Research on frost resistance of seawater sea-stone concrete

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Abstract: In this paper, the frost resistance of C30 seawater sea-stone concrete (SSC) under double corrosion in Marine environment is studied. In this paper, the relative dynamic modulus of elasticity, mass loss, micro morphology and composition of artificial sea water were tested and analyzed. The results show that under the condition of water conservation, SSC mass loss of 5% or more when chloride ions reduce after 40 times of freeze-thaw cycle.The freeze-thaw cycles of the quality loss and relative dynamic modulus of elasticity loss model are established respectively .The microscopic analysis of concrete in sea water stone are done,added to concrete in freeze-thaw and external double seawater corrosion performance.

1. Preface

Tthe freezing and thawing cycle damage is the main reason for the failure of the marine concrete structure. Therefore,the erosive medium in seawater and sea stones is harmful to the performance of concrete and the basic performance of sea-stone concrete(SSC).The influence of seawater on concrete is a complex process involving the ion exchange capacity of cement internal pore solution, cement admixture, chloride ion binding, pore characteristics and chemical composition of external erosive liquid [1].The impact of external seawater on concrete under erosion will be more complicated.

The study of durability energy under the influence of SSC has not been involved. Based on this, this paper aims to study the durability of SSC under the action of chloride ion erosion and freeze-thaw. The relative dynamic modulus of elasticity (RDME) and mass loss rate (MLR) were used to evaluate the durability of the SSC.At the same time, the SSC micro-morphology analysis and composition determination of the number of freeze-thaw cycles were carried out to investigate the changes of SSC performance under seawater and freeze-thaw double corrosion.

2.Test Overview

2.1 Test raw materials

The cement used is P·O 32.5.The fine aggregate used is natural sand, which belongs to medium sand. The coarse aggregates are ordinary gravel and sea stones, and the basic performance parameters are shown in Tab.1.

Table.1.Basic performance parameters of coarse aggregate

category Numerical value parameter	Crushing indicator（%）	Mud content（%）	Bulk density（kg/m³）	Apparent density（kg/m³）
gravel	15.4	0.47	1388	2863

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Sea stone	17.9	0.33	1379	2609

The seawater is artificially configured seawater,mainly prepared according to the chemical composition of seawater in Lianyungang Port. The pH value is 8.02 and specific components are shown in Tab.2. The water reducing agent is a polycarboxylic acid water reducing agent with a solid content of 55%.

Table.2. Chemical composition of artificial sea water

name	Molecular formula	quality（g/L）
Sodium chloride	$NaCl$	46.934
Magnesium chloride	$MgCl_2$	9.962
Sodium sulfate	Na_2SO_4	7.834
Calcium chloride	$CaCl_2$	2.204
Potassium chloride	KCl	1.328

2.2 experimental design

The test design strength grade is C30. The curing conditions adopted are seawater immersion. The combination of ordinary concrete and SSC is shown in Tab.3 below.

Table.3. Proportion design

Concrete strength grade	cement/kg	water/kg	Sand/kg	Stone/kg	Water reducing agent/kg
C30	475.61	195	501.52	1227.9	0.95

The dimensions of the test piece were 100 mm × 100 mm × 400 mm. The antifreeze performance test refers to the fast freezing method in the Standard Test Method for Long-Term Performance and Durability of Common Concrete[7]. In this paper, artificial seawater solution is selected as the freeze-thaw medium.

3. Results and Discussion

3.1 Experimental phenomena

First, the surface cement slurry is smooth in Fig.1(a); and then, the concrete test piece skin cement slurry begins to peel off, revealing sand and stones as in Fig.1(b); At the end, the surface cement slurry is completely peeled off, the sand and stone are completely exposed, and some corners are dropped, as shown in Fig.1(c).

(a) 0 Times (b) 20 Times (c) 50 Times

Figure.1. Surface damage of the specimen after SSC freeze-thaw cycle

3.2 Concrete mass loss rate

In Fig.2,The ordinary concrete fails at 30 times while SSC is at 50, indicates that the incorporation of seawater and sea stones can improve the frost resistance of concrete.Through the analysis of experimental data, we get fig.3.

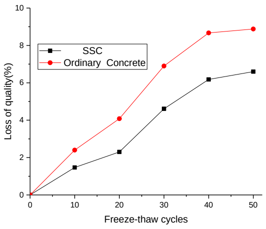


Figure.2. Relationship between mass loss and number of freeze-thaw cycles

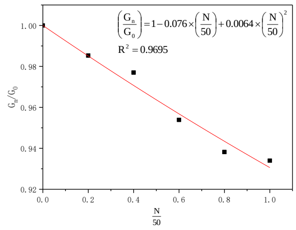


Figure.3. Fit curve of SSC relative mass and number of freeze-thaw cycles

As shown in Fig.3, the fitting curve is highly consistent with the test, and the formula (1) is obtained by fitting the test data:

$$G_n = 9.596\left(1 - 0.076 \times \left(\frac{N}{50}\right) + 0.0064 \times \left(\frac{N}{50}\right)^2\right) \qquad (1)$$

Among them, Gn is the mass of concrete after N freeze-thaw cycles, N is the number of freeze-thaw cycles, and the correlation coefficient is R2=0.9695.

3.3 Relative dynamic modulus of concrete

As fig.4 shows when the ordinary concrete is frozen and thawed 30 times, the relative dynamic elastic modulus has dropped to 54.1%, which is less than 60% of the specification requirements, that is, the number of freezing and thawing failures of ordinary concrete is 30 times, and the number of freeze-thaw cycles of SSC is 40 times.

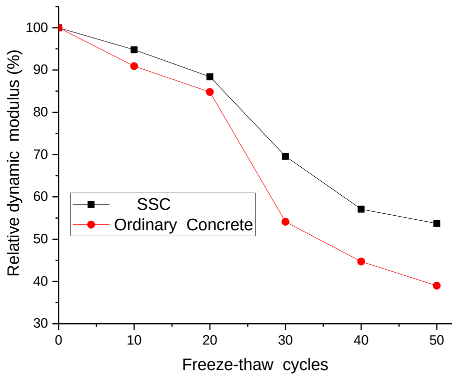


Figure.4.Relationship of relative dynamic and cycles.

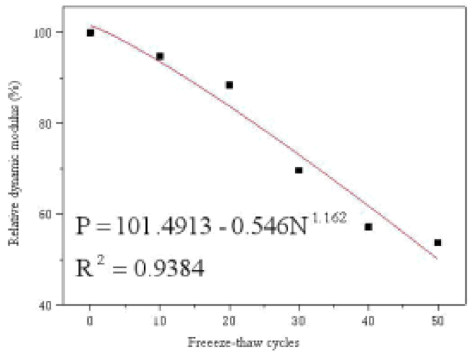


Figure.5.Fit curve of relative modulus dynamic elasticity and cycles

There are many reasons. 1) SSC's real water-cement ratio is lower than ordinary concrete, so its compactness is superior; 2) In the freeze-thaw cycle, ordinary concrete enters a large amount of chloride ions, and react with concrete hydration products.sulfate ions crystallize and swell, result in cracks and pores inside the concrete; 3) Friedel salt inside the SSC, which has a certain curing ability to chloride ions, can block capillary pores and reduce Freeze-thaw expansion failure in capillary pores; 4) From Fig.6(a) and Fig.8(a), the surface of ordinary concrete contains voids and a small amount of cracks, while the surface of SSC is intact.

By regression analysis of them in the test piece, they shows a power function relationship with the number of freeze-thaw cycles, as shown in Fig.5, the fit curve and test fit Higher, this paper gives a functional relationship as Equation 2.

$$E_n = 31.80\left(101.4913 - 0.546N^{1.162}\right) \qquad (2)$$

Among them, En is the dynamic elastic modulus of concrete after N freeze-thaw cycles, N is the number of freeze-thaw cycles, and the correlation coefficient is R2=0.9384.

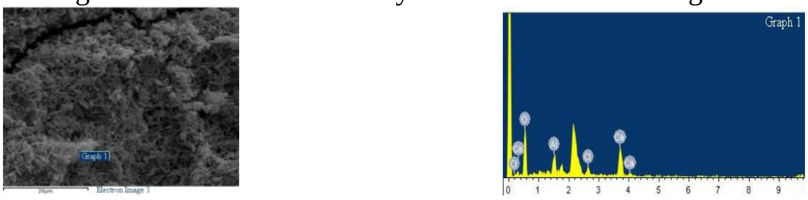
4. Micro Analysis

4.1 Concrete microscopic morphology

Fig.7(a) shows that the hydrate of the concrete forms a dense mass after 50 cycles of ordinary concrete freeze-thaw cycles, and is covered with dense holes and many cracks. The flocs are very loose and have almost no cohesive force. Compared with Fig.6, the CSH gel and $Ca(OH)_2$ crystals are broken, and there are needle-shaped ettringite (AFt) and Friedel salt generate. Elemental analysis of the floe using EDS in the SEM As shown in Fig. 7(b), a large number of elements are Ca, O, Cl and Al, and it can be confirmed from the elemental composition that the product is a Friedel salt.

（a） （b）

Fig.6.SEM image and EDS of C30 ordinary concrete before freezing and thawing



(a) （b）

Figure.7.SEM of C30 ordinary concrete freeze-thaw cycle 50 times and EDS

Obviously, the reaction of Mg+, $S0_4^{2-}$ and CH in the seawater solution consumes a large amount of CH[8].There are a large number of holes and many cracks, the pores of the concrete increase, and the hydration products are seriously damaged. In Fig.9(b), a large number of elements are Ca, O, Al, and S and the product is ettringite.

Fig.7(a) the pores and micro-cracks are larger than Fig.8(a), and the flocs and needles are significantly more than those in Fig.9(b). Microscopically, under the 50th freeze-thaw cycle, ordinary concrete is seriously damaged than SSC.

（a） （b）

Fig. 8 .SEM of C30 sea - sea rock concrete and EDS

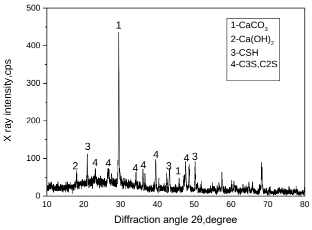
(a) （b）

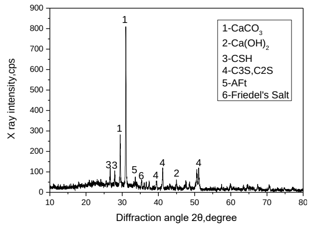
Fig.9 .SEM of 50 times of freeze-thaw cycle of C30 seawater concrete and EDS

4.2 Concrete content

From the X-ray diffraction theory,The presence of Friedel salt and AFt (calcium vermiculite) was not found in the 10(a) XRD test results, indicating that Cl^- and SO_4^{2-} in seawater did not react with concrete.

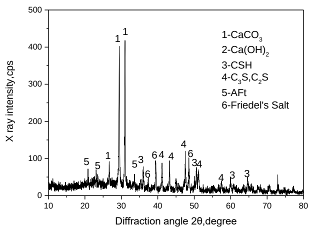
However, a small amount of Cl^- in the seawater enters the interior of the concrete, which may react with CH in the concrete to form $CaCl_2$, and $CaCl_2$ is easily dissolved under the scouring of seawater, which increases the porosity of the concrete. This also indicates that the erosion damage of Cl^- to concrete in the seawater is mainly dissolution-destructive.

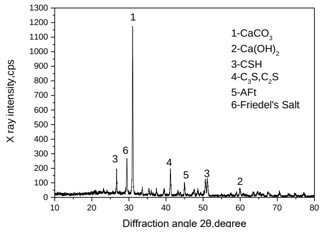




（a）Ordinary concrete 28d XRD diffraction pattern （b）SSC 28dX RD diffraction pattern

Fig. 10.XRD pattern of concrete under seawater corrosion





（a）Ordinary concrete cycle 50 times XRD diffraction pattern （b）SSC cycle 50 times XRD diffraction pattern

Figure.11. XRD pattern of concrete under double corrosion conditions

Comparing Fig.10 and 11, we can see the formation of concrete with a diffraction angle of 2θ=25°~35° and freeze-thawing 50 times. The Friedel salt is significantly more produced due to the damage to the concrete structure when the concrete freezes and thaws. The external Cl- quickly enters the concrete and reacts with the concrete cement to form the Friedel salt.

5. Conclusion

(1) The SSC contains a large amount of Cl^- in the seawater and reacts completely with C3A in the cement to form the Friedel salt. When the external chloride ions enter the concrete, no hydrated calcium aluminate reacts with it, and Cl^- exists in a free state. Or adsorbed on the surface of CSH gel, the concrete pore structure is more compact, hindering the entry of seawater, and the SSC frost resistance is better than ordinary concrete.

(2) The chloride ions doped in the concrete improve the pore structure of the concrete, mainly because the pore size becomes smaller, the pore network system becomes more tortuous, and the SSC frost resistance is better than that of ordinary concrete.

(3) The Friedel salt inside the SSC has a certain curing ability for chloride ions, and can block the capillary pores and reduce the freezing and thawing expansion damage in the capillary pores. The seawater stone concrete has better frost resistance than ordinary concrete.

(4) From the microscopic analysis of concrete seawater immersion curing, the pore structure difference and material composition of hydration products after freezing and thawing, to explain that the SSC frost resistance is better than ordinary concrete.

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