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# Chloride diffusion study of coral concrete in a marine environment

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## HIGHLIGHTS

• Chloride concentration distribution laws of coral concrete soaked in seawater were studied.

• Influence of curing age and exposure time on the durability of chloride in coral concrete were discussed.

• Superior of magnesium sulfate cement in resisting chorine salt erosion were verified.

• Possible applications of coral concrete in marine engineering structures were suggested.

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## ABSTRACT

Using the distribution of free chloride concentration ( $C_{\rm f}$ ) and total chloride concentration ( $C_{\rm f}$ ) measured by different grades and species of coral concrete (CPC) soaking in sea water, the chloride binding capacity (R), surface free chloride concentration ( $C_s$ ) and apparent chloride diffusion coefficients ( $D_a$ ) of CPC were calculated. Then, the influence of curing age and exposure time on the durability of chloride in coral concrete were discussed, and the superior of magnesium sulfate cement (MSC) in resisting chorine salt erosion were verified. The results indicated that the CPC R values increased whereas the C<sub>s</sub> values decreased with the extension of the curing age. The relationship between the exposure time and  $C_s$  followed an exponential form; however, its growth rate was considerably lower than that of ordinary concrete (OPC) due to its high water absorbability. Furthermore, the decreasing relationship between  $D_{\rm a}$  and the exposure time conformed to the power function. The CPC  $D_a$  exposed for 10–25 a under a laboratory-simulated marine environment was 88.9-99.1% lower than that in an actual marine environment. The  $D_a$  of CPC was 0.5-6.6 times higher than that of any other type of concrete but decreased more quickly with the exposure time. After studying the CPC chloride diffusion parameters C<sub>f</sub>, C<sub>t</sub>, R, C<sub>s</sub> and D<sub>a</sub>, the advantages of MSC against the erosion due to chloride salt were fully demonstrated. Hence, for a CPC structure under an actual marine environment, extending the moisture curing age or using MSC will improve its ability to resist chloride diffusion, reduce the speed of chloride intrusion and prolong the service life of the structure. © 2016 Elsevier Ltd. All rights reserved.

#### 1. Introduction

Coral concrete (CPC) consists of coral fragments as a coarse aggregate, coral sand as fine aggregate, seawater, and cement. Coral reefs are abundant in the South China Sea Islands. Due to the rate of ocean development, the construction of marine engineering projects is increasing. Because constructing and repairing concrete projects on a coral island, which is far from the mainland, is expensive and restricted by natural conditions, such as storms, aggregate and fresh water must occasionally be shipped from the mainland. Thus, the construction time is not ensured [1,2]. Without destroying the local environment, it is practical and functional to construct and repair concrete projects by mixing seawater with coral reef sands and

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http://dx.doi.org/10.1016/j.conbuildmat.2016.06.135 0950-0618/© 2016 Elsevier Ltd. All rights reserved. replacing fresh water and common aggregate because seawater and coral sand are local materials on coral islands. Coral is a type of natural porous material that defies anti-chlorine penetration. Research has clearly demonstrated that chloride erosion damages concrete, significantly threatening the security and durability of marine concrete construction [3–5]. In conclusion, there is a great importance in studying the durability of CPC under the erosion of chloride salt.

To study the durability of CPC under the erosion of chloride salt, the penetration process of free chloride into the inner concrete should be first studied [6]. Only free chloride can corrode a steel rebar, and it can penetrate the concrete cover and reach the surface of the steel bar. Because it accumulates, the free chloride concentration ( $C_{\rm f}$ ) in the pore liquid of the steel bar surface gradually increases to a critical chloride concentration ( $C_{\rm cr}$ ), thus eroding the steel rebar. Hence, the steel rebar erosion can be determined







based on the time in which the outside free chloride diffuses and the amount of accumulation. Considering the different types of mechanisms, the diffusion models of chloride and computing methods are presented in relation to Fick's Second Diffusion Law. Three important parameters are the chloride binding capacity (R), surface free chloride concentration ( $C_s$ ) and apparent chloride diffusion coefficient ( $D_a$ ).

Currently, the service life of concrete in a chloride salt can be evaluated using Fick's Second Law and the changed diffusion equation. The theoretical model, which describes the diffusion law of concrete chloride, can be derived by Fick's Second Diffusion Law as follows:

$$C_{\rm f} = C_{\rm s_0} + (C_{\rm s} - C_{\rm s_0}) \left( 1 - erf \frac{\chi}{2\sqrt{\frac{D_{\rm a}}{1+R}t}} \right)$$
(1)

where  $C_{s0}$  is the initial chloride concentration (%);  $C_f$  is the free chloride concentration (%);  $C_s$  is the surface free chloride concentration (%);  $D_a$  is the apparent chloride diffusion coefficient (cm<sup>2</sup>/a); and *erf* is the error function:  $erfu = \frac{2}{\sqrt{\pi}} \int_0^u e^{-t^2} dt$ .

American scholar Howdyshell [7] published a report on the investigation of CPC in 1974. He concluded that it is feasible to form concrete with a coral coarse aggregate; however, the chloride salt concentration of the coral aggregate must be controlled and the steel bar must be protected. Because the CPC is made by seawater, it is easy to erode the steel bar; thus, the thickness of the protective layer must conform to the requirements. American scholar Rick [8] surveyed the durability of three CPC buildings in the Bikini Atoll in the Pacific Ocean in 1991. He believed that the strength of the CPC had to meet the design requirements of the engineering structure, and the primary factors influencing the durability of the CPC were salinity, protective thickness of the concrete and surface crack width of the structure. Indian scholars Arumugam et al. [9] conducted research on the developing rules of the CPC on the cube compressive strength ( $f_{cu}$ ) in 1996. He confirmed that the strength of the CPC increased rapidly in the early stages but slowed its pace in the later stages. In 2003, Japanese scholars Wanchai et al. [10] determined that the  $D_{\rm a}$  of CPC was twice as large as that of ordinary concrete (OPC). If the W/B in CPC decreased to 0.25, then the  $D_a$  of CPC would be similar to that of OPC. The strength and diffusion of the chloride resistance in the CPC would clearly improve if the surface of the coral aggregate was treated. Hence, the C40 CPC was formed. Japanese scholars Tehada et al. [11] in 2005 and Wattanachai et al. [12] in 2009 researched the reinforcement corrosion and chloride diffusion of CPC, respectively. It was determined that the corrosion speed in the CPC was higher than that in the OPC for the same mix proportion. A certain chloride salt may be responsible for this result. Malaysian scholars Kakooei and Iranian scholars Akil et al. [13,14] studied the oxygen permeability and reinforcement corrosion of CPC in 2012. They discovered that the speed of corrosion in the CPC (W/B = 0.48, 28 d  $f_{cu}$  = 16 MPa) was twice as high as that in the OPC (W/B = 0.48, 28 d  $f_{cu}$  = 25 MPa). In 1989, Chinese scholars Zhaolin et al. [15] conducting marine engineering design studies created C15, C20 and C25 CPC and performed a systematic study on their mechanical properties, such as crush resistance, tensile splitting, anti-fracture, axial comprehensive strength. It was determined that when the W/B reached 0.49 and 86% of coral was replaced by gravel, the  $f_{cu}$  of the CPC with gravel could reach that of the C30. Chinese scholars Yanlin et al. [16] systematically studied the basic mechanical properties and flexural fatigue properties of CPC in 2011. It was determined that when W/C = 0.30–0.35, the  $f_{cu}$  of CPC after 28 d reached that of C30. Based on the chloride corrosion reinforcement mechanism, Chinese scholars Fang et al. [17] performed a feasibility study of CPC applied to a concrete-filled steel tube in 2013. It was determined that CPC without treatment could be used

in reinforced concrete. In 2014, Chinese scholars Baolai et al. [18] added 20–30% of silica fume (SF) into C30 CPC from river sand and seawater for 28 d (W/B = 0.40, sand ratio ( $S_p$ ) = 54%). The  $f_{cu}$  was determined to be 34.9 MPa and 35.4 MPa, respectively, which was an increase of 14.9% and 16.4% compared to that of the reference concrete. In 2005, Chinese scholars Bozhou et al. [1] analysed the effects of cement categories and the impact of seawater on the CPC  $f_{cu}$ . The results demonstrated that CPC mixed with anti-sulfate cement and seawater had a better working performance and higher strength. Previous studies on CPC concentrated on the durability investigation, design of mix proportion and basic physical and mechanical properties.

This study included a systematic test on the chloride concentration of coral concrete in different grades, cements, curing age and exposure time using a natural diffusion method and discussed the depth distribution of the chloride concentration. Furthermore, the modified Fick's Second Diffusion Law [19] was used to study the *R*,  $C_{\rm s}$ , and  $D_{\rm a}$  variables as well as the time-dependent index of the apparent chloride diffusion coefficients (*m*) of CPC, and the durability parameters were compared with other types of concrete. These comparisons offered the data and theoretical support for CPC application to coral reef engineering.

#### 2. Experiments

#### 2.1. Raw materials

The coral sand in South China Sea (see Fig. 1) was used, which had a chloride concentration of 0.112%, mud concentration of 0.5%, apparent density of 2500 kg/m<sup>3</sup>, bulk density of 1115 kg/m<sup>3</sup>, fineness modulus of 3.5, and gradation in district I (see Fig. 2). This sand was classified as a type of medium sand. Furthermore, the coral in South China Sea was used (see Fig. 1). Its chloride concentration was 0.0074%, and the largest smashed diameter was 20 mm. A 5-20 mm continuous gradation was formed through sieving (see Fig. 2) with a 2300 kg/m<sup>3</sup> apparent density, 1000 kg/m<sup>3</sup> bulk density and 3.8 MPa cylinder compressive strength. The CPC was made of 52.5 Ordinary Portland Cement, which was produced by the China Jiangnan Cement Co., Ltd or MSC (for chemical composition, see Table 1; for physical and mechanical properties, see Table 2) The Class I FA was produced by Zhenjiang. The Class S95 milled SG was made by the Jiangsu Jiangnan Grinding Company. The JM-B Naphthalene series superplasticizer was made by the Jiangsu Building Science Research Institution and artificial seawater. The artificial seawater was made of chemical reagents NaCl, MgCl 6H<sub>2</sub>O, Na<sub>2</sub>SO<sub>4</sub>, CaCl<sub>2</sub> and KCl in accordance with the provisions of the United States ASTM D1141-2003. For its chemical composition, refer to Table 3.

#### 2.2. Concrete compositions

This experiment designed CPC in 5 different grade strengths based on the studies performed by Yinfeng et al. [20]. The mix proportion is listed in Table 4. The C30S30F15, C40S15F7, C50S15F7 and C55S15F7 concrete specimens used 52.5 Ordinary Portland Cement. Concurrently, to verify the features of the new cement, the C25S15F7 concrete specimen, which had the same mix proportion of C55S15F7, used MSC instead of the 52.5 Ordinary Portland Cement. Because coral is a natural porous light aggregate, it is able to absorb and release water. This improves the effect of "self-curing" in the curing process, which strengthens the density and bonding strength of the set cement over the border and increases the CPC capacity to resist the chloride salt erosion. Thus, pre-absorption is necessary. The  $f_{cu}$  under standard curing for 3 d, 7 d, and 28 d are listed in Table 5.

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