The influence of materials parameters on chloride diffusion coefficient in concrete

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Abstract: In order to investigate the influence of materials parameters on chloride diffusion coefficient in concrete, experiments were conducted by orthogonal design and factorial design, and 15 sets of concrete specimens with different mix proportion were prepared. RCM test for each concrete specimen was performed to determine the chloride diffusion coefficient. Results show that water-to-binder ratio, replacement of mineral admixtures and the ratio of replacement of fly ash to replacement of granulated blast furnace slag have a significant influence on chloride diffusion coefficient, but the water-to-binder ratio is the most important one.

1. Introduction
In the marine environment, chloride ions will diffuse into the interior of the concrete that will cause corrosion of steel bars and result in a decrease in the bearing capacity of the concrete structure. Even it can cause the overall failure of the concrete structure[1]. Therefore, controlling the diffusion rate of chloride ions into concrete interior is particularly critical to ensure the safety of concrete structures. Usually, chloride ion diffusion coefficient is used to characterize the rate of chloride ion diffusion into concrete[2,3,4]. At present, the main methods used to test the chloride diffusion coefficient of concrete including natural immersion method, NEL method and RCM method. Among them, the RCM method has the advantages of short test cycle, simple operation, and close test results to real results, that is widely used internationally.

Researchers have carried out a large number of experimental about chloride ion diffusion coefficient of concrete basing on the RCM method. Studies have shown that curing age, water-binder ratio and mineral admixture content are the main factors affecting the chloride ion diffusion coefficient of concrete[5,6,7].

Yang Fang et al. tested the chloride diffusion coefficient of concrete with different admixtures at the age of 28 days[8]. Jiang Fuxiang et al. tested the chloride diffusion coefficient of concrete with different admixtures at 56d age[9]. Yu and Ye carried out a study on the time-varying chloride ion diffusion performance of fly ash concrete finding that the degree of hydration reaction of fly ash particles at 28d age is limited, and the filling effect of fly ash particles is dominant. The secondary hydration producing very slow, so it is not suitable to use the 28d chloride ion diffusion coefficient evaluating the chloride ion diffusion performance of fly ash concrete, and it is recommended to use 180d as the test age of the chloride ion diffusion coefficient of fly ash concrete[10]. Based on the above analysis, it can be seen that the existing research is mainly focused on the chloride diffusion coefficient of concrete at the curing age of 28d and 56d while the research on the chloride diffusion coefficient of concrete with different admixtures at the age of 28 days[8].
coefficient of concrete at the curing age of 180d is less. Because the hydration process of mineral admixtures lags behind that of cement, the action mechanism of the chloride diffusion coefficient of 180d long-curing concrete has changed due to the water-binder ratio and the content of mineral admixtures. Therefore, it is necessary to study the main influencing factors of chloride diffusion coefficient of mineral admixtures concrete for 180d long curing period.

In view of the above, based on orthogonal experimental design and cause-analysis experimental design, this paper adopts RCM method to test the chloride ion diffusion coefficient of concrete with a standard curing age of 180d, and analyzes the degree of influence of water-binder ratio, total content of mineral admixtures and proportion on the chloride ion diffusion coefficient of concrete.

2. Materials and methods

2.1 Orthogonal test and full series test

In order to study the influence of various factors in 180d concrete on the diffusion coefficient of chloride ion, the experimental scheme of orthogonal test and causal test was adopted. Three mixing ratio parameters were studied as experimental factors about water-binder ratio, total mineral admixture content, fly ash and ore powder content combination. The experimental scheme is shown in Table 1 and Table 2. There are 15 sets of concrete mix proportions are obtained that contains 3 sets of orthogonal test and the whole series of test concrete mix proportions.

2.2 Materials

Cement: PII 42.5 Portland cement produced by China Resources Cement Co., LTD. whose technical indexes are shown in Table 3. Fly ash: F type II grade fly ash performance parameters are shown in Table 4. Slag powder: Grade S95 ore powder performance parameters are shown in Table 5. Fine aggregate: river sand and medium sand that apparent density is 2514 kg/m³ that the fineness modulus is 2.42. Coarse aggregate: crushed stone apparent density is 2709 kg/m³. The particle size ranges from 5 to 25 mm with continuous grading. Admixture: Polycarboxylic acid superplasticizer with 10% solid content.

| Factors | Level | W/C A | Total mineral admixture content B% | Dosage combination \((F_A + S_G)C%\) |
|---------|-------|-------|-----------------------------------|----------------------------------|
| 1       | 0.3   | 50    | 15+X                              |
| 2       | 0.35  | 60    | X+X                              |
| 3       | 0.4   | 70    | X+15                             |

| Factors | W/C | Level | Total mineral admixture content B% | Dosage combination \((F_A + S_G)C%\) |
|---------|-----|-------|-----------------------------------|----------------------------------|
| 0.35    | 1   | 50    | 15+X                              |
| 0.35    | 2   | 60    | X+X                              |
| 0.35    | 3   | 70    | X+15                             |

| Physical properties of cement | Fineness /% | Specific surface area \(/m^2\cdot kg^{-1}\) | SO₃ /% | MgO /% | Chloridion /% | Insolubles /% | Alkali content /% | Loss |
|------------------------------|-------------|---------------------------------------------|------|-------|-------------|--------------|-----------------|------|
| 2.3                          | 379         | 2.16                                        | 1.30 | 0.016 | 0.67        | 0.29         | 2.47            |      |
Table 4 Physical properties of fly ash

| Fineness/% | Water demand ratio /% | Loss |
|-----------|-----------------------|------|
| 10.2      | 98.9                  | 3.3  |

Table 5 Physical properties of granulated blast furnace slag

| Density /g/cm³ | Specific surface area /m²·kg⁻¹ | Fluidity than /% | 7d activity index /% | 28d activity index /% | Loss |
|----------------|--------------------------------|------------------|----------------------|-----------------------|------|
| 2.92           | 432                            | 99               | 76                   | 103                   | 0.7  |

2.3 Age of preparation and curing

The concrete was prepared according to the test schemes in Table 1 and Table 2. The mixing method of concrete preparation refers to the mixing method of high-performance concrete by Professor Okamura. The concrete was formed into $\Phi100 \times 200$m cylindrical concrete specimen. After 1d the mold is removed to the standard curing room (temperature $20 \pm 3^\circ$C, humidity above 90%) for curing to 180 d. The original test piece was cut into 3 cylindrical test pieces of $\Phi100 \times 50$m for RCM rapid electromigration test.

2.4 RCM rapid chloride ion electromigration test

The RCM rapid chloride ion electromigration test is a test method for the unsteady state chloride ion rapid electromigration. The method mainly accelerates the migration of chloride ions in the concrete by applying an external electric field at both ends of the concrete specimen. The instrument used in this experiment is RCM-NTB chloride diffusion coefficient tester produced by Beijing Nerde Co., LTD. The characteristic index of this test is the average value of chloride ion diffusion coefficient measured in 3 concrete specimens of a group of mixture ratio.

3. Analysis of test results

3.1 Analysis of chloride diffusion properties

The RCM test results of 180d concrete are shown in Table 6. It can be seen from Table 6 that the 180d chloride ion diffusion coefficient of each group of concrete does not exceed $3 \times 10^{-12}$m²/s. Indicating that concrete has a good chloride ion erosion resistance performance. Moreover with the increase of curing age, the degree of secondary hydration reaction between mineral admixtures and cement hydration product CH is improved. The amount of hydration gel is increased and the microscopic pore structure inside concrete is optimized. As well as the chloride diffusion resistance of concrete is improved.

Table 6 Mix proportion and RCM test results

| Group | W/C | Fly ash content /% | Slag powder content /% | RCM test value /($\times 10^{-12}$m²/s) |
|-------|-----|--------------------|------------------------|----------------------------------------|
| 1     | 0.3 | 15                 | 35                     | 1.313                                  |
| 2     | 0.3 | 30                 | 30                     | 1.189                                  |
| 3     | 0.3 | 55                 | 15                     | 1.232                                  |
| 4     | 0.35| 25                 | 25                     | 2.495                                  |
| 5     | 0.35| 45                 | 15                     | 2.472                                  |
| 6     | 0.35| 15                 | 55                     | 2.198                                  |
| 7     | 0.4 | 35                 | 15                     | 2.807                                  |
| 8     | 0.4 | 15                 | 45                     | 2.516                                  |
| 9     | 0.4 | 35                 | 35                     | 1.276                                  |
| 10    | 0.35| 15                 | 35                     | 2.537                                  |
| 11    | 0.35| 35                 | 15                     | 2.692                                  |
12  0.35  15  45  2.234  
13  0.35  30  30  2.120  
14  0.35  35  35  0.704  
15  0.35  55  15  1.284  

Note: Groups 1~9 are orthogonal tests. Groups 10~15 are full series of tests in which the water-binder ratio of 0.35 does not coincide with the orthogonal tests.

3.2 Analysis of influencing factors

In orthogonal experiment, the range analysis reflects the influence degree of the corresponding factors on the test index by analyzing the average range of each factor. The greater the range R of a factor is, the greater the fluctuation of the test index will be caused by the change of the value of the factor within the test range. Therefore, in the orthogonal experiment the factor with the largest range is usually taken as the most important influencing factor of the test index. The range analysis of this experiment is shown in Table 7.

9 groups of test values of the orthogonal experiment were selected. The mean value of the 180 d chloride ion diffusion coefficient at each factor level and factor level were taken as the ordinate and abscissa respectively. The trend of factor level was shown in Figure 1.

As can be seen from Table 7, In this orthogonal experiment the water-binder ratio is the main factor affecting the 180d chloride ion diffusion coefficient of concrete. The total content of mineral admixtures and the combination of fly ash and mineral powder are the secondary factors. Among them, the influence of the total content of mineral admixture is slightly greater than the combination of fly ash and mineral powder.
It can be seen from Figure 1 that the chloride ion diffusion coefficient of concrete at 180 d increases with the increasing of water-binder ratio. The smaller the water-binder ratio is within a certain range, the better the chloride ion erosion resistance of concrete at 180 d. It decreases with the increase of the total mineral admixtures and the greater the total mineral admixtures within a certain range, the better the chloride ion erosion resistance of concrete at 180d. With the increase of the relative content of fly ash in mineral admixtures, the chloride diffusion coefficient first decreases and then increases. When the content of fly ash and ore powder is close to 1:1, 180d concrete has the best resistance to chloride ion erosion. When the water-binder ratio is 0.3, the total mineral admixture is 70%, and the fly ash content and the ore powder content are 1:1, it is the optimal combination level of concrete against chloride ion erosion.

9 groups of full-series test data with a water-binder ratio of 0.35 were selected. The 180 d chloride diffusion coefficient values and factor levels under various conditions were taken as the ordinate and abscissic coordinates respectively. The trend of factor levels in the full-series test was shown in Figure 2.
It can be seen from Figure 2 that regardless of the combination of fly ash and mineral powder content, the 180d chloride diffusion coefficient of concrete decreases with the increase of the total mineral admixture content. The greater the total content of mineral admixtures within a certain range, the better the chloride ion erosion resistance of concrete at 180 d. No matter how the total mineral admixture content changes, the chloride diffusion coefficient of concrete at 180 d decreases first and then increases with the increase of the relative content of fly ash in mineral admixtures. When the content of fly ash and ore powder is close to 1:1, the chloride erosion resistance of concrete at 180d is better. When the total content of mineral admixture is 70% and the content of fly ash to ore powder is 1:1, it is the best factor horizontal combination against chloride ion erosion. The results are consistent with the above orthogonal test results and the rationality of the test results is verified.

4. conclusion
Based on orthogonal and full series experimental design, RCM chloride ion rapid electromigration tests at 180d age were carried out on 15 groups of concrete with different mix ratios. The effects of water-binder ratio, total mineral admixture and mixture ratio on chloride diffusion coefficient of 180 d concrete were analyzed. The result of research shows that:

1) when the standard curing period is 180d, the secondary hydration of mineral admixtures is more sufficient, the pore structure of concrete is continuously refined and the chloride diffusion coefficient is less than $3 \times 10^{-12} \text{m}^2/\text{s}$. Concrete has good chloride erosion resistance performance;

2) the water-cement ratio is the main factor affecting the chloride diffusion coefficient of concrete with a curing age of 180d and the total content and combination of mineral admixtures are the secondary factors;
3) the chloride diffusion coefficient of concrete increases with the increase of water-binder ratio, decreases with the increase of total mineral admixtures, and decreases first and then increases with the increase of relative content of fly ash in mineral admixtures. When the water-binder ratio is 0.3, the mineral admixture ratio is 70% and the yield ratio of fly ash and ore powder is 1:1, 180d concrete has the best chloride resistance performance.

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