Effect of coupled deterioration by freeze-thaw cycle and carbonation on concrete produced with coarse recycled concrete aggregates

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This paper presents a study on coupled deterioration mechanisms, including carbonation and frost attack, on concrete prepared with 0, 50 and 100% by weight coarse recycled concrete aggregates (CRCA) to replace coarse natural aggregate (CNA). Fly ash (FA) was also used as 0, 20 and 40% weight replacements of cement. Carbonation depth, relative dynamic modulus of elasticity (RDME) and residual compressive strength were measured during the tests. Nuclear magnetic resonance analysis was performed on the selected samples to identify pores and cracks formed through coupled deterioration. Results showed that freeze-thaw cycle and carbonation affected each other. On the one hand, carbonation can increase strength and reduce permeability to improve freeze-thaw resistance and form new pores, which accelerate freeze-thaw damage. On the other hand, the depth of carbonated concrete increased as the freeze-thaw deterioration increased; this finding could be due to cracking associated with increased internal deterioration caused by freeze-thaw cycle. In contrast to the findings of the single-factor test, concrete subjected to coupled deterioration by freeze-thaw and carbonation showed lower residual compressive strength and residual RDME but higher carbonation depth.

Key-words: Coarse recycled concrete aggregates, Fly ash, Freeze-thaw cycles, Relative dynamic modulus of elasticity, Carbonation depth, Compressive strength, Nuclear magnetic resonance

1. Introduction

With rapid developments in the construction industry, environment-friendly techniques for waste treatment and demolition (C&D) must be developed. Crushing concrete from old structures generates recycled concrete aggregates (RCA), which can be used as a partial substitute of virgin aggregates for producing new concrete. Recycled aggregate concrete (RAC) can also be used as a partial substitute of virgin aggregates in producing new concrete, and is a promising solution for dealing with C&D waste and saving construction materials.1) Laboratory studies on the durability of RAC indicated that freeze-thaw resistance is one of the main causes of concrete deterioration.2)-5) The deterioration of concrete constructions resulting in freeze-thaw damage severely affects the durability and service life of concrete structures. The freeze-thaw resistance of concrete is affected by various factors, such as porosity, water/cement (w/c) ratio, environmental conditions and type of aggregate used.6) Studies have reported the effects of fine recycled concrete aggregates (FRCA) and coarse recycled concrete aggregates (CRCA) on the freeze-thaw resistance of concrete. Bogas et al.7) concluded that incorporation of FRCA is not detrimental to the freeze-thaw resistance of concrete. Moreover, w/c ratio exhibits greater influence on the freeze-thaw resistance than the type of aggregate used, and air entraining elicits slightly beneficial effect on high-strength concrete. Yildirim et al.8) studied the effects of internal curing provided by FRCA on the freeze-thaw resistance of 0.5–0.7 w/c concrete. Lofty and Al-Fayez9) investigated freeze-thaw resistance using 20% CRCA and FRCA as a replacement of natural aggregates; the obtained resistance is as high as that of the reference non-recycled concrete. Liu et al.10) elucidated the effects of the parent concrete and mixing approach on the freeze-thaw resistance of air-entrained recycled aggregate concrete (ARAC). Results indicated that the mixing approach did not affect the frost resistance of both FRCA and CRCA. Industrial by-products, such as fly ash (FA), can also be used both as alternative binders (in partial replacements of Portland cement) and fillers.11) Salem and Burdette12) reported that the resistance of RAC to freeze-thaw cycling can be improved by adding air-entraining agents (AEA) and high amounts of FA.

Several studies on the carbonation of concrete produced with RCA have been published in the last 10 years.13)-16) Amorim et al.17) suggested that RAC presents a higher carbonated depth than concrete produced without recycled aggregates because CRCA have greater water absorption than NCA, and RAC have higher porosity than NAC with the same w/c ratio; therefore, the carbonation resistance of RCA is reduced. This finding was also observed in other studies.18),19) Otsuki et al.20) found that the carbonation resistance of RAC is slightly inferior to that of normal aggregate concrete; the use of double mixing method with high water-binder ratio concrete can achieve the carbonation resistance of RAC. Katz21) found that the depth of carbonation of the recycled concrete is 1.3–2.5 times higher than that of the reference concrete; higher values were also observed in the recycled ordinary Portland cement concrete compared with the white Portland cement concrete. The carbonation resistance of RAC is similar to the source concrete in terms of hydration level. Ryu22) produced concrete mixes with coarse RCA from materials with different strength and contents of adhered cement paste. All RAC mixes with 100% CRCA exhibited 20% higher carbonation depths than

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Kou and Poon26) used FA as a substitute and added cement in CAN mixes. However, some researches suggested that the properties of RCA do not affect RAC. Xiao et al.25) evaluated six tests by using 22 groups of RAC specimens; the results showed that the carbonation behaviour of RAC was not only influenced by the quality of new mortar but also by the properties of RCA. Kou and Poon27) studied the carbonation depths of RAC prepared with 25, 35 and 55% class-F FA as cement replacements. After 10 years of outdoor exposure, 55% FA as cement replacement exhibited high carbonation depth; FA also increased the carbonation depth of concrete.

Most studies have focused on single environmental factor affecting the deterioration of RAC; limited information is available on the interaction between freeze–thaw cycles and carbonation. Themicro structural features of concrete under the coupling effect require further investigation. This paper presents the results of assessing coupled deterioration mechanisms, including frost damage and carbonation. This paper is a basic experimental research on the performance of concrete subjected to three tests: single freeze–thaw cycles; single carbonation test; coupled deterioration test by freeze-thaw and carbonation. Moreover, carbonation depth, relative dynamic modulus of elasticity (RDME), compressive strength, porosity and inter-images of pore information were measured. In brief, this study analysed the influence of replacing CNA with CRCA as well as cement with FA in coupled deterioration of concrete.

2. Experimental program

2.1 Materials

Table 1 shows the chemical compositions of cement and FA provided by the manufacturers. Natural and recycled aggregates were used as coarse aggregates in concrete mixtures. Natural gravel was used as natural aggregate. The fine aggregate used in the concrete mixtures was natural river sand, with a 2.5% silt content. Parent concrete samples were subjected to primary crushing using a jaw crusher. CRCA samples, with diameters of 10 and 20 mm, were selected after screening. Figure 1 shows the photograph of CRCA used in the experiments. Some physical properties of natural sand, CNA and CRCA are shown in Table 2.

2.2 Concrete mixtures

Concrete mixtures were prepared with a w/c ratio of 0.36. FA was used as 0, 20 and 40% by weight replacements of cement, and CRCA was used as 0, 50 and 100% by weight replacements of CNA. Table 3 shows the nine mixtures prepared and properties of the concretes. In concrete mixtures, 10 and 20 mm coarse aggregates were used at a ratio of 1:2. As predicted, the fresh density of concrete was related to the CRCA content of the mixture. The fresh density of the concrete mixtures decreased slightly with increasing CRCA content. The quantity of super-plasticizer (SP) and AEA used in concrete mixtures are also present in Table 3.

Table 1. Chemical compositions of cement and fly ash

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<th>Contents</th>
<th>Cement</th>
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<td>SO₃ (wt%)</td>
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Table 2. Properties of aggregates

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Table 3. Mixture proportions and properties of the concretes

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<th>Fly ash (%)</th>
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<th>Fly ash</th>
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<th>Gravel</th>
<th>CRCA</th>
<th>AEA (%)</th>
<th>SP (%)</th>
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Fig. 1. Coarse recycled concrete aggregates used in experiments: (a) 20 mm, (b) 10 mm.
2.3 Experimental samples
The following specimens were produced for each mixture. Three 100 mm cubic specimens were maintained for compressive strength tests at 28 days. Three 100 mm cubic specimens were maintained in water during testing and tested at the same age as those exposed to deterioration to evaluate the compressive strength loss of concrete. Twelve 100 mm cubic specimens were prepared for compressive strength test according to the standard test method for mechanical properties of ordinary concrete (GB/T 50081-2002). Three 100 mm × 100 mm × 400 mm specimens were obtained for evaluating freeze–thaw resistance according to the standard test methods for long-term performance and durability of ordinary concrete (GB/T 50082-2009). Three 100 mm × 100 mm × 400 mm specimens were used for freeze–thaw tests. Six 100 mm × 100 mm × 400 mm specimens were prepared for coupled deterioration test.

2.4 Freeze–thaw cycle test
The testing procedure for evaluating the freeze–thaw resistance of various samples involved rapid freeze–thaw for 400 cycles according to the GB/T 50082 (2009) standard. The temperature of concrete was controlled with a thermocouple embedded in the centre of the 100 mm × 100 mm × 400 mm specimens. The specimens were placed in a freeze–thaw machine and subjected to freeze–thaw cycles. During each cycle, the temperature was decreased from 5 to −20°C, then increased to 5°C within 4 h. For each group, three specimens of 100 mm × 100 mm × 400 mm prisms and twelve specimens of 100 mm cubes were used. After 50 cycles, the specimens were removed from the testing device, and RDME was measured. Three prisms of each type were tested, and the average values were used for all parameters. After 50, 100, 200 and 400 freeze–thaw cycles, compressive strength was measured. In the test, the prismatic specimens were first inserted in rubber boxes filled with liquid up to 20 mm above the upper face of the concrete specimens. Water was used for liquid solution test for freeze–thaw cycles.

The dynamic modulus of elasticity can be determined by Eqs. (1) and (2), as shown below:

\[
E_d = \frac{1 + \nu}{1 - 2\nu} \frac{E_o}{\rho V^2}
\]

(1)

\[
RDME = \frac{E_{dn}}{E_{do}} = \frac{V_d^2}{V_o}
\]

(2)

where \(E_d\) is the dynamic modulus of elasticity; \(\rho\) is the density of concrete; \(V\) is the ultrasonic pulse velocity; \(\nu\) is the poisson coefficient; \(E_{dn}\) is the dynamic modulus of elasticity at \(n\) cycles (GPa); \(E_{do}\) is the dynamic modulus of elasticity at the beginning of the test (GPa); \(V_d\) is the ultrasonic speed of concrete specimens at the beginning of the test (m/s) and \(V_o\) is the ultrasonic speed of concrete specimens at \(n\) cycles (m/s).

Based on the preceding test, the RDME of the concrete samples was determined. We then detected the concrete porosity and inter-images of pore information for each concrete sample before the test and after 400 freeze–thaw cycles. A low-field NMR spectrometer (MacroMR23-060H-I, Shanghai Niumag Corp.) was used in the test. The main NMR measurement parameters were as follows: echo time was 0.6 ms, waiting time of repeat was 4 s, echo numbers were 8000, and scanning numbers were 64. In addition, the magnetic resonance imaging (MRI) system used for NMR could obtain internal images of concrete samples that indicate the specific pore scales of a cross-section. The main MRI measurement parameters were the following: slice width was 20 mm, cumulative number of times was 16, waiting time of repeat was 500 ms, and echo time was 9.42 ms. Before the MRI test, we saturated the concrete specimens using a vacuum saturation device. The vacuum pressure value of the device was 0.01 MPa, and the water absorption time was 8 h. Then, we soaked the concrete specimens in distilled water for 48 h, which allowed the concrete samples to reach 100% water-saturated condition. During the MRI test, because the temperature of the magnet and probe assembly was 32°C, we wrapped the concrete specimens in a preservative film to eliminate the influence of moisture evaporation on the experiment results.

2.5 Carbonation test
All the specimens were cured in a controlled chamber at 20 ± 2°C and relative humidity of 95%. At 28 days, the specimens were placed in an accelerated carbonation test chamber with (20 ± 3)% CO₂ concentration, 20 ± 5°C temperature and (70 ± 5)% relative humidity. The carbonated concrete showed a different colour compared with other areas; therefore, the depth could be measured by a calliper. The mean values of carbonation depths at 7, 14, 28 and 56 days were measured by the distance from the exposure surface to the place that turned blue. Twelve 100 mm cubic specimens were used for compressive strength tests after 7, 14, 28 and 56 days of carbonation. Before the test and after 56 days of carbonation, the concrete porosity and inter-images of pore information are measured by NMR.

2.6 Coupled deterioration test
Six 100 mm × 100 mm × 400 mm and twelve 100 mm cubic specimens were prepared for freeze–thaw test, followed by carbonation test. In this test, the freeze–thaw cycle was performed first. After 50 cycles of freeze–thaw, all specimens were transferred to the accelerated carbonation test chamber for 7 days. After the carbonation test, the specimens were removed from the test chamber; carbonation depth and RDME were measured. This procedure describes a cycle of coupled deterioration tests, which repeated for a total of eight cycles. Twelve 100 mm cubic specimens were used for compressive strength tests after 7, 14, 28 and 56 days of carbonation. Before and after the coupled deterioration test, the concrete porosity and inter-images of pore information are measured by NMR.

3. Experimental results and discussion
3.1 Carbonation depth
The variation in the average carbonation depth with the replacement ratio of NCA by CRCA and cement by FA shown in Fig. 2. The carbonation depth increased almost linearly with CRCA replacement ratio in Fig. 2(a). At 56 days, the average carbonation depth increased by approximately 11 and 40% for concrete with replacement rates of 50 and 100% CRCA, respectively, compared with that of concrete with NCA. CRCA positively and negatively influenced RCA subjected to carbonation. In the positive effect, CRCA possesses high total binder content and alkaline reserve, which can be carbonated because of the attached mortar of RCA, thereby enhancing carbonation resistance. In the negative effect, CRCA contains old adhered mortar and is porous; therefore, water absorption is higher than that of NCA. Moreover, RAC exhibits increased porosity and reduced carbonation resistance. The negative effect is dominant. The results corroborated with the findings of other researchers, the carbonation depth of concrete increases with increasing replacement ratio of NCA with CRCA.

Figure 2(b) shows the average carbonation depth of concrete mixes with varying FA contents at 7, 14, 28 and 56 days. The in-
The coupled deterioration mechanisms, including freeze-thaw cycle and carbonation, freeze-thaw damage affects the carbonation coefficient, which is defined by the following equation:

$$\lambda_F = \frac{d_{F+C}}{d_C}$$  \hspace{1cm} (3)

Where $\lambda_F$ is the freeze-thaw damage affecting the carbonation influence coefficient, $d_{F+C}$ is the carbonation depth under the coupled deterioration mechanisms including freeze-thaw cycle and carbonation (mm) and $d_C$ is the single carbonation depth (mm). If $\lambda_F = 1$, freeze-thaw damage does not influence carbonation. If $\lambda_F < 1$, freeze-thaw damage positively influences carbonation. If $\lambda_F > 1$, freeze-thaw damage negatively influences carbonation.

The change law of carbonation depth in the coupled deterioration test is similar to that of the single carbonation test. As shown in Fig. 3, the influence coefficient $\lambda_F$ increased with testing time. After 7 and 14 days of carbonation, the influence coefficient increased slightly to more than 1. After 56 days of carbonation, the influence coefficient is higher than 1. It can be explained that the freeze-thaw damage may negatively affect the carbonation of concrete at the beginning of the test. With increasing test time, the negative effect of freeze-thaw becomes significant.

3.2 Relative dynamic modulus of elasticity

As shown in Figs. 4(a)–4(c), the highest percentage reduction in RDME was recorded for R0 and the residual RDME is 86.5%. The lowest percentage reduction in RDME was recorded for R100F20 and the residual RDME is 91.03%. When FA was used, the average RDME of concrete with 20 and 40% FA increased.

Fig. 2. Carbonation depth variation with (a) NCA by CRCA replacement ratio and (b) cement by FA replacement ratio. The number of specimen n = 3.

Fig. 3. Variation in $\lambda_F$ with (a) NCA by CRCA replacement ratio and (b) cement by FA replacement ratio. The number of specimen n = 3.

$\lambda_F$ increases with increasing FA ratio led to high carbonation depths. The extrapolated values of the average carbonation depth after 56 days were 18.33, 20.47 and 21.80 mm for mixtures without FA, with 20% FA and 40% FA, respectively. With FA content of 20 and 40%, the carbonation depth was approximately 1.12 and 1.19 times higher than those of concrete without FA. Using FA improved the interfacial transition zone between the CRCA and the new cement paste as well as the internal pore structure, consequently decreasing the porosity of RAC. However, using FA decreased the total hydraulic pressure caused by ice. Therefore, CRCA exhibited higher permeability, which could be beneficial for the freeze-thaw resistance of concrete. Concrete mixtures with NCA possessed larger internal cracking during freeze-thaw cycles; this feature can improve gradual transport of CO2 from the surface of the concrete inwards.31)
by 6.6 and 4.7%, respectively, compared with that of concrete without FA after 400 freeze-thaw cycles. This result suggests that FA can enhance the internal freeze-thaw resistance of RAC, and the effect can be improved because CRCA provided additional voids in the paste. In the presence of FA, the number of micro-cracks in the CRCA decreased because of the healing effect after prolonged curing of FA-blended cement paste. Therefore, concrete mixtures with CRCA and the quality of the interfacial transition zone were better than those of the old paste and CNA. Moreover, the bond between the new cement paste and CRCA was enhanced. The coefficient of permeability also increased by a small degree when FA was used as replacement, although the values remained satisfactory for durable concrete. Hence, hydraulic pressure caused by ice can easily dissipate. However, 40% FA led to less improvement than 20% FA. After 400 freeze-thaw cycles, excessive amounts of FA, which was used to replace cement, reduced the strength of surface cement paste.

Figure 4(a) shows the highest percentage reduction in RDME was recorded in concrete with NCA, followed by 50 and 100% CRCA. After 400 freeze-thaw cycles, RDME with 50 and 100% CRCA increased by 6.01 and 2.98%, respectively, compared with that of concrete without CRCA. Concrete with CRCA showed higher residual RDME than concrete with NCA. Therefore, CRCA incorporation did not reduce the freeze-thaw resistance of concrete. In fact, permeable aggregates can easily dissipate hydraulic pressure caused by ice. Therefore, CRCA can be beneficial to the freeze-thaw resistance of concrete because of its high permeability and ability to easily accommodate the expansion pressures better than NCA. Therefore, the freeze-thaw action can be less important in concrete with CRCA.

Under the coupled deterioration mechanisms including freeze-thaw cycle and carbonation, carbonation damage affects the freeze-thaw influence coefficient, as defined by the following equation:

$$\lambda_c = \frac{D_{F+ C}}{D_C}$$

Where $\lambda_c$ is carbonation effect of freeze-thaw influence coefficient, $D_{F+ C}$ is coupled internal deterioration including freeze-thaw and carbonation and $D_C$ is single internal deterioration of freeze-thaw cycles. The internal deterioration was determined by the RDME. If $\lambda_c = 1$, carbonation damage did not influence the freeze-thaw cycle. If $\lambda_c < 1$, carbonation damage positively affected the freeze-thaw resistance damage of concrete. After 150 freeze-thaw cycles, the influence coefficients are higher than 1; hence, the carbonation damage negatively affected the freeze-thaw cycle.

The change law of RDME in the coupled deterioration test is similar to that of the single freeze-thaw test. As shown in Fig. 5, the influence coefficient $\lambda_c$ of concrete increased with increasing number of freeze-thaw cycles. The influence coefficient is less than 1 during the initial 100 freeze-thaw cycles. Carbonation positively affected the freeze-thaw resistance damage of concrete. After 150 freeze-thaw cycles, the influence coefficients are higher than 1; hence, the carbonation damage negatively affected the freeze-thaw resistance of concrete in further test times.

Figure 5(a) shows the average influence coefficient $\lambda_c$ variation with NCA by CRCA replacement ratio in the coupled deterioration test. The concrete mixtures prepared with 100%
CRCA showed 1.07 and 1.06 times higher average $\lambda_c$ than NCA and 50% CRCA, respectively. After 400 freeze-thaw cycles, concrete mixtures prepared with 0, 50 and 100% CRCD exhibited average $\lambda_c$ values of 1.51, 1.60 and 1.76, respectively. The $\lambda_c$ of concrete increased with increasing replacement ratio of CNA with CRCA. This finding may be attributed to the recycled porous aggregates. Therefore, the internal density of concrete mixtures with CRCA was not good and can accelerate CO$_2$ transfer from the surface of concrete inwards, resulting in internal damage.

Figure 5(b) shows the average influence coefficient $\lambda_c$ variation with cement by FA replacement ratio in coupled deterioration test. The concrete mixtures prepared with 40% FA were 1.28 and 1.09 times of concrete mixtures with no FA and 20% FA in the average $\lambda_c$ respectively. After 400 freeze-thaw cycles, the concrete mixtures prepared with 0, 20 and 40% FA had the average $\lambda_c$ of 1.39, 1.74 and 1.74, respectively. The $\lambda_c$ increased as the FA content increased, and 40% FA mixed with concrete have the largest $\lambda_c$ after the test. This may be also attributed to the lower Ca(OH)$_2$ content in the concrete with FA, which decreased the amount of constituents capable of becoming carbonated.

3.3 Residual compressive strength

The compressive strengths of the concrete mixtures after curing for 28 days summarised in Table 3. As the CRCA content increased from 0 to 100%, the compressive strength decreased accordingly. Furthermore, when FA was added, the strength gains of all the concrete mixtures at 28 days were less than those of the concrete mixtures without FA; moreover, the compressive strengths decreased with the increased FA as a replacement of cement. The effect of the compressive strength on the carbonation behaviour subjected to coupled deterioration tests were analysed and the results are shown in Fig. 6. The carbonation depth increased and the compressive strength decreased with the increased CRCA replacement ratios.

The compressive strengths of the concrete mixtures of after 7, 14, 28 and 56 days carbonation are summarised in Table 4. The compressive strength of concrete exhibited the following stages: (I) increased stage (II) decreased stage. The residual compressive strengths are shown in Fig. 7(a). In general, the concrete mixtures with CNA and no FA showed the highest residual compressive strengths. This corroborated the better behaviour shown by recycled aggregate mixes, in terms of carbonation depth changes.

The compressive strengths of the concrete mixtures of after 50, 100, 200 and 400 freeze-thaw cycles are summarised in Table 4. The compressive strength of concrete exhibited the following stages: (I) slowly decreased stage (II) decreased stage. The residual compressive strengths are shown in Fig. 7(b). The concrete mixtures with replacement rates of 50% CRCA and 20% FA showed the highest residual compressive strengths, and the concrete mixtures with 100% CRCA and 40% FA showed the lowest residual compressive strengths.

Table 4. Compressive strengths in the single carbonation and freeze-thaw tests

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<td>52.65</td>
<td>56.97</td>
</tr>
<tr>
<td>R100F20</td>
<td>47.79</td>
<td>52.82</td>
</tr>
<tr>
<td>R0F40</td>
<td>52.03</td>
<td>54.99</td>
</tr>
<tr>
<td>R50F40</td>
<td>48.21</td>
<td>52.32</td>
</tr>
<tr>
<td>R100F40</td>
<td>37.63</td>
<td>42.15</td>
</tr>
</tbody>
</table>

Fig. 6. Relationship between carbonation depth and compressive strength. The number of specimen $n = 3$.

Fig. 7. Residual compressive strength after (a) single carbonation test, (b) single freeze-thaw test and (c) coupled deterioration test. The number of specimen $n = 3$. 

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The compressive strengths of the concrete under coupled deterioration tests are summarised in Table 5. The compressive strength of concrete also exhibited the following stages: (I) slowly increased stage (II) accelerating decreased stage. However, compared with the single carbonation and freeze-thaw tests, the increased rates were less in stage I, and the decrease rates were higher in stage II. The concrete mixtures with 50% CRCA and 20% FA showed the highest residual compressive strengths [Fig. 7(c)]. However, the concrete mixtures with 100% CRCA had much less residual compressive strength. This finding can be explained by the increased recycled aggregates in the concrete, which might have increased the damage in surrounding paste after coupled deterioration test, there by leading to a lower residual strength.

3.4 Concrete porosity and permeability

Porosity refers to the specific value between the pore volume and the total volume of the concrete. Porosities of the concrete samples upon NMR are shown in Table 6. Porosities of the concrete increased with the increase in CRCA replacement ratios before the tests, and the increase rates in the R50 and R100 were 10 and 23% compared with that of the R0. Furthermore, the porosity of the concrete increased with the decrease on FA replacement ratios before the test, and the decrease rates in the R0F20 and R0F40 were 4 and 5% compared with that of the R0.

In single carbonation test, the changes of porosity in the R0, R50 and R100 before and after carbonation were 9.1, 6.0 and 10.6%, respectively. Furthermore, the changes of porosity in the R0, R0F20 and R0F40 before and after carbonation were 9.1, 15.4 and 17.2%, respectively. This corroborates the better behaviour shown by recycled aggregate mixes, in terms of carbonation depth (section 3.1). From these results, it can be concluded that the partial incorporation of CRCA and FA can reduce the carbonation resistance of concrete.

In coupled deterioration test, the change rates of porosity in the R0, R50 and R100 before and after coupled deterioration test were 36.2, 31.7 and 35.1%, respectively. Furthermore, the change rates of porosity in the R0, R0F20 and R0F40 before and after coupled deterioration test were 36.2, 37 and 47%, respectively. Compared with the single test results, the coupled deterioration test pore change rates were higher than the single environmental factor test; therefore, the internal damage of coupled deterioration test were more than single carbonation or freeze-thaw tests.

The permeability of the concrete samples upon NMR is also shown in Table 6. The change law of permeability is similar to the law of change of porosity. Variation curves of concrete porosity and permeability curve after coupled deterioration test are shown in Fig. 8. As demonstrated in Fig. 8(a), the increased porosity and permeability of the concrete are similar after the coupled deterioration, and the porosity and permeability in the R100 was the highest. As demonstrated in Fig. 8(b), the increased porosity and permeability of the concrete are different after the coupled deterioration, the porosity in the R0 was the highest, and porosity in the R0F40 was highest. These are due to the fact that concrete permeability is controlled not only by porosity, but also by pore size distribution and mineral additions, such as FA,32).

3.5 Magnetic resonance imaging

Figure 9 shows the results of the MRI of R0, R50 and R100 mix notations before and after tests. In Fig. 9, bright regions in the image represent water molecule region and surrounding black area is the background; the brightness of the image reflects the concrete water content. If the colour is brighter, there is more water inside; therefore, the area has larger pores or cracks.

The bright spot zones of the concrete before tests were small, and that in the R100 was slightly larger, followed by those of the R50 and R0, which is consistent with the results of CRCA being more porous and can absorb more water than NCA [Fig. 9(a)]. Figure 9(b) shows MRI of concrete after 56 days of carbonation. The images have small bright spots, indicating that concrete having low water content. Furthermore, the area with bright spots increased with the increasing CRCA replacement ratios. R100 has several large pores in a small area, but small pores occupy most parts. The reason for this is that RAC is a porous medium.
CaCO₃. The carbonation products can block the internal porosity within the cement matrix. Moreover, the carbonation will also gradually increase and develop. Increase in carbonation time, the internal micro cracks will permeability as a result of the deposition of CaCO₃ in the voids. This process results in a slightly increased strength and reduced permeability of concrete to a certain extent, and decreased the porosity of concrete. However, Ca(OH)₂ which dissolved in the pore solution is consumed in the reaction, and it will continue dissolved out from the cement matrix. Part of the cementations was also the consumption by the carbonation reaction; therefore, the carbide particles continuously dissolved and were consumed from the matrix, thereby forming new pores. Most of these new pores were not closed, and these pores will become larger after freeze-thaw cycles; therefore, these are not conducive to the frost resistance of concrete. This explains the initial test, due to carbonation of concrete becoming dense and the compressive strength and RDME of concrete slightly increasing; however, with further test time, the compressive strength and RDME had a rapid downward trend.

Freeze-thaw cycle can inflict different degrees of internal deterioration in concrete, as determined by RDME. The results revealed some correlation between the internal deterioration (RDME) and carbonation degrees. Compared with the single carbonation and coupled deterioration, as the freeze-thaw deterioration increased from approximately 3.72–5.80%, the depth of carbonated concrete increased from 11.51 to 21.83 mm. As freeze-thaw internal deterioration increased, so did the depth of carbonated concrete. The cause of this increased penetration can be attributed to increased internal pores and cracks associated with the increase in internal deterioration caused by freeze-thaw, as observed by MRI in Fig. 9.

4. Conclusions

This research shows the following conclusions derived from studies on single and coupled damage of concrete tested under laboratory conditions of freeze–thaw cycle and carbonation.

1. In single carbonation test, the carbonation depth of concrete increased with the increased replacement ratio of CNA with CRCA and cement with FA. In general, the carbonation depth of the concrete decreases with the increase in the strength grades of the original concrete, and concrete mixtures with CNA and no FA showed the highest residual compressive strength.

2. The internal freeze-thaw resistance of CRCA was found to be of at least equal internal freeze-thaw resistance to concrete manufactured with NCA. Right amount of FA (20%) as a replacement of cement was able to reduce the RDME loss and compressive strength loss of the concrete. The concrete mixtures with 50% CCA and 20% FA showed the highest residual compressive strength.

3. Carbonation has both positive and negative effects on the concrete subjected to freeze-thaw cycles. The positive effect is that carbonation can increase strength and reduce permeability in the initial freeze–thaw cycles. The negative effect is that the chemical reaction of carbonation leads to new pores, which results in the microcracks in concrete and accelerates the freeze-thaw damage process. The compressive strength and RDME of concrete in coupled deterioration was found to be more than in single freeze-thaw test during the initial freeze–thaw cycles because the positive effect was dominant. In further freeze-thaw cycles, the negative effect of carbonation was more significant and the damage of concrete was more severe.
100% CRCA and 40% FA, carbonation had the most effect on freeze-thaw.

(4) Freeze-thaw cycle negatively affects concrete subjected to carbonation. The depth of carbonated concrete increased with increasing freeze-thaw deterioration. This finding could be due to surface cracking associated with increased internal deterioration caused by freeze-thaw. The carbonation of concrete in coupled deterioration was found to be higher than in single carbonation test overall. The residual compressive strength in coupled deterioration was less than in single freeze-thaw or carbonation tests. During coupled deterioration, in the mixture with NCA and 40% FA, the freeze-thaw had the most effects on the carbonation. New laboratory standards for freeze-thaw testing should be generated to account for the carbonation effect.

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