



Study on the resistance to seawater corrosion of the cementitious systems containing ordinary Portland cement or/and calcium aluminate cement



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HIGHLIGHTS

- CAC mortar compressive strength cured in seawater is higher than that in tap water.
- The addition of FA and SG can improve the resistance to seawater corrosion of system.
- The OPC-CAC-gypsum-SG system offers the best seawater corrosion resistance.

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ABSTRACT

The resistance to seawater corrosion was investigated for OPC, CAC, OPC-CAC-gypsum, OPC-SG-FA, and OPC-CAC-gypsum-SG. The specimens were cured in tap water for 28 days and then immersed in artificial seawater for 30, 90, and 180 days. Compressive strength, weight change, apparent porosity, free and total chloride content were measured. The results demonstrated that the compressive strength of all specimens immersed in seawater increased up to 90 days and then decreased up to 180 days. Additional, the compressive strength of CAC immersed in seawater is higher than that in tap water. The OPC-CAC-gypsum-SG system had the highest resistance to seawater corrosion.

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1. Introduction

An increase in the use of cement and concrete in the marine environments may be concomitant to renewed interest in marine structures. However, the corrosion of buildings in the seawater should not be ignored. The main phases in the traditional ordinary Portland cement (OPC) contain tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). The compounds C_3S and C_3A contribute to the early hydration, and produce a large amount of calcium hydroxide ($Ca(OH)_2$, CH), calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H), which are easily attacked by SO_4^{2-} , Cl^- , CO_3^{2-} , Mg^{2+} , etc. in seawater [1–4]. The erosion products, including ettringite, Friedel's salt, magnesium hydroxide ($Mg(OH)_2$, MH), magnesium silicate hydrate (M-S-H), calcium carbonate ($CaCO_3$), etc. can lead to the destruction of the concrete structures and the

reduction of the durability. Therefore, the application of OPC in marine environment is limited.

Compared to OPC, the main phases in calcium aluminate cement (CAC) mainly contain calcium aluminate (CA), calcium dialuminate (CA_2). The reaction products of CAC do not contain $Ca(OH)_2$, C-S-H, which alleviates erosion of ions in the seawater. In addition, CAC offers the good resistance to the sulfate attack owing to the following reasons: the absence of $Ca(OH)_2$, the presence of a protective coating of alumina gel, and the low reactivity of its reaction products with sulfate ion [5]. Furthermore, the rapid hydration of CAC can achieve a very dense matrix [6]. But Edmunds [7] studied the hydration of CAC and found that the initial reaction products of both components (CA and CA_2) are calcium aluminate hydrate (CAH_{10} or C_2AH_8) with alumina gel. These can subsequently convert to another form of calcium aluminate hydrate (C_3AH_6) (called katoite) (Eqs. (14)) [8]. This process is accompanied by increasing porosity due to the higher densities of these stable phases, consequently reducing the mechanical properties of the cementitious system [9]. Therefore, it can be inferred that CAC

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may not be conducive to the application in the marine environments.



In addition to the OPC or the CAC is used alone, the binary system (OPC-CAC) should also be cause for concern. Ping Gu [8] reported that the formation of ettringite in the binary system was at very early hydration times. The studies of SEM and EDXA indicated that fast setting in the binary system was due to the formation of ettringite, which is unfavorable to construction. In order to retard the setting time and improve the early strength, gypsum was considered to be added. Up to now, the different proportions of the ternary system (OPC-CAC-gypsum) had been widely used as special cements [10–14] and repair materials [15]. But the hydration products of the ternary system contain $\text{Ca}(\text{OH})_2$, C-S-H, and ettringite, which are easy to be corroded by seawater.

In order to improve the seawater corrosion resistance of the above cementitious systems, mineral admixtures are considered to be added. There are three main reasons: (a) The mineral admixtures have small particle size and can be filled in the voids of the reaction products to make the structure more compact, and finally slow down the invasion of ions in seawater. (b) Mineral admixtures replace part of cement, which reduces the amount of cement and hydration products that are susceptible to be corroded by seawater. (c) Mineral admixtures have the pozzolanic activity, and produce the additional C-S-H gel later which makes the structure more compact and hinders the ingress of ions, these will improve the resistance to seawater corrosion of the systems. Especially, fly ash (FA) and slag (SG) are widely used due to the large output and obtain easily. In addition, a large number of studies have shown that the incorporation of FA and SG can significantly improve the seawater corrosion resistance of OPC system [16–19]. Moreover, slag as a mineral admixture, in addition to the above three reasons, itself contains a large number of alumina [20]. Chloride ion can be solidified in the reaction, which slows the corrosion of free chlorine ion on the reinforcement [17]. There-

fore, it is necessary to introduce suitable slag into the ternary system to improve the resistance to seawater of the ternary system.

In view of the application of the above materials in seawater. Fly ash and slag were considered to be added in them to improve the resistance to seawater corrosion of the cementitious systems. In the present paper, the following five systems were prepared: (1) OPC. (2) CAC. (3) OPC-CAC-gypsum. (4) OPC-SG-FA. (5) OPC-CAC-gypsum-SG. The OPC-SG-FA system was proposed to improve the pure OPC system. In addition, the OPC-CAC-gypsum-SG system was put forward to improve the resistance to seawater corrosion of OPC-CAC-gypsum system. An evaluation of the compressive strength from different systems was described. To make further study on these systems, weight change, free chloride content, total chloride content and apparent porosity were measured. Furthermore, the evolution of phases was also studied from XRD spectra.

2. Experimental

2.1. Materials

The cements used in the study were ordinary Portland cement (P-O 42.5 according to Chinese standard) and calcium aluminate cement (CA-50 according to Chinese standard), respectively. The chemical analysis and physical properties of them are shown in Tables 1, 2, and 3, respectively. The mineral admixtures (FA and SG) used and their chemical analysis are given in Table 1. The fineness of SG is 7.12%, density is 2.65 g/cm³. The specific surface area of OPC, FA, and SG are 350 m²/kg, 381 m²/kg, 521 m²/kg, respectively. The purity of gypsum is 99.01 wt %. And β -Naphthalenelonic acid-based superplasticizer (BNS) powder was also used in this study.

2.2. Mix proportions

The mix proportions of different systems are shown in Table 4. The cement paste without aggregates was prepared with the water to binder ratio of 0.29. The cement mortars with the water to binder ratio of 0.3 and the binder to sand ratio of 1:1.5 by weight were prepared, respectively. Tap water was used as mixing water. The content of BNS was 1.5 wt% cementitious materials.

2.3. Preparation and curing process

After casting, the specimens were cured at a moist room (temperature 20 ± 1 °C, and RH 100%) for 24 h before demolding. And then, the specimens were cured in tap water for a further period of 27 days. The initial compressive strength and weight (for 28 days) were recorded before they were placed in the test solution. The artificial seawater was determined as the test solution, the compositions of the artificial seawater used were given in Table 5 according to ASTM D1141. The volume of arti-

Table 1
Chemical analysis of OPC, CAC, SG, and FA (wt%).

Components	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	Loss
OPC	22.32	5.84	3.15	61.23	2.02	0.39	0.15	2.00	1.66
CAC	7.81	52.40	2.42	34.25	0.02	0.24	0.13	0.05	0.21
SG	32.56	25.77	0.62	42.08	5.63	0.96	1.22	1.01	0.93
FA	51.07	30.86	5.26	5.75	2.72	1.13	0.79	1.48	2.80

Table 2
Physical properties of the OPC used in experiment.

Density (g/cm ³)	Setting time (min)		Flexural strength (MPa)		Compressive strength (MPa)	
	Initial	Final	3 d	28 d	3 d	28 d
3.18	65	120	5.3	9.2	23.2	47.7

Table 3
Physical properties of the CAC used in experiment.

Specific surface area (m ² /kg)	Setting time (min)		Flexural strength (MPa)			Compressive strength (MPa)						
	Initial	Final	6 h	1 d	3 d	6 h	1 d	3 d	7 d	28 d		
580	33	95	3.3	5.9	6.9	6.7	6.5	22.8	49.6	60.2	58.3	55.6

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