



# Ground granulated blast furnace slag effect on the durability of ternary cementitious system exposed to combined attack of chloride and sulfate



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## HIGHLIGHTS

- Durability of the ternary system exposed to combined NaCl and Na<sub>2</sub>SO<sub>4</sub> attacks is tested.
- GGBS can improve the resistance to sulfate and chloride attacks of the ternary system.
- The optimum amount of GGBS in 5% NaCl, 5% Na<sub>2</sub>SO<sub>4</sub>, and 5% NaCl–5% Na<sub>2</sub>SO<sub>4</sub> solutions were 35%, 25%, and 25%.

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## ABSTRACT

This paper presents a study on the durability of the ternary cementitious system (TCS) containing ordinary Portland cement, calcium aluminate cement and calcium sulfate with different content of ground granulated blast furnace slag (GGBS) when subjected to 5% NaCl, 5% Na<sub>2</sub>SO<sub>4</sub>, and 5% NaCl–5% Na<sub>2</sub>SO<sub>4</sub> attacks. The results showed that the partial replacement of TCS by GGBS increased bound chloride, enhanced compressive strength, and decreased apparent porosity. Besides, the presence of chloride mitigated sulfate attack. The presence of sulfate decreased the contents of free and total chloride, and limited the formation of Friedel's salt.

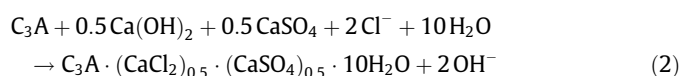
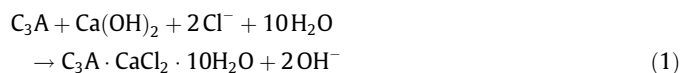
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## 1. Introduction

A lot of damages have been reported for concrete structures in marine and groundwater environments [1–3], which are very aggressive due to the presence of high concentration chloride and sulfate ions. Both ions are very harmful for the durability of constructions. It is mainly due to the chemical reaction between ions and hydration products in cement. Therefore, it is necessary to study the corrosion reaction for improving the durability of concrete structures.

In general, the presence of chloride ion mainly causes corrosion of reinforced concrete, which is mainly through the diffusion of free chloride ion in the pore solution to the surface of the reinforcing bar [4]. In addition to the free chloride ion, bound chloride ion is another form of existence. The existing of bound chloride ion is mainly due to the reaction of free chloride ion in pore solution and hydration products in cement to produce chloroaluminate compounds, such as Friedel's salt and Kuzel's salt (Eqs. (1) and (2)),

which have no expansion and are absorbed to the calcium silicate hydrate (C-S-H) [5,6]. The process is also called chloride binding, which is beneficial to mitigate the reinforcement corrosion caused by free chloride ion. In the study of free chloride ion and bound chloride ion, free chloride ion can cause corrosion initiation [7,8]. On the other hand, bound chloride ion can also lead to corrosion initiation. This is mainly due to the release of bound chloride ion to free chloride ion [9,10].



Apart from chloride attack, concrete structures in marine and groundwater environment are also subjected to sulfate attack. It is well known that sulfate ion in the pore solution can react with calcium hydroxide (CH) in cement to form gypsum (Eq. (3)), and the gypsum will have a further react with calcium aluminate hydrated phases in cement to form ettringite (Eq. (4)) which has a big expansion property. This process may result in expansion

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and cracking of hardened concrete structures. In addition, the degree of damage in sulfate attack relates to the concentration of sulfate in environment [11].



In the case of seawater and groundwater, sulfate and chloride ions coexist and influence each other. Some studies [11–19] showed that the specimens stored in chloride-sulfate solution performed better compare to that in sulfate solution alone for the following reasons: (a) Free chloride ion can be captured by tricalcium aluminate ( $\text{C}_3\text{A}$ ) in the cement to produce chloroaluminate compounds, which do not cause any expansion. The significantly reduction of  $\text{C}_3\text{A}$  in cement can decrease the damage caused by sulfate attack due to ettringite reduction. (b) The diffusion rate of chloride is higher than that of sulfate. This indicated that chloride can quickly penetrate into concrete and react first with the  $\text{C}_3\text{A}$ , limiting the formation of ettringite. (c) The solubility of ettringite in chloride solution is higher than that in water, which leads to the decreasing of ettringite formation. On the other hand, the sulfate ion relates to the products of chloride attack. The presence of sulfate can weaken the ability of chloride binding. The bound chloride ion is partially released to produce free chloride ion. Moreover, the presence of sulfate can limit the formation of Friedel's salt and make Friedel's salt change into ettringite [20,21].

Because the concrete structures in marine and groundwater environments are vulnerable to erosion and damage, the durability of construction was put forward. In general, the different types of mineral admixtures, such as slag, fly ash, silica fume, are considered to be added to the ordinary Portland cement (OPC) in order to enhancing the service life of construction, and the addition of pozzolanos in OPC for enhancing the seawater resistance is well known. However, the ternary cementitious system (TCS), which is a mixture of ordinary Portland cement, calcium aluminate cement and calcium sulfate, is different from OPC. Compared with OPC, the ternary system contains amounts of ettringite and small number of calcium hydroxide. The formation of ettringite may come from the following aspects: (1) The hydration of OPC itself produce. (2) The reaction between the hydration products of OPC and added gypsum produce. (3) The interaction between the reaction product of calcium aluminate cement (CAC) and added gypsum produce. In ternary system, the reason for the small number of calcium hydroxide is due to the replacement of CAC and gypsum. Compared with OPC, the increasing of ettringite is beneficial to improve the compactness and strength of the ternary system, and the decrease of calcium hydroxide can mitigate the sulfate attack in ternary system. In addition, the ternary system had been widely used as special cements [22–24] and repair materials [25], which is very promising.

Although the ternary system offers excellent performance, the study of the ternary system in marine environment is lacking. In theory, the hydration products of the ternary system contain calcium hydroxide, calcium aluminate hydrate, and ettringite, which are easy to be corroded by sulfate and chloride ions. Considering the ion erosion resistance, ground granulated blast furnace slag (GGBS) is added to the ternary system for the following reasons: (a) Increasing chloride binding ability [18,26]. (b) Reducing of permeability. (c) Improving the distribution porosity [27,28]. But the content of GGBS in system is a critical parameter. Some researchers [29] asserted that concrete containing 35 wt% GGBS in chloride-containing environment showed a lower corrosion rate. While others [30] founded that the system containing 15 wt% and 30 wt % GGBS performed better. Therefore, in this study, the different

amount of GGBS was added in the TCS to improve the resistance to ions corrosion of TCS.

The main aim of this study is to improve the durability of TCS in chloride and sulfate environments and establish the interaction between chloride and sulfate. Thus, the effect of different content of GGBS (5 wt%, 15 wt%, 25 wt%, 35 wt%) on TCS exposed to combined attack of chloride and sulfate was studied. Molded specimens were cured in tap water at the temperature of 20 °C for 28 days, and then immersed in 5% (by mass) NaCl solution, 5% (by mass)  $\text{Na}_2\text{SO}_4$  solution, 5% (by mass) NaCl + 5% (by mass)  $\text{Na}_2\text{SO}_4$  solution for 1, 7, 14, 30, 90, and 180 days. The compressive strength, mass change, apparent porosity, free chloride content, and total chloride content of specimens were tested. The identification of reaction products was studied from X-ray Diffraction (XRD).

## 2. Materials and methods

### 2.1. Materials and mix proportions

Materials used in this study consisted of ordinary Portland cement, calcium aluminate cement, gypsum (calcium sulfate (CS)), and ground granulated blast furnace slag (GGBS). The chemical compositions of OPC, CAC and GGBS are summarized in Table 1. The state of gypsum is dihydrate gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) with the purity of 99.0 wt%. The chemical compositions of gypsum are shown in Table 2. The physical properties of OPC and CAC are given in Tables 3, and 4, respectively. Naphthalenesulfonic acid-based superplasticizer (NS) powder was added to the mixture to obtain a slump between 150 mm and 180 mm.

The mix proportions are shown in Table 5, where the system G15 means mortar specimens with the binder ( $\text{OPC} + \text{CAC} + \text{CS} = \text{B}$ ) replaced by GGBS at the dosage of 15% by weight, while the G0 means mortar specimens without GGBS. The water to binder ratio (W/B) of mortar specimens was maintained at 0.3 and the binder to sand ratio (B/S) at 1:1.5 by weight.

### 2.2. Preparation and curing process

Mortar specimens were cast in steel molds of 20 mm cubes (used for compressive strength and apparent porosity) and 20 mm × 20 mm × 80 mm prisms (used for mass measurement), cured at 20 °C and 95% RH for 24 h. After that specimens were demolded and cured in tap water at 20 °C for 27 days. After 28 days, the half of specimens were put into corrosion solution, the rest of half of specimens continued to store in tap water used as reference. The corrosion solutions are as follows: 5% NaCl solution, 5%  $\text{Na}_2\text{SO}_4$  solution, 5% NaCl–5%  $\text{Na}_2\text{SO}_4$  solution. Specimens were cured in the four solutions (three corrosion solutions and tap water) at 20 °C for 1, 7, 14, 30, 90, and 180 days. The volume of the test solution was about 0.025 L/cm<sup>2</sup>. The test solutions were changed once a month. Before each test, the samples were washed three times with deionized water to eliminate the salts on the surface of the specimens.

### 2.3. Testing methods

#### 2.3.1. Mass measurement

Mortar specimens of 20 mm × 20 mm × 80 mm prisms were prepared for mass measurement. The test method is in accordance with the literature [31]. Mass of the specimen before ( $m_0$ ) and after ( $m_n$ ) immersion in test solution (except for tap water) was recorded every two weeks. Before each test, specimens were washed by running tap water and dried by blotting with a paper towel. After that, the specimens were allowed to dry for 30 min ( $20 \pm 2$  °C, and RH  $50 \pm 10\%$ ) and measured the mass with an accuracy of 0.01 g. The mass change (M) was calculated as follows.

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