarithmic coordinate system with \( \log r \) as the abscissa and \( \log N_r(A) \) as the ordinate was obtained by the least square linear regression method. This slope is the box-counting dimension (fractal dimension).

Figure 10 shows the box dimension method used to analyze the air-void structure data measured by TR-AHS hardened concrete air-void structure tester, and the relationship between sulfate attack ages and fractal
With the increase of attack ages, the fractal dimension of three groups of fly ash content concrete specimens all increased to the maximum after 30 days, and then gradually decreased, which is consistent with the above macro physical and mechanical properties analysis, indicating that the fractal dimension analysis of sulfate attack of concrete specimens is available.

**Figure 9.** Variation trend of air–void structure parameters under different sulfate attack ages.

**Figure 10.** Relationship between fractal dimension and sulfate attack ages.

dimension can be obtained. With the increase of attack ages, the fractal dimension of three groups of fly ash content concrete specimens all increased to the maximum after 30 days, and then gradually decreased, which is consistent with the above macro physical and mechanical properties analysis, indicating that the fractal dimension analysis of sulfate attack of concrete specimens is available.
The fractal dimension can reflect the complexity of the air-void structure of concrete to some extent. The larger the fractal dimension is, the more complex the air-void structure is, the smaller the number of large pores is. In contrast, the smaller the fractal dimension is, the simpler the air-void structure is, the more the number of large pores is. The fractal dimension gradually increases to the maximum in the process of 0 days to 30 days, the reason is that the products of hydration reaction in the early stage of concrete specimen were filled in the concrete, and the fractal dimension of concrete with fly ash is higher than that of concrete without fly ash. At the same time, a series of physical and chemical reactions among fly ash, Ca(OH)$_2$ and water in cement occurred, which made the internal structure of concrete filled, the porosity decreased. Therefore, the fractal dimension of concrete with fly ash is higher. After 30 days, the fractal dimension gradually decreased. This is because with the increase of attack time, more and more sulfate ions in the solution invaded into the concrete, resulting in a large amount of crystallization pressures and expansion stress. The small pores were connected and broken, the large pores were gradually formed and the number of large pores gradually increased, resulting in the pore structure deteriorated [50]. Therefore, fractal dimension of air-void structure can well describe the development of internal pore structure of concrete under sulfate attack environment. The results agreed with the findings of the previous study [50].

3.5. Establishment of damage model under sulfate attack

3.5.1. Damage model of sulfate attack based on each evaluation index

According to the relationship between ultrasonic velocity and dynamic elastic modulus of concrete materials [32], the relative dynamic elastic modulus of hybrid fiber fly ash concrete specimen can be obtained by equation (7). At the same time, the test showed that with the increase of attack age, the mechanical properties of hybrid fiber fly ash concrete changed, and the changes of macro properties can indirectly reflect the internal damage degree of concrete materials. In order to quantitatively reflect the change law of mechanical properties of hybrid fiber fly ash concrete under sulfate attack, and comprehensively evaluate the change state of concrete, the relative dynamic elastic modulus and relative compressive strength are selected as damage variables by using damage mechanics [22, 51], so the damage caused by sulfate attack can be calculated by equations (8) and (9).

$$E_r = \frac{E_n}{E_0} = \frac{V_n^2}{V_0^2}$$

(7)

Where $n$ is sulfate attack time. $E_i$ is the relative dynamic elastic modulus after $n$ days sulfate attack. $E_n$ and $E_0$ are respectively after $n$ days of sulfate attack and initial dynamic elastic modulus (N m$^{-1}$). $V_n$ and $V_0$ are respectively after $n$ days of sulfate attack and initial ultrasonic velocity (m s$^{-1}$).

According to the macro damage mechanics, the damage deterioration of hybrid fiber fly ash concrete after sulfate attack can be evaluated by the damage values $D_v$ and $D_c$.

$$D_v = 1 - E_r$$

(8)

$$D_c = 1 - f_{cr}$$

(9)

Where $D_v$ and $D_c$ are sulfate attack damage variables corresponding to relative dynamic elastic modulus and relative compressive strength respectively.
As shown in figure 11, the sulfate attack damage variables corresponding to the relative dynamic elastic modulus and relative compressive strength calculated by equations (8) and (9) increased continuously with the increasing of sulfate attack time. The results indicated that the damage and deterioration rate of the concrete with fly ash was obviously less than that without fly ash, and the deterioration rate of the concrete with 10% fly ash is slower.

According to figure 11, the correlation coefficient of the fitting formula between the sulfate attack damage variables and the sulfate attack time is high, which can better reflect the damage evolution law of the hybrid fiber fly ash concrete specimen with time under the sulfate attack. The relationship between sulfate attack damage of each performance index and sulfate attack time is subjected to exponential function. The fitting formula can be obtained by equation (10).

\[ D_t = a_1 + b_1 e^{c_1 n} \]  

(10)

Where \( n \) is the sulfate attack time. \( a_1, b_1 \) and \( c_1 \) are the coefficients in the fitting formula.

As shown in figure 12, the sulfate attack damage variables corresponding to the relative dynamic elastic modulus and relative compressive strength calculated by equations (8) and (9) increased continuously with the increasing of sulfate attack time. The results indicated that the damage and deterioration rate of the concrete with fly ash was obviously less than that without fly ash, and the deterioration rate of the concrete with 10% fly ash is slower.

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\[ D_t = a_1 + b_1 e^{c_1 n} \]  

(10)

Where \( n \) is the sulfate attack time. \( a_1, b_1 \) and \( c_1 \) are the coefficients in the fitting formula.

Considering that compressive strength is commonly used to evaluate the mechanical properties of concrete in practical engineering, the relationship between the sulfate attack damage variables \( D_v \) and \( D_c \) was established. As shown in figure 12, \( D_v \) and \( D_c \) have the well relationship of exponential function, and the function
relationship can be obtained by equation (11). Therefore, the wave velocity of non-destructive testing can be used to predict the strength performance and damage of hybrid fiber fly ash concrete structure.

\[ D_v = a_2 + b_2 e^{c_2 D_v} \]  

(11)

Where \(a_2, b_2\) and \(c_2\) are the coefficients in the fitting formula.

3.5.2. Prediction model of sulfate attack damage based on fractal dimension and fly ash content

The meso-structure changes of concrete materials can reflect its overall performance, and the meso-structure is associated with macroscopic properties of concrete, hence it can describe the development of internal defects of concrete.

According to the analysis in the above section, the fractal dimension can quantitatively describe the complexity of the air-void structure under sulfate attack, and the damage variable can evaluate the corrosion resistance of concrete with different fly ash content. In order to better study the relationship among the air-void structure, the effect of fly ash and sulfate attack damage of hybrid fiber fly ash concrete, the prediction model of sulfate attack damage based on fractal dimension and fly ash content was presented in this study. It provides an important role for the durability of concrete to evaluate the sulfate attack resistance of concrete through the damage prediction of concrete materials.

The scatter diagram of fly ash content, damage value and the fractal dimension of hybrid fiber fly ash concrete specimen, and the sulfate attack damage model based on regression analysis are shown in figure 13. The mathematical model of sulfate attack damage is shown in equation (12). The correlation coefficient of data regression analysis is 0.938, and the fitting coefficient is high, which indicates that this model can be used to predict the quantitative relation among sulfate attack damage, air-void structure and fly ash content of hybrid fiber fly ash concrete after sulfate attack, so as to evaluate the sulfate attack resistance durability of hybrid fiber fly ash concrete.

\[ z = 47.084 - 52.037x + 0.139y + 14354x^2 - 0.00105y^2 - 0.0653xy \]

\[ R^2 = 0.938 \]  

(12)

4. Conclusions

In this paper, the sulfate resistance of hybrid fiber concrete with different fly ash content at different ages was studied, and macro mechanical properties of concrete were evaluated by mass loss, wave velocity and strength changes. The pore structure characteristics were evaluated by pore structure parameters and fractal dimension. The damage prediction model under sulfate attack was established based on the above indexes. The specific conclusions are as follows:

(1) At the same sulfate attack age, compared with other fly ash content, the hybrid fiber concrete with 10% fly ash content had the smaller mass loss, and presented the larger relative wave velocity and the stronger mechanical properties. This phenomenon is particularly obvious at 30 days of sulfate attack ages.

(2) Fly ash has a positive effect on refining the internal pores of concrete and reducing the air content, and the effect was significantly at 30 days. The fractal dimension showed a trend of decrease after an initial increase with the increasing of sulfate attack ages, and became the largest at 30 days of ages, which is similar with the changes of macro mechanical properties.

(3) The damage degradation rate of concrete with fly ash is obviously lower than that of concrete without fly ash, and the degradation rate of concrete with 10% fly ash is lower. The sulfate attack damage variables corresponding to relative dynamic elastic modulus and relative compressive strength have the exponential function relationship through data regression, and correlation coefficient was above 0.9, concrete containing 10% fly ash content was 0.962. The sulfate attack damage model was established based on fractal dimension and fly ash content, which can quantitatively predict the sulfate resistance of hybrid fiber fly ash concrete.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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