# Characterization of the Interfacial Transition Zone between Carbonated Recycled Aggregates and New Cementitious Matrix: The Cement Type Influence on Carbonation

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Abstract. One sustainable destination for demolished concrete is the extraction of aggregates for subsequent reuse. The performance of recycled concrete, produced with 100% recycled aggregates (RA), is limited by the existence of the attached mor-tar, resulting in multiple, weaker and larger interfacial transition zones (ITZ). One promising improvement approach is the accelerated carbonation of RA. In this technique, CO2 reacts with the adhered cementitious phase of RA, changing its chemical and physical properties. Many studies reported beneficial developments in mechanical and durability performances of recycled concrete produced using RA from Ordinary Portland Cement demolished concrete (N-RA). Therefore, in this study, chemical and physical changes caused by carbonation of RA from Ground Granulated Blast Furnace Slag blended cement demolished concrete (BB-RA) were also investigated, and the influence of demolished concrete's cement type on accelerated carbonation treatment of RA was discussed. Then, the new ITZ, between non-carbonated and carbonated RA and the new cement paste of modeled recycled concretes, was characterized by microhardness test. From experimental results, an increase in dry density and a decrease in Calcium ions re-leased from RA after carbonation evidenced that CaCO<sub>3</sub> formation occurred effectively for both aggregates. However, while in N-RA's carbonation, the filling effect was predominant, reducing RA's water absorption and evaporation ratios and strengthening the ITZ of the modeled recycled concrete, carbonation treatment applied to BB-RA increased water absorption and evaporation ratios, resulting in a wider new ITZ and indicating significant microstructural changes, where the filling effect was surpassed by porosity coarsening caused by carbonation shrinkage.

**Keywords:** Recycled Aggregate, Accelerated Carbonation, Interfacial Transition Zone, Ground Granulated Blast Furnace Slag, Carbonation Shrinkage.

# 1 Introduction

With the aging of existing concrete structures, demolition and reconstruction have been progressively cogitated as a more feasible option than maintenance and repair. The large amount of demolished concrete generated can be reprocessed into recycled aggregates (RA) usually by mechanical crushing and grinding techniques to extract the coarse and fine aggregates. It is still a high cost & energy demanding process, but as the residues can be reincorporated into the life cycle of concrete, it can be considered a sustainable destination for this construction and demolition waste.

Mechanical and durability performances of the recycled concrete, produced by replacing 100% of the aggregates by RA, are inferior compared to normal concrete, mixed using natural aggregates. The limitation is attributed to the existence of the attached old mortar in RA, which also suffered mechanical impact during the aggregates extraction process, resulting in RA having low density, high porosity and high water absorption. This in turn forms multiple (Fig. 1) and, in general, weaker and larger new interfacial transition zone (ITZ) in recycled concrete [1]. ITZ is considered the weakest part of concrete, with higher porosity than the bulk cement paste and where microcracks often initiate and propagate. Therefore, modifying the surface properties and pore structure of RA, by refining the microstructure of the old and especially the new ITZ, can improve the performance of recycled concrete [2].



Fig. 1. Identification of multiples ITZ in recycled aggregate.

One improving method applied to RA is the  $CaCO_3$  precipitation by accelerated carbonation treatment. Carbonation of cementitious materials is a chemical reaction between  $CO_2$  and calcium bearing phases, such as calcium hydroxide (CH), producing  $CaCO_3$ . This specific reaction causes solid volume expansion, reducing the porosity of hydrated cement pastes. But carbonation of calcium silicate hydrate (C-S-H), the major cement hydration product, has been investigated extensively and there are conclusive studies about carbonation shrinkage's negative effects in the microstructure, when decalcification of C-S-H reduces Ca/Si to values lower than 1.2 [3, 4].

It has been reported that carbonation of RA can refine the attached paste/mortar phase and the ITZ between carbonated RA and the new cementitious matrix, resulting in significant improvements in mechanical and durability performance of the recycled concrete. However, most of the investigations were conducted for RA from Ordinary Portland Cement demolished concrete. Considering that chemical and physical changes occur in the RA with carbonation treatment, RA can be more chemically

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active than natural aggregates [5], and the potential carbonation shrinkage in RA may also influence the performance of recycled concrete. Therefore, in the present study, the effect of carbonation treatment in RA was also investigated for Ground Granulated Blast Furnace Slag Cement demolished concrete, which is characterized for having a low Ca/Si. The potential chemical reactivity and the physical changes in the paste phase of RA were first evaluated and then, the ITZ between non-carbonated and carbonated RA and the new cementitious matrix in modeled recycled concrete samples was characterized by microhardness test.

# 2 Materials and Methods

## 2.1 Recycled Aggregate

**Preparation**. Coarse RA was produced by manual crushing of cylinder concrete specimens (Fig. 2). Two types of binders were used in demolished concrete: Ordinary Portland Cement (N) and 50% replacement Ground Granulated Blast Furnace Slag Cement (BB). The water to binder ratio (W/B) was set as 0.45, 0.55 and 0.65, and the sand to aggregate ratio (s/a) was fixed at 0.46. The concrete specimens were water cured for 35 days, assuring good hydration conditions. After crushing, the particle size distribution of the produced RA was adjusted by sieving and selection, from 5mm to 20mm, according to Japanese Industrial Standard JIS 5023:2018. Then, RA were placed in an accelerated carbonation chamber 5% CO<sub>2</sub> concentration, 20°C and 60% relative humidity (RH) for 7 days. Carbonation of the attached paste of RA was confirmed by the reduction in the alkalinity, spraying phenolphthalein solution. Finally, carbonated and non-carbonated RA were saturated in a vacuum chamber at 0.1 MPa and partially dried to produce saturated surface dry (SSD) state aggregates before testing and mixing. The RA types are identified in Table 1, according to the mix design of demolished concrete and the carbonation treatment.

| Coarse recycled aggregate |                     |                          | Demolished concrete |                               |            |               |                       |                                  |
|---------------------------|---------------------|--------------------------|---------------------|-------------------------------|------------|---------------|-----------------------|----------------------------------|
| Identification            |                     | Carbonation<br>treatment | Binder              | Water<br>(kg/m <sup>3</sup> ) | W/B<br>(%) | Slump<br>(mm) | Air<br>content<br>(%) | Compressive<br>Strength<br>(MPa) |
| 1<br>2                    | N-RA65<br>N-CRA65   | No<br>Yes                | N                   | 170                           | 65         | 18.5          | 4.8                   | 20.7                             |
| 3<br>4                    | N-RA55<br>N-CRA55   | No<br>Yes                |                     |                               | 55         | 19.0          | 3.8                   | 33.9                             |
| 5<br>6                    | N-RA45<br>N-CRA45   | No<br>Yes                |                     |                               | 45         | 15.5          | 5.5                   | 41.3                             |
| 7<br>8                    | BB-RA65<br>BB-CRA65 | No<br>Yes                | BB                  | 170                           | 65         | 19.5          | 4.0                   | 22.5                             |
| 9<br>10                   | BB-RA55<br>BB-CRA55 | No<br>Yes                |                     |                               | 55         | 19.5          | 3.8                   | 30.9                             |
| 11<br>12                  | BB-RA45<br>BB-CRA45 | No<br>Yes                |                     |                               | 45         | 12.5          | 4.5                   | 39.1                             |

Table 1. Coarse RA's identification according to the demolished concrete.



Fig. 2. Steps for the recycled coarse aggregate's preparation.

**Calcium (Ca) Ions Release Test.** 100 g of RA was mixed with 200 ml of pure water and kept sealed for 7 days under 20°C and 60% RH controlled conditions. A portable compact Ca ion meter Horiba LAQUAtwin-Ca-11 was used to measure the concentration of Ca ions released from RA into the solution. Before sampling, the suspension was gently mixed and superficial water was used. The results presented are the average of three consecutive measurements.

Water Evaporation Test. SSD RA were placed in 20°C and 60% RH controlled conditions and the mass variation caused by the water evaporation was measured periodically. The water evaporation ratio ( $W_{evap}$ ) was determined for 3 weeks of evaporation, when the mass change stabilized, and it was calculated using Eq. (1).

$$W_{evap} = (M_{sat} - M_i)/M_{dry}$$
(1)

Where:  $M_{sat}$  = SSD mass;  $M_i$  = mass after 3 weeks' evaporation;  $M_{dry}$  = 100°C oven dried mass.

#### 2.2 Modeled Recycled Concrete Specimens

**Preparation.** Modeled concrete specimens were prepared without fine aggregate (only cement paste and SSD coarse RA), to facilitate the visual identification of the new ITZ between the RA and the new cement matrix. First, OPC paste with W/B of 0.50 was prepared by manual mixing and then SSD RA were added to the mixture, with aggregate content of approximately 60%. Cylinder specimens Ø50x100 mm were cast in two layers to ensure good filling and were cured in sealed conditions for 2 days. After being removed from the mold, they were cured in water until the age of 14 days, when specimens were cut orthogonally to their longitudinal axis in 3 cylinders samples for the microhardness test (Fig. 3).

**Microhardness Test.** The surfaces of cut cylinders were adequately prepared by #120 to #15000 abrasive paper grinding and polishing equipment. The test was performed using Akashi Vickers hardness machine (load of 0.9807 N; penetration velocity of 1  $\mu$ m/s; full loading time of 10 seconds). For each specimen, a coarse RA aggregate was selected, the hardness values were measured in 4 directions. For each direction, 10 measurements were made from a visually identified attached mortar, at a linear distance of 200  $\mu$ m, spacing in 20  $\mu$ m. After literature review and previous experimentation, the ITZ width was determined as the distance between consecutive measurements with hardness values smaller than 80 HV. Finally, the average of the ITZ width determined in 4 directions was calculated.



Fig. 3. Samples cut from modeled concrete specimens for microhardness test.

# **3** Experimental Results

#### 3.1 Physical Properties of RA

Dry density and water absorption of RA were determined before and after accelerated carbonation (Table 2). The increase in dry density after carbonation treatment was confirmed for all types of RA. This was expected and it is related to the formation of  $CaCO_3$  in the attached hydrated cement paste phase of RA, increasing the solid volume and reducing its porosity. However, carbonation treatment led to a different trend in water absorption, as carbonation reduced water absorption of N-RA but increased it in BB-RA, even though the dry density was reduced for both (Fig. 4).

#### 3.2 Ca Ions Release Test

The possibility of chemical reactivity of the RA was evaluated by measuring the concentration of Ca ions released in pure water (Fig. 5). The significant reduction in the Ca ions concentration for all carbonated RA confirmed that CaCO<sub>3</sub> formation occurred for both aggregate types, indicating that carbonation can transform the Ca ions from hydration products into the chemically stable CaCO<sub>3</sub> in RA.

#### 3.3 Water Evaporation Test

As RA are required to undergo a pre-wetting treatment before being mixed to produce recycled concrete, the possibility of the aggregate supplying water to the ITZ was investigated by a simple water evaporation test. Results (Fig. 6) showed a similar tendency compared to the water absorption results. For N-RA, the carbonation impact was positive, and it reduced the water evaporation ratio (and water absorption), but for BB-RA the effect was an increase in water evaporation ratio (and water absorption) after accelerated carbonation treatment of BB-RA.

## 3.4 Microhardness of the new ITZ in Modeled Concrete Samples

Changes caused by the carbonation treatment of RA on the new ITZ width, measured between the attached mortar of RA and the new paste phase of modeled concrete samples, were evaluated (Fig. 7). Depending on the cement type of the demolished concrete originating RA, carbonation treatment resulted in opposite behaviors in the modeled ITZ. For N-RA, ITZ width decreased with carbonation treatment, for all W/B. But in the case of BB-RA, there was an increase in the ITZ width, especially noticeable for high W/B ratios, which are easily carbonated. This indicates that a high degree of carbonation achieved by carbonation treatment may have negative effects

|           | -               |             |            |  |
|-----------|-----------------|-------------|------------|--|
|           | Recycled        | Dry density | Water abs. |  |
| aggregate |                 | $(g/cm^3)$  | (%)        |  |
| 1         | N-RA65          | 2.25        | 6.45       |  |
| 2         | N-CRA65         | 2.27        | 5.81       |  |
| 3         | N-RA55          | 2.24        | 5.05       |  |
| 4         | N-CRA55         | 2.27        | 4.83       |  |
| 5         | N-RA45          | 2.28        | 4.95       |  |
| 6         | N-CRA45         | 2.34        | 4.80       |  |
| 7         | BB-RA65         | 2.24        | 5.55       |  |
| 8         | BB-CRA65        | 2.28        | 6.29       |  |
| 9         | BB-RA55         | 2.21        | 5.44       |  |
| 10        | <b>BB-CRA55</b> | 2.33        | 5.79       |  |
| 11        | BB-RA45         | 2.25        | 5.40       |  |
| 12        | <b>BB-CRA45</b> | 2.27        | 5.54       |  |

7.0 •N-RA **O**N-CRA Water absorption (%) 6.5 BB-RA Δ △BB-CRA 6.0 0 Λ 5.5 5.0 0 ŏ 4.5 2.25 2.35 2.15 Dry density (g/cm<sup>3</sup>)

**Fig. 4.** Relationship between dry density and water absorption of N-RA and BB-RA.



Evaporation ratio (%) 6.0 4.0 2.0 0.0 N-CRA45 N-RA55 N-CRA55 N-RA45 BB-RA65 **BB-CRA65** BB-RA55 N-RA65 N-CRA65 **BB-CRA55 BB-RA45 BB-CRA45** 

**Fig. 5.** Ca ions released in pure water by N-RA and BB-RA.

Fig. 6. Water evaporation of N-RA and BB-RA.



on RA produced from demolished concrete with C-S-H with low Ca/Si, such as when

Fig. 7. ITZ width of modeled concrete specimens produced using N-RA and BB-RA.

# 4 Discussions

#### 4.1 CaCO<sub>3</sub> formation and the filling effect of accelerated carbonation of RA

The change in Ca ions' concentration released from RA before and after carbonation (Fig. 8) was calculated. The reduction in Ca concentration for all RA after carbonation indicates that ionizable Ca from the hydrated paste phase in the attached mortar of RA was transformed into chemically stable CaCO<sub>3</sub>. For the fixed period of 7 days' carbonation treatment, N-RA was more sensitive to the differences in W/B and carbonation was less effective for W/B of 0.45. This occurs because in lower water con-

Table 2. Physical properties of RA.

supplementary cementitious materials are used.



**Fig. 8.** Change in Ca ions' concentration released in pure water, caused by carbonation treatment of N-RA and BB-RA.



**Fig. 9.** Water evaporation ratio/Absorption capacity of RA.

tent, the cementitious phase contains more Ca to be consumed by carbonation and has reduced porosity, which affects the CO<sub>2</sub> diffusion and limits the carbonation degree, remaining Ca ions that could not react to form CaCO<sub>3</sub>. In contrast, the change in Ca ions concentration for BB-RA was similar for all W/B, indicating that the degree of carbonation, measured by the Ca ions availability, achieved a saturation point for the set carbonation conditions. However, despite the similar carbonation degree of the 3 types of BB-RA, the ITZ width between the carbonated BB-RA and the new cement paste varied (see Fig. 7). Considering it, the water evaporation ratio/absorption capacity of RA was calculated (Fig. 9). It is evident that highly carbonated RA (all BB-CRA and N-CRA65), showed pronounced loss of absorbed water from the SSD state. This result indicates a coarsening of porosity, which is in opposition to the filling effect of CaCO<sub>3</sub> formation inside the pores, expected for highly carbonated hardened cementitious materials.

The results presented in this section suggested that the CaCO<sub>3</sub> formation and the filling effect from accelerated carbonation of RA cannot be the only parameter influencing the change in the ITZ width of the modeled concrete samples.

## 4.2 Decalcification of C-S-H effect of accelerated carbonation of RA

The decrease in water absorption and evaporation ratios for N-RA after carbonation treatment, and the increase in these ratios for carbonated BB-RA are unambiguous evidence of dissimilar physical changes caused by carbonation, depending on the binder type of the demolished concrete. The demolished concrete that originated BB-RA had 50% content of slag as a binder, and consequently, the Ca/Si ratio of C-S-H is low, and the CH content is low, compared to the demolished concrete of N-RA. The combination of these two factors is reported as the main accelerator of the extent of carbonation shrinkage. When low Ca/Si C-S-H is subjected to carbonation, Ca ions are removed by decalcification of C-S-H, reducing the Ca/Si to values lower than 1.2 and leading to relevant structural changes in C-S-H. This can produce visible microcracks and the final volume contraction can reach 7.8mm/m [3,4]. In this study, the C-S-H phases' Ca/Si of the attached paste in RA was not investigated and there is no methodology to measure the shrinkage of carbonated attached mortar of RA, with irregular shapes. However, the increase in BB-RA's water absorption and evaporation ratios, combined with previous reports about carbonation shrinkage of pastes, makes clear that significant microstructural changes occurred when RA were carbonated. This can be explained by the variation of volume due to the carbonation of CH (also

 $C_2S$  and  $C_3S$ ), which tends to cause a volume expansion, whereas C-S-H phases (and ettringite) lead to significant volume contraction, since the molar volume of C-S-H reduces as Ca/Si decreases. Also, in the case of carbonation of the attached paste of RA, the presence of aggregate particles may act as a restriction to shrinkage, increasing the cracking development, more than in plain pastes' shrinkage, as reported in the literature. In opposition to it, another aspect that may have influenced the ITZ is the interaction between the new binder of the cementitious phase and the accelerated carbonation products from RA, such as CaCO<sub>3</sub> and the (Al-)Si rich gel which can exhibit a pozzolanic reaction and affect the ITZ.

In summary, in N-RA's carbonation, the filling effect was predominant, and this resulted in strengthening of the ITZ; but in BB-RA case, the filling effect was surpassed by the formation of additional and/or coarsening of the existing porosity, as a consequence of C-S-H decalcification induced by carbonation, and this affected the microstructure of the carbonated cementitious paste phase, increasing the water absorption and evaporation of BB-RA, even the dry density was improved. As all RA were used in the SSD state to produce modeled concrete samples, carbonated BB-RA supplied more water to the new ITZ, increasing its width.

## 5 Conclusions

Recycled aggregates from OPC demolished concrete (N-RA) and from slag blended cement demolished concrete (BB-RA) were subjected to accelerated carbonation treatment. Experimental results showed that in N-RA's carbonation, the filling effect from CaCO<sub>3</sub> formation was predominant; but in BB-RA's case, in parallel to it, microstructural changes caused by decalcification shrinkage of C-S-H induced by the accelerated carbonation occurred, resulting in increasing the ITZ width between SSD carbonated BB-RA and the new cementitious matrix of modeled concrete samples.

Even if cement type is a high weight influencing factor of accelerated carbonation treatment of RA, the overall balance of the effects needs to be evaluated. Also, the interaction between the new cementitious phase's binder and the CaCO<sub>3</sub> and (Al-)Si rich gel which can affect the new ITZ, is under investigation.

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