The Doping of Mineral Additions SF, FA and SL on Sulfate Corrosion Resistance of the HIPC Cements

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Abstract. To prepare highly durable cement concrete for marine infrastructure, the effect of silicon powder (SF), fly ash (FA) and mineral powder (SL) on sulfate corrosion resistance of the high iron and low calcium portland cement (HIPC) were studied. In this paper, a series of experiments were carried out using HIPC cements as the raw material and 20 °C, 5% Na₂SO₄ solution as the conservation environment. The effect on the sulfate resistance of the system is determined by analysing the mechanical properties of the sample and measuring the corrosion resistance coefficient K to characterize the system’s resistance to corrosion. The results show that the anti-erosion coefficient of HIPC systems with different mineral admixtures has been enhanced to varying degrees, among which the optimal amount of SF is 3%; the optimal amount of SL is 40%; the optimal amount of FA 20%.

1. Introduction
At present, cement-based materials are the most widely used building structural materials in the world. They are called “food” in the field of construction and play an important role in the national economic construction. The long-term contact of concrete with sulfate rich soil, groundwater or sea water will lead to chemical reaction between sulfate ion and hydrate in concrete, and accompany by cracking, spalling, mass loss, expansion, reduction of strength and elastic modulus of concrete [1], which will degrade the durability of concrete. For the concrete structures in service in the marine environment, the concrete in the tidal and splash areas are important parts of durability design. They not only suffer from the corrosion of sulfate in the sea water, but also are in the external environment of alternation of dry and wet for a long time, which leads to the accumulation of sulfate ion in the concrete surface [2-3], and it greatly intensifies the erosion of sulfate and makes sulfuric acid accumulate. Salt erosion is more complex and serious, which is an important factor for the durability of marine concrete to decline, so it is necessary to study some mechanical properties of concrete under sulfate erosion. Considering that the corrosion of sulfate to concrete is mainly the erosion of cementitious materials, cement mortar specimens instead of concrete specimens in the experiment, and the experimental results can provide reference and basis for concrete sulfate resistance. Cement concrete material is an elastic viscoelastic composite. The change of the proportion of each component, the difference of manufacturing technology, and the randomness of hardened concrete structure affect the properties of agglomerates. Scholars at home and abroad have conducted extensive research on sulfate corrosion of concrete by different methods. The results show that [4-7], due to the filling of mineral admixtures and the effect of secondary reaction, the compactness of cement-based materials can be improved, the pore structure can be improved, the connectivity between pores can be reduced, and the sulfate resistance of cement-based materials can be improved.
2. Experiment

2.1. Raw Materials for Experiment
The high iron and low calcium cement (HIPC) with a specific surface area of 423.50 m²/kg produced by Guangxi Yufeng cement plant, which contains 37.06 wt% C₃S, 32.86 wt% C₂S, 4.32 wt% C₃A and 15.17 wt% C₄AF. Fly ash (FA) is grade I fly ash with a specific surface area of 352.50 m²/kg; The mineral powder (SL) is provided by Wuhan Wuxin new building materials Co., Ltd. with a specific surface area of 385.19 m²/kg; The specific surface area of silicon powder (SF) is 1318.45 m²/kg. The specific ingredients of the raw materials are shown in table 1.

| Materials | Chemical substance content (%) |
|-----------|-------------------------------|
|           | CaO  | SiO₂  | Al₂O₃ | Fe₂O₃ | MgO  | K₂O  | TiO₂ | SO₃ | IL  |
| HIPC      | 58.08 | 21.20 | 4.21  | 4.99  | 1.20 | 0.54 | 0.20 | 1.75 | 1.02 |
| SF        | 0.60  | 92.86 | 0.52  | 0.02  | 0.21 | 0.56 | 0.21 | 0.32 | 0.01 |
| FA        | 5.49  | 48.67 | 23.18 | 12.33 | 0.99 | 1.67 | 2.40 | 1.70 | 2.76 |
| SL        | 40.27 | 36.77 | 16.15 | 0.30  | 8.27 | 0.58 | 0.72 | 1.82 | 1.20 |

The composite material used in the test is composed of cementitious material and quartz sand. The total mass of the cementitious material is 450 g. The quartz sand adopts ISO standard sand with a mass of 1350 g. The system has a water-to-gel ratio of 0.4. In the method of replacing cement, the amount of SL and FA is 20%, 40%, and 60%, and the amount of SF is 3%, 5%, and 8%, respectively.

2.2. Sample Forming and Curing
Before molding, wipe the 40 mm × 40 mm × 160 mm molds and apply butter evenly, and assemble tightly. Calculate and weigh the amount of various materials. Samples were made through the steps of stirring, loading, shaking, and demolding. The test block was first cured in 20 °C water for 7 days, and then cured in a Na₂SO₄ salt solution with a concentration of 5% to a specified age, and the mechanical strength test was performed immediately after removal.

2.3. Coefficient of Erosion Resistance K
The flexural strength and compressive strength of the samples were measured using a DYE-10 cement mortar flexural tester and a TSY-2000 pressure tester, respectively. The erosion resistance coefficient of the sample is expressed by the ratio of the flexural/compressive strength of the sample in the salt solution to the flexural/compressive strength of the corresponding sample in pure water.

3. Results and Analysis of the Experiment

3.1. The Effect of Different Dosages of SF on Sulfate Attack Resistance of HIPC System
As shown in figure 1, the changes of the sulfate resistance coefficient K of the HIPC system when the SF content is 3%, 5%, and 8%, respectively. The results show that: (1) The anti-corrosion coefficient of HIPC systems with different amounts of SF increased before 90 d and decreased after 90 d; (2) Before 90 d, the anti-sulfate erosion coefficient of the test specimens did not change with the increase in the amount of silica fume Large; when the curing age is greater than 90 d, the K value of the corresponding age will decrease; (3) When the SF replacement amount is 3%, the corrosion resistance coefficient at 180 d is 1.15, which is 5% compared with the SF replacement amount And 8%, and the early anti-corrosion coefficient is lower than the other two when the silica fume content is 3%, but the difference is small, so the improvement effect is 3% SF > 5% SF > 8% SF; (4) When tested When the sample immersion age is 180 d, the erosion coefficient of the SF-HIPC system is greater than 1; (5) Because the specific surface area of silica fume is small and the activity of the particles is high, the
early resistance to sulfate attack of the HIPC system can be significantly improved after incorporating silica fume.

![Figure 1](image1.png)

**Figure 1.** The change of anti-erosion coefficient of HIPC system with different dosage of SF in Na$_2$SO$_4$ solution.

### 3.2. Effect of Different Dosages of SL on Sulfate Attack Resistance of HIPC System

The change of K-corrosion resistance coefficient K of different SL-HIPC systems with curing time is shown in figure 2. The following conclusions can be drawn: (1) The sulfate resistance coefficient K of the SL-HIPC system with different dosages increases before 120 d and decreases after 120 d; (2) When the amount of SL substitution is less than 40%, the high content of the sulphate erosion resistance coefficient K of the HIPC system increases before curing for 120 days; when the SL replacement amount is greater than 40%, the sulphate erosion resistance coefficient of the high-content SL-HIPC system decreases before 120 days of curing; (3) The corrosion resistance coefficient of 40% SL-HIPC system is significantly higher than the test block with 20% and 60% dosage before 120d; after 120d, the K value is lower than the test block with 20% dosage. The overall improvement effect: 40 %SL > 20%SL > 60%SL; (4) When the immersion age is 180 d, the anti-sulfate erosion coefficient of the SL-HIPC system is greater than 1; (5) In the system, hexagonal plate-like Ca(OH)$_2$ crystals and AFt crystals intersect and grow, eventually forming an integrated cement stone, thereby improving the ability of the HIPC system to resist sulfate attack in the later stage.

![Figure 2](image2.png)

**Figure 2.** The change of anti-erosion coefficient of HIPC systems with different dosages of SL in Na$_2$SO$_4$ solution.
3.3. The Effect of Different Dosages of FA on Sulfate Attack Resistance of HIPC System

Figure 3 shows the change of the sulfate resistance coefficient K of different dosage FA-HIPC systems with curing time. We can draw the following conclusions: (1) The K value of FA-HIPC system with different dosages increased before 90d and decreased after 90 d; (2) Before curing for 60 days, the 40% FA-HIPC system has a high resistance to sulfate attack; after 60 days, the 40% FA-HIPC system has a high sulfate resistance coefficient, and the overall improvement effect: 20% FA > 40% FA > 60% FA; (3) When the immersion age is 180 days, the erosion coefficient of the FA-HIPC system is higher than 1; (4) Compared with the pure HIPC system, because of the low reactivity of FA, after incorporating FA, it can improve the resistance to sulfate attack during the whole curing process.

![Figure 3](image.png)

**Figure 3.** The Variation of anti-erosion coefficient of HIPC systems with different dosages of FA in Na₂SO₄ solution.

4. Conclusions

(1) According to the results of different dosages of SF-HIPC system in sulfate attack solution, the optimal dosage of SF is 3%. The addition of SF mainly uses the high activity of silicon powder particles to improve the resistance of early HIPC system to sulfate attack.

(2) In the experiment of anti-sulfate corrosion resistance of SF-HIPC system with different content, the optimal content of SL is 40%. Compared with pure HIPC system, Ca (OH)₂ and AFt can generate structurally stable cement stone to strengthen the system Resistance to sulfate attack.

(3) By observing the sulfate-resistance experiments of different dosages of FA-HIPC system, it can be seen that the optimal dosage of FA is 20%. Because fly ash hardly participates in the reaction in the early stage, it is beneficial to enhance the resistance of sulfuric acid in the later stage of HIPC Salt erosion performance.

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