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Effect of mixed chlorides on the degradation and sulfate diffusion of cast-in-situ concrete due to sulfate attack

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HIGHLIGHTS

- Effect of mixed chlorides in concrete on the sulfate-induced attack is studied.
- The higher the sulfate concentration, the greater the degradation in concrete.
- Mixed chlorides promote the diffusion and accumulation of sulfates in concrete.
- Mixed chlorides accelerate the sulfate-induced degradation of concrete.

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ABSTRACT

This paper reports the results of a detailed experimental study conducted to investigate the influence of mixed chlorides on sulfate-induced corrosion in cast-in-situ concrete. Concrete specimens with or without mixed chlorides were exposed to sulfate solutions for a period of 365 days. The concentration of sulfate solutions varied from 0% to 10%. Concrete degradation was assessed by measuring the expansion, mass loss and strength loss at regular intervals. Scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), thermogravimetry-derivative thermogravimetry (TG/DTG), and differential scanning calorimetry (DSC) were used to analyse the microstructural changes and the complex mineral assemblage of concrete. The results indicate that mixed chlorides in concrete play a positive role in inhibiting the strength formation of concrete in the early stages and hence decreasing the strength of concrete. The acceleration effect of mixed chlorides on the expansion and mass loss of concrete caused by external sulfate attack is noted. Furthermore, the presence of mixed chlorides in concrete increases the diffusivity and accumulation of sulfates. Therefore, mixed chlorides in cast-in-situ concrete play a significant role in accelerating the degradation process of cast-in-situ concrete due to sulfate attack.

1. Introduction

Concrete is a type of construction porous material that is widely used in both superstructure and underground structures. Degradation of concrete structures is one of the major problems facing the construction industry in both saline and offshore areas [1–3]. One of the main causes of concrete deterioration is its exposure to harmful chemicals, which are normally found in groundwater, soil and sea water [4–6]. Among the aggressive chemicals found, sulfates and chlorides are reported to be the most aggressive ions that influence the durability of concrete structures.

It is well documented that sulfate ions react with the cement matrix to form expansive corrosion products, leading to expansion, cracking, spalling and failures to the structures [7–9]. Ettringite formation has always been reported as the main cause of concrete expansion; however, controversies still remain since some reports found that gypsum formation is also responsible for concrete expansion [10,11]. The formation of ettringite occurs even when the concentration of sulfate is low [12], and the formation process depends on the variations in environmental temperature and the solubility of calcium aluminate hydrate phases in the pore solution [13]. Thaumasite is also reported to cause cracking and expansion when subjected to sulfate attack, with the processes strongly dependent on variations in pH and temperature [14]. In addition, concrete also suffers from internal chloride attack by chlorides

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mixed into fresh concrete at the time of its preparation [15,16], as a strong accelerator of the early stages of cement hydration [17]. The binding of chloride ions with C_3A forms Friedel's salt, which causes chloride corrosion [18].

Although the effects of chlorides on sulfate attack in concrete has been studied for many years, it remains a controversial issue. It is well accepted that chloride ions diffuse faster than sulfate ions into concrete [19], and competition occurs between chloride ions and sulfate ions when they coexist in concrete [20]. Some researchers [21,22] indicated that chlorides mitigate sulfate diffusion and inhibit sulfate attack by retarding the formation of ettringite, gypsum or thaumasite [23–25]. Moreover, conversion of Friedel's salt to ettringite is noted for the case of sodium ions in solution [26,27]. Furthermore, other researchers [28] found that chloride ions could actually weaken the concrete resistance against sulfate and could accelerate the sulfate attack. The effect of chlorides on concrete degradation due to sulfate attack can be attributed to the diffusivity of ions [20], the solubility of ettringite in pore solutions [21] and the formation of Friedel's salt [29,30]. The relevant studies mentioned above were of great importance to understand the degradation of concrete subjected to sulfate, chloride and sulfate-chloride combined attacks and laid a necessary foundation for further study. However, it should be noted that the concrete specimens mentioned in the previous studies are primarily precast concrete with standard curing. In contrast, underground concrete structures in saline and offshore areas are mainly cast-in-situ structures. In addition, the phenomenon of chlorides being mixed into fresh concrete at the time of preparation has been widely reported. Until recently, the effect of mixed chlorides on the sulfate-induced degradation and sulfate diffusion in cast-in-situ concrete was unclear. In this regard, a systematic study on the effect of mixed chlorides on sulfate attack in cast-in-situ cement concrete deterioration is required to develop guidelines on the precautions to be taken when structures are exposed to soil or groundwater with complex chemical components.

This paper investigates the effects of mixed chlorides on the degradation and sulfate diffusion in cast-in-situ concrete due to external sulfate attack. Specimens, with 3% mixed chlorides or without mixed chlorides, were exposed to sulfate solutions, with the concentration varying from 0% to 10% for 12 months. Related tests regarding the expansion, mass loss and compressive strength were conducted. Microstructure analysis and mineral assemblage of concrete were observed by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), thermogravimetry-derivative thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) tests. The sulfate concentrations at different time intervals were determined by chemical titration.

2. Experimental program

2.1. Materials and mixture proportions

In this study, Portland cement (P.C. 32.5R, similar to ASTM Type I [31,32]), made in China, was used as the binding material. The chemical compositions of the cement are given in Table 1. The maximum size of the gravels used to make the specimens was 10 mm. River sand was used to make the concrete specimens. The fineness modulus of sand was 2.6, and the maximum particle size was 2.36 mm. The water used in the experiments was distilled water. The mixture proportion of concrete specimens is listed in Table 2.

2.2. Curing conditions and sample preparation

Four types of curing conditions were selected to simulate the different types of corrosive environments. Four tanks, CK, 3S, 5S and 10S, were prepared as solution containers. The solution in the tank CK was distilled water as a control group to provide a reference condition. The tanks 3S, 5S and 10S were filled with sodium sulfate solutions, and the mass fractions were set as 3%, 5% and 10%, respectively. The solute concentrations of the aforementioned solutions were checked and were adjusted monthly to ensure that the solute concentrations in the solutions remained constant. Moreover, the liquid levels of each tank were checked monthly to ensure that the specimens were completely immersed in the solutions at all times.

After measuring the weight of the raw materials, the dry components, including cement, river sand and aggregates, were first mixed at a high speed for 3 min. Water was then added and mixed for approximately 6 min at a low speed. For specimens with 3% mix chloride ions, NaCl powder was weighted and mixed in water before being mixed into the fresh concrete. To simulate the corrosion condition of cast-in-situ concrete piles, cylinder specimens were designed, and the sizes of these specimens were ϕ100 mm × 200 mm (diameter × height). The specimens with moulds were then stored in a curing cabinet at 20 °C and RH > 95% for 6 h. After demoulding, the top and the bottom sides of each specimen were sealed with epoxy resin immediately. After another 12 h of standard curing, all the specimens were then numbered and placed into the 4 containers mentioned above. The details of all the tested specimens and the corresponding corrosion conditions are listed in Table 3.

2.3. Test methods

After being immersed in tanks for 1, 3, 6, 9 and 12 months, the specimens were removed and then placed in an oven at 40 °C for 48 h to dry. Afterwards, the size change, mass loss, compressive strength and sulfate concentration were determined. The microstructures and mineral components of the specimens were also investigated after immersion for 12 months.

Table 1
Chemical composition of cementitious materials.

Chemical composition	Al_2O_3	SO_3	TiO_2	Fe_2O_3	Na_2O+K_2O	MgO	Cl	CaO	C_3A	C_4AF
Content (%)	6.51	1.98	0.365	2.06	0.907	1.85	0.05	58.5	13.77	6.26

Table 2
Mixture design of concrete specimens.

w/c Ratio	Water (kg/m^3)	Cement (kg/m^3)	Sand (kg/m^3)	Gravel (kg/m^3)
0.485	175	360	635	1235

Table 3
The specimens and the corresponding working conditions.

Tested specimen	Mixed chlorides	Solution	Tested specimen	Mixed chlorides	Solution
CK	0% NaCl	Distilled water	3C	3% NaCl	Distilled water
3S		3% Na_2SO_4	3S + 3C		3% Na_2SO_4
5S		5% Na_2SO_4	5S + 3C		5% Na_2SO_4
10S		10% Na_2SO_4	10S + 3C		10% Na_2SO_4