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## Chloride ions transportation behavior and binding capacity of concrete exposed to different marine corrosion zones

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### HIGHLIGHTS

- The order of chloride ion content and binding capacity in different marine zones.
- The chloride ion profiles difference between separate samples and one whole sample.
- The optimized replacement ration of fly ash and GGBS in marine environment.

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### ABSTRACT

Transport of chloride ion into concrete can induce depassivation of reinforcement, which seriously threatens the durability of concrete subjected to marine environment. In this paper, the chloride ion transport and binding capacity of different concrete samples located in marine atmosphere zone, splash zone, tidal zone and submerged zone for 9 and 13 months were tested. And the chloride ion profiles of one whole concrete sample exposed to all the corrosion zones for 13 months was also detected. The effect of fly ash and ground granulated blast furnace slag (GGBS) on the chloride ion transport and binding capacity of all the concrete samples were studied and the optimized replacement ratios of mineral admixtures in marine environment was proposed. The contents of  $\text{Ca}(\text{OH})_2$  and Friedel's salt in paste exposed to different corrosion zones were also tested by XRD and DSC-TG. Results showed chloride ion content in separate concrete samples exposed to splash zone and atmosphere zone were lower than that of the other zones, but the opposite results were observed for one whole concrete sample throughout all the corrosion zones. For separate samples, the chloride binding capacity of concrete in atmosphere zone was the lowest, and would decrease with corrosion time in marine environment. The washing effect by tidal action would lead to the loss of  $\text{Ca}(\text{OH})_2$ , abrasion of surface, and decrease of compressive strength of concrete.

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### 1. Introduction

As we all know, most of concrete structures used in bridges, subsea tunnels and harbors were exposed to marine environment containing large amount of chloride ion, sulfate ions, oxygen, etc, which can result in severe corrosion of concrete structures [1]. As previously reported, the corrosion rates of steel in tidal zone even exceed  $500 \mu\text{m}/\text{year}$  [2]. In China, the total corrosion cost exceeded 2 trillion yuan in 2014, which accounted for 3.34% of its GDP [3]. In the marine environment, the ionic concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  are the highest [4]. The chloride ion will transport to the surface of the steel bar and induce its depassivation and corrosion [5–8],

resulting in corrosive crack, loss of load carrying capacity and damage of the structures ultimately [9,10]. Therefore, the corrosion of reinforcement induced by chloride ion is a huge risk for the security of reinforced concrete in marine environment.

The damaged factors in marine environment include chloride ion induced corrosion of steel bar, sodium sulfate and magnesium sulfate attack, salt crystallization, abrasions and erosions by the waves, and so on. A significant number of studies that focus on chloride transport mechanism of concrete immersed into salt solution or exposed to drying-immersion cycles have been carried out in the laboratory [11–14]. Experimental results from long-term field exposure might be conforming to the actual situations. Forty-six months of atmosphere zone field exposure experiments by G.R. Meira indicated that chloride profiles of concrete exposed to atmosphere zone tend to be convection-diffusion zone profiles,

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with a maximum chloride concentration a few millimeters inside [15]. Four specimens of metals and reinforced concrete exposed to atmosphere zone in the South and Northeast Brazil were studied by D.P.Cerqueira [16]. In the tidal zone, the most severe deterioration likely occurs in the structures because all kinds of physical and chemical attacks may happen [17]. In nearly 7 years, tidal zone exposure experiments about fly ash concrete have been carried out by W. Chalee and more long-term field exposure in Thailand has also been developed by T. Cheewaket [5,18]. In order to obtain the resistance capacity of concrete to ocean corrosion, exposure experiments about high performance concrete, and concrete with corrosion inhibitor or coating have been directed by researchers [19–22]. The chloride ion transport mechanism of concrete exposed to tidal zone for 10–30 years has also been studied by other researchers [23–27]. The detection results from long-term service concrete structures provide more powerful data for the analysis of chloride transport mechanism of concrete exposed to marine environment [28,29]. But for the wharf or the caps of sea-crossing bridges, the reinforced concrete structures pass through the full marine corrosion zones, which will provide the channels for water and ion transmission to the high direction. Therefore, the distribution of chloride ion in concrete exposed to separate marine corrosion zone and the total corrosion zone will be significantly different.

When chloride ion migrated into concrete, part of chloride ion would be bound in hydrated cement paste with Friedel's salt and calcium oxochlorides [30]. Herein, the predicted service time of reinforced concrete could be increased by 93% and 200% due to the existence of bound chloride ion [31]. However, the mineral admixture, temperature, relative humidity and chloride ion concentration would influence the chloride binding capacity of concrete [32]. Seven years' marine exposure of fly ash concrete indicated that the chloride binding capacity would be dramatically decreased as the concrete was located in the marine environment for 3–4 years [33]. In addition, there is a chemical equilibrium between the combined chloride ion and the ACDC change of the amount of combined chloride ion in concrete [34–36]. The environmental temperature, humidity and carbonization degree of each corrosion area are different, especially, lots of sulfate ions exist in the sea water, which will lead to the difference of the chloride ion binding capacity between concrete in the marine environment and the common chloride environment, moreover, the chloride ion binding capacity of the concrete in each corrosion zone will also be different.

A larger number of ocean structures have been built in Qingdao during the last 20 years including the cross-sea Bridge, harbors, subsea tunnels and ocean wind plants [37]. These reinforced concretes are exposed to different marine corrosion zones or throughout all the corrosion zones. In different corrosion zones, the oxide concentration, humidity, temperature, corrosion ion content, and wave effect are various, and these factors will affect chloride ion transport and binding capacity of reinforced concrete. In order to maximize the service life of the structures, different concrete raw materials and protection technologies were used for individual corrosion zones [38]. At the same time, mineral admixtures such as fly ash and GGBS have been used widely in concrete in order to improve the sustainability of construction

[39,40]. High volume mineral admixture would decrease the hydration heat and improve the shrinkage resistance capacity of concrete, which helps to promote the durability of reinforced concrete. However, light-degree freezing and 50 days/year of sea fog existent in Qingdao seawater is different from Thailand and other seawater environment. Additionally, there are differences in the chemical composites and production technology of fly ash and GGBS between China and other areas. Therefore, suitable volumes of fly ash and GGBS to concrete should be proposed based on resistance capacity of chloride ion migration in Qingdao ocean environment.

The overall aim of this paper is to reveal the chloride transport and binding capacity of concretes in different marine corrosion zones including atmosphere zone, splash zone, tidal zone and submerged zone, and to compare the chloride migration process of separate concrete samples exposed to different corrosion zones and one whole concrete throughout all the corrosion zones based on long-term marine exposure. And then, the optimized replacement dosage of fly ash and GGBS in concrete in marine environment was proposed based on chloride transport resistance capacity and binding capacity.

## 2. Experimental program

### 2.1. Materials and specimen preparation

P.I. 52.5 Portland cement with a compressive strength of 59.8 MPa after curing for 28 days was used in this study. Mineral admixtures including Class I fly ash and S95 GGBS were used for replacement of Portland cement. The chemical compositions of cement, fly ash, and GGBS are shown in Table 1. And the particle size distributions of cement, fly ash and GGBS were shown in Fig. 1.

The coarse aggregate used in this study was crushed granite with the size of 5–25 mm, the river sand with fineness modulus of 2.6 was used as fine aggregate. The dosage of polycarboxylic super plasticizer was adjusted for keeping the slump of fresh concrete 140 mm–180 mm. In order to improve the frost resistance capacity of concrete in Qingdao seawater, an air entraining agent was used, and its dosage was controlled to guarantee the air content of fresh concrete in the range of 3.5–5.0%. The concrete mixtures were made with an effective water-to-cement ratio (w/c) of 0.35 and total binder content of 470 kg/m<sup>3</sup>. Based on lots of previous mechanical and durability experiment studies, high content mineral admixtures including GGBS and Fly ash could enhance the workability of fresh concrete and crack resistance capacity of harden concrete. Therefore, the optimized mixture proportion LF50 mixed with about 32% GGBS and 17% fly ash was identified and used in piling concrete structure in Qingdao. The control concrete L50 including the same w/c and total cement content as LF50 was prepared. Additionally, concretes were cast using fly ash or GGBS to substitute cement at 15–65% by weight of binder with the same W/B ratio of the control concrete. The mixture proportions of the concretes and their compressive strength, air content are given in Table 2.

The concrete cube specimens for each mix proportion with size of 100 mm × 100 mm × 100 mm and the reinforced concrete for L50 and LF50 with size of 150 mm × 200 mm × 1000 mm were cast and placed at room temperature in the mold, and demoulded after 48 h, then cured for 28 days at the condition of 20 ± 3 °C and 95% relative humidity. Four sides of the cube specimens were sealed by using epoxy resin to ensure one-dimensional diffusion. Then specimens were transferred to the marine exposure field of Qingdao Wheat Island and placed on the corrosion zones including atmosphere zone, splash zone, tidal zone and submerged zone for nearly 2 years. For the specimens exposed to separate corrosion zones, 3 samples with the size of 100 mm × 100 mm × 100 mm were taken at each age for determination of chloride ion distribution. And for the specimens exposed throughout all the corrosion zones, 1 sample with the size of 150 mm × 200 mm × 1000 mm was taken for test. The reinforced concretes with height of 1000 mm were transferred to the simulated marine environment exposure filed and exposed throughout all the corrosion zones for 13 months.

**Table 1**  
Chemical compositions of cement, fly ash and GGBS.

Constituent, wt%	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	TiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	SO <sub>3</sub>	Cl
Cement	21.8	5.42	3.44	63.85	1.26	0.36	0.57	0.33	2.26	0.00
GGBS	32.87	13.40	1.34	41.06	5.64	1.59	0.45	0.54	2.68	0.01
Fly ash	51.28	32	4.23	3.76	0.75	1.43	1.02	0.38	2.5	0.02

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