Study on the curing behavior of chloride ion in sea sand concrete

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Abstract： Study on chloride ion adsorption and combined with the characteristics of sea sand concrete， through the determination of free chlorine ion content in sea sand concrete. The sea sand concrete microstructure and Friedel salt were characterized by using X-ray diffraction (XRD) , scanning electron microscopy (SEM) and thermal analysis methods (TG/DTA). Research results show that: the extraction temperature of solution is positively correlated with free chloride concentration in sea sand concrete. Physical binding of chloride ion in fly ash mortar shows low dissolution in lower temperatures. TG / DTA curve does not appear endothermic peak on the Friedel salt in sea sand concrete, while the XRD and SEM pictures show the existence of Friedel salt in the sea sand. Probably, it's the result of less Friedel salt, leading to the formation of the Friedel salt is unstable.

Introduction

Desalination of sea sand is natural sand which by water washing and purification formation. Due to extensive use of sea sand in coastal areas and even appear "sea sand house", the domestic and foreign corrosion experts attach great importance to study on the durability of sea sand concrete[1-4] . In general, chloride ion in sea sand concrete exists in three forms:free chlorine ion, physical curing chloride ion and chemical curing chloride ion[5] . Only free chloride ions in the three forms of chloride ions play a role in the corrosion of steel bars, when free chlorine ions in the surface area of the reinforced concrete, even if the concrete is greater than 12 pH, it will also cause or exacerbate the corrosion of steel[6-7]. The based on a survey of status of Ningbo City sea sand desalination, curing rule of sea sand concrete chloride ion binding, and fly ash on the free chloride ion concentration influence,clarify the sea sand concrete micro structure and Friedel's salt characteristics, and provide a theoretical basis for the durability of sea sand concrete structure.

Experiment

1.Materials and Forming

(1)Cement: 42.5 ordinary portland cement; (2) Fly ash:two ash; (3) River sand: The medium sand, fineness modulus of 2.27, water content is 0.67%. Desalination of sea sand and not desalination of sea sand in 5 desalination of sea sand sampling plant,the chloride ion content was determined as shown in Table 1. Mortar mix ratio is cementitious materials: sand: water =1:2.5:0.45,Specimen size is 70.5mm×70.5mm× 70.5mm,the curing age of 28 days, as shown in Table 2.

Table 1 Chloride ion contents in sea sand *W*/%

Sample	1	2	3	4	5
DSS	0.0062	0.0019	0.0055	0.0114	0.0107
SS	0.0293	0.0279	0.0302	0.0575	0.0539

* DSS——Desalted sand; SS-Sea sand

Table 2 Mix proportions of the mortar

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

* RS-River sand

2.Methods

Determination of chloride ion content in sand:The sand with four points to 1500g on the shrinkage oven at 105 DEG C dried to constant weight, cooling to room temperature.Using the balance to accurately weigh the 500g, respectively, into the capacity of 1000ml with a plug in the bottle, add 500ml distilled water, plus the lid, shake once, place 24h.Then, shaking once every 5min, a total of 3 times, to facilitate the full leaching of chloride salt.Grinding mouth bottle top has clarified solution by filter through the funnel inflow into the beaker, with the pipette aspiration of 50 ml of the filtrate injected into Erlenmeyer flask, add 1ml of 5% potassium chromate indicator, with 0.0lmol/L $AgNO_3$ standard solution titration to brick red in colour.Record the consumption of silver nitrate standard solution by ml, content of chloride ion in sea sand is calculated.

Determination of free chlorine ion in mortar:Determination of free chloride content in mortar specimens with curing to 28 days by moire method. Using K_2CrO_4 as indicator and silver nitrate titration, and the pH value of the solution should be neutral.Taking into account the effect of temperature on the solubility of free chlorine, the determination of chloride ion concentration was carried out at 15℃ and 65℃ respectively.

Analysis of microstructure and products of mortar:Desktop scanning electron microscope (SEM) production from Japan Hitachi, the samples of non observation of spraying, using low vacuum, using back scattered electron image observation and performance between advanced optical microscope and traditional scanning electron microscopes, when the magnification of 8000, but also clearly scanning the sample morphology;Polycrystalline X - ray diffraction and thermal weight/differential thermal analysis were produced by the German Brook company and the United States Elmer-Perkin company,determination of internal product and content of mortar by combining analysis with the two party[8].

Results and discussion

1.Free chlorine ion content of mortar

Content of chloride ion in sea sand:Can be seen from Table 3.1, different sand chloride content of sea sand desalination plant has certain difference.Dilute the content of chloride ion in sea sand is far less than the non desalination of sea sand;Not dilute the sand content of chlorine ion in more, by dilution of the residual chlorine ion concentration is high, it is fully embodies the necessity of desalted sea sand.

Table 3 Existing status of chloride ion at different temperatures

Sample	Soluble ratio of Cl^-/%		Bonding ratio of Cl^-/%		TCl^-/% *	Sample	Soluble ratio of Cl^-/%		Bonding ratio of Cl^-/%		TCl^-/% *
	15℃	65℃	15℃	65℃			15℃	65℃	15℃	65℃	
HCA0	22.1	54.7	77.9	45.3	0.0071	HCD0	22.9	58.8	77.1	41.2	0.0714
HCA20	28.3	57.8	71.7	42.2	0.0071	HCD20	27.8	57.3	72.2	42.7	0.0714
HCB0	22.1	57.8	77.9	42.2	0.0214	D0	29.5	63.0	70.5	37.0	0.0077
HCB20	24.1	52.6	75.9	47.4	0.0214	D20	33.4	64.7	66.6	35.3	0.0077
HCC0	26.4	60.1	73.6	39.9	0.0428	W0	30.3	56.7	69.7	43.3	0.0385
HCC20	31.2	63.5	68.8	36.5	0.0428	W20	32.0	58.8	68.0	41.2	0.0385

* TCl^-——Total contents of $Cl^-$for mortar

Free chlorine ion content:sea sand and river sand with chlorine salt in 15ºC and 65ºC in the state are shown in Table 3.It can be seen that the free chlorine ion concentration is closely related to the extraction temperature, when the extraction temperature is 15ºC, the free chloride dissolution rate of 22%～34%, and the free chlorine ion dissolution rate of 52%～65% in 65ºC.That is,free chlorine dissolution rate is two times more than that of 65ºC when the temperature is 15ºC.It is showed that the difference of total chloride ion content and free chlorine ion content is not accurate.The chlorine ion inside the mortar includes chemical and physical forms,when the material is grinding and immersion, a large part of the physical curing of chloride ions will be dissolved and become "free chloride ion",sea sand concrete, mix remains adsorbed in micro particles on the surface of the chloride ion should belong to the physical curing of chloride ion, after grinding and soaking the majority will dissolution,and the higher the temperature, the higher the dissolution rate.

In addition, the dissolution rate of the mortar mixed with 20% fly ash is higher than without any fly ash mortar when the extraction temperature is 15ºC; But at 65ºC, the dissolution rate of chloride ion in fly ash mortar is similar to without any fly ash mortar,as shown in Fig.1.This may be related to the lower temperature of the fly ash mortar in combination with less chemical curing chlorine ion content,and the adsorption of the physical cure chlorine ion dissolution rate is higher.

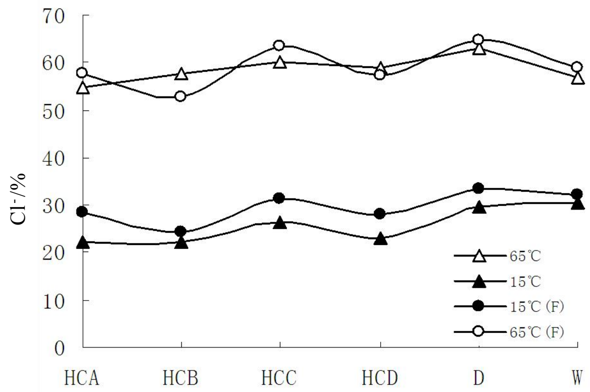
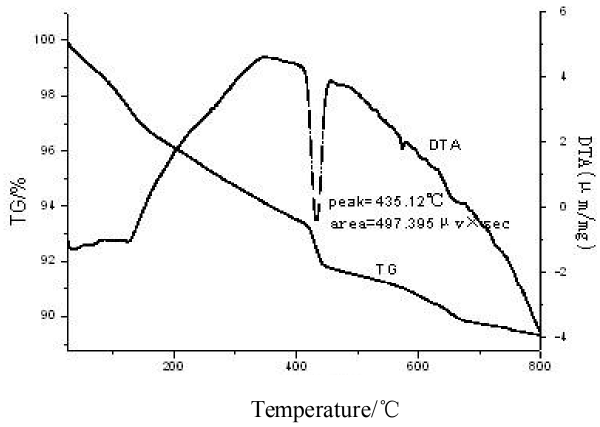
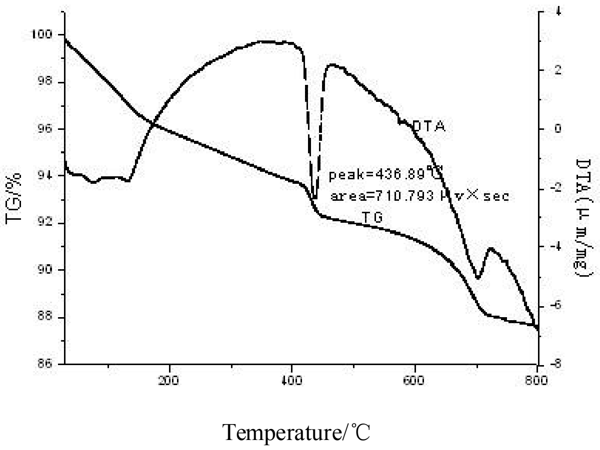


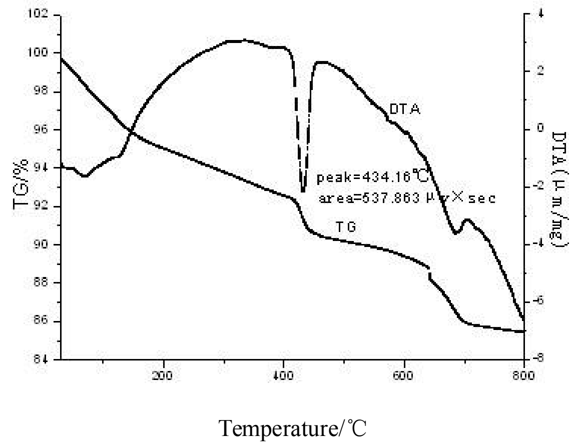
Fig.1. Relationship between the temperature and soluble chloride ion concentrations



(a) TG/DTA curves of HCD0



(b) TG/DTA curves of D0



(c) TG/DTA curves of W0

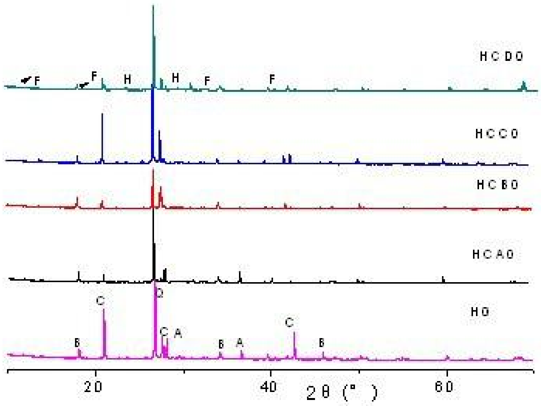
Fig.2 . TG/DTA curves of mortar

2.F salt product features of sea sand concrete

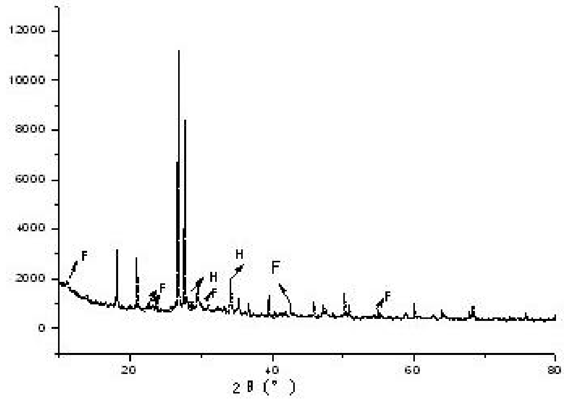
Chloride ions in the cement based materials will be chemically combined with the formation of F salt,however, in the relevant research, most of them are dissolved in the mixing water to the introduction of chloride ions.When the chloride ion content in concrete is not reached a very high concentration, under such conditions will produce F salt, and whether it can be observed, there is no relevant research report[11].

In general,the decomposition endothermic peak of F salt on the TG/DTA curve appeared at about 360ºC[9,12].Fig.2 for TG/DTA curves of mortar with river sand, dilute sand and did not dilute the sand,the content of Cl^- is 0.1%, 0.01% and 0.054% respectively.Unfortunately, there are no endothermic peaks in the F salt decomposition region of the three DTA/TG curves.

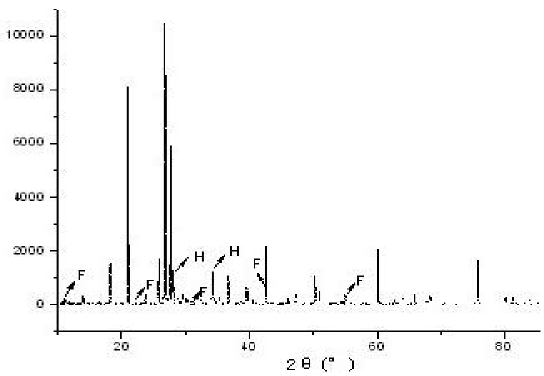
In order to further reveal the sea sand concrete whether F salt formation, the age 28 day sampling of mortar is grind and the XRD tested, the results are shown in Fig.3.Can be seen, the sand F salt of diffraction peak intensity with $Ca(OH)_2$ material than is very weak, or can be found F salt obvious evidence of existence.No matter the desalination of sea sand desalination of sea sand, can be found in the peak diffraction intensity of multiple F salt.This shows that in the sea sand mortar, chloride ion adsorption in the sand particle surface, and the total amount is not large but will still generate a certain amount of F salt[13] .The TG/DTA curve does not appear on the F salt endothermic peak, probably because the amount of F salt formation is too low, the formation of the F salt is not stable.Obvious peak value was observed in the river sand with the chloride ion content greater than 0.03%, while the chloride ion content was less than 0.03% and the peak value of F salt was not obvious.



(a) XRD patterns of mortars with river sand

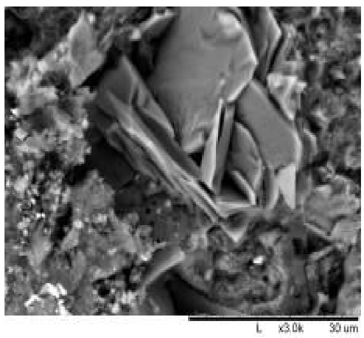


(b) XRD patterns of mortars with desalted sea sand

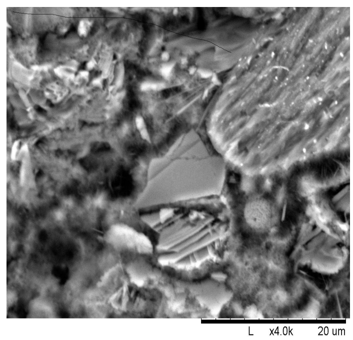


(c) XRD patterns of mortars with sea sand

Fig.3. XRD patterns of mortars with chloride



(a) Sea sand mortar



(b) Desalted sea sand mortar

Fig.4. SEM micrographs of Friedel salt in sea sand mortars

Fig.4 is the internal sand mortar hydration products morphology,can clearly see the formation of the F salt for the size of 10～20μm six square crystal,and the combination of XRD and SEM showed that the formation of more F salt in the sea sand[14].

Conclusion

(1)Water soluble free chlorine ion concentration and solution temperature in sea sand concrete is closely related to the extraction.The higher the temperature, the greater the concentration of free chlorine ion.When the extraction temperature is 65ºC, the concentration of free chlorine ion is about two times of that of 15ºC.

(2)When the extraction temperature was 15ºC, the dissolution rate of free chlorine ion of fly ash mortar was higher than without any fly ash mortar.But at 65ºC, the dissolution rate of chloride ion in fly ash mortar is similar to without any fly ash mortar.This may be related to the lower temperature of the fly ash mortar in combination with less chemical curing chlorine ion content,and the adsorption of the physical cure chlorine ion dissolution rate is higher.

(3) The TG/DTA curve does not appear on the F salt endothermic peak, probably because the amount of F salt formation is too little, the formation of the F salt is not stable.Therefore,we should combine with X-ray diffraction pattern and SEM map to determine the existence of F salt by TG/DTA curve.

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