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Carbonation of concrete made with dredged marine sand and its effect on chloride binding



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HIGHLIGHTS

• Interaction between DMS chloride in concrete and concrete carbonation was studied.

• Chloride ions introduced by DMS can reduce the porosity of cement paste.

• Carbonation can improve free Cl⁻ concentration in DMS concrete.

• Initial total Cl⁻ concentration of DMS concrete is very important to steel bar corrosion.

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$A \hspace{0.1in} B \hspace{0.1in} S \hspace{0.1in} T \hspace{0.1in} R \hspace{0.1in} A \hspace{0.1in} C \hspace{0.1in} T$

River sand (RS) has been overly exploited to meet demand in the construction industry, particularly in China. Chloride salt in dredged marine sand (DMS) is the primary concern that limits the use of DMS in reinforced-concrete (RC) structures. This paper developed an interaction model between the carbonation behaviour and chloride ions in DMS concrete compared with RS concrete. In this research, the test results indicated that the chloride ions introduced by DMS can reduce 20–50% carbonation of the DMS concrete. The process of concrete carbonation can alter the state of chloride ions in the concrete. The process of concrete carbonation process, the bound chloride ions would become free, and their concentration in carbonated concrete could increase by up to 200% compared to that of uncarbonated concrete when the chloride ions must be considered with respect to the durability when DMS concrete is designed for use in RC structures.

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1. Introduction

With the rapid growth of the construction industry in recent decades, the demand for fine aggregate has increased significantly. River sand (RS) is the most widely used fine aggregate in China, and the overexploitation of RS to meet this demand has led to various harmful consequences, such as increasing depths of river beds, lowering water levels, and salinity intrusion into rivers. Due to these environmental problems, river sand mining activities must be restricted, particularly in vulnerable locations. As a remedial measure, the Chinese government has imposed various restrictions

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http://dx.doi.org/10.1016/j.conbuildmat.2016.05.011 0950-0618/© 2016 Elsevier Ltd. All rights reserved. on the extraction of RS, which has produced significant increases in prices. In China, where coastal areas are rich in dredged marine sand (DMS), DMS has been widely used in local concrete construction due to the convenience of mining and transportation, its relatively mature technology, and lower costs (50–70% of the cost of imported freshwater sand).

Chloride salt from DMS is the primary reason for limiting its use in reinforced-concrete (RC) structures. Using unwashed DMS may lead to serious degradation in concrete quality or steel corrosion in RC structures [1–4]. At present, the use of DMS in RC structures without washing has become a significant engineering quality problem in coastal areas of China [5].

The passive film on the steel bar can typically protect the steel from corrosion in a high-alkalinity (pH > 12.5) environment in concrete. However, the passive film will be destroyed when either the concrete cover is carbonated or the chloride ions attack the surface

Abbreviations: RS, river sand; DMS, dredged marine sand; RC, reinforced-concrete.

of the steel bars above a certain threshold. During carbonation, the presence of chloride ions can damage the steel's passive film, promoting the electrochemical process of steel corrosion. Therefore, the influence of chloride ions on the durability of carbonated concrete structures tends to be greater than that to the uncarbonated concrete structures [1,6,7]. There are many studies on concrete carbonation and the effects of chloride on concrete durability [8–14]. Carbonation can reduce the pH of concrete and influence the stability of the bound chloride ions [15,16]. The chloride ions critical threshold is directly related to many factors, such as the chloride ions concentration and pH [1]. Therefore, even if the initial concentration of chloride ions introduced into the concrete by DMS is lower than the critical threshold, RC structures with DMS are still more vulnerable to corrosion due to the interaction of carbonation and chloride ions. Saillioa et al. [17] investigated the effect of partial and total carbonation on chloride binding by various macroscopic and microscopic techniques. The research showed that there is a competition between chlorides and carbonates to react with AFm phases. Ramezanianpoura et al. [18] studied the effect of combined carbonation and chloride ion ingress by an accelerated test method on microscopic and mechanical properties of concrete. Although these researches explained that effect of carbonation on the change of chloride concentration in concrete, carbonation and chloride ion ingress were studied individually. Chloride ion ingress can improve anti-carbonation capacity of concrete and reduce concrete carbonation, whilst carbonation can lead to the increase of chloride ion concentration. Therefore, the carbonation and chloride ion ingress interacting in different direction for steel bar corrosion in concrete. However, few studies have considered the interaction between concrete carbonation and chloride ions introduced by the ingredient of concrete. DMS is a kind of raw materials for manufacturing concrete in many areas in the world. Therefore, this research originally explores the interaction between DMS chloride in concrete and concrete carbonation. A schematic drawing was displayed in Fig. 1 for explaining the originality of this study visually. The results of this research can contribute to the risk estimation of DMS concrete application in infrastructure.

2. Experimental

2.1. Materials

In this paper, RS, DMS, and washed DMS were used to study the carbonation of the concretes and the characteristics and roles of chloride ions in the carbonated concretes. A mercury intrusion porosimeter (MIP), X-ray diffraction (XRD) and differential thermal analysis were employed to study the mechanism of interaction between carbonation and chloride ions in concrete. The typical DMS in this research was mined from the South China Sea near the mouth of the Pearl River, located in Guangdong Province in South China. The specific location is marked by the dashed circle in Fig. 2.

Through field sampling tests, 60 DMS samples were collected from the mouth of the Pearl River at different times and from different piles of sand in the area. Based on statistical analyses, the physical properties of the mined DMS were obtained and are shown in Table 1.

The morphologies of RS and DMS were studied by optical microscopy and scanning electron microscopy (SEM). An energy dispersive X-ray (EDX) detector was used to analyse the elements on the surface of the sand. The mineral and petrographic composition of DMS were also analysed using XRD and petrographic analyses.

The cement used was ordinary Portland cement (OPC) that conformed to British Standard BS 12 and had a 28-day mortar compressive strength of 61 MPa. The specific gravity was 3.1 g/cm^3 , and the fineness was $3190 \text{ cm}^2/\text{g}$. The initial and final setting times were 145 and 200 min, respectively. The oxide composition is given in Table 2.

Three types of sand (RS, DMS, and washed DMS) were used as fine aggregates to produce the concretes studied. The properties of the three sand samples are shown in Table 3. Methods from standards of ASTM C1218/C1218M-99 (Standard Test Method for Water-Soluble Chloride in Mortar and Concrete) and ASTM C1152/C1152M-04 (Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete) were employed to obtain the chloride content in concrete.



Fig. 1. Schematic drawing for research works on the interaction between concrete carbonation and chloride ions concentration. (a) Most of current researches focus on carbonation and chloride ions ingress; (b) Originality of this study is to investigate interaction between concrete carbonation and concentration of chloride ions introduced by DMS.

Crushed gravel was used as the coarse aggregate with a grading of 10–20 mm. The apparent density is 2630 kg/m³. To eliminate the chloride ions in the tap water used, distilled water without chloride was used to mix all of the concrete specimens. The chemical admixture was a high-efficiency water-reducing agent made of polycarboxylic acid.

2.2. Mixture proportions

The concrete mixture proportions for the carbonation tests are shown in Table 4. Concrete specimens were classified by different sand materials. A, B and C represent RS, DMS, and washed DMS, respectively; the number refers to the type of mixture proportion.

To eliminate the influence of aggregate on test results, plain cement paste was used to study the effect of chloride on the porosity of the hardened cement paste and the mechanism of carbonation and chloride interaction. The mixture proportions are displayed in Table 5. NaCl was added to certain cement pastes in proportions of 1% and 5% by cement mass during mixing, as shown. The equivalent chloride ions percentage (0.6% and 3%) can be calculated through the concentration of NaCl and is divided by 1.648, which is the value of the molecular weight of sodium chloride divided by the atomic weight of chloride. Compared with chloride ion concentration in the selected concrete mix proportion, the 0.6% and 3% chloride ion concentration are remarkably high. In fact, higher chloride ion concentration can be helpful to identify the changes of Friedel's salt under carbonation clearly. Although the chloride ion concentrations are different between the concrete and the neat cement paste, these differences have not shown any negative effect on this research results.

2.3. Specimen preparation and test methods

All specimens were cast in steel moulds and compacted using a vibration table. The specimens were then demoulded after curing for 24 ± 2 h in a controlled indoor environment at 99% relative humidity (RH). To eliminate the effect of chloride in curing water, all demoulded specimens were sealed using a plastic film and then put in a curing room at 20 ± 2 °C and 99% RH until testing.



Fig. 2. Location from which the DMS was collected.

Table 1 Physical properties of DMS in the Pearl River Mouth area.

Properties	Data range	Mean	Standard deviation
Fineness modulus (µ _f) Bulk density (kg/m ³) Apparent density (kg/m ³) Silt content (%)	1.6-3.2 1320-1490 2580-2680 0.8-3.8	2.65 1394 2632 1.7	0.30 55 20 0.67

Concrete carbonation test was performed in accordance with the Chinese National Standard GB/T 50082-2009 "Standard for test methods of long-term performance and durability of ordinary concrete". The CO₂ concentration in the cabinet was $20 \pm 3\%$, and the RH and temperature were $70 \pm 5\%$ and 20 ± 5 °C, respectively. Although the 20% concentration of CO₂ is far higher than the natural condition and under such a high CO₂ the carbonated hydration products may be different from the natural carbonation concentration, in this study, the high CO₂ concentration can make testing results more obvious and the results are conservative for DMS engineering application. The specimen size was 100 mm \times 100 mm \times 100 mm, and three samples were used for each mixture. Carbonation tests were performed after the samples cured for 28 days.

After 28 days of standard curing, the hardened plain cement paste was ground into powder. In order to avoid samples of plain cement paste to be carbonated during the grinding process, all samples were ground in alcohol solution. Before the next test, the ground powders were dried in an oven with 50 °C. Then the samples were put into the accelerated carbonation cabinet under same carbonation condition as that of the concrete samples. Then, the carbonated powders were ground for XRD and differential scanning calorimetry (DSC)/thermogravimetry (TG) analyses.

The chloride ions content in the concretes were studied according to the standards of ASTM C1218/C1218M-99 (Standard Test Method for Water-Soluble Chloride in Mortar and Concrete) and ASTM C1152/C1152M-04 (Standard Test Method for Acid-Soluble Chloride in Mortar and Concrete). The water soluble chloride ions in the concretes and the total chloride ions were measured. A Switzerland Metrohm 809 Titrando potentiometric titration apparatus was used to measure the chloride ions content. The electrode used was a compound silver electrode (Part No. 6.0450.100 or 6.0430.100). The concentration of the titration solution AgNO₃ was 0.01 N. The chloride ions content was expressed as the percentage of the dry weight of each concrete.

Table 2

С

Chemical analysis of the cement (%).

Washed DMS

2.83

Π

Content	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ Oeq	<i>f</i> -CaO	Cl^{-}
%wt	20.30	5.15	2.67	65.25	1.21	2.34	0.69	0.51	<0.01

I	Primary	properties of the	e sands.					
	No.	Sand type	Fineness modulus	Grading zones	Apparent density (kg/m ³)	Bulk density (kg/m ³)	Shell content (wt%)	Chloride content (wt%
	А	RS	2.66	II	2660	1510	<1.0	<0.001
	В	DMS	2.83	П	2580	1580	4.40	0.210

1580

2580

A2/B2/C2

Type of concrete

based on sand type A1/B1/C1

Table 5

Table 4

Mixture proportions of the net cement paste.

Mixture proportions of the concrete (kg/m³).

Cement

360

460

Type of net cement paste	W/C	NaCl (wt% of cement weight)	% Equivalent chloride ions*
Blank	0.5	0	0
1% NaCl	0.5	1%	0.6%
5% NaCl	0.5	5%	3.0%

Sand

797

636

Gravel

1057

1152

Water

170

162

W/C

0.47

0.35

Plasticiser

2.85 (0.79%)

5.06 (1.10%)

% Equivalent chloride ions = %NaCl/1.648.

A Mercury AutoPore IV 9500 injection apparatus was used for the pore analysis of the plain cement paste, and the XRD analysis was conducted using a Dandong Fangyuan DX – 2500 X-ray diffractometer. These tests involved a Cu target, 3 kW of power, 0.03° per step and a scanning range from 5° to 70°. A DSC/TG STA-409 PC comprehensive thermal analyser was used for the analysis of the thermal properties. The sample was heated in a range of 100–1000 °C at a heating rate of 10.0 °C/ min; the protective atmosphere was nitrogen.

3. Results and discussion

3.1. Comparison between DMS and RS

In this study, the physical, chemical and microstructure properties of DMS were examined. Fig. 3(a) and (b) displays the morphology of RS and DMS, respectively, using optical microscopy. The RS

4.40

< 0.001



(a) RS



(b) DMS

Fig. 3. Optical microscopy of the morphology of RS and DMS.

surface is rough and matte. In contrast, the surface of DMS is smooth and lustrous. Fig. 4 shows an EDX test result of RS particle. From the test result, it can be known that there was no chloride in the RS. Fig. 5(a) and (b) presents the EDX test results of DMS. The square scan in Fig. 5(a) illustrates that the DMS has chloride ions, which is a potential factor for steel bar corrosion. From the elemental analysis, the chloride content was found to be 3.14 wt%. But the EDX results can not represent the true picture of the chloride content in DMS. They just give micro level chloride concentration. The method in BS EN 1744-1:2009 (Tests for chemical properties of aggregates. Chemical analysis) was employed for total chloride ion concentration and free chloride ion concentration of the concretes. Fig. 5(b) shows the enlarged microstructure of a selected area in Fig. 5(a) and the EDX test results of the crystal materials attached on the surface of DMS. From the elements in this EDX results, the cubic crystals can be identified as NaCl.

According to the XRD diagrams shown in Fig. 6, both RS and DMS have strong diffraction characteristic peaks of quartz (SiO₂) (d = 0.4241, 0.3336, and 0.1816 nm); in addition, characteristic feldspar ((K, Ca, Na) (AlSi)₄O₈) diffraction peaks are also evident (d = 0.3472, 0.3233 and 0.2985 nm). The XRD patterns show that DMS and RS possess similar mineral compositions and that their primary minerals are quartz and feldspar.

3.2. Carbonation of the concretes

3.2.1. Carbonation depth

Fig. 7 presents the results of the carbonation depth of concrete samples under the accelerated carbonation test for 365 days. In this figure, concretes A, B and C are manufactured with RS, DMS and washed DMS, respectively.

The concrete carbonation behaviour can typically be represented by the carbonation depth at a fixed time or by the change in carbonation depth over time. Most previous studies assumed



Electron Image 1



Fig. 4. EDX test results for RS.

that the carbonation depth of concrete is proportional to the square root of the carbonation time [19–21]. Eq. (1) shows this mathematical expression:

$$Xc = k \cdot t^{1/2} \tag{1}$$

where Xc is the carbonation depth and K is the carbonation coefficient.

The concrete carbonation coefficient *k* can be obtained using the fit carbonation curve based on Eq. (1). Comparing the A, B and C series in Table 4, concrete A, which is made with RS, has the largest carbonation depth, and its carbonation coefficient is the greatest compared to those of concretes B and C, which are made with DMS and washed DMS, respectively. Through the comparison of concrete carbonation coefficient k between concretes A (made with river sand) and concrete B (made with DMS), it can be deduced that the chloride ions introduced by DMS can increase the concrete's carbonation resistance. For concretes with W/C = 0.47, K value diminished from 0.70 to 0.61 and the reduced range is about 13%. The 1 year's concrete carbonation depth diminished from 12.5 mm (concrete A1) 9.8 mm (concrete B1) and the reduced range is about 21.6%. For concrete A2 and B2 with W/C = 0.35, the reduced range of K value is about 58.3% (dropped from 0.12 to 0.05) and 1 year's carbonation depth is reduced by about 52.6% (dropped from 1.9 mm to 0.9 mm). Therefore, it can be known that the chloride ions have not adversely effected the concrete's carbonation resistance.

Although both river sand and washed DMS contained negligible amount of chlorides in this study, their properties such as fineness modulus, particle size and shell content are different (see Table 3). Specially, the shell content of DMS is higher than that of river sand obviously. The abovementioned differences are the possible reasons to explain why concretes with DMS and river sand have







Fig. 6. XRD diagrams of RS and DMS.

different carbonation performances. Effect of chloride ion on concrete carbonation can be displayed clearly through the comparison between carbonation performance of concrete made with DMS and concrete made with washed DMS.

Compared Fig. 7(a) with (b), it can be known that higher water/ cement ratio decreases the differences of carbonation depth between the different concretes. The reason for this phenomenon is that higher water/cement ratio leads to higher porosity of the concretes, which makes concrete carbonation depth increased [22,23].

3.2.2. Pore analysis for cement paste

Plain cement paste (see Table 5) was used to study the effect of chloride on the porosity of hardened cement paste and the mechanism of carbonation and chloride interaction. The pore

distribution characteristics of the plain cement pastes with different chloride contents are shown in Fig. 8.

Fig. 8(a) shows that the inclusion of chloride ions in cement paste does influence the total porosity of the hardened cement paste. The comparison of the chloride ions contents among the three different types of plain cement paste illustrates that the total porosities of the plain cement pastes containing 1% and 5% NaCl are considerably lower than that of the blank cement paste. This result demonstrates that adding a small amount of chloride ions reduces the total porosity of hardened cement paste. Green circle area 1 in Fig. 8(b) illustrates that the volume of 100–300 nm coarse capillary pores in the cement paste decreases significantly with the addition of chloride ions. The amount of capillary pores less than 100 nm shown in the green oval area 2 in Fig. 8(b) was found to increase with increasing content of chloride ions. The volume changes of coarse and fine capillary pores illustrate that the addition of chloride ions is beneficial for reducing the content of coarse capillaries and thus optimising the pore distribution in the cement. Previous studies have shown that chloride ions can increase the strength of concrete [24] and that NaCl crystals can fill capillary and gel pores in concrete [25]. The effects of chloride ions on the early strength of concrete are described by the following three aspects: (1) chloride ions react with the cement hydration product of tricalcium aluminate (3CaO·Al₂O₃, C₃A) to generate refractory chlorine aluminate hydration, accelerating C₃A hydration; (2) chloride ions react with Ca(OH)₂ produced by cement hydration to generate calcium chloride, which has a low solubility in water, further accelerating tricalcium silicate (C_3S) hydration to generate composite salt and increase the solid phase proportion in cement pastes; and (3) chloride salts can increase the solubility of Portland cement clinker and thus accelerate concrete hardening [26].

The change phenomena presented in Fig. 8 have shown that chloride ions can reduce the porosity of hardened cement paste and pore size distribution of hardened cement paste leading to fine capillary pores. In concrete, a lower total porosity and higher ratio



(a) Concretes with W/C=0.47, cement 360 kg/m³



Fig. 7. Comparison of carbonation for concretes made with different sands.

of capillary pores can reduce the diffusion rates of CO_2 and moisture in the atmosphere. Furthermore, the chloride ions carried by DMS in concretes can improve the carbonation resistance of the resulting concrete.

3.3. Interaction model between carbonation and concentration of chloride in concrete

3.3.1. Effects of carbonation on chloride ions in cement paste

Chloride ions exist in concrete in free or bound states. Because only free chloride ions are effective in the steel corrosion process, a larger amount of chloride ions that are in a bound state yields a smaller risk of steel corrosion. The formation of bound chloride ions can be considered as chemical binding and physical adsorption; chemical binding refers to the reaction between chloride ions and aluminate to generate chlorine hydrated calcium aluminate (C₃A·CaCl₂·10H₂O), which is also known as Friedel's salt [27]; the physical adsorption primarily refers to cement hydration products or microporous adsorbed chloride ions.

Table 6 shows the content of total chloride ions and free chloride ions and the binding ratio of chloride ions in uncarbonated and carbonated zones in DMS concrete. The chloride ions bound ratios in the carbonated zones of concretes B1 and C1 made with DMS were significantly lower than the chloride ions bound ratio

Fig. 8. Pore distribution characteristics of cement paste.

 Table 6

 Chloride contents in concrete (wt% of concrete).

Concrete	Uncarbonated zone			Carbonated zone (1 year)			
type	Total (%)	Free (%)	Ratio of bound	Total (%)	Free (%)	Ratio of bound	
B1 C1	0.076 0.011	0.049 0.007	35.5% 36.4%	0.088 0.012	0.086 0.011	2.3% 8.3%	

in the uncarbonated zone. The chloride ions bound ratio of the C1 samples decreased from 36.4% to 8.3%, and that of the B1 samples decreased from 35.5% to 2.3%. The test results indicated that in the carbonated zone, the amount of free chloride ions was close to the total amount of chloride ions. For DMS concrete, free chloride ion concentration in carbonated zone (1 year age) is nearly about 200% of that of uncarbonated zone. Therefore, concrete carbonation can enable the release of most bound chloride ions to become free chloride ions. This observation is similar to the results of other studies. Kayyali and Haque [28] found that carbonation can increase the concentration of chloride ions in the pore solution of mortar. This may also explain the corrosion risk presented by the presence of chlorides at low concentrations, which is generally negligible in uncarbonated concrete but becomes increasingly significant in carbonated concrete. Considering the influence of carbonation on chloride ions binding, the interaction between carbonation and chloride ions on steel corrosion should be considered,

even if the amount of chloride ions introduced by DMS is lower than the critical threshold value and particularly in DMS concrete structure with higher W/C ratios. Due to there is threshold value of chloride ion for steel bar corrosion in reinforced concrete, therefore, initial chloride ion concentration introduced by DMS is considerably important for DMS concrete. From Table 6, it can be known that C1 concrete with washed DMS, which has a low initial chloride ion concentration, has a remarkably lower free chloride ion concentration than that of B1 concrete with DMS. Therefore, initial total chloride ion concentration of DMS concrete is very important to assessing the risk of steel bar corrosion.

3.3.2. Mechanism of the interaction between concrete carbonation and chloride ions

The mechanism of the interaction between concrete carbonation and chloride ions in concrete is critical for understanding the effect of DMS concrete on steel bar corrosion in concrete.

3.3.2.1. XRD analysis. Fig. 9 shows the XRD graphs of the plain cement pastes. A comparison of the primary diffraction peaks of the XRD graphs before and after concrete carbonation illustrates

Fig. 9. XRD patterns of the net cement pastes.

that for three types of uncarbonated cement paste samples, positions near d = 0.4900, 0.2627, 0.1925 and 0.1794 nm have significant Ca(OH)₂ diffraction peaks. After carbonation, the primary diffraction peaks of Ca(OH)₂ disappeared, and positions near d = 0.3859, 0.3034, 0.2495, 0.2285 and 0.2495 nm exhibit strong CaCO₃ diffraction peaks. These results show that most of the cement hydration products Ca(OH)₂ are transformed into CaCO₃ after carbonation.

Fig. 9(a) shows the XRD diagram of the plain cement pastes with added chloride ions (see curves (2) and (3)); diffraction peaks are present at d = 0.789 nm $(2\theta = 11.21^{\circ})$ and d = 0.787 nm $(2\theta = 11.24^{\circ})$. A higher chloride ion content yields a higher diffraction peak intensity. However, in the blank cement paste, there is no diffraction peak for curve (1). Suryavanshi [29] and Goñi [27] found similar diffraction peaks in the vicinity of d = 0.790-0.800 nm; these peaks are characteristic of Friedel's salt; therefore, the diffraction diagram of curves (2) and (3) in Fig. 9(a) at $2\theta = 11.21^{\circ}$ and 11.24° are likely Friedel's salt. However, Suryavanshi [29,30] suggested that the characteristic peak of the hydration of calcium aluminate (C₄AH₁₃) should be near d = 0.790 nm $(2\theta = 11.21^{\circ})$. The determination of Friedel's salt requires differential scanning calorimetry (DSC) analysis; this finding is reported in the next section.

The XRD diagram of carbonated plain cement paste is shown in Fig. 8(b). Curves (2) and (3) indicate that the diffraction characteristic peaks of the Friedel's salt have disappeared, suggesting that carbonation causes the chloride ions in its binding state to be unstable. Suryavanshi [29] stated that Friedel's salt stability is related to pH; carbonation reduces the pH and can thus cause the solubility of Friedel's salt to increase. Friedel's salt may follow the dissolution of the following equation:

$$\begin{aligned} 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaCl}_2 \cdot 10\text{H}_2\text{O} &\rightarrow 6\text{Ca}^{2+} + 6\text{Cl}^- + 60\text{H}^- \\ &\quad + 2\text{Al}(0\text{H})_3 + 4\text{H}_2\text{O} \end{aligned} \tag{2}$$

Because the dissolution of OH^- and Al $(OH)_3$ from Friedel's salt can react with CO_2 , the carbonation process can cause the reaction in Eq. (2) to occur. In this process, chloride ions bound by the Friedel's salt are gradually released and become free chloride ions. Thus, the Friedel's salt diffraction characteristic peaks disappeared as a result of Friedel's salt decomposition due to carbonation.

3.3.2.2. DSC/TG analysis. Fig. 10 shows the results of DSC and TG of the plain cement paste. In Fig. 10(a), $Ca(OH)_2$ endothermic peaks are observed for uncarbonated samples in the temperature range of 480–496 °C. However, $Ca(OH)_2$ endothermic peaks are not present in carbonated concrete; $CaCO_3$ endothermic peaks are observed in the temperature range of 771–799 °C. This phenomenon shows that after carbonation, most $Ca(OH)_2$ cement hydration products have been transformed into $CaCO_3$, which is consistent with the results of the XRD diagram analysis.

The endothermic peaks of Friedel's salt might appear anywhere in the range of 300–370 °C [29–32]. Fig. 10(a) shows that before carbonation, cement paste containing 5% NaCl has an endothermic peak at 333 °C. However, the plain cement paste does not have a similar endothermic peak. In addition, the diffraction characteristic peak of Friedel's salt is near the endothermic peak of hydrated calcium aluminate (C₄AH₁₃) in the range of 185–200 °C [27,29]. Combined with the previous corresponding XRD diagram analysis, the endothermic peak can be identified as that of Friedel's salt.

After carbonation, the endothermic peak of Friedel's salt of the plain cement paste containing 5% NaCl disappeared. This phenomenon coincided with the characteristic Friedel's salt diffraction peak in the XRD diagram. This shows that Friedel's salt is present after carbonation decomposition and releases chloride ions via chemical binding.

Fig. 10. DSC/TG analysis of the paste samples.

Assuming that all $Ca(OH)_2$ is converted into $CaCO_3$ in the carbonated plain cement pastes, TG data can be used to calculate the $Ca(OH)_2$ content in the uncarbonated plain cement paste. The $CaCO_3$ content in the plain cement paste and the $CaCO_3$ content from the reaction generated by $Ca(OH)_2$ in Fig. 10(b) using a semi-quantitative method. The results are shown in Table 7.

Table 7 shows that, for non-carbonated samples, the Ca(OH)₂ contents of samples having chloride ion are greater than that of the blank cement paste. The paste with 1% NaCl has 14.9% Ca (OH)₂, in contrast, the blank paste has 13.0% Ca(OH)₂. Meanwhile, it can be known that the CaCO₃ content of carbonated cement paste was significantly greater than the CaCO₃ content of carbonated by Ca(OH)₂. For blank cement paste, total CaCO₃ content of carbon-ated sample is 25.8%, but CaCO₃ generated from Ca(OH)₂ is only 16.8%. This phenomenon suggested that both Ca(OH)₂ and other hydration products became CaCO₃ after carbonation. Due to carbonation, the hydrated calcium silicate gel (C-S-H) can react with

 CO_2 to produce amorphous silica gel (silica gel) and transient or steady-state $CaCO_3$ (i.e., vaterite and aragonite or Calcite) [21,33,34]. The reaction equation can be represented as

$$\text{C-S-H} + 2\text{CO}_2 \rightarrow \text{SiO}_2 \cdot \text{H}_2\text{O} + 2\text{CaCO}_3 + \text{H}_2\text{O} \tag{3}$$

The C-S-H gel layer flocculent structure has a large specific surface area that can provide considerable physical adsorption. Florea [31] proposes that the chloride ions physical ability of cementbased material is related to the high specific surface area of C-S-H gel. Tang [35] found that the quantity of C-S-H gel affected the chloride ions binding ability when the adsorption equilibrium method is used to study the bound chloride ion. However, after the carbonation decomposition of C-S-H gel, its specific surface area could be reduced significantly [36]. Regarding the physical adsorption of a solid surface, a low specific surface area indicates low physical adsorption ability. Therefore, parts of the physical adsorption of chloride ions were released again under the effect of carbonation.

3.3.3. Model of the interaction between carbonation and chloride ions

Chloride ions introduced by DMS can reduce the carbonation depth; higher carbonation resistances can reduce the possibility of steel bar corrosion in concrete. In contrast, concrete carbonation behaviours can change the state of chloride ions in concrete and their concentration. Carbonation can make bound chloride ions become free chloride ions. Fig. 11 shows the model of the interaction between concrete carbonation and chloride ions states in DMS concrete based on the above discussion. After 1 year of carbonation, the carbonation depth is reduced by approximately 20-50% (see mark ①). Thus, the variation in this range is likely caused by different mixture proportions and different DMS types. For concretes with higher water-to-cement (W/C) ratios, the reducing range is greater than that of concrete with lower W/C ratios. The reducing range for concrete with DMS is greater than that of concrete made with washed DMS. For concretes made with DMS and washed DMS, carbonation can increase the concentration of free chloride ions by nearly twofold (see mark 2). Free chloride ions can cause steel bar corrosion when their concentration is above a certain threshold. Carbonation behaviour can clearly increase the possibility of steel bar corrosion in DMS concrete. Therefore, regarding the durability of RC using DMS, the effect of carbonation on changes in chloride ions behaviours must be considered.

Fig. 11. Interaction model between concrete carbonation and chloride ions states in DMS concrete.

Semi-quantitative analysis of the Ca(OH)₂ and CaCO₃ contents by the mass of paste.

Table 7

Paste	Paste Non-carbonated		Carbonated		$CaCO_3$ generated from $Ca(OH)_2$ (%)
	Loss of water (%)	Ca(OH) ₂ (%)	Loss of CO ₂	CaCO ₃ (%)	
Blank	-3.17	13.0	-11.33	25.8	16.8
1% NaCl	-3.63	14.9	-10.58	24.0	19.2
5% NaCl	-3.43	14.1	-8.64	19.6	18.2

4. Conclusions

- Chloride ions introduced by DMS can reduce the porosity of cement paste and optimise the pore distribution. Therefore, chloride ions have some beneficial effects on the carbonation resistance of concretes.
- 2) According to the results of XRD and DSC/TG analyses, the decomposition of Friedel's salt is the primary reason for the chemical binding of chloride ions into free chloride ions; the decomposition of C-S-H gel is also shown to be the primary reason for the physical adsorption of chloride ions into free chloride ions.
- 3) Considering the influence of carbonation on chloride ions binding, the interactive behaviour between carbonation and chloride ions on steel corrosion should be considered, even if the amount of chloride ions introduced by DMS is lower than the critical threshold value and particularly in DMS concrete structure with higher W/C ratios.

Conflicts of interest

The authors declare no conflict of interest.

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