The Resistance of Novel Concrete Prepared by Gap-Graded Blended Cement under Chloride-Sulfate Attack

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Abstract. The resistance of concrete under chloride-sulfate attack dominates the durability of marine constructions. The binder played a more important role in chloride-sulfate resistance of concrete due to the dynamic hydration process. Incorporating supplementary cementitious materials (SCMs) was beneficial to the microstructure densification of cement paste, but the low hydraulic activities of SCMs resulted in the decrease of mechanical properties, activating activities of SCMs would raise the cracking risk of cement paste. On the basis of close packing theory, a gap-graded blended cement contained calcined hydrotalcite and metakaolin was adopted to prepare concrete with high resistance under chloridesulfate attack in present study. The gap-graded blended cement concrete presented comparable strength with Portland cement concrete, even though only 25% clinker used in the blended cement. Because of the continuous hydration of alumina-rich SCMs and functional components, the secondary hydration products with high chloride binding capacity helped blocking ions ingress, resulting in the one-magnitude decrease of chloride diffusivity. At the early period of soaking duration in chloride-sulfate solution, the sulfate ions were beneficial to delaying the migration of chloride. And the cracks introduced by expansive products from sulfate attack would observably accelerate the release and continuous ingress of chloride at late period.

1. Introduction

The degradation of concrete in marine environment was essentially caused by the attacks of aggressive media, such as chloride and sulfate. Since the aggregates were inert and stable during the service of concrete, and the characteristics of cement paste were the primary factor to dominate the properties of concrete. Then, improving the durability of concrete by increasing the resistance of cement paste under ions attack was a useful solution. Commonly, incorporation of supplementary cementitious materials (SCMs) was a widely accepted method to improve the chloride and sulfate resistances. But the mechanical properties of blended cement usually decreased due to the low activity of SCMs[1]. So, finely ground SCMs were adopted because of their acceleration effects of pozzolanic reaction. However, utilization of ultra-fine cementitious materials usually resulted in the rapid development internal stress and the increase of cracking risk, which would lead to the 1~3 magnitude increases of aggressive media diffusivity[2]. It can be inferred that improving the activity of cementitious materials merely cannot...
modify the resistance under ions attacks exactly. Our group has proposed a gap-graded distribution model based on the close packing theory, and the highly active SCMs, cement clinker, and poorly active SCMs or inert fillers were respectively arranged in the fine, mid-sized, and coarse fractions of gap-graded blended cement, to improve the initial packing density of fresh paste and densify the microstructure of hardened paste[3-4], and the denser microstructure and higher compressive strength were achieved[5-6]. In present study, a modified gap-graded blended cement incorporated metakaolin and calcined hydrotalcite was prepared, then the mechanical properties, chloride diffusivity, and resistance under chloride-sulfate attack concrete contained modified gap-graded blended cement were measured, and the modification mechanism of prepared concrete was investigated in accordance with the pore structures and the stability of hydration products.

2. Experimental

Portland cement clinker (C), blast furnace slag (B), and fly ash (F) were classified into several fractions to prepare gap-graded blended cement (Table 1). The five-fraction and three-fraction blended cements were denoted as bbcff and bcf, respectively. And the modified gap-graded blended cement (gcm) was prepared by incorporating 1% calcined hydrotalcite (CHT, 550 °C) and 5% metakaolin (MK) into 94% bbcff. The clinker content of blended cement was constant at 25%.

Table 1. Mix proportions of gap-graded blended cements.

|        | Fraction/μm | Content% | Material |
|--------|-------------|----------|----------|
| bbcff  | <4          | 25       | B        |
|        | 4-8         | 11       | B        |
|        | 8-24        | 25       | C        |
|        | 24-45       | 19       | F        |
|        | 45-80       | 20       | F        |
| bcf    | <8          | 36       | B        |
|        | 8-32        | 25       | C        |
|        | >32         | 39       | F        |
| gcm    | 94%bbcff+1%MHT+5%MK |

The concrete was prepared by cement content of 412 kg/m³ and water-to-binder (W/B) ratio of 0.43, and the proportions of coarse aggregate and sand were 1030.0 kg/m³ and 750.8 kg/m³, respectively. The superplasticizer addition was adjusted to keep the slump of concrete ranged in 150~165 mm. The concrete specimens were cured in saturated lime solution until targeted ages.

The Φ100mm×100mm specimens were used in chloride diffusivity measurements (Rapid chloride migration test, in accordance with GB/T 50082-2009), and the mechanical properties and ions attack (0.598 mol/L NaCl-0.352 mol/L Na₂SO₄ solution) resistance evaluations were carried out on 100×100×100mm³ specimens. The drying-wetting cycles were applied to accelerate attack. The soaking duration was set at 72 h for one cycle, then the specimens were dried in 60 °C for 21 h, then a cooling stage (3 h) was introduced. The chloride and sulfate profiles were determined by layer-by-layer sampling for each 2mm from specimen surface. Then mixing concrete powder and nitric acid (10%) and 24h standing, the Cl⁻ and SO₄²⁻ concentration of filtrates were obtained by ion chromatography. The pore structure of concrete was tested by mercury intrusion porosimetry (MIP). The surface tension of mercury and contact angle were 0.485 N/m and 130° at 25 °C[7], respectively.

3. Results

As shown in figure 1, the 28 d compressive strength of PC (60.4 MPa) was higher than the blended cement concrete as expected. And the differences among concrete prepared by gap-graded blended cements was negligible, the 28 d compressive strength of blended cement concrete were varied slightly in range of 46.6 to 47.7 MPa. It was well-known that the activity of cement clinker was much higher than those of SCMs, then the strength decrease of blended cement concrete can be attributed to the significant dilution effect of high content of SCMs, especially the incorporation of 39% fly ash. And the slight difference among blended cement concrete indicated the negligible contribution of calcined hydrotalcite and metakaolin in such a low content.
Figure 1. Compressive strength of concrete at 28 days.

Figure 2. Chloride diffusion coefficient of concrete specimens.

The RCM chloride diffusion coefficient of PC was high as $1.09 \times 10^{-12}$ m$^2$/s, which was one magnitude larger than those of blended cement concrete. The diffusion coefficient of BBCFF decreased 84% compared with PC, it can be attributed to the densified particle packing and efficient hydration of gap-graded blended cement. Moreover, with the addition of calcined hydrotalcite and metakaolin, the diffusion coefficient of GCM reduced furtherly to $0.14 \times 10^{-12}$ m$^2$/s, indicating the remarkable modification of functional components on the chloride resistance of concrete, which also agreed with available publications [8-9].

With the increase of soaking duration in chloride-sulfate solution, the compressive strength of concrete increased at the first month and then reduced sharply (figure 3). Obviously, the strength increase of PC after 28 d soaking was only 5.1 MPa, it was caused by the secondary hydration of unhydrated aluminate phase and external sulfate ions[10]. As external sulfate ions migrated into the internal continuously, the oriented growth of ettringite led to the significant reduction of compressive strength of PC after 90d. And the strength increase of BBCFF at the first 28 days was much higher, it relied to the higher content of active aluminate phase in BFS and fly ash, and more ettringite would generate to filled up the pores in microstructure. The delayed pozzolanic reaction of SCMs and Ca(OH)$_2$ was also beneficial to the formation of hydration products. As for the GCM specimens, the strength increase at early period was slightly higher than BBCFF, which can be attributed to the more aluminate introduced by calcined hydrotalcite and metakaolin.

Figure 3. Compressive strength of concrete after soaking in chloride-sulfate solution.

Figure 4. Appearance of concrete after 0, 1, 3, 6 months soaking in chloride-sulfate solution.
As shown in figure 4, there were visible cracks and spalling at the edges and surfaces of specimens of BCF and BBCFF, and the GCM specimens showed higher resistance under ions attack, as the cracks appeared at later period. To assess the deterioration degree of concrete under chloride-sulfate attack, a quantitative evaluation of deterioration scale proposed by Sotiriadis [11] was adopted, and the deterioration degree of concrete was illustrated in figure 5. The damage of concrete was intensified as the soaking time increased, and the deterioration degree of GCM was always slighter than those of BCF and BBCFF. For instance, there was remarkable spalling observed on BBCFF after 4 month soaking, and only narrow cracks appeared at the edges or corners of GCM at the same soaking duration. Besides, the development of concrete mass during soaking in chloride-sulfate solution also indicated the positive effects at early period introduced by the formation of ettringite, and the rapid decrease of concrete mass at late period was attributed to the continuous formation of ettringite, which resulted in the significant expansion stress and spalling of specimens (figure 6).

The sulfate and chloride profiles of concrete after 6 month soaking in composite solution were illustrated in figure 7. With the increase of distance from surface, the concentration of sulfate decreased rapidly when the distance smaller than around 6 mm, then the concentration reduced generally until leveled off. Obviously, the sulfate concentrations of PC were always higher than those of blended cement concrete at each distance, and the difference of sulfate profile between BBCFF and GCM was not so significant, except at the surface layer (<2 mm). Moreover, for the concrete did not attack by sulfate (>16 mm), the sulfate concentration of PC still higher than the others, it was owing to the higher original sulfate content of Portland cement which was not diluted by SCMs. Differ from sulfate profile, the chloride concentration concrete at 2~4 mm from surface was even higher than the surficial concentration, then showed diminishing reduction with the increase of distance from surface of specimen. The decrease of chloride at surface can be attributed to the enriched sodium chloride dissolved into external solution during drying-wetting cycles. For the concrete at 4~8 mm, the concentration of chloride showed no significant variation. The chloride of GCM reached the limitation earlier, and the equilibrium concentration was also much lower than BCF and BBCFF. Briefly, the resistance of GCM under chloride-sulfate attack was higher than the other concrete.

![Figure 5. Deterioration degree of concrete soaking in chloride-sulfate solution.](image1)

![Figure 6. Mass of concrete related to soaking duration in chloride-sulfate solution.](image2)
Figure 7. Ions profiles of concrete after 6-month soaking in chloride-sulfate solution.

4. Discussion
As listed in Table 2, the porosity of PC was high as 13.66%, and the porosity of BBCFF (11.39%) decreased as the modification of particle packing and hydration processing[3, 4]. With the incorporation of calcined hydrotalcite and metakaolin, more hydration products (especially C-S-H) were generated by pozzolanic reaction, indicating more pores were filled and less pathways for ions penetration. Moreover, the lamellar products, such as monocarboaluminate, monosulphoaluminate, and hydrotalcite-like mineral, formed from hydration of functional components were in favor of the modification of chloride binding, then the amount of free chloride to migrate into internal was reduced. Thus, the GCM presented higher resistance under ions attack.

Table 2. Porosity of concrete after 28-day curing.

| Sample | PC   | BCF  | BBCFF | GCM |
|--------|------|------|-------|-----|
| Porosity (%) | 13.66 | 13.33 | 11.39 | 10.05 |

Since SO$_4^{2-}$ in solution reacted with Ca$^{2+}$ and monosulphoaluminate, the expansive products, like ettringite and gypsum, were generated to induce formation of microcrack and macroscale spalling[12], the chemical reactions in the above erosion processes were shown as follows:

$$\text{Ca(OH)}_2 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{NaOH} \quad (1)$$

$$3(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 26\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \quad (2)$$

$$2(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 12\text{H}_2\text{O} + 16\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \quad (3)$$

Due to the low alumina content, the expansive products in PC were gypsum under ions attack. Formation of gypsum cannot increase internal stress significantly, but it decreased the stability of hydration products and led to weak bond between aggregate and matrix, then the residual compressive strength decreased sharply at the late period of soaking duration. As much active alumina was introduced by SCMs and functional components, the expansive products of BBCFF and GCM under sulfate attack were ettringite mainly, so the internal stress caused by oriented growth of ettringite in narrow pore space aggravated the degradation of BCF and BBCFF. Because the hydration of functional components densified the microstructure, it not only blocked the ingress of aggressive media, but also improved the stability to resist the expansive stress, then the appearance and residual strength of GCM always better than those of BCF and BBCFF after soaking in chloride-sulfate solution. Furthermore, the interaction between chloride and sulfate ions also played an important role in the degradation process of concrete. At the early period, the existence of sulfate ions was beneficial to blocking the migration of chloride. To maintain the electric neutrality of pore solution, the competition between negative ions delayed the ingress of chloride. And the expansive products generated at early period lessened the pathway for ions
migration and helped to decrease the diffusivity of chloride. At the late period, the cracks caused by sulfate attack would observably accelerate the ingress of chloride, and the bound chloride in hydration products was also released due to the transformation from hydration products to erosion products.

5. Conclusion
The main conclusions that can be drawn from the present study are summarized as follows:

(a) A novel concrete with high resistance under chloride-sulfate solution was prepared by using gap-graded blended cement (25% clinker content) contained calcined hydrotalcite and metakaolin. The prepared concrete has comparable mechanical properties and much more high chloride-sulfate resistance compared with Portland cement concrete.

(b) Due to the modification of particle packing and hydration process, the significant pore refinement of gap-graded blended cement concrete was observed, and the alumina-rich products also contributed to the chloride binding, resulting in the improvement of chloride-sulfate resistance.

(c) At the early period of soaking duration, the sulfate ions were beneficial to blocking the migration of chloride. And the cracks introduced by expansive products from sulfate attack would observably accelerate the release and continuous ingress of chloride at late period.

(d) The chloride-sulfate resistance and durability of concrete were improved significantly by using gap-graded blended cement, and the carbonation and life-cycle analysis of the proposed concrete would be paid more attention in the further investigation.

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