



# Article Influence of Carbon Dioxide Curing on the Corrosion Resistance of Reinforced Cement Mortar under the External Erosion of NaCl Freeze–Thaw Cycle

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Abstract: Carbon dioxide (CO<sub>2</sub>)-cured concrete is a novel material that can effectively reduce CO<sub>2</sub> emissions in the atmosphere. However, limited research has been found to investigate the corrosion behavior of CO2-cured reinforced concrete. In this paper, the corrosion resistance of reinforced cement mortar is investigated. The mortars were cured in CO<sub>2</sub> for 1 day~28 days. Water-cement ratios (w/c) of 0.3, 0.4 and 0.5 were designed. The corrosion resistance of inner steel bars was researched by the methods of ultrasonic velocity, electrical parameters (AC electrical resistance, Tafel curve method and AC impedance spectroscopy). Moreover, scanning electron microscope was selected for observing the micro-morphology of CO2-curing mortar. X-ray diffraction spectrum was used to characterize components of steel bars' passive films. The results show that CO2 can effectively increase electrical resistivity and ultrasonic velocity, thus improving the corrosion resistance of reinforced cement mortar. The enhancement of carbon dioxide curing increases with the increasing w/c. The mass-loss rate, the electrical resistivity and the decreasing rate of ultrasonic velocity increase with the increasing sodium chloride freeze-thaw cycles, indicating the continuous increase in the corrosion degree of reinforcement. The corrosion deterioration degree of steel bars decreases with the increasing  $CO_2$ -curing time. Specimens with w/c of 0.3 and 0.4 show the highest and lowest corrosion deterioration resistances after sodium chloride freeze-thaw cycles. Microscopic characterization found that CO<sub>2</sub> curing could increase the corrosion resistance of the inner steel bars by improving the compactness of the cement matrix. Moreover, the iron oxides on the surface of the passivation film decreased after CO<sub>2</sub> curing.

**Keywords:** carbon dioxide; corrosion resistance; water-cement ratios; NaCl freeze-thaw cycles; electrical parameters; microscopic experiments

# 1. Introduction

With the cumulative emission into the atmosphere, the tremendous amount of carbon dioxide (CO<sub>2</sub>) has led to serious greenhouse effects and the of endangering human life [1–3]. Commonly, CO<sub>2</sub> can be used for manufacturing high-value chemicals, such as In<sub>2</sub>O<sub>3</sub> catalysts and light olefins overmixed with Fe-Co-K-Al oxide catalysts. In civil engineering, CO<sub>2</sub>-curing concrete, which can store the CO<sub>2</sub> in concrete, may provide an effective method to alleviate this issue [4–8].

Alkaline substances in cement-based materials can react with  $CO_2$  to generate dense carbonate, and thus enhance cement-based materials' mechanical properties and durability [9,10]. As pointed out in several pieces of research,  $CO_2$  curing on cement-based materials could effectively improve its mechanical properties [11,12]. Meanwhile,  $CO_2$  curing could decrease the chloride–ion penetration of the cement paste with mineral admixtures [13,14]. Cao et al. [15] reported that the mechanical properties and NaCl freeze–thaw



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). resistance of the reactive powder concrete (RPC) produced by compound cement were improved by  $CO_2$  curing. At a high-mass ratio of ordinary Portland cement, the improvement was more prominent. An investigation was conducted to determine the effect of curing temperature on the mechanical strength and durability of high-performance mortar containing binary mixes of cenosphere and waste glass powder. Researchers found that a curing temperature of 80 °C was appropriate for developing the mechanical strength and durability of high-performance mortar [16]. Zhu et al. [3] reported that  $CO_2$  curing could shorten the setting time, decrease the drying shrinkage rate and significantly improve the compactness of the cement stone structure of cement-based materials. Although,  $CO_2$  curing has been applied to manufacturing cement-based materials for several years [17], limited research has been conducted on whether  $CO_2$  curing increases the corrosion resistance of steel inside cement-based materials.

Usually, plain cement concrete can not be used in actual projects. The cement concrete in engineering structures must be reinforced with steel bars. When electrons are lost in steel bars within the cement concrete, the steel bar becomes corroded [18–20]. Marine concrete engineering structures are frequently subjected to complex marine corrosion environments [21–25]. Coastal seawater contains chlorine salts that can corrode the passive films of steel bars, therefore accelerating the corrosion process of reinforced concrete [26,27]. The steel bars inside cement concrete may be seriously eroded under the corrosion action of seawater [28–32]. Many methods have been developed to improve steel bars' corrosion resistance. As pointed out in some studies, the incorporation of rice husk ash and silica fume could improve steel bars' chloride corrosion resistance [33-35]. Sodium nitrite, sodium molybdate and other rust inhibitors can effectively increase steel bars' corrosion resistance [36]. The ultra-high-performance concrete should have good corrosion resistance.  $CO_2$  curing can improve the compactness of cement concrete. Thus, the corrosion resistance of steel bars inside cement concrete may be increased [37]. It has been well acknowledged that, as cement concrete services in the environment of deicing by deicing salt and coastal environment, the inner steel bars may be severely corroded. However, the degradation of cement concrete is still unclear, and very few studies have been conducted on this topic.

A study was conducted on the effect of  $CO_2$  curing on the corrosion resistance of steel bars embedded in cement mortar. The curing time of carbon dioxide increased from 1 day to 28 days. In the presence of a 3% NaCl solution, freeze and thaw cycles were conducted on the specimens. Electrical methods, ultrasonic methods, mass-loss methods and microscopic technologies were used to evaluate the corrosion rate of steel bars. This study guides the reinforced concrete design for seawater freeze–thaw cycle corrosion.

# 2. Materials and Methods

#### 2.1. Raw Materials

Table 1 shows all the raw materials' chemical compositions, and Table 2 displays the particle-size distributions of ordinary Portland cement. The cement used in this research has a strength rating of 42.5 MPa and an apparent density of  $3.05 \text{ g/cm}^3$ . The standard sand with a silica content of 98% whose loss on ignition, moisture content and chloride ion content are less than 0.40%, 0.18% and 0.007%, respectively, was used as the aggregate. CO<sub>2</sub> with a concentration of 99.999% provided by Hebei Jiehang Test Instrument Co., Ltd., Cangzhou, China, was used to cure the cement mortar.

**Table 1.** Chemical composition of the raw materials/%.

Types	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	SO <sub>3</sub>	Loss on Ignition
P·O cement	20.86	5.47	3.94	1.73	62.23	2.66	3.11
Standard sand	99.2	0	0.42	0	0	0	0.38

Tunoc		Particle Size/µm						
Types —	0.3	0.6	1	4	8	64	360	
P·O cement	0	0.33	2.66	15.01	28.77	93.59	100	

**Table 2.** Particle passing percentage of cement/%.

# 2.2. The Preparation of Samples

The following steps can be used to prepare RPC specimens. The mixing proportions are shown in Table 3 [22].

|--|

Water	Cement	Sand
157.9	526.3	1315.8
210.5	526.3	1315.8
263.2	526.3	1315.8

A UJZ-15 mixer was used for preparing the cement mortar. The cement power and standard sand were first mixed for 1 min at  $60 \pm 2$  R/min in the mixer. After adding the water, the mixture was mixed again for another 3 min at  $80 \pm 4$  R/min. Molds ( $50 \times 50 \times 50$  mm<sup>3</sup>) were filled with the freshly prepared mortar. The specimen was centered on an 8 mm-wide plain round bar. At the same time, 316 L stainless-steel mesh with 4.75 mm square holes served as conductive electrodes. The distance from the stainless-steel mesh to the central axis of the specimen was 40 mm. Six replicates were used for each test.

# 2.3. Measurement Methods

In this study, a rapid freeze–thaw testing machine was used to perform the freeze–thaw test. The temperatures of this experiment ranged from -18 °C to 5 °C. Each freeze–thaw cycle lasted for 2 h. NaCl solution (3%) was used as the freeze–thaw medium. All specimens were immersed in the NaCl solution (3%) for 4 days before the rapid freeze–thaw experiment. Subsequently, the specimens were moved to the rubber tubes filled with 3% NaCl for the freeze–thaw test.

#### 2.3.1. The Measurement of pH

The solid–liquid extraction method was chosen to evaluate the pH of the cement mortar. The following are the specific steps. The test block was crushed to powder along the carbonation depth direction. Before the first 5 mm, the sample was collected every 1 mm, then every 2 mm after that. After passing through a filter (0.08 mm square-hole sieve), 5 g of the dried sample was obtained from the ground sample. To prevent carbonation, the sieved sample was dissolved in 50 mL of distilled water and sealed with a rubber stopper. After 24 h of stirring every 5 min and stewing for 2 h, the pH of the filtered solution was measured using a pH meter (PHSJ-6L type) provided by Beijing Dongnan Yicheng laboratory equipment Co., Ltd., Beijing, China. The depth direction of the pH is shown in Figure 1.



Figure 1. The depth direction of pH.

# 2.3.2. Electrical Parameters

Electrical parameters (AC electrical resistance, AC impedance spectrum and Tafel curves) were measured with two electrode methods. For determining the AC electrical resistivity, an LCR digital bridge with 10<sup>4</sup> Hz and 1 V was used. PARSTAT 3000 A, provided by AMETEK Trading (Shanghai) Co., Ltd., Shanghai, China, was used for determining the AC impedance spectrum and Tafel curves. Figure 2 illustrates the testing process. Following the test, the following equation could be used to calculate the AC electrical resistivity.

ρ

$$=\frac{RA}{L}$$
(1)



Figure 2. The measurement of electrical parameters.

The resistance *R* represents the average electrical resistance of the specimen, and *A* and *L* are the area and length of the electrical current passing through the testing specimen's cross section, respectively.

#### 2.3.3. Ultrasonic Velocity

The SUB-100 ultrasonic flaw detector provided by Wuxi Jiebo Instrument Technology Co., Ltd., Wuxi, China was applied in the measurement of the ultrasonic velocity. The forming sides of the specimen were evenly smeared with Vaseline. Subsequently, the SUB-100 ultrasonic flaw detectors were pressed tightly on the sides and smeared with Vaseline. Finally, the sound velocity of the ultrasonic flaw detector was recorded after ultrasonic emission. The measuring process of the ultrasonic velocity is shown in Figure 3.



Figure 3. The schematic diagram of ultrasonic measurement.

#### 2.3.4. Percentage of Mass Loss

The mass-loss rate of cement mortar can be determined as follows. During each 50 NaCl freeze–thaw cycle, the surface of the specimens was wiped dry with a rag. Subsequently, the mass of the specimen was tested. However, the steel bars should be ground before the following mass was measured. The mass-loss rate can be calculated by Equation (2).

$$\frac{\Delta m}{m} = \frac{m - m_0}{m_0} \tag{2}$$

where *m* and  $m_0$  are the mass of cement mortar or steel bars before and after each 50 freeze–thaw cycle, respectively.

# 2.3.5. Microscopic Tests

The scanning electron microscope (SEM) was used for observing the micro-morphology of samples. Meanwhile, X-ray diffraction (XRD) was selected to investigate the crystal component of the steel bars' passive film. To block the cement's hydration, four days' immersion in absolute ethanol was provided for the samples after reaching the planned curing age. The powdered sample whose particle size was smaller than 74  $\mu$ m was used for the XRD tests. Soybean-sized samples extracted from the large specimen were dried in the vacuum drying oven. After drying, the samples were taken out and sprayed with gold in a vacuum environment. The samples were coated with a gold film to conduct the SEM test. The Hitachi S-4800 cold field emission scanning electron microscope, Hitachi, Tokyo, Japan, was applied for the measurement of SEM images. The D8 ADVANCE X-ray diffractometer, manufactured by Bruker Corp., Tokyo, Japan, was used to conduct the XRD measurement.

# 3. Results and Discussions

# 3.1. The pH of the Cement Mortar

The pH of the cement mortar is depicted in Figure 4 at various depths. All the specimens were cured in  $CO_2$  for 28 days. Figure 4 shows that the pH value on the surface of the specimens is between 9.0 and 11. With the rising depth and lowering w/c, however, the pH value rises. This was due to  $CO_2$  reacting with calcium hydroxide and lowering the alkalinity of the cement mortar. The pH value of the surface section of the cement mortar is lower because it is more prone to react with  $CO_2$ . Calcium carbonate, which is generated when  $CO_2$  reacts with calcium hydroxide, can increase the compactness of cement mortar, inhibiting  $CO_2$  penetration. As a result, as the depth of the specimen grows, so does the alkalinity, and the pH value rises. Furthermore, because of the greater compactness, the lower w/c can raise the pH value [38].



Figure 4. The pH value of cement mortar along different depths.

### 3.2. Macroscopic Properties before Sodium Chloride Action

In this section, the specimens' curing occurred for 1, 3, 7 and 28 days in a chamber where the  $CO_2$  concentration was 8% and the temperature was 20 °C. These specimens were then cured further in conventional curing environments for 27, 25, 21 and 0 days. One-, three-, seven- and twenty-eight-day cured samples were designated as  $D_1$ ,  $D_2$ ,  $D_3$  and  $D_4$ .

The electrical resistivity of cement-mortar specimens is shown in Figure 5. In Figure 5, the electrical resistivity of steel bars reinforced with cement mortar increases with the longer CO<sub>2</sub>-curing time. This improvement can be attributed to the generated calcium carbonate due to the reaction between calcium hydroxide and CO<sub>2</sub> [39]. Due to this reaction, conductive ions can decrease in the pore solution, so electrical conduction is reduced and electrical resistivity is increased. As the water-to-cement ratio (w/c) increases, the electrical resistivity decreases. More water and conductive ions are found in cement mortar with a high w/c, thus improving the electrical conduction [40]. As obtained from Figure 5, the increasing rate of electrical resistivity improves as the curing period increases. A higher w/c demonstrates a positive effect on the increasing rate of electrical resistivity. This increase could be ascribed to the more free water and pores in the cement mortar with a higher w/c. Therefore, more calcium hydroxide in the cement mortar could react with CO<sub>2</sub>, thus forming calcium carbonate to improve the compactness of the mortar [41].



Figure 5. The electrical resistivity of specimens before NaCl freeze-thaw cycles.

The ultrasonic velocity of specimens is presented in Figure 6. It is evident that the ultrasonic velocity of the specimens increases as the curing age of the  $CO_2$  increases. This improvement is because the longer  $CO_2$ -curing age improves the calcium carbonate content (hydration products with high compactness). The speed of ultrasonic propagation in compact materials is rapid [42]. Therefore, the ultrasonic velocity increases with the increasing  $CO_2$ -curing time. Due to the positive effect of the w/c on the  $CO_2$  effect, the increasing rate of ultrasonic velocity of specimens increases with the w/c.



Figure 6. The ultrasonic velocity of specimens before NaCl freeze-thaw cycles.

# 3.3. Macroscopic Properties during Sodium Chloride Action

Figure 7 depicts the electrical resistivity of specimens during NaCl freeze–thaw cycles. According to Figure 7, the electrical resistivity decreases within the first 100 freeze–thaw cycles. The increase in NaCl concentration in pore solution in response to increasing freeze–thaw cycles may explain this improvement. However, the electrical resistivity increased as the number of freeze–thaw cycles increased from 100 to 300 cycles, owing to the formation of additional interior cracks following the NaCl freeze–thaw cycles [43]. Figure 7 shows that the longer the CO<sub>2</sub>-curing time, the lower the growing rate of electrical resistivity becomes. This is due to the fact that after CO<sub>2</sub> curing, the steel bars reinforced cement mortar's NaCl freeze–thaw corrosion resistance improves [44].



Figure 7. The electrical resistivity of specimens during NaCl freeze-thaw cycles.

Figure 8 depicts the variation rate of ultrasonic velocity of specimens during NaCl freeze–thaw cycles. As shown in Figure 8, the ultrasonic velocity increases with the freeze–thaw cycles ranging from 0 to 50. It is believed that the cement's continuous hydration leads to the increase in compactness of cement mortar [45]. However, with the freeze–thaw cycles increasing from 50 to 300, the ultrasonic velocity decreases obviously. The further NaCl freeze–thaw cycles may induce the corrosion of steel bars and yield the inner cracks of cement mortar [46]. Besides, the frozen-thaw stress resultant from NaCl freeze–thaw cycles may also extend the propagation of internal cracks in cement mortar, hindering the transmission of ultrasound in concrete [47]. Therefore, the ultrasonic velocity of specimens decreases obviously with the freeze–thaw cycles increasing from 50 to 300. Figure 6 illustrates that when the  $CO_2$ -curing age increases, the lowering rate of ultrasonic velocity decreases due to the better compactness of the higher  $CO_2$ -curing age. Moreover, the increasing w/c increases the variation rate of ultrasonic velocity. This can be attributed to the increased compactness of cement mortar with the decreasing w/c.

Figure 9 shows the mass-loss rate of specimens during NaCl freeze–thaw cycles. Figure 9 depicts how the mass grows as the number of freeze–thaw cycles. The continuous hydration of cement mortar during freeze–thaw cycles may be responsible for this increase. The continuous hydration of cement mortar increases the mass of hydration products. However, with freeze–thaw cycles increasing from 50 to 300, the mass of cement mortar decreases. The frozen-heave stress and reinforcement corrosion caused by NaCl freeze–thaw cycles may increase specimens' spalling and thus reduce the mass of cement mortar [48]. The mass-loss rate decreases at a longer  $CO_2$ -curing age, due to the improved compaction of hydration products [49]. Moreover, specimens with a w/c of 0.3 display the lowest mass-loss rate. This is because a lower w/c may improve the compactness of cement mortar. However, the mass-loss rate of specimens with a w/c of 0.5 is lower than

the specimens with a w/c of 0.4. This is because the higher carbonation degree of cement mortar with a w/c of 0.5 leads to higher compactness and less mass loss.



Figure 8. The variation rate of ultrasonic velocity of specimens during NaCl freeze-thaw cycles.



Figure 9. The mass-loss rate of specimens during NaCl freeze-thaw cycles.

The mass loss rate of steel bars through NaCl freeze–thaw cycles is shown in Figure 10. As illustrated in Figure 10, the mass-loss rate of steel bars increases with the freeze–thaw cycles. This is due to the fact that NaCl freeze–thaw cycles hasten the corrosion of steel bars, resulting in an increase in rust mass. However, the mass loss rate of steel bars increases with a higher w/c because the electrical conduction is improved with the increasing w/c [50]. Moreover, the mass-loss rate of steel bars decreases with the longer CO<sub>2</sub>-curing time due to the improved corrosion resistance.

The electrochemical impedance spectroscopy (EIS) curves are exhibited in Figure 9. As demonstrated in Figure 11, the imaginary part  $(-Z_i)$  of EIS curves first decreases and then increases with the increasing real part  $(Z_r)$ . Meanwhile, the CO<sub>2</sub>-curing time makes the extreme point of the impedance spectrum shift from left to right due to the decreased electrical conduction by CO<sub>2</sub> curing, thus increasing the electrical resistivity [51]. Therefore, the EIS curves shifted from left to right with the increasing CO<sub>2</sub>-curing time. Moreover, specimens with a w/c of 0.3 show the highest real part of the extreme point of impedance spectrum. This is because the free water inside the specimens increases with the w/c, and,

thus, the free water of specimens with a w/c of 0.3 shows the lowest conduction and the highest electrical resistance. However, the corresponding real part of the extreme point of impedance spectrum of the specimens with a w/c of 0.5 is higher than a w/c of 0.4. This can be attributed to the improved carbonation degree of a higher w/c [52].



Figure 10. The mass-loss rate of the inner steel bars during NaCl freeze-thaw cycles.



Figure 11. EIS curves of steel bar-reinforced cement mortar before NaCl freeze-thaw cycles.

Figure 12 depicts the specimens' EIS curves following 300 NaCl freeze–thaw cycles. As illustrated in Figure 12, similar tendencies of the EIS curves to Figure 11 can be observed. Comparing Figure 11 with Figure 12, the corresponding real part of the extreme point of impedance spectrum of the specimens increases with NaCl freeze–thaw cycles, due to the inner cracks generated after freeze–thaw cycles, and thus results in the reduction in electrical conduction of cement mortar [53]. Furthermore, CO<sub>2</sub> curing reduces the rate at which the actual portion increases during NaCl freeze–thaw cycles. This is because  $CO_2$  curing of cement mortar might improve the hydration products' compactness, thereby boosting the resistance to NaCl freeze–thaw cycles [54,55]. Because of improved compactness and less free water due to a lower water–cement ratio, the actual portion of specimens with a w/c of 0.3 shows the slowest rise. The rise in the real part of specimens with a w/c of 0.5 is lower than that of specimens with a w/c of 0.4, due to the higher carbonation degree.



Figure 12. EIS curves of steel bar-reinforced cement mortar after 300 NaCl freeze-thaw cycles.

To investigate the corrosion degree of steel bars, the equivalent circuit diagram was generated by fitting the experimental curves with Zsimpwin, according to the equivalents of Figures 11 and 12. The equivalent circuits derived from the AC impedance spectrum are shown in Figure 13 [56–58]. As indicated in Figure 13, the corresponding circuits may be separated into four electrical components in series. The first part was the contact electrical resistance between electrodes and specimens. The other three parts were parallel electrical resistance and reactance of pore solution, cement mortar and passive film. The chi square of each specimen was less than or equal to the value of 0.045, indicating that this equivalent circuit model was rational and appropriate to the conductive mechanism.



Figure 13. Corresponding equivalent circuits of steel bar-reinforced cement mortar.

Figure 14 depicts the electrical resistance of the steel bars' passive film, pore solution and cement-mortar matrix calculated using equivalent circuits. Figure 14a shows how the electrical resistance of passive film increases with the number of freeze–thaw cycles and reduces with  $CO_2$ -curing age. This is because the NaCl freeze–thaw process can accelerate the corrosion of the passive film on steel bars, and rust on the surface of steel bars can impede electron transmission, lowering electrical conductivity [59]. A longer  $CO_2$ -curing period, on the other hand, improves the compactness of cement mortar, enhancing corrosion resistance and lowering electrical resistance. Finally, the electrical resistance of passive film of inner specimens with the w/c of 0.3 is the lowest due to enhanced compactness by the decreased w/c. However, the electrical resistance of the passive film of inner specimens with w/c of 0.4 is the highest, due to the lowest carbonation degree and compactness. The electrical resistances of the pore solution and cement mortar matrix are shown in Figure 14b,c. The electrical resistance of pore solution rises with increasing CO<sub>2</sub>-curing age. Because the CO<sub>2</sub> reacts with calcium hydroxide from the pore solution, the concentration of the pore solution decreases, as does the subsequent electrical conduction. The electrical resistance of pore solution decreases with the increasing w/c, due to higher free water. Furthermore, because of the increasing concentration of NaCl in the pore solution, the electrical resistance of pore solution is lowered by the number of NaCl freeze–thaw cycles. Finally, as shown in Figure 14c, the electrical resistance of the cement mortar matrix increases with increasing w/c. This may be attributed to the increased conductivity of the gel-pore solution by w/c [60–62].



(c) The cement mortar matrix

Figure 14. The electrical resistance through equivalent circuit diagram.

The corrosion rates of steel bars during NaCl freeze–thaw cycles are presented in Figure 15. It can be observed that increasing the NaCl freeze–thaw cycles can noticeably accelerate steel bars' corrosion rates. As illustrated in Figure 15, the increasing  $CO_2$  curing reduces the corrosion rate of steel bars. Moreover, steel bars of specimens with a w/c of 0.3 and 0.4 show the lowest and highest corrosion rates, respectively. This can be attributed to the compactness of hydration products and the carbonation degree of the cement mortar.



Figure 15. The corrosion rate of steel bars during NaCl freeze-thaw cycles.

# 3.4. Microscopic Analysis

Figure 16 shows the microstructural morphologies of specimens with 1, 3 and 28 days of CO<sub>2</sub>-curing ages through the SEM tests. It can be observed from Figure 16 that flocculent hydration products are universally observed in the SEM photos at a w/c of 0.3. As shown in Figure 16a–c, the flocculent hydration products decrease, and hydration products become more compact with the increasing CO<sub>2</sub>-curing age. Needle-like hydration products are found in the SEM photos. With the increase in CO<sub>2</sub>-curing age, the needle-like hydration products in SEM photos gradually decrease, and the flocculent hydration products increase, improving the compactness of hydration products. Additionally, as observed in Figure 16, the compactness increase follows the order as follows: w/c-0.4 < w/c-0.5 < w/c-0.3. The specimen with a w/c of 0.3 has low free water, thus forms higher compactness. However, the carbonation degree of cement mortar with a w/c of 0.5 is higher, thus showing higher compactness.

Figure 17 shows the X-ray diffraction (XRD) of the passivation film of the inner steel bars of cement mortar. As illustrated in Figure 17, the diffraction peaks of  $Fe_2O_3$  and  $Fe_3O_4$  can be obviously observed due to the corrosion of steel bars, which leads to the formation of iron oxides. Moreover, increasing the  $CO_2$ -curing age decreases the intensity of the diffraction peaks of  $Fe_2O_3$  and  $Fe_3O_4$ . This is because of the corrosion resistance of steel bars inner cement mortar.



(a) w/c-0.3-CO<sub>2</sub> cured-1 day



(d) w/c-0.4-CO<sub>2</sub> cured-1 day



(g) w/c-0.5-CO<sub>2</sub> cured-1 day



**(b)** w/c-0.3-CO<sub>2</sub> cured-3 days



(e) w/c-0.4-CO<sub>2</sub> cured-3 days



(h) w/c-0.5-CO<sub>2</sub> cured-3 days



(c) w/c-0.3-CO<sub>2</sub> cured-28 days



(f) w/c-0.4-CO<sub>2</sub> cured-28 days



(i) w/c-0.5-CO $_2$  cured-28 days

Figure 16. SEM microstructure photos of CO<sub>2</sub> cured specimens.



Figure 17. The X-ray diffraction (XRD) spectra of steel bars' passivation films.

# 4. Conclusions

The corrosion of steel bars inside cement mortar exposed to the NaCl freeze-thaw cycles was investigated. The conclusions can be summarized as follows.

The electrical resistivity and ultrasonic velocity increase with the more extended carbon dioxide  $(CO_2)$  curing, which improves the corrosion resistance of reinforced cement mortar.

The water–cement ratio demonstrates a positive effect on enhancing  $CO_2$  curing. The increasing NaCl freeze–thaw cycles increase the mass-loss rate, the electrical resistivity of steel bars reinforce cement mortar, but decrease the rate of ultrasonic velocity, which indicates the continuous increase in corrosion degree of reinforcement. The  $CO_2$ -curing time demonstrates a positive effect on the resistance of the corrosion deterioration degree of steel bars. Specimens with a water–cement ratio of 0.3 show the best corrosion resistance of steel bars. However, specimens with a water–cement ratio of 0.4 present the worst.

The scanning electron microscope results show that  $CO_2$  curing could improve the compactness of the hydration products, thus improving the corrosion resistance of the inner steel bars. Additionally,  $CO_2$  curing decreases the content of iron oxides on the surface of the passivation film. Specimens with a water–cement ratio of 0.3 show the best compactness. However, the compactness of specimens with a water–cement ratio of 0.4 are the worst.

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