Article

Effect of Freeze–Thaw Cycles on Carbonation Behavior of Three Generations of Repeatedly Recycled Aggregate Concrete

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Abstract: Multiple recycling of waste concrete has attracted widespread attention. This study presented the carbonation behavior of repeatedly recycled aggregate concrete (RRAC) used in a micro-frozen region. The effects of freeze–thaw cycles on the carbonation depth of three generations of RRAC with 25%, 75%, and 100% of replacement rate were evaluated. All RRAC specimens after different numbers of freeze–thaw cycles were rapidly carbonated for 28 d indoors to test the carbonation resistance of concrete. The results suggested that the carbonation depth of RRAC subjected to freeze–thaw cycles is higher than that in the non-freeze–thaw condition. This is because the freeze–thaw damages cause the internal structure of RRAC to become porous and prone to cracking, thus providing convenient channels for CO₂ to react with the alkali in the cementitious materials. With the growth of replacement rate or recycling number, RRAC reveals serious freeze–thaw damage and inferior carbonation resistance, which is due to the continuous deterioration repeatedly recycled concrete aggregate (RRCA) quality. However, when the replacement rate was 25%, the carbonation depth for the third generation of RAC was comparable to the second generation of RAC at a 75% replacement rate, and even the first generation of 100% RAC. To ensure better carbonation resistance durability of multiple recycling RAC, the low replacement rate of RRCA should be considered. For the third generation of RAC with the 100% replacement rate, its highest carbonation depth after freeze–thaw cycles was 9.16 mm, which still met the design requirements for structural use in a micro-frozen region. This indicates that it is feasible for three generations of RRAC to be used in the micro-frozen environment and that RRAC has great engineering application potential and promotional value.

Keywords: repeatedly recycled aggregate concrete; carbonation behavior; freeze–thaw cycles; multiple generations of recycling; replacement rate

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1. Introduction

Many countries are experiencing dramatic and swift urbanization in the worldwide, the result of which is followed by massive construction and demolition wastes (C&DWs) and a huge demand of natural aggregate (NA). These C&DWs cause serious environmental loads. The demand of NA results in overexploitation and shortage of NA resources, which greatly damages the ecological balance of aggregate-producing areas [1,2]. Utilizing these C&DWs as recycled aggregates to prepare the recycled aggregate concrete (RAC) is an effective and proven method to solve the environmental and resource crises and realize a circular economy in conventional concrete industries [3–7]. Many countries around the world

including USA, China, and EU are gradually extending RAC to practical projects [8–11]. At present, RAC has been widely used in building structures and pavements [12–14]. In this situation, the RAC utilization rate around the world is growing progressively with each passing year [15,16]. However, when such RAC reaches its service life, it will face the problem of being dismantled and becoming waste concrete again. To achieve the strategy of sustainable development, multiple recycling of RAC emerges, attracting widespread attention from scholars. Obtaining the utmost out of waste RAC and converting it to produce repeatedly recycled aggregate concrete (RRAC) will further improve the utilization rate of C&DWs and conserve natural resources effectively. Therefore, it is quite necessary to explore the multiple recycling potential of RAC.

Carbonation resistance is a key index affecting the durability of reinforced concrete structures [17,18]. Exploring the carbonation behavior of RRAC is an indispensable step which determines the application potential of RRAC. Concrete carbonation is a process in which CO_2 in the atmosphere reacts with the alkali in the cement to make the pore water more acidic, thus lowering the pH and leading to the loss of passivation film for reinforcements [19,20]. In the previous work, the carbonation behavior of three generations of RRAC with 100% replacement rate were reported [21]. It was found that with the increasing of the recycling number, the repeatedly recycled concrete aggregate (RRCA) quality degraded seriously and the carbonation resistance of RRAC gradually declined. But this study only considered the effect of a single factor on the carbonation resistance of RRAC. In an actual engineering, the occurrence of concrete carbonation is always accompanied with other environmental factors [22,23]. In a micro-frozen region whose average monthly temperature of the coldest month is between $0\sim-4\text{ }^\circ\text{C}$, the concrete always inevitably suffers from freeze–thaw cycles. These regions make up about a third of China’s territory. Therefore, it is necessary to investigate the effect of freeze–thaw cycles on the carbonation behavior of concrete used in micro-frozen regions.

Previous research has pointed out that the carbonation resistance of concrete in the cold region was worse than that only in the atmospheric environment [24–26]. This is attributed to the damages caused by freeze–thaw cycles in the cold environment. Guo et al. [27] and Yildirim et al. [28] reported that the mechanical properties and relative dynamic elastic modulus of RAC decreased and the mass loss increased with the rise of freeze–thaw cycles. Deng et al. [29] concluded that the porosity of recycled concrete increased with the increasing number of freeze–thaw cycles and proportion of recycled coarse aggregate. The freeze–thaw cycle is believed to bring about some micro- or macro-cracks in the concrete, which can immediately provide pathways for further migration of CO_2 [24]. Xiao [30] studied the carbonation behavior of natural aggregate concrete (NAC) in freeze–thaw circumstances. When NAC was firstly subjected to freeze–thaw cycles and then carbonized for a few days, the carbonation depth of NAC was obviously larger than that of NAC in a carbonized environment. Similar results have been found in the references of [23,24]. Mao et al. [31] reported the durability of recycled fine aggregate concrete under the actions of freeze–thaw and carbonation. The results indicated that crack propagation in concrete caused by the freeze–thaw damage resulted in the carbonation intensification of concrete, while the carbonation refining the pore structure could delay the freeze–thaw damage in the initial cycle. It is well known that compared with NA, recycled concrete aggregate (RCA) owns worse physical and mechanical properties due to the old attached mortar on its surface [32]. It has been proven that the carbonation resistance of RAC is inferior to that of NAC after freeze–thaw cycles due to the inferior properties of RCA [33]. If RAC is further repeatedly recycled into RRAC, with the growth of recycling number, it can be predicted that the carbonation resistance of RRAC would be degraded seriously. But their utilization rate and possible service life used in the micro-frozen region is not clear. Hence, it is of great academic and applied value to fill in the research gap regarding whether RRAC could be used in the micro-frozen region and to verify the utilization potential of RRAC.

In this study, three generations of RRAC were prepared by different replacement rates (25%, 75%, and 100%) of RRCA. The carbonation depth of three generations of RRAC under different freeze–thaw cycles (100–800 times) was measured to explore the effect of freeze–thaw damage on the carbonation resistance of RRAC. A research hypothesis that three generations of RRAC can be applied in actual projects in a micro-frozen region was verified by evaluating the carbonation resistance of RRAC during the whole service life.

2. Experimental

2.1. Materials

The experimental materials used in this study were consistent with ones in previous work [21]. P·O 52.5 Portland cement manufactured by Jiangsu Yangzi Cement Co. Ltd. (Changzhou, China) was used to prepare the three generations of RRAC. Granulated blast-furnace slag (GBFS), fly ash (FA), and silica fume (SF) were added as mineral admixtures. Considering strength, durability, and workability, etc. of concrete, the content of FA, GBFS, and SF was 20%, 10%, and 5% by weight of all cementitious materials, respectively. River sand whose apparent density was 2586 kg/m³ and fineness modulus was 2.4 was adopted as a fine aggregate. Natural coarse aggregate (NCA) with a particle size of 4.75–26.5 mm was applied to cast NAC as the control group. In addition, air entraining admixture (AEA) and polypropylene fiber (PP) were used as additives in the preparation process of RRAC. Polycarboxylic acid (PCA) as superplasticizer was used in all concrete groups. The dosage of polycarboxylic was 1.8 wt.% of cementitious material to ensure that the workability of all concrete could meet the slump value requirement of 150 mm.

2.2. Preparation of RRCA and RRAC

Figure 1a reveals the preparation process of three generations of RRCA and RRAC. A design service life of 50 years for RAC was defined as a generation in this study. The first-generation recycled aggregate (4.75–26.5 mm) marked as RCA-1 was provided from Jiangsu Lvhe Environmental Technology Co. Ltd. (Changzhou, China) to prepare the first generation RAC (RAC-1). To achieve the equivalence of a 50-year service life of concrete and prepare the second (RCA-2)- and third (RCA-3)-generation recycled aggregates by a laboratory acceleration process, the multi-environmental time similarity theory [34] was adopted. The cured RAC-1 was carbonated for 17 d indoor under 30% of its ultimate tensile stress, which was equal to concrete carbonated for 50 years in the natural environment. The loading procedure of RAC-1 followed the previous study [35], and the loading device is shown in Figure 1b. Then the RAC-1 was crushed by a two-grade crushing technique and sieved to obtain the RCA-2 (4.75–26.5 mm). Similarly, RCA-3 and the second (RAC-2)- and third (RAC-3)-generation RAC were prepared. The physical properties, phase compositions, and morphologies of three generations of RRCA had been described in the previous research [21]. All RRAC could meet the requirements for medium quality aggregates. The grading curves of NCA and RRCA are shown in Figure 2. All the cumulative sieve residual rates of NCA and RRCA conformed to the continuous grading requirements of a 5–20-mm aggregate diameter in accordance with GB/T 25177-2010. Three generations of RRAC with 40 MPa of target strength were prepared using the corresponding RRCA at different replacement rates (25%, 75%, and 100%), which were labeled as RRAC-25, RRAC-75, and RRAC-100.

Figure 1. (a) Schematic for preparation process of recycled concrete aggregate (RCA) and repeatedly recycled aggregate concrete (RRAC) and (b) loading device of RRAC.

Figure 2. Grading curve of natural aggregate concrete (NCA) and RRCA.

The mixed proportions of NAC and RRAC are given in Table 1. Cube specimens ($100 \times 100 \times 100$ mm) of RRAC were prepared for measuring compressive strength. Twenty-seven $100 \times 100 \times 400$ mm prism samples for each group of RRAC and NAC were cast for the freeze–thaw cycle and accelerated carbonation test. All specimens were demolded after 24 h and preserved in a standard curing room (20 ± 3 °C, RH > 90%) until the age of 28 d. The specimens for freeze–thaw cycles needed to be taken out 4 days in advance and soaked in (20 ± 2 °C) water until the freeze–thaw cycle began. The freeze–thaw cycles (100–800 times) of RRAC were carried out by the quick-freezing method in the laboratory. After subjecting to the freeze–thaw cycles, the NAC and RRAC specimens were carbonated in a standard carbonation box ($20 \pm 3\%$ of CO_2 concentration, $70 \pm 5\%$ of RH and 20 ± 2 °C of temperature) for 28 d.

Table 1. Mixed proportions of NAC and RRAC.

Concrete Types	Cement	NCA	RCA	Sand	GBFS	FA	SF	AEA	PCA	PP	Water
NAC	270	946	776	-	41	83	21	0.21	7.42	0.41	185.7
RAC-1-25	270	709.5	795	217.8	41	83	21	0.21	7.42	0.41	195.4
RAC-2-25	270	709.5	881	189.3	41	83	21	0.21	7.42	0.41	195.5
RAC-3-25	270	709.5	904	170.5	41	83	21	0.21	7.42	0.41	191.3
RAC-1-75	270	236.5	795	653.3	41	83	21	0.21	7.42	0.41	215
RAC-2-75	270	236.5	881	567.8	41	83	21	0.21	7.42	0.41	215.2
RAC-3-75	270	236.5	904	511.5	41	83	21	0.21	7.42	0.41	202.6
RAC-1-100	270	-	795	871	41	83	21	0.21	7.42	0.41	224.8
RAC-2-100	270	-	881	757	41	83	21	0.21	7.42	0.41	225
RAC-3-100	270	-	904	682	41	83	21	0.21	7.42	0.41	208.2

GBFS: Granulated blast-furnace slag; FA: Fly ash; SF: Silica fume; AEA: Air entraining admixture; PCA: Polycarboxylic acid; PP: Polypropylene fiber.

2.3. Measurements

The workability of fresh concrete was tested in accordance with standard ASTM C143 [36]. The compressive strength of NAC and RRAC was tested by standard ASTM C109 [37]. In each group, three specimens were tested to obtain the average compressive strength.

The carbonation resistance of NAC and RRAC before and after subjecting freeze–thaw cycles were assessed using rapid carbonation method according to standard GB/T 50082-2009 [38].

SEM images were taken by Zeiss SUPRA55 to observe the micro-morphology of RRAC under the action of freeze–thaw cycles and carbonation.

3. Results

3.1. Workability and Compressive Strength of RRAC

3.1.1. Workability

The workability of all concrete was set as 150 ± 15 mm and the measured values are shown in Figure 3. To ensure the well workability of fresh concrete, the dosages of additional water were adjusted according to the water absorption of RRCA.

Figure 3. Workability of RRAC with different replacement rates.

As shown in Figure 3, all the slump values of RRAC were more than 150 mm, which satisfied the design index. But the slump values of RRAC were lower than that of NAC, and showed a downward trend when the replacement rate or recycling number of RRCA increased. Compared with NAC, the slump values of RAC-1-25, RAC-2-25, and RAC-3-25 reduced by 4.2%, 5.8%, and 10.0%, respectively. For RAC-3, the slump values declined by

10.0%, 14.2%, and 20.5% with the increase of replacement rate. Both the high replacement rate and recycling number led to more loss in the workability of concrete, which was attributed to the increase of attached mortar contents and the number of fissures in RRCA. The high content of the attached mortar and loose and porous structure of RRCA resulted in an increase in water demand of RRAC, thus reducing the workability. In addition, RCA was more irregular in shape and rougher on the surface [39], which also reduced its mobility in concrete to reduce the workability.

3.1.2. Compressive Strength

The compressive strength of all concrete groups and the strength loss rate of RRAC relative to NAC are shown in Figure 4. The loss rate of compressive strength for RRAC increased, and its compressive strength gradually decreased with the growth of RRCA replacement rate and recycling number. The loss rates of RAC-1 were only 1.43%, 2.86%, and 3.68%, indicating that RAC-1 owned well strength close to that of NAC, especially at a low replacement rate (25%). But the strength loss rate of RAC-2 and RAC-3 increased significantly with the increase of the RRCA replacement rate. At a 100% replacement rate, RAC-3 had the largest loss rate, reaching 17.38%. Even though the compressive strength of RRAC decreased severely at a high replacement rate and great recycling number, all three generations of RRAC reached the target strength of 40 MPa. Therefore, it was feasible to prepare RRAC by using multiple recycling RCA for structural use in terms of compressive strength.

Figure 4. Compressive strength (a) and its loss rate (b) of RRAC at 28 d.

The falloff of the mechanical property of RRAC was attributed to the degraded quality of RRCA, such as high porosity, low density, high water absorption, etc., as well as the complex interfacial transition zone (ITZ) in RRAC (Figure 5). NAC owned only new ITZ between NCA and new mortar. However, as shown in Figure 5a, for the first generation RAC, three types of ITZs were introduced: (1) The old ITZ (O-ITZ) between the old attached mortar and original aggregate in RCA (black line); (2) the new ITZ (N-ITZ) between the original aggregate and new mortar (blue line); and (3) the mortar ITZ (M-ITZ) between the old attached mortar and new mortar (orange line). O-ITZ and M-ITZ produced by the attached mortar were the weakest part in recycled concrete [40]. Thus, new cracks in RAC were more likely to appear under the action of external force. When the waste concrete was multiple recycled, the ITZ became more complex, as displayed in Figure 5b, because another old mortar ITZ (marked as OM-ITZ) between the old attached mortar and next generation attached mortar appeared (green line). In addition, a great number of micro-cracks occurred in the attached mortar even inside the aggregate due to the iterative crushing processes in the preparation of RRCA [41]. These factors aggravated the decline in the quality of RRCA and compressive strength of RRAC.

Figure 5. Schematic diagram of interfacial transition zones (ITZs) in (a) RAC-1 and (b) RAC-2.

3.2. Carbonation Behavior of RRAC after Freeze–Thaw Cycles

Carbonation is an inevitable reaction during the use of cement concrete in a natural atmospheric environment. Carbonation depth indicates the carbonation resistance durability of concrete. Figures 6–8 exhibit the carbonation depth of RRAC with different replacement rates before and after freeze–thaw cycles.

Figure 6. Carbonation depth of RAC-1 with different replacement rates (a) before and (b) after freeze–thaw cycles.

Figure 7. Carbonation depth of RAC-2 with different replacement rates (a) before and (b) after freeze–thaw cycles.

Figure 8. Carbonation depth of RAC-3 with different replacement rates (a) before and (b) after freeze–thaw cycles.

3.2.1. The First Generation

The time-evolution of carbonation depths for RAC-1 at different replacement rates is displayed in Figure 6a. It is no doubt that the carbonation depths of concrete increased as time went on, and the carbonation resistance of RAC-1 became poor when the replacement rate increased. On the whole, the carbonation depth of RAC-1-25 and RAC-1-75 was similar to that of NAC, indicating that the carbonation resistance of RAC-1 with non-100% of replacement rate was comparable to that of NAC. Especially at low replacement rates (25%), the carbonation depths of RCA-1 were even lower than the NAC ones. This was due to the attached mortar on the surface of RCA, which reacted with CO_2 to form the carbonation products. These products filled in the micro-pores and micro-cracks in the attached mortar to enhance the weak ITZs [42], thus blocking the CO_2 penetration in concrete to some extent. But with the increase of attached mortar content namely replacement rate, the poor performance of attached mortar and ITZs in RAC began playing the leading role. The increasing pores and cracks in the attached mortar and the loose ITZs made it easier for CO_2 to penetrate into RAC [43]. Therefore, when the total attached mortar content in RAC exceeded a certain degree, the carbonation depth of RAC was greater than that of NAC [44].

The concrete structures used in micro-frozen regions are inevitably subjected to more or less freeze–thaw cycles. Predictably, freeze–thaw damage for concrete accelerates its carbonization. Figure 6b shows the 28-d carbonation depth variations of NAC and RAC-1 after different freeze–thaw cycles. The carbonation depth of all concretes increased gently as the freeze–thaw cycle went on. For NAC, the carbonation depth grew slowly before 600 freeze–thaw cycles, and the depth value increased by 41.4% compared to that of specimens under non-freeze–thaw conditions. But when freeze–thaw cycles increased unceasingly to 800 times, the carbonation depth reached 2 times as much as that of unfreeze–thaw specimens. Such a variation trend was also applicable to RAC-1-25. The carbonation depth of RAC-1-25 was close to the NAC one, showing that RAC-1 with low replacement rate owned comparable carbonation resistance durability of NAC. At a 75% replacement rate, the carbonation depth of RAC-1 increased rapidly after 300 freeze–thaw cycles. When the replacement rate was 100%, the carbonation depth of RAC-1 showed an exponential growth trend. This indicated that freeze–thaw damage and high contents of RCA-1 weakened the carbonation resistance of RAC-1. But for the first generation RAC, its carbonation resistance was acceptable especially at 25% and 75% replacement rates. In addition to the attached mortar of RCA retarding the CO_2 penetration in RAC, the relatively few micro-cracks and micro-pores in RCA accommodated more free water, which greatly alleviated the seepage pressure and expansion stress caused by icing in the early stage of freeze–thaw process. Minor freeze–thaw damage appeared in the RAC-1, resulting in a lower carbonation depth. But with the raise of replacement rate, the contents of attached mortar, micro-cracks, and micro-pores increased, which provided more channels for water and CO_2 media, leading to major freeze–thaw damage and poor carbonation resistance.

3.2.2. The Second Generation

Figure 7 shows the carbonation depths of second-generation RAC before and after freeze–thaw cycles. As shown in Figure 7a, the carbonation depth of RAC-2-25 was close to that of NAC. Similar to RAC-1, the attached mortar in RCA-2 slightly retarded the carbonation reaction of RAC-2. But when the replacement rate continued to rise, the carbonation depths of RAC-2 increased linearly. At the replacement rate of 100%, the carbonation depth of RAC-2 rose by 75.8% compared with the NAC one at a 28-d carbonation age. With the rise of the carbonation age, the overall growth trend was relatively gentle. The carbonation depth and carbonation time were approximately proportional to each other.

RAC-2 after freeze–thaw cycles was more likely to be carbonated, as displayed in Figure 7b. The carbonation depth of RAC-2 after freeze–thaw cycles increased faster than those of NAC and RAC-1, especially when the freeze–thaw cycle exceeded 300 times. The carbonation depth of RAC-2-100 showed a linear growth trend after 300 times of freeze–thaw cycles and the carbonation depth reached 7.15 mm after 700 times of freeze–thaw, which increased by 2 times compared with that before the freeze–thaw cycle. Freeze–thaw cycles resulted in the deterioration of pores and cracks in the concrete structure and the spalling of its surface mortar, which allowed CO₂ to penetrate into the concrete and increase the CO₂ diffusion coefficient [24]. Therefore, the RRAC specimens after freeze–thaw cycles were more susceptible to be carbonated, compared to those exposed in the non-freeze–thaw condition.

3.2.3. Third Generation

For the third-generation RAC, its carbonation resistance deteriorated sharply. With the increase of replacement rate, the carbonation depths of RAC-3 increased significantly (Figure 8a). In other words, the influence of the replacement rate on the carbonation resistance of RAC-3 was particularly severe. When the replacement rate reached 100%, the carbonation rate of RAC-3 showed a substantial increase compared with that at a low replacement rate. The carbonation depth of RAC-3 with 100% replacement rate at a 28-d carbonation age was 3.65 mm, which was 1.85 times higher than that of NAC. This was caused by the poor quality of RCA-3 and the cumulative effect of carbonation [21]. In the preparation process of every generation RCA, the matrix concrete was carbonated under the 30% of ultimate tensile stress for 17 d to simulate the real service life, thus leading to the partially attached mortar being carbonated. The greater the generation, the more obvious the accumulation effect of carbonation.

In Figure 8b, the carbonation resistance of RAC-3 falls off further with the increase of replacement rate and number of freeze–thaw cycles. After 400 times of freeze–thaw cycles, the carbonation depths of RAC-3-25, RAC-3-75, and RAC-3-100 were 3.12, 6.53, and 9.16 mm, respectively. Compared with the NAC one, the carbonation depth increased by 84.6%, 286%, and 442%, respectively, and the maximum carbonation depth of RAC-3 was 2.5 times higher than that in the non-freeze–thaw condition. It was found that the effect of freeze–thaw cycles on the carbonation resistance of RAC-3 was more detrimental. In the micro-frozen regions, the freeze–thaw cycle could be a significant factor to the deterioration of pore structure of concrete [45]. Under different pore structures, the difference of CO₂ diffusion coefficient resulted in the changes of carbonation resistance of RAC [46]. In addition, the poor properties of RCA-3 also played a prominent role in the deterioration of carbonation resistance of RAC-3 [47]. The new mortar on the RAC-3 surface fell off easily after freeze–thaw cycles due to the weaker ITZs caused by the RCA-3, and CO₂ was much easier to penetrate in the concrete, increasing the CO₂ diffusion coefficient. Therefore, freeze–thaw damage and the quality of RCA were the critical factors to affect the carbonation resistance of RAC.

3.3. SEM Analysis

It can be seen from the above that RAC-1 possessed the best carbonation resistance which was equivalent to that of NAC. Therefore, RAC-1 with different replacement rates

subjected to freeze–thaw cycle for 600 times and carbonized for 28 d was chosen for SEM analysis, which are shown in Figure 9. After freeze–thaw and carbonation processes, the micro-morphology of RAC-1 had changed with different replacement rates. When the replacement rate was 25%, the internal structure of RAC-1 was relatively dense with almost no pores and micro-cracks, and a small amount of carbonation reaction products such as CaCO_3 existed on the surface to fill in the pores. With the increase of replacement rate, the internal structure of specimen began to become loose and the cracks appeared. When the replacement rate was 100%, cracks in concrete were formed and developed in large quantities to provide the reaction channels for carbonation. In addition, a large number of carbonation reaction products were attached on the surface of concrete, but these carbonation products were not enough to fill these cracks (Figure 9c). Therefore, the carbonation resistance of RAC-1-100 was worse than that of RAC-1-25 and RAC-1-75.

Figure 9. SEM images of RAC-1 with different replacement rates carbonated for 28 d after 600 times of freeze–thaw cycles: (a) 25%; (b) 75%; (c) 100%.

This is mainly because that the freeze–thaw cycle is essentially a process in which the hydration products of concrete change from compact to loose. The freeze–thaw damages of RAC were aggravated with an increase of the replacement rate due to the inferior properties of RCA, which have been verified as previous work [6]. These damages intensified the development of internal pores and micro-cracks in concrete, thus providing more channels for CO_2 to initiate a carbonation reaction, thus decreasing the carbonation resistance of RAC.

To explore the effect of the freeze–thaw cycles on the carbonation resistance of RAC, the morphologies of RAC-2-75 carbonated for 28 d after different freeze–thaw cycles were observed by SEM (Figure 10). After 200 times of freeze–thaw cycles, RAC-2 was still relatively dense. Its surface contained a small amount of CaCO_3 , SiO_2 , and other substances formed by carbonation. But micro-cracks and pores began to form inside of RAC-2, and RAC-2 became loose and porous after 400 times of freeze–thaw cycles, which accelerated the carbonation of concrete. A growing number of carbonation products appeared on the concrete surface. When the freeze–thaw cycle reached 600 times, the pores generated in the early stage of concrete gradually expanded, forming large holes and cracks, causing the structure of RAC to significantly deteriorate. The ITZs in concrete gradually became fuzzy, and a large number of carbonation products attached to the surface of concrete.

With fewer freeze–thaw cycles, the presence of micro-pores and micro-cracks in RCA provided more space for free water; thus, RAC showed good freeze–thaw resistance. However, with the increasing number of freeze–thaw cycles, free water migrated and was frozen repeatedly inside the pores of RAC-2. The freeze–thaw damages caused by hydrostatic pressure on pore wall were gradually accumulated and the internal structure gradually became porous [48]. These porous structures caused by freeze–thaw damages provided quick channels for CO_2 to accelerate the carbonation reaction of concrete. Therefore, the freeze–thaw of concrete was the key factor to determine the carbonation resistance durability of RAC at the same replacement rate in a micro-frozen region.

Figure 10. SEM images of RAC-2-75 carbonized for 28 days after different freeze–thaw cycles: (a) 200; (b) 400; (c) 600.

4. Discussion

It was found that the replacement rate and the recycling number of RRCA and freeze–thaw cycles of RRAC played critical roles in the carbonation resistance of RRAC used in the micro-frozen regions, as shown in Figure 11 and Table 2. The carbonation resistance of all three generations of RRAC gradually deteriorated with the growth of the replacement rate and recycling number of RRCA, and the freeze–thaw cycles.

Figure 11. The 28-d carbonation depth of NAC and RRAC after 0–300 times of freeze–thaw cycles.

Table 2. Growth rate of carbonation depth for RRAC with different replacement rates relative to NAC after 0–300 times of freeze–thaw cycles.

Number of Freeze–Thaw Cycles	0	100	200	300
RAC-1-25	−11.7%	−1.4%	−1.3%	1.9%
RAC-1-75	7.8%	7.0%	5.3%	6.8%
RAC-1-100	44.5%	43.4%	45.0%	52.5%
RAC-2-25	9.4%	6.3%	7.3%	13.6%
RAC-2-75	53.9%	47.6%	54.3%	48.8%
RAC-2-100	75.8%	66.4%	76.8%	82.7%
RAC-3-25	47.7%	38.5%	49.7%	63.0%
RAC-3-75	130.5%	161.5%	202.0%	254.9%
RAC-3-100	185.2%	237.8%	307.3%	389.5%

At the same replacement rate, whether or not it went through the freeze–thaw cycles, the carbonation depths of RRAC increased with the growth of the recycling number of RCA. The carbonation depths of RAC-1-25, RAC-2-25, and RAC-3-25 under the non-freeze–thaw condition were 1.13, 1.40, and 1.89 mm, respectively. After 100 times of freeze–thaw cycles, the carbonation depths of RAC-1-100, RAC-2-100, and RAC-3-100 were 2.05, 2.38, and 4.83 mm, respectively. This was attributed to the deterioration of RRCA quality, such as the decreasing apparent density, increasing attached mortar content and crushing index, and the increasing of recycling number [21]. Compared with NCA, the apparent density of RCA-1, RCA-2, and RCA-3 decreased by 5.9%, 9.4%, and 15.9%, respectively, and the attached mortar content of RRCA increased from 40.3% to 55.4%, as reported in a previous study [21]. The poor qualities of RRCA caused higher porosity and cracks in RRAC than the NAC one, which facilitated the diffusion of CO₂ in RAC.

In a micro-frozen region, the freeze–thaw damage is another inevitable factor contributing to the degradation of carbonation resistance for RRAC. The more serious such damage, the worse the carbonation depth of RRAC. After 100, 200, and 300 times of freeze–thaw cycles, the carbonation depth of RAC-3-100 increased by 32.3%, 68.5%, and 117.3% compared to that of concrete not subjected to freeze–thaw cycles. As reported by Wu et al. [49] and Deng et al. [29], the freeze–thaw damages of concrete are usually manifested as the growth of porosity and micro-cracks caused by the appearance of frost heaving and osmotic pressure. These damages result in cracking and spalling of cement mortar on the surface of concrete, thus providing more convenient channels for CO₂ penetrating into concrete. It should be noted that, according to equivalent principle between laboratory freeze–thaw cycle and that in natural environment proposed by Jin et al. [50], the damage caused by 300 times of accelerated freeze–thaw cycles indoors is equal to the damage of concrete used in micro-frozen areas for 50 years. No RRACs, even RAC-3-100, suffered freeze–thaw failure after such freeze–thaw cycles, which has been verified by Zhu et al. [21].

Although the carbonation resistance of RRAC was degraded due to the freeze–thaw damage, RRCA replacement rates and recycling numbers, and the carbonation depth of all RRAC, even RAC-3-100, were still much lower than the protective thickness of reinforced concrete based on the standard for design of concrete structure durability of GB/T 50476-2019 [51]. This suggested that the three generations of RRAC can be used in micro-frozen regions for engineering applications for at least 50 years.

5. Conclusions

In this study, three generations of RRAC were prepared from the multiple recycling of C&DW concrete with different RRCA replacement rates (25%, 75%, and 100%). The properties of fresh and hardened concrete, carbonation behavior, and micro-morphologies of three generations of RRAC before and after freeze–thaw cycles were investigated. The conclusions can be drawn from this research as follows:

- The workability and compressive strength of RRAC decreased with the increase of RRCA replacement rate and recycling number. The workability and compressive strength of RRAC were inferior to that of NAC, but could still reach the target slump value of 150 mm and strength of 40 MPa. It was feasible to prepare RRAC using multiple recycling RCA for structural use in terms of strength;
- The RRAC under different replacement rates and different recycling numbers showed diversity in carbonation resistance. The increasing of both the replacement rate and recycling number resulted in the degradation of RRAC carbonation resistance. But RAC-3-25 and RAC-2-75 displayed a comparable carbonation resistance to the RAC-1-100 one. For the multiple recycling RAC, it could achieve similar carbonation resistance as the previous generation's by reducing the substitution rate;
- The degradation of RRAC carbonation resistance was attributed to the continuous dropping in RRCA quality and weak ITZs caused by RRCA in concrete. But at a low replacement rate and low recycling number, such as RAC-1-25, the carbonation resistance of RAC was comparable or even superior to the NAC one. This resulted

from the attached mortar on the surface of RCA which reacted with CO₂ to refine the pore structures of RAC;

- The RRAC specimens after freeze–thaw cycles were more susceptible to be carbonated due to the freeze–thaw damages. The spalling of cement mortar and micro-cracks as a consequence of freeze–thaw cycles aggravated the degradation of carbonation resistance of RRAC, especially at a high replacement rate ($\geq 75\%$) and recycling number ($\geq$ two generations). This was verified by results of SEM analysis;
- The carbonation depth of RRAC after freeze–thaw cycles was much lower than the protective thickness of reinforced concrete in the design code. All three generations of RRAC could be used in micro-frozen regions for engineering applications.

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