Assessment of the freeze–thaw resistance of concrete incorporating carbonated coarse recycled concrete aggregates

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This study aims to characterise the freeze–thaw resistance of concrete incorporating carbonated coarse recycled concrete aggregate (C-CRCA) at partial or full replacement rates of coarse natural aggregate (CNA). Experimental work is conducted for C-CRCA with varying CO₂ curing time (0 day, 3 day, 7 day) and C-CRCA weight replacement percentages (0, 20, 50, 100 %) for concrete production. Weight loss, relative dynamic modulus of elasticity (RDME) and residual compressive strength were monitored after 300 freeze–thaw cycles. Pore size distribution and crack volume variation were also measured via nuclear magnetic resonance to investigate changes in the microstructure of the concrete interior. The compressive strength of concrete decreases with the replacement percentage of CNA by the C-CRCA. The internal freeze–thaw resistance of concrete with C-CRCA was higher or equal to those of concrete with CRCA and CNA. The total replacement of CNA by C-CRCA led to the highest RDME and residual compressive strength were monitored after 300 freeze–thaw cycles. However, the weight loss was more severe with the increasing replacement of CNA by C-CRCA. Increasing CO₂ curing time improved the frost resistance of C-CRCA concrete. The analyses of concrete mesostructure based on pore size distribution and crack volume variation agreed with the results of RDME and the compressive strength of concrete.

Key-words : Carbonated coarse recycled concrete aggregates, Freeze–thaw cycle, Weight loss, Relative dynamic modulus of elasticity, Residual compressive strength, Mesostructure

1. Introduction

Breakthrough developments in the construction industry have increased construction rates and the demand for concrete in the construction of new buildings. Hence, an eco-friendly method for handling construction and demolition (C&D) waste is necessary. Recycled concrete aggregate (RCA) can partially substitute for virgin aggregates in the production of new concrete, thus providing a promising solution for handling C&D waste and saving construction materials.1

Some studies have reported on the production and characterisation of recycled aggregates.2–5 The mesostructure of a RCA is far more complex than that of conventional concrete owing to the adhering mortar on the surfaces of RCA particles.6 The presence of micro-cracks and residual cement paste increases the porosity of RCA, thus lowering its density and enhancing water absorption.7

The deterioration of concrete constructions from freeze–thaw damage is a severe problem that affects the durability and service life of concrete structures. Various factors influence the freeze–thaw resistance of concrete, such as porosity, water/cement (w/c) ratio and type of aggregate used.8

Some studies have reported on the effect of fine recycled concrete aggregates (FRCA) and coarse recycled concrete aggregates (CRCA) on the freeze–thaw resistance of concrete. Bogas et al.9 concluded that incorporation of FRCA is not detrimental to the freeze–thaw resistance of concrete. Instead, w/c ratio has a greater influence on freeze–thaw resistance than the type of aggregate used and air entraining has a slightly beneficial effect on high-strength concrete. Yildirim et al.10 investigated the effect of internal curing provided by FRCA on the freeze–thaw resistance of a 0.5–0.7 w/c concrete. Lotfi and Al-Fayez11 reported that the freeze–thaw resistance of concrete containing CRCA and FRCA at replacement rates of 20% natural aggregate is as high as that of the reference non-recycled concrete. Lotfi et al.12 investigated low-strength and moderate-strength concrete that both contained an air-entraining agent (AEA). The frost resistance of concrete samples containing normal aggregate or 100% RCA has been tested. Results indicated that only low-strength concrete is negatively affected by the incorporation of CRCA. Moreover, Tuyan et al.13 studied the influence of CRCA on the freeze–thaw resistance of self-compacting concrete (SCC). They reported that RCA-containing mixtures exhibit significantly increased viscosity. Moreover, the addition of up to 40% CRCA slightly improves the compressive strength of SCC mixtures. Ajdukiewicz and Alíma14 reported that a high-performance concrete prepared with RCA and a high-performance parent concrete endures freeze–thaw cycles better than conventional concrete. Yildirim et al.15 concluded that the performance of an RCA-containing concrete after exposure to 300 freeze–thaw cycles is comparable to that of concrete containing only virgin aggregate.

Strategies to improve RCA quality and performance have received considerable research attention in the past few decades16–18 to efficiently facilitate waste management through the reuse of RCA. Three main technical methods are utilized to improve RCA properties: (I) the removal of residual cement mortars from RCA; (II) the modification of mixing method; and (III) CO₂ curing. These methods significantly reduce the water absorption and increase the compressive strength of the new concrete.19–24 Liu et al.25 found that the two-stage mixing method improves the mechanical properties of RCA but has no significant effect on freeze–thaw resistance. Abbas et al.26 reported that applying the
assess the frost resistance of recycled aggregate concrete,\(^9\) In addition, macroscopic indices, such as mass loss and the relative dynamic modulus of elasticity (RDME) are currently used to evaluate the frost resistance of recycled aggregate concrete after freezing–thawing. However, limited research has been performed on the effects of carbonated coarse recycled concrete aggregates (C-CRCA) on the freeze–thaw resistance of recycled aggregate concrete.

The present study aims to investigate the effects of C-CRCA on the frost resistance of recycled aggregate concrete at the macroscale level and to reveal the failure mechanism during freezing–thawing based on mesostructural analyses. First, a systematic study was performed to elucidate the effects of CRCA and C-CRCA incorporation on the frost resistance of recycled aggregate concrete as reflected by the macroscopic indices of mass loss, RDME and compressive strength. Then, a possible mechanism for the failure recycled aggregate concrete after freezing–thawing is proposed based on the results of mesostructural analyses.

### 2. Experimental details

#### 2.1 Materials

The mixture proportion of the parent concrete for CRCA is provided in **Table 1**. After 6 months of external curing, the concrete was crushed at the same construction waste recycling plant. Concrete was prepared with two coarse fractions of 5–10 and 10–20 mm CRCA. The size fractions of coarse natural aggregate (CNA) were 10–20 and 5–10 mm. The 10–20 and 5–10 mm size fractions of the crushed materials were designated as 20 and 10 mm CRCA, respectively. In concrete mixtures, 20 and 10 mm coarse aggregates were used at a ratio of 1:2. C1-CRCA and C2-CRCA were carbonated for 3 and 7 days, respectively. The coarse concrete aggregates used in the experiments are shown in **Fig. 1**.

**Table 1.** Mixture proportion of the CRCA parent concrete

| Mix proportions (kg/m³) | W/C | Water | Cement | Sand | Natural aggregate (10–20 mm) | AEA (%) | fcm, 28d (MPa) |
|-------------------------|-----|-------|--------|------|-----------------------------|--------|----------------|
|                         | 0.4 | 512.5 | 205    | 605  | 1120                        | 0.03   | 55.4           |

**Fig. 1.** Coarse concrete aggregates used in the experiments: (a) CNA and (b) CRCA.

**Table 2.** Chemical composition and properties of cement

| Contents | Cement |
|----------|--------|
| SiO₂ (%) | 21.45  |
| Al₂O₃ (%)| 6.45   |
| CaO (%)  | 61.5   |
| Fe₂O₃ (%)| 3.09   |
| MgO (%)  | 1.21   |
| K₂O (%)  | 1.38   |
| Na₂O (%) | 0.25   |
| SO₃ (%)  | 2.01   |
| Loss on ignition (%) | 4.05 |
| Specific gravity (g/cm³) | 3.15 |
| Specific surface area (cm²/g) | 3412 |

**Table 3.** Properties of coarse aggregates

| Property          | Particle size (mm) | CNA | CRCA | C1-CRCA | C2-CRCA |
|-------------------|--------------------|-----|------|---------|---------|
| Loose bulk density (kg/m³) | 20                | 1453| 1290 | 1311    | 1320    |
|                   | 10                | 1453| 1290 | 1318    | 1325    |
|                   | 20                | 0.78| 6.78 | 4.52    | 4.41    |
| Water absorption (%) | 10               | 0.81| 6.95 | 4.76    | 4.59    |
|                   | 20                | 1.10| 18.85| 11.06   | 10.25   |
| Porosity (%)      | 10                | 1.10| 18.52| 9.98    | 9.42    |
conventional concrete; R group denotes concrete with CRCA (mixes R20, R50 and R100); C1-R group refers to concrete with C1-CRCA (mixes C1-R20, C1-R50 and C1-R100); and C2-R group refers to concrete with C2-CRCA (mixes C2-R20, C2-R50 and C2-R100). An effective w/c ratio of 0.45 indicated that sufficient water is available for cement hydration. The concrete was produced via a two-stage mixing approach to maintain the target workability.\(^{10}\) The absorption of CRCA in the mix was estimated beforehand to correct for the total mixing water in accordance with Shi et al.\(^{10}\) AEA and superplasticiser (SP) with a water-reducing rate of 20% by weight were also used in the concrete mixtures.

Twenty-one 100 mm cubes and three prisms with dimensions of 100 mm \(\times\) 100 mm \(\times\) 400 mm were prepared from each mixture. Three cubes were used to test compressive strength on the 28th day of curing. Three of the prisms were used to measure weight loss and RDME, whereas eighteen cubes were used to determine compressive strength during freeze-thaw cycles. The three prisms of the 100 mm \(\times\) 100 mm \(\times\) 400 mm samples were also produced for mesostructural analyses via nuclear magnetic resonance (NMR). For each test, three specimens were tested under identical conditions, and the average values were used for the discussion of the results.

### 2.4 Compressive strengths

The compressive strengths of concrete were determined using a compression machine with a loading capacity of 3000 kN. The loading rates applied in the compressive strengths tests were 50 kN/min.

### 2.5 Freezing and thawing cycle tests

The testing procedure used to evaluate the freeze-thaw resistances of the various samples involved 300 rapid freeze-thaw cycles. The temperature of the concrete specimens was controlled with a thermocouple embedded in the centre of the prisms. Specimens were placed in a freeze-thaw machine, where they were subjected to freeze-thaw cycles. During each freeze-thaw cycle, the temperature was decreased from 5 to \(-20^\circ\text{C}\) and then increased to \(5^\circ\text{C}\) within 4 h. Water was used in the liquid solution test for freeze-thaw cycles. The specimens were removed from the testing device every 50 freeze-thaw cycles for the measurement of weight loss, RDME and compressive strength.

The weight loss can be determined using Eq. (1) as follows:

\[
W_n = \frac{G_0 - G_n}{G_0} \times 100
\]

(1)

where \(W_n\) is the weight loss of specimens at \(n\) freeze-thaw cycles (%), \(G_0\) is the average weight of concrete specimens at the beginning of the test (kg) and \(G_n\) is the average weight of concrete specimens at \(n\) freeze-thaw cycles (kg).

The relative dynamic modulus of elasticity was calculated as follows:

\[
RDME = \frac{f_2^2}{f_0^2} \times 100
\]

(2)

where \(RDME\) is the relative dynamic modulus of elasticity at \(n\) freeze-thaw cycles (\%), \(f_0\) is the initial transverse frequency at \(n\) freeze-thaw cycles (Hz) and \(f_2\) is the initial transverse frequency at the beginning of the test (Hz).

### 2.6 Nuclear magnetic resonance analysis

The NMR system, which has an accuracy of \(\pm 5\%\), was supplied by Niumag Corporation (Shanghai, China). The pore parameters of concrete specimens at different freeze-thaw cycles were determined using the NMR system. Before the test, the concrete specimens were saturated for 8 h by using a vacuum saturation device. Concrete specimens were subsequently soaked in distilled water for 24 h prior to NMR analysis. The main NMR measurement parameters were as follows: echo time, 0.6 ms; waiting time for repeat measurement, 4 s; scanning number, 64; and echo number, 8000. Three 100 mm \(\times\) 100 mm \(\times\) 400 mm specimens were taken out of the testing device every 50 freeze-thaw cycles to acquire pore information.

NMR transverse relaxation (\(T_2\)) distributions are strongly related to concrete and rock pore-crack structures.\(^{31}\) As a result, the fluids in different cracks and pores show different relaxation times. The NMR relaxation method\(^{31,32}\) is suitable for characterising the pore structures of concrete and rock. The physical properties of concrete and rock, such as pore size distribution and pore volume variation, can be analysed based on \(T_2\) spectral peaks and relaxation time. \(T_2\) distribution is similar to pore size distribution; thus, the pore radius \(r\) (\(\mu\text{m}\)) that corresponds to \(T_2\) can be determined as follows:\(^{33-36}\)

\[
r = CR_2
\]

(3)

where \(C\) is a constant conversion coefficient (\(\mu\text{m}/\text{ms}\)) that can be calculated from a constant-speed mercury injection capillary pressure test. According to the literatures\(^{35,37}\) the value of \(C\) is \(8 \times 10^{-3}\) \(\mu\text{m}/\text{ms}\).

### 3. Results and discussion

#### 3.1 Compressive strength

Figure 2 shows the relative compressive strength of all mixtures at 28 days. At 28 days, the compressive strengths of concrete mixtures prepared with C-CRCA and CRCA were lower than that of concrete prepared with CNA. The compressive
strength of concrete mixtures was dependent on the percentage of CNA replaced by C-CRCA and CRCA. Compared with concrete prepared with CNA, the compressive strengths of concrete samples prepared with 100% CRCA, C1-CRCA and C2-CRCA decreased by 17.7, 9.9 and 8%, respectively, as shown in Fig. 2. As expected, the compressive strength of concrete decreased with the increasing replacement ratio of CNA with CRCA and C-CRCA owing to CRCA being weaker and more porous than the natural aggregate. Previous studies have reported similar findings.38)

Compared with concrete prepared with CRCA, the compressive strength of concrete prepared with C-CRCA improved. Compared with concrete mixed with 100% CRCA, the compressive strength of C2-R100 increased by 7.9%, which resulted from the improved physical and mechanical properties of CRCA cured via the CO2 curing method. Table 3 shows that the water absorption of 20 mm C1-CRCA and C2-CRCA was 33.3 and 34.9% lower than that of CRCA, respectively. Moreover, the porosity of 20 mm C1-CRCA and C2-CRCA was 41.3 and 45.6% lower than that of CRCA, respectively. Figure 3 shows the results from phenolphthalein spraying on the cross-sectional image of split concrete at 28 days. As illustrated in Fig. 3(a), the whole surface of the split concrete with untreated CRCA was red except for CNA. However, no colour change occurred when 1% phenolphthalein alcohol solution was sprayed [Fig. 3(b) and 3(c)], indicating the carbonation of CRCA in the concrete. Therefore, the CO2 curing method enhanced the strength of concrete prepared with C-CRCA.

The compressive strength of C2-R100 only increased by 1.9% compared with that of C1-R100, indicating that prolonging CO2 curing time increases compressive strength. In accordance with the results by Kou et al.,39) a longer CO2 curing time allows additional CO2 uptake by C-CRCA, thus yielding a less porous, less absorbent and denser aggregate; generating a desirable chemical reaction during hydration; and leading to a superior and denser bond matrix. Concrete with 100% C2-CRCA was only marginally better than concrete with C1-CRCA. Subjecting CRCA to CO2 curing for 3 days almost fully carbonated the adhering mortar on the surfaces of CRCA particles.

3.2 Weight loss

Figure 4 illustrates that the curves of weight losses for the average three groups (R, C1-R and C2-R) increased with increasing freeze–thaw cycles. The damage process of the three groups during freeze–thaw cycles consisted of two stages. The initial weight change (0–100 cycles) resulted from water that penetrated
the inner cracks of concrete samples after freezing–thawing. This stage proceeds slowly as the water fills in the pores and interfacial transition zones (ITZs), which reduces weight loss. Then, a linearly increasing stage occurs with the spalling of the surface paste when the freeze–thaw expansion stress exceeds the tensile strength of concrete. Given that the spalling of the surface paste also sped up the freeze–thaw cycles, weight loss accelerated in 100–300 cycles.

Compared with the incorporation of CRCA, the incorporation of C-CRCA decreased the weight losses of specimens under freeze–thaw cycles. After 300 freeze–thaw cycles, the weight losses of concrete samples containing C1-CRCA and C2-CRCA were lower by 0.3 and 0.45%, respectively, than those of concrete containing CRCA. This outcome was related to the pop-outs effect, which results from the disintegration of the surrounding cement paste and the expansion of saturated aggregates near the surface of the specimen. When the water inside the aggregate freezes, the generated pressure causes the aggregate to fail or disrupts the surrounding cement paste. Given their porous nature, recycled aggregates absorb considerable amounts of water, thus delaying drying and increasing the saturation level of the concrete.40)41) As the mortar with CRCA near the surface decreased in strength and absorbed more water than C-CRCA, the R group became more prone to pop-outs and surface destruction. The C2-R group only had a slightly beneficial effect compared with the C1-R group because the frost resistance of the former was already high.

Figure 5 shows the influence of CRCA and C-CRCA contents on the variation in weight losses after 300 freeze–thaw cycles. After 300 freeze–thaw cycles, the weight losses of R100, R50 and R20 were respectively 0.84, 0.69 and 0.18% higher than those of concrete with CNA. After 300 freeze–thaw cycles, the weight loss values of C1-R100, C1-R50, and C1-R20 were 0.39, 0.32 and 0.1% higher than that of concrete with CNA, respectively. The concrete with 100% CRCA and C-CRCA exhibited the highest weight losses, while concrete with CNA had the lowest weight losses. The weight loss of concrete increased with the increasing replacement ratio of CNA with CRCA and C-CRCA because the incorporation of CRCA and C-CRCA in concrete weakened the mortars and caused the concrete to experience more pop-out effects. The surface scaling tended to be less severe in concrete with CNA because its mortar was more resistant.

### 3.3 Relative dynamic modulus of elasticity

Figure 6 shows the variations in the RDME of the concrete mixtures under freeze–thaw cycles. The RDME curves for the three average groups (R, C1-R and C2-R) decreased with increasing freeze–thaw cycles. The RDME of concrete specimens in the three groups showed a similar trend. However, as the number of freeze–thaw cycles increased, the C-CRCA mixtures exhibited a higher RDME than the CRCA mixtures. Incorporating C-CRCA improved the RDME of recycled aggregate concrete during the freeze–thaw cycles. As shown in Fig. 6, the RDME of the three groups exhibited two stages: (I) a slowly decreasing stage, where the differences among the RDME values of R, C1-R and C2-R groups were small during 0–100 freeze–thaw cycles; and (II) an accelerating decreasing stage, where the differences obviously increased with further freeze–thaw cycles. After 300 freeze–thaw cycles, the RDME of C1-R increased by 6.2% compared with that of R. The RDME of C2-R increased by 1.6% compared with that of C1-R. Subjecting CRCA to 7 days of CO₂ curing had a slightly beneficial effect. As mentioned above, 3 days of CO₂ curing already provided high freeze–thaw resistance. Thus, C1-R and C2-R had less dissimilar RDME values.

The incorporation of RCA exerted positive and negative effects on concrete samples subjected to freeze–thaw cycles. The positive effect is the production of a more permeable aggregate that easily dissipated the hydraulic pressures exerted by frozen water. Negative effects include the high porosity of adhered mortar and the generation of micro-cracks during RCA production. These defects influenced the strength of the concrete. Given that CRCA incorporated concrete samples have lower water absorption and looser structures than C-CRCA incorporated concrete samples, less water proceeded inwards from the surface of the concrete. Hence, the negative effect on CRCA-incorporated concrete samples was slightly less than those on C-CRCA mixtures during the initial freeze–thaw cycles and slightly increased the RDME of the latter compared with that of the former. In further freeze–thaw cycles, the positive effect was dominant. The positive effect of C-CRCA mixtures was more obvious than in CRCA mixtures based on the spalling of the surface paste and the filling of pores and cracks with water. Therefore, the incorporation of C-CRCA attenuates the deterioration of concrete properties during Stage II of freezing–thawing.

Figure 7 shows the influence of CRCA and C-CRCA contents on the variation of RDME after 300 freeze–thaw cycles. After 300 freeze–thaw cycles, the RDME values of R100, R50 and R20 were respectively 8.8, 1.2 and 0.2% higher than those of concrete with CNA. RDME increased with increasing replacement rates of CRCA with CNA. The results agree with those reported by Debieb et al.,42) which showed that RCA obtained from air-entrained concrete had a drastic effect on freeze–thaw resistance and had better performance than concrete with CNA. RDME curves essentially led to the same conclusion about the frost resistance of concrete with C-CRCA: given that increasing the
amount of incorporated C-CRCA in concrete leads to a more positive effect, concrete with the 100% replacement mixtures have high residual RDME. After 300 freeze–thaw cycles, the RDME values of average C1-R100 and C2-R100 were respectively 18 and 18.7% higher than that of concrete with CNA. Hence, the internal freeze–thaw resistance of concrete did not decrease with the incorporation of C-CRCA.

Compared with CNA mixes, the performances of CRCA and C-CRCA mixes were worse in terms of weight loss but better in terms of RDME because weight loss is a surface phenomenon, whereas RDME is internal. On the one hand, concrete samples with CRCA and C-CRCA mortars were weaker and thus more easily damaged, especially near the surface. On the other hand, the freeze–thaw action could be less important in either concrete with CRCA and C-CRCA because these inclusions can easily dissipate hydraulic pressures.

3.4 Residual compressive strength in response to freeze–thaw cycles

The curves of compressive strength for the three average groups (R, C1-R and C2-R) decreased with the increasing freeze–thaw cycles, as presented in Fig. 8. The compressive strength of concrete specimens in the three groups exhibited a similar trend. Increasing the number of freeze–thaw cycles decreased the strength of concrete samples given that the evolution of cracks in the paste and ITZs in the concrete samples loosened the paste and weakened the bond between the paste and the aggregates.

As illustrated in Fig. 8, the compressive strength of concrete in freeze–thaw cycles exhibited the following two stages: (I) decreasing stage (0–100 cycles), where the compressive strengths of C1-R and C2-R groups were slightly greater than that of the R group; (II) accelerated decreasing stage (100–300 cycles), where the compressive strengths of C1-R and C2-R groups were greater than that of R group. After 300 freeze–thaw cycles, the 5.7% increase in the compressive strength of C1-R was obvious compared with that in compressive strength of the R group. However, the RDME of C2-R increased only by 1.4% compared with that of C1-R. The results of compressive strength loss agreed with the RDME values shown in Section 3.3. More importantly, both the positive and negative effects of RCA significantly affected the frost resistance of concrete.

Figure 9 shows the influence of CRCA and C-CRCA contents on the variation in compressive strength after 300 freeze–thaw cycles. In the R group, the values for residual compressive strength increased as CRCA content increased by up to 20%. Mixes containing CRCA at replacement rates of 20% showed the highest residual compressive strength. However, the values for residual compressive strength increased as C-CRCA content increased by up to 50% in the C1-R and C2-R group. Mixes containing C-CRCA at replacement rates of 50% showed the highest residual compressive strength. The compressive strength values of C2-R100 were 4% higher than that of CNA, despite the compressive strength values of R100 being 0.7% lower than that of the latter. From these results, it can be concluded that the partial and fully incorporation of C-CRCA does not reduce the freeze–thaw resistance of concrete. However, the mixes with 100% RCA had the worst performance. One explain is that even a small level of damage in the paste can be enough to cause an important participation of the porous aggregates in the concrete strength, leading to a lower residual strength.

3.5 Mesostructural analysis

3.5.1 Pore size distribution

The pore structure and ITZ of concrete are important factors that affect the durability and macromechanics of concrete. Freeze–thaw cycles change the internal pore structure of concrete, consequently affecting the physical and mechanical properties of concrete.\(^{[25]}\) Pore structure, especially the morphology of the connected pores, is critical to ice formation in concrete samples.\(^{[43,44]}\) Figure 10 shows the pore distribution patterns of different concrete mixtures before the freeze–thaw test. Four categories of pores are identified based on pore size distribution: micro-pores with \(r < 0.01 \mu m\); mesopores with \(r \approx 0.01\) and \(0.05 \mu m\); macropores with \(r \approx 0.05\) and \(1 \mu m\); and cracks larger than \(1 \mu m\).

As shown in Fig. 10(a), the pore size distribution of the concrete samples had three peaks, namely, higher left peak area, moderate middle peak area and lower right peak area. The pore radii were mainly between 0.001 and 0.05 \(\mu m\). These pore size distributions indicated that the pore structures of the concrete
mixtures were mainly occupied by micropores, mesopores and macropores. By contrast, cracks were not well developed. The trimodal distribution also indicated that enclosed multi-pores existed in the concrete mixtures. Furthermore, the left peak slightly shifted to a small pore radius when the C-CRCA was incorporated into concrete. Moreover, the volumes of micropores and mesopores in the concrete mixtures followed the descending order of C1-R50 > R50 > N [Fig. 10(b)]. This trend indicated that the most probable pore sizes of C1-R50 were smaller than those of R50 and N, thus demonstrating that CO2 curing improved the pore microstructure of concrete. Few initial cracks existed within the mortar before the freeze-thaw test owing to the self-shrinkage of the concrete samples and the formation of micro-cracks in the CRCA because of crushing.

Figure 11 shows the pore distribution patterns of concrete specimens after 300 freeze-thaw cycles. The patterns revealed that the majority of pore sizes in different mixtures remained almost unchanged. As shown in Fig. 11(a), in the N concrete mixture, the value of the left peak decreased, whereas the values of the middle and right peaks significantly increased. This result indicated that the micropore and mesopore volumes decreased, whereas the macropore and crack volumes significantly increased after the freeze–thaw cycles. In the R50 and C1-R50 concrete mixtures, the value of the left peak also decreased, whereas the values of the middle and right peaks slightly increased. These changes resulted from the enlargement of small pores to large pores or cracks in response to freezing–thawing. As shown in Figs. 10(b) and 11(b), the average crack growth rates in N, R50 and C1-R50 concrete mixtures were 13.3, 5.6 and 3.4%, respectively. This result indicated that the variation rate of the cracks in C1-R50 were considerably smaller than those in R50 and N. Thus, the incorporation of C-CRCA decreased the extent of freeze–thaw damage in concrete.

### 3.5.2 Variation in concrete pore volume

The area of the NMR $T_2$ spectrum is directly proportional to the total amount of fluid in the concrete. Therefore, the total area of the $T_2$ spectrum is generally equal to or less than the pore volume of the concrete sample. This relationship can intuitively reflect the variations in pore volume. The $T_2$ spectrum area of concrete before and after 300 freeze-thaw cycles was extrapolated from Figs. 10 and 11 and is presented in Table 5.

The $T_2$ spectrum areas of the N, R50 and C1-R50 mixtures increased after 300 freeze–thaw cycles relative to those before the test (Table 5). This result indicated that the total pore volumes of the three mixtures all increased after frost damage. The total pore volume of the R50 and C1-R50 concrete mixtures increased by only 1.4 and 1.8%, respectively, after 300 freeze–thaw cycles. However, the total pore volume of the N concrete mixture drastically increased by 7.7% after frost damage. It also revealed that the volumes of micropore and mesopore decreased cubically,
the volumes of macropore and crack began to increase cubically after frost damage, as shown in Table 5. This result likely occurred because the freeze–thaw effect of ice caused small pores to expand towards and connect with large pores. The total pore volumes of the C1-R50 and R50 mixtures slightly increased after 300 freeze–thaw cycles, indicating that the total pore volumes of the two mixtures were not severely affected by freeze–thawing. Thus, small pores in the C1-R50 and R50 concrete samples were less likely to expand into larger pores. In addition, under the freeze–thaw effect, new micropores would continuously initiate, develop and expand into macropores and cracks. The N mixture exhibited the highest increase in total pore volume because new micropores in this mixture rapidly developed during freeze–thaw cycles. Thus, the N mixture experienced more freeze–thaw damage than the R50 and C1-R50 mixtures. After 300 freeze–thaw cycles, the C1-R50 mixture exhibited the least variation in crack volume, which increased by 2.6 times of the initial value before the test. The performance of the C1-R50 concrete specimen was better than those of the N and R50 concrete specimens. This result further emphasised that the concrete that incorporates C-CRCA has better freeze–thaw resistance.

### 3.5.3 Failure mechanism

The pore structure is the primary mesostructural feature of concrete that considerably affects freeze–thaw resistance.50) Tiny enclosed micropores and mesopores, which are harmless, dominated the pore structure of C-CRCA in recycled aggregate concrete.51) These pores helped prevent ice formation and relieve ice pressure, consequently decreasing the extent of freeze–thaw damage in the mortar. Concrete with CRCA and CNA had fewer micropores and mesopores, which are less resistant to freeze–thaw cycles. As a result, the concrete structure easily weakened during freeze–thaw cycles. According to Aft et al.,52,53) the better performance of concrete with C-CRCA resulted from the reactions between CO2 and the hydration products Ca(OH)2 and calcium silicate hydrate (C-S-H) in hardened cement pastes and concrete. Ca(OH)2 and C-S-H react with CO2 to produce CaCO3:

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}
\]

\[
\text{C-S-H + CO}_2 \rightarrow \text{CaCO}_3 + \text{SiO}_2 + n\text{H}_2\text{O}
\]

CaCO3 then precipitates in the pore spaces of C-CRCA concrete samples, thus densifying the concrete microstructure, increasing the number of micropores and improving resistance to freeze–thaw cycles.

The increases in the crack volume of concrete in response to increasing freeze–thaw cycles are shown in Fig. 12. C1-R50 exhibited good resistance during freeze–thaw cycling. Its final crack volume increased to 3.6 times that of the initial value, indicating slight damage. By contrast, the crack volume of R50 after 150 freeze–thaw cycles was more than 2 times the initial value and subsequently increased to 4.8 times the initial value. These results indicated that R50 received severe damage during freezing–thawing. However, the crack volume of N after 300 freeze–thaw cycles was 7.5 times that of the initial value and was higher than those of concrete samples that incorporated CRCA and C-CRCA. This result indicated that N samples received more severe damage CRCA and C-CRCA samples. The microstructure of concrete with C-CRCA was more compact than that of concrete with CRCA and CNA. These results support those reported in Sections 3.3 and 3.4, where the residual RDME value and the compressive strength of concrete with C-CRCA were higher than those of concrete with CRCA and CNA.

### 4. Conclusions

The freeze–thaw resistance of concrete incorporating C-CRCA was characterised. C-CRCA decreases the negative effects of high porosity and defects of RCA during initial freeze–thaw cycles and increases the positive effects of hydraulic pressure dissipation during later freeze–thaw cycles. The following conclusions are drawn:

1. Concrete with C-CRCA exhibited higher compressive strength and density, as well as lower water absorption, than concrete with CRCA. The compressive strength of concrete decreased with the increasing replacement ratio of CNA with C-CRCA.
2. The 100 and 50% replacement of CNA by C-CRCA led to the highest RDME and residual compressive strengths after 300 freeze–thaw cycles, respectively. However, the weight loss was more severe with the increasing replacement of CNA by C-CRCA.
3. Freeze–thaw damage is more severe in concrete with CRCA than in concrete with C-CRCA irrespective of the replacement rates of CNA with C-CRCA. The internal freeze–thaw resistance of concrete with C-CRCA was higher or equal to that of concrete with CRCA and CNA.
4. Increasing CO2 curing time improved the freeze–thaw resistance of concrete with C-CRCA. The frost resistance of concrete with C2-CRCA was only marginally better than that of concrete with C1-CRCA, which already exhibits high frost resistance.
5. Incorporating C-CRCA improved frost resistance given that C-CRCA enhanced the pore structure of concrete by increasing the number of harmless pores. The reaction among CO2, Ca(OH)2 and C–S–H formed CaCO3 and silica gel. These products refined the pore structure and strength gain of concrete.

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