A Novel Corrosion Inhibitor for Preventing the SO_4^{2-} Transportation in Concrete

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Abstract. Chemical erosion of reinforced concrete by SO_4^{2-} in saline soil is the main factor of steel corrosion and concrete damage. Therefore, we synthesized a novel corrosion inhibitor based on barium salts for improving the SO_4^{2-} resistance property of concrete. In this study, the effects of corrosion inhibitor on the workability, compressive strength and SO_4^{2-} corrosion resistance property of concrete have been investigated. The results showed that with increased of corrosion inhibitor the slump of concrete has increased firstly and then decreased, compressive strength also showed a trend of firstly increasing and then decreasing. More importantly, with the increase of corrosion inhibitor, the SO_4^{2-} corrosion resistance property of concrete have improved obviously.

Keywords: Chemical erosion; corrosion inhibitor; corrosion resistance property.

1. Introduction

Concrete structures generally play an important role in the infrastructure construction. The corrosion of reinforcing steels in concrete structures is one of the main causes of the degradation and reduction of their service life, especially when they are exposed to marine environment or de-icing salts. An understanding of the process of SO_4^{2-}, Cl^- transportation in concrete is of great importance for engineers to predict the service life of concrete structures[1,2,3].

The corrosion of SO_4^{2-} to reinforced concrete is a complex process, which contains chemical reaction and physical action. SO_4^{2-} corrosion is a kind of expansive damage, which can induce to the crack of concrete, concrete spalling, and exposing of steel. All these results can make bad effects on the service life of concrete structure [4].

The resources of sulfate contain two types: (1) the concrete itself contains SO_4^{2-}, which can react with hydrated products to form ettringite, gypsum, tombstone, and other corrosions. (2) the SO_4^{2-} comes from environment, which invades into concrete and reacts with hydrated products. According to the generated products' crystalline, the corrosion mechanisms are different. Although the type and crystalline of generated products are different, the volume of products will increase during the formation process. Therefore, this solid phase reaction can increase the volume significantly, inducing to a large internal stress and make the crack of concrete increasing the diffusion of SO_4^{2-}.

There are many studies focused on improving the sulfate resistance of concrete. Researcher [5] studied the effect of silica fume on the properties of concrete. They found that the introduced silica fume could increase the early strength of concrete, meanwhile the final strength of concrete was also improved. The mechanism showed that the introduced silica fume increased the density of concrete, hindered the segregation and bleeding of concrete. Therefore, the sulfate resistance property of concrete mixing silica fume improved obviously. Moreover, researcher [9] [6]studied the effect of water-reducing agent's type on concrete's sulfate resistance property, they found that compared with naphthalene-based water reducing agent, the concrete containing polycarboxylate superplasticizer showed better sulfate resistance property.

According to the previous studies and based on the diffusion character of SO_4^{2-} in concrete, we synthesized a novel corrosion inhibitor for improving the SO_4^{2-} resistance of concrete.

2. Materials, specimen preparation and test method

2.1 Materials

The cement was used Portland cement CEM-1 42.5, and its chemical and physical properties are shown in Table 1 and 2. The river sand with 2680 kg▪m^{-3} apparent density and 2.8 fineness modulus was used as fine aggregate. The other components were tap water and polycarboxylate superplasticizer using as water reducing agents.

Table 1 Chemical compositions of cement (wt./%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O_{eq}	LOI	f-CaO	Cl^-
21.32	4.31	3.38	61.26	2.47	2.55	0.57	1.31	0.86	0.014

Table 2 Physical properties of cement

Density / kg·m^{-3}	Specific surface / kg·m^{-3}	Setting time / min		Flexural strength / MPa		Compressive strength / MPa	
		Initial	Final	3 d	28 d	3 d	28 d
3160	340	99	159	5.7	8.8	26.2	50.4

2.2 Preparation of corrosion inhibitors

The main components of corrosion inhibitors are barium salts. The preparation process of corrosion inhibitors as following: The mass ratio of barium nitrate, barium hydroxide, and barium carbonate is 2:2:6, the mixture of three barium salts were dissolving in an aqueous solution of 100 mL at 85 ℃. And then adding 250 g silica emulsion and stirring well at 50 ℃, finally the sample was dryed in vacuum oven at 60 ℃.

2.3 Preparation of specimen

The mix proportion of concrete specimen with different dosage of corrosion inhibitors were shown in Table 3.

Table 3 Concrete mix proportion (kg/m^3)

Specimen	PCE	Cement	Coarse aggregate			Fine aggregate	Water	Mass ratio of corrosion inhibitors
			＞ 20mm	（10～20）mm	（5～10）mm			
F-0	1.6	444	105.2	526.4	421.2	763	160	0%
F-1	1.6	430.8	105.2	526.4	421.2	763	160	3%
F-2	1.6	417.6	105.2	526.4	421.2	763	160	6%
F-3	1.6	404.4	105.2	526.4	421.2	763	160	9%
F-4	1.6	390.8	105.2	526.4	421.2	763	160	12%

2.4 Curing method of concrete

(1) Standard curing of concrete: After forming, the specimens were placed in a room with a temperature of (20 ± 3) ℃ and relative humidity > 50% for 24 h. After mold removal, the specimens were immediately placed in a standard curing room with a temperature of (20 ± 2) ℃ and relative humidity > 95% until the specified age.

(2) Corrosion solution curing of concrete: After forming, the specimens were placed in a room with the temperature at (20 ± 3) ℃ and the relative humidity > 50% for 24 h. After removing the mold, the specimens were immediately put into a container with water and the temperature of water was at (50 ± 1) ℃ for curing for 7 days. After curing, the specimens were taken out. Each number was divided into four groups with three specimens in each group, and then transferred to the curing conditions A and B.

Curing condition A: The two groups were placed in a container with (20 ± 1) ℃ to continue water curing.

Curing conditions B: The two groups were immersed in the erosion solution at (20 ± 1) ℃ for curing. When the specimen is soaked in the container, the liquid level is more than 10mm higher than the specimemn to avoid evaporation, and the container is capped. During the soaking process of the specimens, the erosion solution should be titrated with 20 wt.% sulfuric acid to neutralize the calcium hydroxide released by the specimens in the solution everyday, and the pH value of the erosion solution was about 7.0.

After curing for 60 days and 90 days, a group of specimens were taken out from the containers to test the diffusion coefficient of chloride ions.

2.5 Compressive strength

The standard curing age for testing the compressive strength pf concrete is 28 days. Experiment process was according to GB/T 50081-2019; The size of the test block is 100 mm×100 mm×100 mm, with 3 specimens in each group.

2.6 Sulfate erosion resistance property of concrete

The test was followed according to GB/T 50082-2009; The size of the specimen is 100 mm×100 mm×100 mm, with 3 pieces in each group.

3. Results and discussion

3.1 The effect of dosage of corrosion inhibitors on the workability of concrete

As shown in the Figure 1, it can be seen that with the dosage of corrosion inhibitor increasing from 0%~9%, the slump of concrete firstly increased and then decreased. Especially, when the mass ratio of corrosion inhibitor was over 3%, with the dosage further increasing, the slump of concrete have decreased a lot. Comparing with reference F-0, the slump of F-2, F-3, and F-4 have decreasd 43%, 58% and 76%, respectilvely. The higher specific surface area of corrosion inhibitor induced to a larger water amount for dispering the cement particle and decreased the workability of concrete.

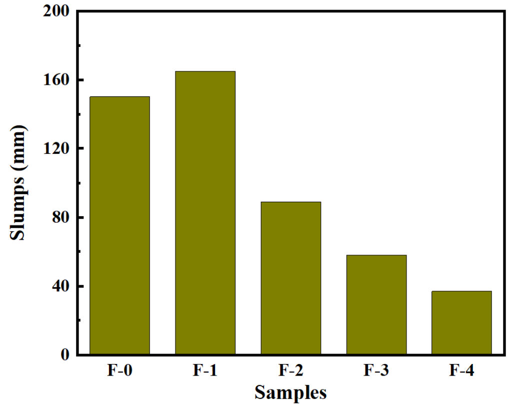

Figure1 The slump of concrete with different dosages of corrosion inhibitor

3.2 The effect of dosge of corrosion inhibitors on the concretes' compressive strengths

Moveover, the compressive strength of concretes have been also tested and tes results were shown in Figure 2, it can be found that with the corrosion inhibitor increasing, the compressive strengths of concretes were also improved firstly and then decreased. But comparing with reference F-0, the specimen containing corrosion inhibitor still showed higher compressive strength, Comparing with F-0, the compressive strength of F-1, F-2, F-3, and F-4 have increased 2.1%, 9.8%, 19.9% and 13.0%. Test results implies that the introduced corrosion inhibitor promoted the mechanical properties of concrete.

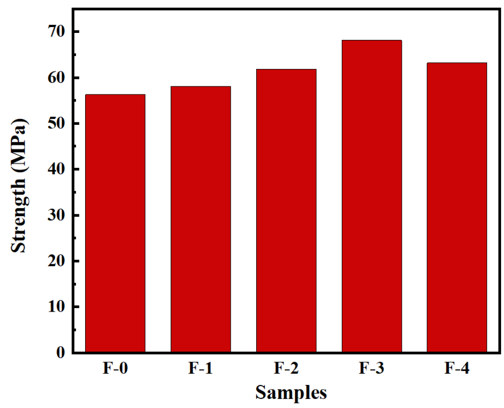

Figure 2 The compressive strength of concrete in the presence of different dosgaes of corrosion inhibitors

3.3 The effect of corrosion inhibitors on the compressive strength of concrete after curing in the erosion solution

Moreover, the compressive strength of concrete after curing in the erosion solution for 60 d and 90 d have also been investigated and test results were shown in Figure 3 and Figure 4, respectively. Comparing with reference F-0, it can be seen that the introduced corrosion inhibitors improved the compressive strength of concrete even in the erosion solution, which indicates that the erosion solution improved the sulfate corrosion resistance property of concrete due to the chemical reaction between SO_4^{2-} and Ba^{2+}, which can effectively decreased the diffusion of SO_4^{2-} and produced the insoluble barium salt ($BaSO_4$) to enhance the density of concrete.

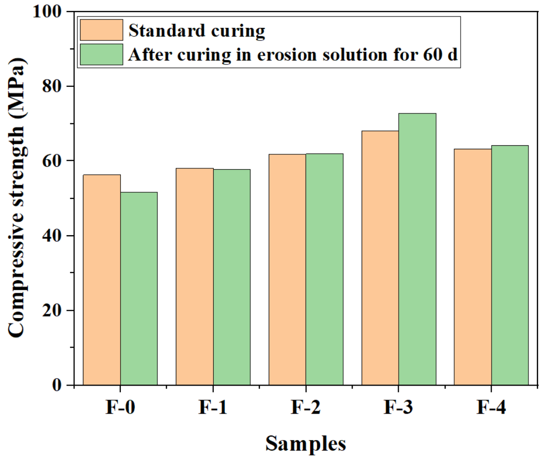

Figure 3 The compressive strength of concrete in the presence of different dosgaes of corrosion inhibitors after curing in erosion solution for 60 d

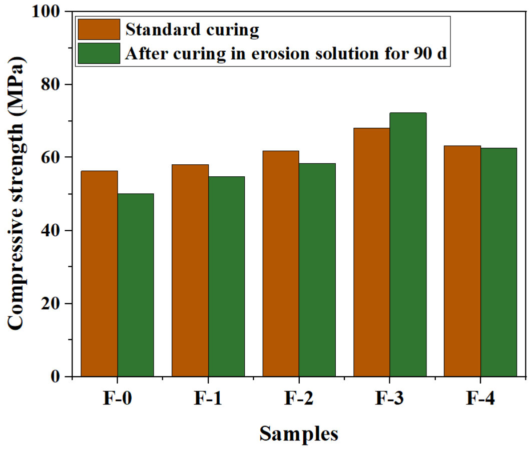

Figure 4 The compressive strength of concrete in the presence of different dosgaes of corrosion inhibitors after curing in erosion solution for 90 d

4. Conclusion

According to the test results, it can be concluded that the corrosion inhibitor made effects on the workability of concrete, the slump of concrete firstly increased and then decreased with dosage of corrosion inhibitor increasing from 0%~12%. The compressive strength results showed that the introduced corrosion inhibitor would improve the compressive strength of concrete even curing in erosion solution. All of test results indicated that the introduced corrosion inhibitor can promote the SO_4^{2-} resistance property of concrete.

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