

# Examining the Binding Mechanism of Chloride Ions in Sea Sand Mortar

Nengjun Gong<sup>1, A</sup>, Xintang Wang<sup>2, b</sup>

<sup>12</sup> School of Civil Engineering, Ningbo University, Ningbo, Zhejiang China

<sup>a</sup>[444068255@qq.com](mailto:444068255@qq.com) <sup>b</sup>wxtnbdx@163.com

**Keywords:** sea sand mortar, water soluble chloride ions, micro structures, Friedel's salt.

**Abstract:** The adsorption and binding mechanisms of chloride ion in sea sand mortars were investigated through measuring the water-soluble chloride ion content in this paper. In addition, the microstructure of Friedel's salt were characterized by three approaches : X-ray diffraction (XRD), thermal analysis method (TG/DTA) and scanning electron microscopy (SEM). The results show that water soluble chloride ion concentration in the sea sand mortar is closely related to the extraction temperature. The water soluble chloride ion concentration increases with the extraction temperature increasing. When extraction temperature is 65°C, the concentration of water soluble chloride ion is about the double of mortars at 15°C. Physically bound chloride ion in fly ash mortar shows low dissolution in lower temperatures. In the sea sand mortar, the endothermic peak of Friedel's salt does not appear on the TG/DTA curve, while the existence of Friedel's salt was determined by SEM and XRD picture. This is probably owing to the small amount of instable Friedel's salt content in the sea sand mortar.

## 1. Introduction

Coastal areas often contains rich resources of sea sand. The sea sand washed by freshwater to remove impurity has already been widely used in coastal concrete industry in China due to its convenience in mining and transportation. Chloride-induced reinforcement corrosion in reinforced structures is a crucial problem to the concrete professionals. The residual chloride in the desalted sea sand, potentially threatens the durability of reinforced concrete structures [1-5]. Generally, there are three types of chloride ions in the sea sand concrete: free chloride ions, physically bound and chemically bound chloride ions. Only the first type is responsible for the corrosion of rebars. Even though the pH of concrete is more than 12, the free chloride ions accumulated on the surface of rebars can cause or aggravate the corrosion [6-7]. Base on the survey of the utilization of the desalted sea sand in Ningbo city, this paper studied the binding mechanism of chloride ion and the effect of fly ash used as a partial replacement of cement on the free chloride ion concentration in the regular sea sand and desalted sea sand mortars. The characteristic of Friedel's salt and microstructure of mortars contained chloride were clarified in order to provide the theory base for durable sea sand concrete structures.

## 2. Experimental Procedure

**2.1 Materials and Mix Proportions.** Grade 42.5 ordinary Portland cement produced by Ningbo shunjiang Cement Plant was used in this study; Grade II Fly ash (FA) used in this research was supplied by Ningbo Zhenhai Power Plant. River sand (RS) was used as fine aggregate, and its fineness modulus is 2.27. Regular sea sand (SS) and desalted sea sand (DSS) came from five plants and its chloride ion contents are shown in Figure 1.

Mixture proportions are shown in table 1. The mortar cube specimens 70.7mm×70.7mm×70.7mm in volume were prepared for testing after being placed in a fog room to cure for 28 days .

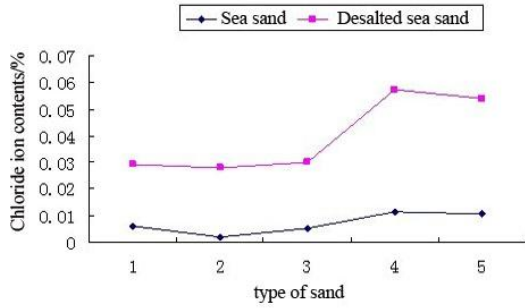


Figure 1. Chloride ion contents in sea sand (W%) Sample

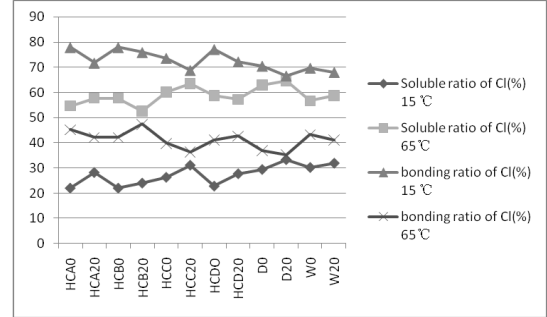


Figure 2. Existing status of chloride ions at different temperatures

## 2.2 Test Method

**2.2.1 Test of total Chloride Content in Regular Sea Sand and Desalted Sea Sand.** The sand was quartered to 1500g and dried in an oven with 105°C. Then the sand was cooled to room temperature. 500g sand was put in a reagent bottle with rubber stopper then 500ml distilled water was added. For the complete extraction of chloride in sand, the bottle was vibrated once in 24h and thereafter three times every five minutes. After a certain time, the clear solution in the bottle was filtered and let the filtrate flow into a glass beaker. 50ml filtrate was transferred into a triangular flask by pipette. Then the filtrate was titrated by 0.01mol / L standard silver nitrate solution. And the solution was mixed with 5% potassium chromate which was acted as indicator. The course of titration would be ended until the color, which should be kept for 5 – 10s, of the solution became red. In the course of titration, the amount of standard silver nitrate solution consumed was recorded and the total chloride content in sea sand can be calculated according to the amount.

**2.2.2 Test of Free Chloride Ion Content in Mortar.** The mortar cubes were cured in the standard curing condition for 28 days. The mole method was adopted to test the free chloride ion content. The pH of the solution under the test must be near neutral according to the requirement of mole method, however, the solution of mortar is alkaline. The dilute sulfuric acid was used for the neutralization in this study. To inquire into the effect of extraction temperature on the total or free chloride concentration of mortar, the tests of chloride ion content were carried out at 15°C and 65°C, respectively.

Table 1 Mix proportions of the mortar

Sample	Sand type	Cl-contents in sand (%)	Fly ash (%)	Mix proportion (C: S: W)
H0	RS	0	0	1:2.5:0.45
H20	RS	0	20	1:2.5:0.45
HCA0	RS	0.01	0	1:2.5:0.45
HCA20	RS	0.01	20	1:2.5:0.45
HCB0	RS	0.03	0	1:2.5:0.45
HCB20	RS	0.03	20	1:2.5:0.45
HCC0	RS	0.06	0	1:2.5:0.45
HCC20	RS	0.06	20	1:2.5:0.45
HCD0	RS	0.1	0	1:2.5:0.45
HCD20	RS	0.1	20	1:2.5:0.45
D0	DSS	0.01	0	1:2.5:0.45
D20	DSS	0.01	20	1:2.5:0.45
W0	SS	0.054	0	1:2.5:0.45
W20	SS	0.054	20	1:2.5:0.45

RS—River sand

**2.2.3 Product Analysis and Microstructure of Mortar.** The proportions of three samples HCD0, W0, D0 for TG/DTA and XRD tests were shown in Table 2. The mortar used for the SEM test was mixed with regular sea sand. The scanning electron microscope was produced by Japan Hitachi Company. The polycrystalline X-ray diffraction and TG/DTA thermal analyzer were produced by German Brueck and America Perkin Amelmer Company. The inner products, microstructure and its content in mortars can be determined by use of these analyzers.

### 3. Experimental Results and Discussion

#### 3.1 Free Chloride Ion Content In Mortar

**3.1.1 Total Chloride Ion Content In Regular Sea Sand And Desalted Sea Sand.** Figure 1 shows chloride ion contents of samples derived from the five plants are different. The chloride ion content in desalted sea sand is significantly lower than regular sea sand. It also shows that the the higher the original chloride ion content, the higher the residual content is after the sea sand is desalted.

**3.1.2 Free Chloride Ion Content in Sea Sand Mortar.** Figure 2 shows the soluble and bonded chloride ion contents at 15°C and 65°C in mortars. It can be seen from Table 3 that there is a close correlation between free chloride concentration and extraction temperatures. At 15°C, free chloride concentration content varies from 22%-34% and at 65°C, it varies from 52%~65%. This indicates that the free chloride concentration of mortars at extraction temperature 65°C is about twice as mortars at 15°C. This may be due to that the extraction rate of physically bound chloride ion increase with an increase in temperature. Therefore, taking the differential between total chloride ion content and free chloride ion content as the amount of chemically bound chloride is somewhat inaccurate.

Majority of the chloride ion is in the form of physically bound to ion exchange sites of C-S-H gel and there exists a significant degree of reversibility. In fact, for a physical adsorption, an increased temperature accelerates the thermal vibration of absorbates, bring about more free chloride [3].

In addition, Figure 3 shows the free chloride extraction rate of the mortar with 20% fly ash is higher than that of the cement mortar without fly ash at extraction temperature 15°C, however, the free chloride extraction rate of the mortars with or without fly ash is almost the same at extraction temperature 65°C. This may be due to less chemical bound and more physical bound chloride ions at lower extraction temperature.

**3.2 The Characteristic of Friedel's Salt in sea Sand Mortar.** As chloride enters the cementitious material, it may be converted to Friedel's salt due to chemical binding. Chloride ion can be introduced into concrete by two methods: (1) mixing as an additional agent (internal chloride); (2) penetrating from outside (external chloride). In the literature review, the chloride was frequently dissolved in the mixing water and then entered the mixture. At the same time, the amount of chloride introduced varies 2%~10% by weight of the cementitious material. Many researchers investigated the Friedel's salt with the abovementioned condition. However, because the chloride contents in the regular sea sand and desalted sea sand are much lower than that of abovementioned researches, it has not been reported if the Friedel's salt exists in regular sea sand or desalted sea sand mortars and concretes and if it can be observed [8].

Generally, Friedel's salt yields an endothermal effect at about 360°C [9]. Figure 4 shows the TG/DTA curves of mortars with river sand (sample HCD0), regular sea sand (sample W0) and desalted sea sand (sample D0), and the chloride content of these sands were 0.1%, 0.054% and 0.01%, respectively. Unfortunately, no clear endothermal peaks of Friedel's salt appear for the three TG/DTA curves of mortars.

To further clarify whether Friedel's salt exists in regular sea sand and desalted sea sand mortar, the XRD tests were carried out for the grounded mortars samples at 28 days of age and the results are shown in Figure 5. From Figure 5, regardless of the mortars with regular sea sand or desalted sea sand, several intensity peaks of Friedel's salt come out at the corresponding situation. However, the intensity peak of the Friedel's salt is quite lower than the other compositions (for example  $\text{Ca}(\text{OH})_2$ )

of the mortar. This indicates that the chloride ions introduced by regular sea sand or desalted sea sand still form some Friedel's salt in the mortars.

Because the total chloride content in regular sea sand or desalted sea sand is relatively low, the intensity peak of Friedel's salt is very low. Moreover, the abovementioned TG/DTA curves of mortars do not show the endothermic peak of Friedel's salt. This is because the small amount of chloride ions introduced by regular sea sand or desalted sea sand formed a very small amount of unstable Friedel's salt. In this paper, the intensity peak of Friedel's salt can be clearly observed in the mortars with river sand containing more than 0.03% chloride content, and not in the mortars with river sand containing less than 0.03% chloride content.

The SEM micrographs of Friedel's salt in regular sea sand mortars is showed by Figure 6. It is clear to see that Friedel's salt's morphology is hexagonal slice in size of about 2~3 $\mu\text{m}$ . Base on the investigation of XRD and SEM, we can conclude that Friedel's salt exists in sea sand mortars.

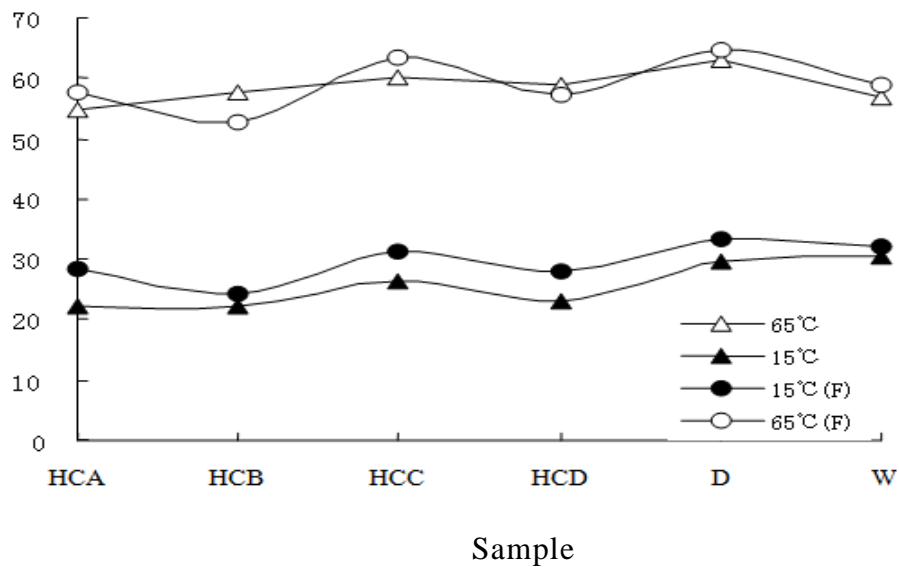
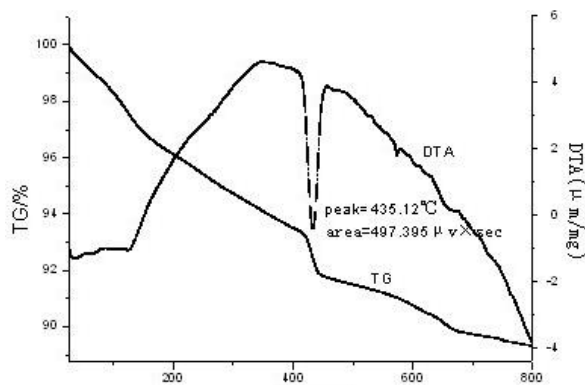
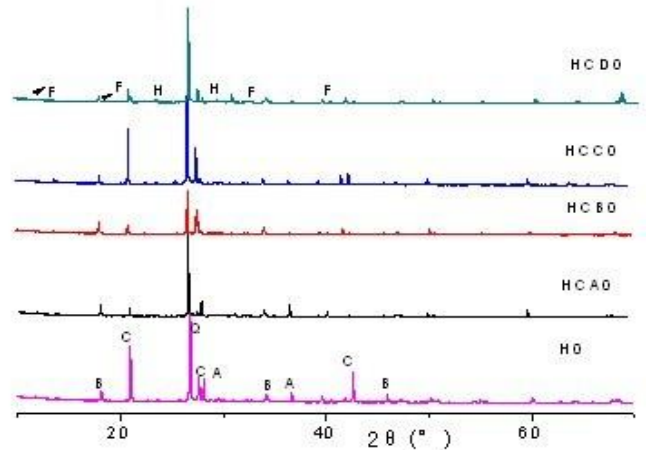


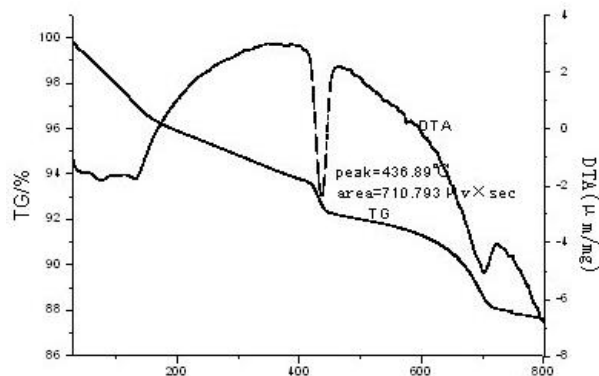
Figure 3. Relationship between the temperature and soluble chloride ion concentrations



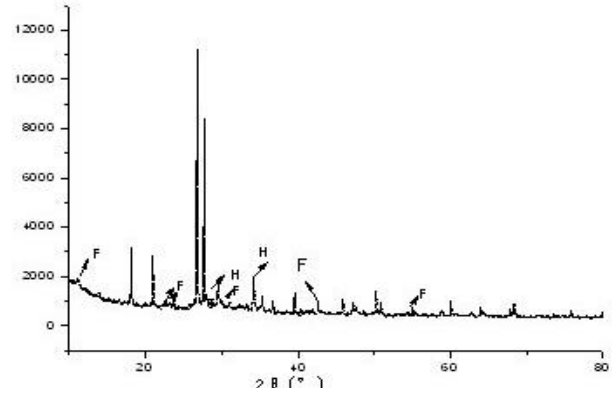
(a) TG/DTA curves of HCD0



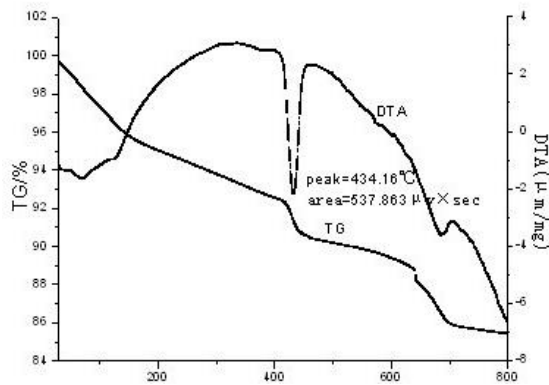
(a) XRD patterns of mortars with river sand



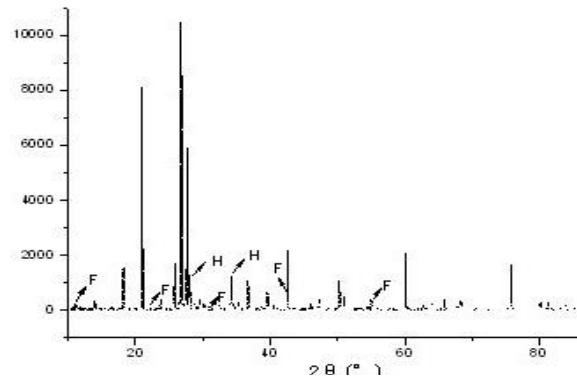
(b) TG/DTA curves of D0



(b) XRD patterns of mortars with desalted sea sand



(c) TG/DTA curves of W0



(c) XRD patterns of mortars with sea sand

Figure 4. TG/DTA curves of mortar

Figure 5. XRD patterns of mortars

#### 4. Conclusions

(1) Regardless of the mortars with river sand, regular sea sand or desalted sea sand, the free chloride content correlates closely to the extraction temperature. The concentration of free chloride increases with the rise of extraction temperature, and the free chloride concentration increases by about two times when the extraction temperature varies from 15°C to 65°C.

(2) The free chloride concentration of the mortar with fly ash is higher than that of the mortar without fly ash at 15 extraction temperature. This may be due to the chemically bound chloride ion content is low and the physically bound chloride ion content is relatively high.

(3) Small quantity of unstable Friedel's salts exists in the mortars. It explains why the TG/DTA curves of regular sea sand and desalted sea sand mortars do not show endothermic peaks. Thus, it is unreasonable to determine the existence of Friedel's salt only using TG/DTA curves, and the investigation of XRD and SEM should be carried out at same time.

## References

- [1] S. Pack, M. Jung, H. Song, S. Kim, K. Ann. Prediction of time dependent chloride transport in concrete structures exposed to a marine environment. *Cement and Concrete Research*, 2010,40(2) 302-312.
- [2] J.J SHI, W. SUN. Recent research on steel corrosion in concrete Chinese Ceramic Society, 2010,38(9)1753-1764. countries. *Concrete* 2000,9 23-26.
- [3] Q. Yuan, C.J.Shi, G.D. Schutter, K. Audenaert, D.H. Deng. Chloride binding of cement-based materials subjected to external chloride environment-A review. *Construction and Building Materials*, 2009,23(1)1-13.
- [4] K.V. Subramaniam, M.D. Bi. Investigation of steel corrosion in cracked concrete: Evaluation of macrocell and microcell rates using Tafel polarization response. *Corrosion Science*, 2010,52(8) 2725-2735.
- [5] Jianbin Chen, Junzhe Liu, Guoliang Zhang, Zhimin He. Study on the strength of sea sand concrete introduced by chloride ions, 2011 Second International Conference on Mechanic Automation and Control Engineering, 2011,250-253 262-265
- [6] Z.Q.JIN, W. SUN, T.J. ZHAO, Q.Y.LI. Chloride binding in concrete exposed to corrosive solutions. *Chinese Ceramic Society*, 2009,37(7)1068-1072.
- [7] S.M. Abd El Haleem, S. Abd El Wanees. Environmental factors affecting the corrosion behavior of reinforcing steel. IV. Variation in the pitting corrosion current in relation to the concentration of the aggressive and the inhibitive anions. *Corrosion Science*, 2010,52(5)1675-1683.