Research on the Sulfate-resistant Chemical Attack Mechanism of Concrete with Mineral Admixture

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Abstract. Durability is the most important factor for evaluating the service life of concrete, and the chemical attack of sulfate is an important factor affecting the durability of concrete. In this paper, fly ash, slag, metakaolin and silica fume were used as mineral admixtures to explore their impact on sulfate chemical attack, and the chemical attack mechanism of sulphate was deeply analyzed, the results showed that: the incorporation of fly ash, slag, and silica fume effectively improves the sulfate-resistant chemical attack capacity of concrete. The concrete was chemically attacked 30d in sulfate solution, which will increased its compressive strength and quality, it was mainly due to the secondary hydration reaction of fly ash and slag, part Ca(OH)2 reacted with Na2SO4 solution to generate gypsum and ettringite, and made the internal structure of concrete more compact. As the age of sulfate chemical attack increases, the ettringite expands with water, and causes concrete to be expanded or peeled. Silica fume mainly provides more active SiO2 for the secondary hydration reaction, consumes more Ca(OH)2, and reduces the formation of ettringite.

Keywords: Sulfate; chemical attack; concrete; chemical attack mechanism; ettringite.

1. Introduction
The strength and durability of concrete are the most basic indicators for studying concrete; durability determines the service life of concrete, therefore, the durability of concrete more and more valued by researchers [1-4]. Both the marine environment and the saline soil environment in the west contain a large number of sulfate ions, and the chemical attack process of sulfate is the most destructive and complicated attack mechanism in concrete durability [5-8]. Yin et al. [9] established the diffusion reaction model of sulfate ions in concrete based on Fick's law and chemical reaction kinetics, the chemical damage extent caused by sulfate chemical attack presented the gradient distribution from concrete surface to interior. Liu et al. [10] studied the influence of sulfate concentration on strength and microscopic properties of concrete, the study found that the compressive strength of concrete and sulfate concentration presented functional relationship of Pearson IV, and the main hydration products were ettringite and gypsum when sulfate chemical attacked cement concrete.

There are many factors that affect the sulfate chemical attack, including mineral admixtures, the concentration of sulfate chemical attack fluid and the corrosive environment and so on [11-13]. Skaropoulou et al. [14] found that the incorporation of natural volcanic ash materials can improve
sulfate-resistant chemical attack property of concrete. Adriana et al. [15] studied the difference between artificial sulfate and biological sulfate on concrete attack, under the action of two kinds of sulfate chemical attack, the main leaching elements of concrete were quite different, the chemical attack of biological sulfate caused the production of new compounds on the concrete surface to be more significant than chemical attack of chemical sulfate. Nehdi et al. [16] found that the incorporation of silica fume also effectively improved the sulfate-resistant chemical attack property of concrete. At present, there are many studies on the sulfate chemical attack mechanism of ordinary concrete; however, the chemical composition and volcanic ash activity of mineral admixtures are different from cement, therefore, it is necessary to conduct in-depth study on the sulfate chemical attack capacity and chemical attack mechanism of large-volume mineral admixtures. In this paper, fly ash, slag, metakaolin and silica fume were used as mineral admixtures to explore their influence on sulfate chemical attack, and chemical attack mechanism sulfate was deeply analyzed.

2. Test Materials and Methods

2.1. Test raw materials and mix proportion

The cementitious materials used in the test include P.O. 42.5 ordinary silicate cement, Class F fly ash, slag and silica fume. The main chemical components of each cementitious material tested by X-ray fluorescence spectrometer are shown in Table.1. Fine aggregate uses standard sand, its fineness modulus is 2.7; coarse aggregate uses ordinary crushed stone, and the particle size distribution uses 5-10mm and 10-20mm continuous distribution crushed stone, and the incorporation ratio of the two crushed stones is 3:7. The chemical reagents selected sodium sulfate analytical pure of Sinopharm Chemical Reagent Co., Ltd, and the sodium sulfate content is not less than 99%. The mixing proportion of all concrete in this paper is 0.34, the incorporation amount of water reducing agent is 0.5%, the incorporation amount of fly ash and slag is 10%, 20%, 30%, 40%, 50% and 60%, and the incorporation amount of silica fume is 10%, and the specific mix proportion is shown in Table 2.

| Materials | SiO₂ | Al₂O₃ | CaO | Fe₂O₃ | SO₃ | MgO | Na₂O | LOI |
|-----------|------|-------|-----|-------|-----|-----|------|-----|
| SiO₂      | 20.09| 6.15  | 62.13| 2.78  | 3.27| 1.10| 0.12 | 4.36|
| Al₂O₃     | 29.79| 52.03 | 7.10 | 1.96  | 0.07| 0.21| 0.46 | 8.38|
| CaO       | 31.29| 15.03 | 37.43| 0.29  | 2.27| 10.51| 0.42 | 2.76|
| Fe₂O₃     | 94.2 | 0.64  | 0.40 | 0.10  | 0.10| 0.36 | 0.56 | 3.64|

Table 2. Mix proportions of concrete kg/m³

| No. | Cement | Fly ash | Slag | Silica fume | Coarse aggregates | Fine aggregates | Water |
|-----|--------|---------|------|-------------|-------------------|----------------|-------|
| C   | 550    | —       | —    | —           | 967               | 575            | 187   |
| FA-10 | 495  | 55      | —    | —           | 967               | 575            | 187   |
| FA-20 | 440  | 110     | —    | —           | 967               | 575            | 187   |
| FA-30 | 385  | 165     | —    | —           | 967               | 575            | 187   |
| FA-40 | 330  | 220     | —    | —           | 967               | 575            | 187   |
| FA-50 | 275  | 275     | —    | —           | 967               | 575            | 187   |
| FA-60 | 220  | 330     | —    | —           | 967               | 575            | 187   |
| S-10 | 495   | —       | 55   | —           | 967               | 575            | 187   |
| S-20 | 440   | —       | 110  | —           | 967               | 575            | 187   |
| S-30 | 385   | —       | 165  | —           | 967               | 575            | 187   |
| S-40 | 330   | —       | 220  | —           | 967               | 575            | 187   |
| S-50 | 275   | —       | 275  | —           | 967               | 575            | 187   |
| S-60 | 220   | —       | 330  | —           | 967               | 575            | 187   |
| FA-SF | 220  | 275     | —    | 55          | 967               | 575            | 187   |
| S-SF | 220   | —       | 275  | 55          | 967               | 575            | 187   |
2.2. Sample preparation and test method

According to the specifications of "Long-term Properties and Durability of Ordinary Concrete" (GB/T50082-2009), after the cementitious material, fine aggregate and coarse aggregate were mixed evenly, water and water reducer were poured to mix and stir for five minutes. The fresh concrete was put into the 100mm*100mm*100mm mold, and vibrated 60s in shaking table, then covered with film and moved to the standard curing room (t=20±2℃, RH=95±1%) for curing 24h, and then moved to the standard curing room for curing to the test age after demolding. The compressive strength and sulfate chemical attack capacity of 28d and 90d samples were tested, respectively.

1. Compressive strength: 100mm*100mm*100mm sample was selected and used in the compressive strength test, and the YAM-500 press was used for testing, the loading speed is 0.5MPa/s. The compressive strength value selected and used the average value of three test blocks.

2. Sulfate chemical attack test: sulfate was immersed in natural way, the samples which were cured to 28d age were put into the plastic box for sulfate chemical attack test, continuously immersed for 30d and 150d, the immersion solution used 5% Na$_2$SO$_4$ solution, the Na$_2$SO$_4$ chemical attack solution was replaced every 30d. Each group of the same sample continued to be cured for 30d and 150d in the standard curing room, the compressive and attack-resistant coefficient K and the mass loss rate ΔW as the measurement criteria. The calculation of K is shown in formula 1:

$$K = \frac{f_s}{f_0} \times 100\%$$

In the formula: $f_s$ represent the compressive strength value/MPa after sulfate chemical attack; $f_0$ represent the compressive strength value /MPa of the standard curing sample.

Mass loss rate $\Delta W$: $\Delta W = (W_0 - W_t)/W_0 \times 100\%$ (2)

In the formula: $W_0$ and $W_t$ represent the mass before and after the chemical attack, respectively.

3. Results and Discussion

3.1. Compressive strength

Compressive strength is the most intuitive and direct index to measure concrete[17]. Fig.1 is the compressive strength value of each sample; Fig.1 (a) is the content factor of fly ash, it can be clearly seen that as the content of fly ash increases, the compressive strength of both 28d and 90d decreases. Compared with the fly ash with 0% content, the 28d compressive strength of fly ash with 10%, 20%, 30%, 40%, 50% and 60% content decreased by 3.02%, 8.85%, 11.07%, 16.10%, 22.93% and 27.16%, respectively; its 90d compressive strength decreased by 0.34%, 2.74%, 7.19%, 10.79%, 12.33% and 15.58%, respectively. Fig.1(b) is the slag content factor, when the slag content is 10% or 20%, its 28d or 90d compressive strength value is greater than that of the concrete sample without slag; when the slag content is greater than 20%, the compressive strength value of concrete increases with the increase of slag content. Compared with the slag sample with 0% content, the 28d compressive strength of slag with 10%, 20%, 30%, 40%, 50% and 60% content decreased by -2.82%, 0.80%, 6.84%, 11.07 %, 15.69% and 20.12%, respectively, and the 90d compressive strength decreased by -6.85%, -2.06%, 1.88%, 3.60%, 8.05% and 10.79%, respectively. It can be found by contrast that the compressive strength value of the fly ash or slag increased faster in the later period. Fig.1(c) is the incorporation of silica fume factor, it can be clearly seen that 28d and 90d compressive strength values increased after 10% silica fume was incorporated.
3.2. Sulfate-resistant chemical attack

The secondary hydration reaction time of large-volume mineral admixtures is longer in concrete; therefore, its strength and quality changes in 5% Na$_2$SO$_4$ chemical solution are different from cement concrete [18]. Fig.2 is the compressive and attack-resistant coefficient values of concrete after attacked 30d and 150d by Na$_2$SO$_4$. Fig.2(a) shows the factor of fly ash content, it can be clearly seen that with the increase of fly ash content, the compressive and attack-resistant coefficient value of concrete after chemically attacked 30d by sulfate shows an increasing trend, and all the compressive and attack-resistant coefficient values are greater than 1, it shows that the compressive strength value of concrete increases when the sulfate chemical attack is 30d. When the sulfate is chemically attacked 150d, the compressive and attack-resistant coefficient values of all concrete are less than 1, it shows that chemical attack loss occurs in the compressive strength value, but the damage degree of sulfate chemical attack of concrete decreases with the increase of fly ash content, namely the concrete which was incorporated with fly ash has stronger sulfate-resistant chemical attack capacity. The slag content factor in Fig.2(b), whose change law is similar to fly ash, with the increase of slag content, and sulfate-resistant chemical attack capacity of concrete is stronger. By contrasting fly ash concrete and slag concrete with the same content, sulfate-resistant chemical attack capacity with slag is stronger. Fig.2(c) is the factor of incorporating silica fume, under the same mineral admixture conditions; the incorporation of 10% silica fume can significantly improve the sulfate-resistant chemical attack effect.

Fig.3 is the change law of concrete mass loss rate under the sulfate chemical attack effect, Fig.3(a) is the factor of fly ash content, Fig.3(b) is the factor of slag content, it can be clearly seen that the mass of concrete increase when all concrete samples are chemically attacked 30d by sulfate, but the increase is very small; after 150d sulfate chemical attack, part concrete expanded and peeled in sulfate solution,
it caused the loss of concrete mass, and the mass loss of all samples exceeded 5%. The incorporation of fly ash or slag can reduce the mass loss of concrete, as a whole, the mass loss rate of concrete decreases with the increase of the content of fly ash or slag, but the difference is not significant on the whole. Fig.3(c) is the factor of incorporating silica fume, it can be clearly seen that the incorporation of 10% silica fume further reduces the mass loss rate of concrete. Overall, the incorporation of mineral admixtures further reduces the mass loss rate of concrete.

Fig.2 The compressive attack resistance coefficient of concrete
4. Mechanism Analysis of Sulfate Chemical Attack

The studies on mechanism of sulfate chemical attack of ordinary cement concrete were more [19, 20], mostly the chemical erosive ions reacted with cement hydration products to form ettringite, as the attack age attack increased, the ettringite expanded with water and caused cracking and peeling of concrete, thus causing the deterioration and destruction of concrete, which belongs to the process of chemical attack and destruction. However, the secondary hydration of high-volume mineral admixtures was delayed, and its sulfate chemical reaction was different from cement. The concrete sample with 28d curing age was placed in 5% Na$_2$SO$_4$ solution, owing to the incorporation of high-volume fly ash and slag, Ca(OH)$_2$ produced by cement hydration decreased and part of cement hydration product Ca(OH)$_2$ participated in the secondary hydration reaction, and another part reacted with Na$_2$SO$_4$ solution to generate gypsum and ettringite, as shown in formula 3

$$\text{Ca(OH)}_2 + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{OH}^- \tag{3}$$

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 3\text{CaSO}_4 + 26\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \tag{4}$$

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca(OH)}_2 \cdot x\text{H}_2\text{O} + 2\text{CaSO}_4 + \text{SO}_4^{2-} + (31-x)\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \tag{5}$$

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca(OH)}_2 \cdot 2\text{H}_2\text{O} + 2\text{CaSO}_4 + (32-x)\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \tag{6}$$

Of course, the generation of gypsum and ettringite depends on the SO$_4^{2-}$ concentration in the attack solution and the Ca(OH)$_2$ concentration inside the concrete, The study found that the lowest SO$_4^{2-}$ concentration for generating CaSO$_4 \cdot 2$H$_2$O was 1400mg/L. This is also the reason why the compressive strength and mass addition of the concrete samples after chemically attacked by sulfate 30d, but because the CaO content inside the slag was higher than that of fly ash, caused the content of gypsum and ettringite produced by the slag sample to be more, the ettringite did not show expansion effect when attacked 30d.

As the age of sulfate chemical attack increased, the ettringite with needle-like crystals expanded with water, caused cracking, peeling and damage of the concrete, resulting in larger compressive strength value and mass loss of concrete when the sulfate chemical attack 150d. With the progress of secondary hydration reaction of fly ash and slag, the PH value inside the concrete decreased, resulting in the decalcification reaction of the cement hydration product C-S-H gel and ettringite:

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} + 4\text{SO}_4^{2-} + 8\text{H}^+ \rightarrow 4\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{Al(OH)}_3 \cdot 12\text{H}_2\text{O} \tag{7}$$

The specific surface area of silica fume was several times that of cement, fly ash and slag and other cementitious materials, the incorporation of 10% silica fume into concrete provided active SiO$_2$ for the secondary hydration reaction and also increased consumptio of Ca(OH)$_2$, reduced the generation of ettringite and gypsum, thereby reducing the expansion or peeling of concrete; moreover, the finer silica fume acted as filling, resulting in more compact pore structure inside the concrete, and reduced circulation of sulfate inside the concrete. The incorporation of slag had a stronger sulfate-resistant chemical attack advantage than that of fly ash, the incorporation of silica fume further improved the sulfate-resistant chemical attack capacity of sulfate.
5. Conclusion
The effects of mineral admixtures: fly ash, slag and silica fume on sulfate-resistant chemical attack of concrete were analyzed in this paper, and the mechanism of sulfate chemical attack was analyzed in detail. The specific conclusion can be expressed as:

(1) The incorporation of fly ash and slag will cause the compressive strength value of 28d concrete to decrease, as the second hydration reaction progressed in the later stage, the compressive strength value of concrete increased, and the incorporation of 10% silica fume further improved the compressive strength value.

(2) The incorporation of fly ash, slag and silica fume will enhance the sulfate-resistant chemical attack capacity of sulfate, in the range of studying content, as a whole, with the increase of fly ash and slag content, the sulfate-resistant chemical attack capacity of sulfate was stronger, however, the incorporation of slag has a stronger sulfate-resistant chemical attack capacity than that of fly ash.

(3) In the early stage of sulfate chemical attack, the cement hydration product Ca(OH)$_2$ will participate in the secondary hydration reaction, thereby reducing the generation of ettringite and gypsum, with the progress of sulfate chemical attack, the ettringite with needle-like crystal expands with water, resulting in cracking, peeling and damage of concrete.

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