Article

Carbonation of Recycled Concrete Aggregates for New Concrete and Concrete Fines to Make Cement-Free Hollow Blocks

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Abstract: Mineral carbonation provides a way to increase the recycling of concrete waste in added-value products, and contributes to the principles of the circular economy. At present, most concrete waste is still downcycled. The high water absorption of recycled concrete aggregates, among other factors, impedes their recycling in the concrete industry. The quality of coarse recycled concrete aggregates (RCA) can, however, be enhanced by carbonation. Even when starting with high-grade RCA obtained from a selective demolition process, the carbonation process can decrease the water absorption of the RCA to as low as 3.0%. Concrete with a 50% replacement rate of carbonated RCA can be produced without a significant compressive strength reduction. The research further shows that carbonation can be performed at atmospheric pressure and low CO₂ concentrations (e.g., 10%). The recycled concrete fines (RCF, 0–4 mm) in combination with 25% stainless steel slag were used to make zero-cement hollow blocks (39 × 19 × 9 cm) by carbonation curing without using any hydraulic binder. The hollow blocks have a compressive strength of 15.4 MPa at the lab scale. Both technologies were demonstrated on a pilot scale. In both processes, CO₂ is immobilized in the resulting construction product. The developed production processes use less primary raw materials and cause less greenhouse-gas emissions than the production of traditional concrete products.

Keywords: carbon-capture utilization and storage; carbonation; recycled concrete aggregate; recycled concrete fines; adhered cement mortar

1. Introduction

The European Union is responsible for the generation of more than 850 million tons of construction and demolition waste (C&DW) per year [1]. Experts estimate that up to 56% of this C&DW is concrete [2]. In the Flemish region in Belgium, about 17 million tons (2.6 tons/capita) of stony fraction from C&DW is generated yearly. The amount of pure concrete is about 38% [3]. Recycled concrete aggregates (RCA) are derived from the crushing and processing of concrete C&DW. The crushing process produces agglomerations of the concrete’s original primary aggregates with adhered mortar. The fraction of adhered mortar by volume of the sample decreases with the increasing size of the recycled concrete aggregates [4–6]. The crushing process also produces recycled concrete fines (RCF), the amount being largely controlled by the strength of the original concrete and the used crushing technology. New high-end crushing technologies and equipment have been developed to produce cleaner recycled aggregates, i.e., aggregates with less adhered mortar [7]. These new crushing technologies, however, also generate more RCF. These are fines consisting mainly of hydrated cement paste and sand. In this study, the boundary between RCA and RCF is set at 4 mm, with RCA having all aggregates > 4 mm, and RCF having all material < 4 mm.
Although the Flemish region in Belgium recycles 97% of its produced C&DW, only 3% of the RCA is recycled as aggregates in ready-mix or prefab concrete [3]. However, some countries are already facing a problem of saturation of low-quality aggregate in the aggregates market [8]. The optimum solution is to recycle the RCA in the concrete industry. Currently, the replacement of virgin coarse aggregates is by most standards limited to 30% or less for most concrete classes [9]. The use of higher replacement levels is in practice not well developed due to the anomalies in the fresh and hardened properties of the concrete produced. This is mainly due to the high water-absorption capacity of the RCA, which can range between 3 and 12% compared to <2% for natural aggregates [10]. In Spain, the water absorption for recycled aggregates in recycled concrete is limited to <7% [11]. In Belgium and the Netherlands, high-grade concrete aggregates have a maximal water absorption of 10% and 6%, respectively [12] and [9]. The Belgian and Dutch standards also have limit values on the Los Angeles coefficient, a coefficient that evaluates the hardness of aggregates (respectively, <35% and <40%). One solution to avoid downcycling is to increase the quality of the RCA by accelerated carbonation. This treatment can both decrease the water absorption and increase the hardness of RCA because of the formation of calcium carbonation through the reaction of CO$_2$ with portlandite or calcium silicate hydrates. Calcium carbonate has a higher hardness and volume, leading to the filling of pores [13,14]. This technology has been demonstrated for various RCAs, with initial water-absorption values of around 5–7%. In most studies, a 20–30% reduction in water absorption was achieved [15–20]. Pu et al. (2021) have shown that the carbonation extent and physical properties of carbonated RCA using flue gases with ±20% CO$_2$ are comparable to the carbonation extent and physical properties of carbonated RCA using a 20% CO$_2$ gas mixture [16]. This research focuses on a complete carbonation process at atmospheric pressure and low CO$_2$ concentrations, as low as 10% CO$_2$. This would allow for the direct use of exhaust or flue gases, for instance from cement manufacturing.

The application of RCF is even further limited, due to the higher water-absorption capacity compared to RCA [21]. Significant work has been done on the removal of the cement paste from the RCF to obtain high-quality recycled sand [22,23]. Furthermore, the RCF can be treated by accelerated carbonation using the wet (direct and indirect aqueous) carbonation method, which is based on a liquid–solid reaction, or the semi-dry method, which is based on a gas–solid reaction. In the direct aqueous carbonation method, the CO$_2$ is injected into a high liquid-to-solid (L/S) ratio mixture of 10 or more [24]. The CO$_2$ is converted to carbonate species in the liquid and is readily available to diffuse into all reaction sites. The indirect method is a two-step mineral carbonation process. In the first step, Ca$^{2+}$ is extracted from the waste, and in the second step, CaCO$_3$ is precipitated [25]. On the other hand, in the semi-dry method, the moisture content of the solid (typical L/S of 0.8 to 0.12) facilitates the precipitation of carbonates due to the reaction of dissolved Ca$^{2+}$ and CO$_3^{2-}$ [26]. Each of these methods comes with advantages and disadvantages [27,28]. The accelerated carbonation of the RCF will carbonate the residual C3S, C2S clinker, and slag grains, and the cement hydrates, forming calcium carbonates and reactive silica gel. The carbonated RCF can then be upcycled to replace part of the cement in concrete as a supplementary cementitious material (SCM). However, still more research is needed to (1) obtain a cleaner RCF where the paste fraction is well separated from the sand fraction and (2) be able to upscale the SCM approach, since the wet carbonation method is not yet economically viable.

In this paper, the approach was to use the semi-dry carbonation method to enhance the quality of the RCA and the resulting concrete produced with them, and to use the RCF to make zero-cement hollow blocks (39 × 19 × 9 cm) with a minimum compressive strength of 4 MPa by carbonation curing. No prior literature exists on the production of carbonated blocks from RCF. Enhancing the quality of the RCA would allow for higher replacement rates of RCA in concrete production, the zero-cement hollow blocks consist of 100% of the secondary raw materials. In both processes, CO$_2$ is immobilized in the resulting construction product. Both technologies were demonstrated on a pilot scale,
starting with the selective demolition of a former warehouse store and selective collection of the highest-quality concrete waste (beams and columns), and ending in the production of concrete with RCA and zero-cement carbonated blocks on a pilot scale. By starting with material obtained from this selective demolition process, the initial quality of the RCA will already be high. This research aims to investigate the feasibility of further improving these high-grade RCAs.

2. Materials and Methods

The recycled concrete was obtained from the selective demolition of a former warehouse store from 1982. Concrete columns and beams were collected separately because they were the highest-quality concrete products in the demolished building, and the steel rebars were removed after pre-crushing the concrete with a hydraulic concrete shear, resulting in 20 tons of pure concrete waste. This material was transported to a certified concrete recycling company, crushed, and sieved with an impact crusher into two size fractions: 0–4 mm (RCF) and 4–16 mm (RCA). Both fractions were used in the research presented in this paper. The used production processes are given in Figure 1.

![Figure 1. Flowchart of the used production processes.](image)

2.1. RCA

The RCA (3 m³) that originated from the former warehouse was carbonated for 24 h in an autoclave at the Orbix pilot facilities (Figure 2). The carbonation was performed at atmospheric pressure with a 30% CO₂ atmosphere at 60 °C. The duration of carbonation was set to 24 h. A small sample of RCA (0.5 kg) was also carbonated in a lab-scale reactor for a longer time (72 h) to compare the carbonation degree. As for the pilot scale, the carbonation was performed at atmospheric pressure with a 30% CO₂ atmosphere at 60 °C. To ensure optimal carbonation conditions, the RCA was put in a monolayer, and a tray of a saturated NaBr solution was put in the carbonation reactor to obtain a relative humidity of ±60% [29].

For the concrete production with the RCA, the following other materials were used: the RCA that originated from the warehouse demolition, CEM III/A 42.5N from Cemminerals, river sand 0/5.6, and limestone aggregates 4/16. The particle size distributions (PSD) of the fine and coarse aggregates were determined by sieving (Figure 3). Classification of the RCA [30] showed that the RCA was, for >99%, composed of concrete particles and natural aggregates.
The particle density and water absorption of the original and carbonated RCAs were measured with the pycnometer method [31]. Total carbon was measured using infrared detection after incineration. The resistance to fragmentation was measured by the Los Angeles test method [32] and the freeze–thaw resistance of the RCA was measured by subjecting the RCA (8–16 mm) to 10 freeze–thaw (−17.5 °C to 20 °C) cycles of 24 h in water and reporting the mass of the fragmented particles (particles smaller than 8 mm) [33]. Since carbonation could also affect sulfate-containing cement phases (e.g., ettringite, calcium sulfoaluminate hydrates), causing more water-soluble sulfate to be present, the amount of water-soluble sulfate in the RCA was measured [34]. A test portion was put in water (liquid–solid ratio = 2), and the sample was shaken for 24 h. Afterward, sulfate is precipitated from the extraction water using BaCl$_2$ at the boiling point (pH: 1–1.5).

The carbonated RCA (cRCA) is used to produce concrete samples. The cRCA is watersaturated to surface-dry conditioned by adding the adsorption water to the cRCA, mixing the cRCA, and letting it rest for 24 h in a closed container. Afterward, the river sand, the natural limestone aggregates, and the cRCA are mixed for 30 s. The cement is added to the mix and water is gradually added (W/C = 0.53) while mixing (total mixing time: 3 min). The compositions of the produced concrete are given in Table 1.
Table 1. Compositions of the concrete produced with carbonated recycled concrete aggregates (in kg/m$^3$).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Reference</th>
<th>30% cRCA</th>
<th>50% cRCA</th>
<th>70% cRCA</th>
<th>100% cRCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM III/A 42.5</td>
<td>340</td>
<td>340</td>
<td>340</td>
<td>340</td>
<td>340</td>
</tr>
<tr>
<td>Sand 0/5.6</td>
<td>770</td>
<td>770</td>
<td>770</td>
<td>770</td>
<td>770</td>
</tr>
<tr>
<td>Limestone 4/16</td>
<td>1097</td>
<td>754</td>
<td>533</td>
<td>316</td>
<td></td>
</tr>
<tr>
<td>cRCA 4/16</td>
<td>323</td>
<td>533</td>
<td>737</td>
<td>1034</td>
<td></td>
</tr>
<tr>
<td>Water (W/C = 0.53)</td>
<td>178.5</td>
<td>178.5</td>
<td>178.5</td>
<td>178.5</td>
<td>178.5</td>
</tr>
</tbody>
</table>

After mixing, the workability of the concrete was measured with the slump test [35] and the air content of the fresh concrete was measured with the water column method [36]. Afterward, the fresh concrete was poured into cubes with edges of 150 mm using a vibrating table, and after 28 days of curing underwater, the apparent density and compressive strength [37] of the concrete cubes were measured.

To investigate the influence of the CO$_2$ concentration on the carbonation process, commercially available high-grade RCA (4–16 mm) from EK Recycling was carbonated in a lab-scale reactor. The RCA had a different origin (demolition sites) than the RCA used in the demonstration process, but they were both produced in the same crushing plant (same particle size distribution). An amount of 0.5 kg RCA (0.5 kg) was placed in the reactor. The carbonation was performed for 24 h at atmospheric pressure and 60 °C. The CO$_2$ concentration was varied in the different carbonation experiments (10%, 20%, 30%, and 70%). To ensure optimal carbonation conditions, the RCA was put in a monolayer and a tray of a saturated NaBr solution was put in the carbonation reactor to obtain an optimal relative humidity of ±60% [29]. The particle density and water absorption of the original and carbonated RCA were measured with the pycnometer method according to EN 1097-6.

2.2. RCF

The following materials were investigated: (1) the RCF from recycled concrete of the demolished Colruyt warehouse (Deinze, Belgium) and (2) Carbinox, a treated stainless-steel slag powder from Orbix NV (Genk, Belgium) that was used as a binder to replace cement. The as-received materials were dried upon arrival at VITO (Mol, Belgium) to avoid aging (carbonation). The stainless steel slag (Carbinox) was dried at 105 °C and then deagglomerated using a disc mill, with the discs set at an approximately 500-micron gap. After homogenization followed by quartering, the RCF was dried in an N$_2$ atmosphere at 55 °C until constant mass.

The chemical composition of the materials was determined by XRF in a fused bead prepared by mixing Li$_2$B$_2$O$_7$ with the sample at a ratio of 1/10. The measurements were carried out with EDXRF under a helium atmosphere. The loss on ignition (LOI) was measured by ashing the sample for 4 h at 1000 °C. The results of XRF and LOI are given in Table 2.

Table 2. Main chemical composition of the materials by XRF. Note that LOI (loss on ignition) was measured by ashing the sample for 4 h at 1000 °C.

<table>
<thead>
<tr>
<th>Material</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>TiO$_2$</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCF Colruyt</td>
<td>23.4</td>
<td>52.6</td>
<td>2.88</td>
<td>0.86</td>
<td>&lt;1</td>
<td>0.325</td>
<td>&lt;0.15</td>
<td>17.43</td>
</tr>
<tr>
<td>Carbinox</td>
<td>45.8</td>
<td>27.5</td>
<td>6.63</td>
<td>0.80</td>
<td>9.65</td>
<td>&lt;0.15</td>
<td>0.86</td>
<td>2.88</td>
</tr>
</tbody>
</table>

The mineralogy of the materials was determined by XRD analysis. Measurements were made using an Empyrean diffractometer equipped with a CoK$_\alpha$ X-ray tube (Malvern Panalytical, Eindhoven, The Netherlands) operated at 40 kV and 45 mA. XRD data were analyzed using Rietveld refinement using X’Pert Highscore Plus v 4.7a to quantify the crystalline phase composition. An external standard was used to calculate the amorphous content of the samples.
Total carbon was measured on the as-received materials and after carbonation using infrared detection after incineration.

The CO₂ uptakes were calculated based on the formula taken from [38]:

\[
\text{CO}_2 \text{ uptake (\%)} = \left( \frac{\text{CO}_2 \text{ final (%)} - \text{CO}_2 \text{ initial (%)}}{100 - \text{CO}_2 \text{ final (%)}} \right) \times 100
\]

A Quantachrome Nova 3000 instrument with Brunauer–Emmett–Teller (BET) N₂ sorption method was used to measure the specific surface area of the powders. The powders were pre-treated by degassing at 40 °C under a N₂ atmosphere for 16 h. The BET-specific surface areas of Carbinox and RCF were, respectively, 3.82 and 6.80 m²/g.

A Micromeritics AccuPyc II 1340 He-pycnometer device was used to obtain the true density of the materials. Approximately 1.5 to 2 g of powders were used to carry out the analysis. The true densities of the Carbinox and RCF were, respectively, 3.1 g/cm³ and 2.6 g/cm³.

The PSD of the Carbinox was evaluated using a Horiba LA-350 Laser Diffraction Particle Size Analyzer (Kyoto, Japan). In a 50 mL plastic tube, a few mgs of material were dispersed in 20 mL of isopropanol (IPA). To ensure full dispersion of the material, 1 min external ultrasonication at 200 Watts was carried out before pouring the dispersion in the Horiba’s sample holder and rinsing the 50 mL tube with IPA to ensure no particles are left behind. Optical parameters of 1.7-0.100i were used. The particle size distribution of the Carbinox was measured by sieve analysis. Figure 4 shows the PSD of the materials.

![Particle size distribution of Carbinox and Colruyt RCF in duplicates.](image)

**Figure 4.** Particle size distribution of the Carbinox and Colruyt RCF in duplicates. The curves of both duplicate measurements are given in the figure.

The research was carried out in three phases to gradually build up the experience of using a vibropress for block-making with the carbstone process:

1. In the first phase, a Knauer laboratory-scale block-making machine with a vibrating table (vibropress) was used to make prisms of 40 × 40 × 160 mm. This stage provided a better understanding of the vibropress settings that can influence the compaction. Different mixtures of RCF and Carbinox were made;

Table 3 summarizes the mix formulations investigated. For each mixture, the RCF and Carbinox were mixed and brought to a pre-specified moisture content using a 5 L Eirich intensive mixer. The moist mixture was then immediately compacted by the vibropress. The apparent density after vibropressing and the compressive strength after carbonation were measured to determine the moisture content at which the highest compressive strength can be obtained.
Table 3. Summary of the mix formulations investigated at each phase of the research.

<table>
<thead>
<tr>
<th></th>
<th>Mixes</th>
<th>RCF (%)</th>
<th>Carbinox (%)</th>
<th>Moisture Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lab phase on prisms</td>
<td>Mix 1/95/5/MC10%</td>
<td>95</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Mix 1/95/5/MC12%</td>
<td>95</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Mix 1/95/5/MC13%</td>
<td>95</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Mix 2/85/15/MC6.5%</td>
<td>85</td>
<td>15</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>Mix 2/85/15/MC8.75%</td>
<td>85</td>
<td>15</td>
<td>8.75</td>
</tr>
<tr>
<td></td>
<td>Mix 2/85/15/MC10%</td>
<td>85</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Mix 2/85/15/MC12%</td>
<td>85</td>
<td>15</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Mix 3/75/25/MC10%</td>
<td>75</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Mix 3/75/25/MC12%</td>
<td>75</td>
<td>25</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Mix 3/75/25/MC13%</td>
<td>75</td>
<td>25</td>
<td>13</td>
</tr>
<tr>
<td>Lab phase on hollow blocks</td>
<td>Mix 2/85/15/MC10%</td>
<td>85</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Mix 2/85/15/MC11%</td>
<td>85</td>
<td>15</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Mix 3/75/25/MC10%</td>
<td>75</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>Pilot phase on hollow blocks</td>
<td>Mix 3/75/25/MC11%</td>
<td>75</td>
<td>25</td>
<td>11</td>
</tr>
</tbody>
</table>

The carbonation of the compacted samples (prisms in stage 1 or hollow blocks in stage 2) was carried out in a 105-L PREMEX reactor (Lyss, Germany) (Figure 5b). The reactor was pressurized to 0.3 MPa with commercial CO₂ (with a purity of >99.9%) and a temperature of 50 °C; the pressure and temperature were kept constant during the carbonation process. A tray of water was used to keep the relative humidity inside the reactor at or above 85%. The carbonation duration was 48 h. After carbonation, a sample was cut in half. To see if the samples were fully carbonated, a solution of phenolphthalein was sprayed on the surface. If the sample was fully carbonated, no pink area was observed. All samples were tested for compressive strength using a 1000 kN Tonitechnik servo-hydraulic testing machine. The loading rate was set at 2.4 kN/s [39]. From stage 1, a mixture formulation was selected for upscaling in stage 2.

Figure 5. Illustration of the steps taken to make a hollow block in VITO: (a) vibropressing, (b) carbonation of the compacted blocks, (c) compressive strength test.

(2) In the second stage, the Knauer laboratory-scale block-making machine was used to make hollow blocks (≈ length 290 mm, height 212 mm, width 90 mm) (Figure 5a). A series of tests were carried out to optimize the mold-filling steps (pre-vibration, intermediate, and final compaction) of the vibropress to ensure the proper height of the blocks, and green strength is achieved. The mixtures coming from the screening test were fine-tuned (Table 3), and the samples were compacted and carbonated as described in the first stage (Figure 5b,c). A 4 MN Tonitechnik servo-hydraulic testing machine was used for compressive strength testing (Figure 5c). The loading rate was set at 0.96 kN/s [40];
In the third stage, the upscaling was carried out at Masterbloc (Gubbels Beton, Belgium) with modified dimensions of the hollow block (≈ length 387 mm, height 191 mm, width 87 mm). The mixture with 75% RCF and 25% Carbinox was selected for the upscaling to ensure the minimum strength of 4 MPa would be reached in the pilot-scale production of the two-ton demonstration material (Figure 6). Unlike stages 1 and 2, where the compaction was carried out in three different steps, the mixture was compacted in one step using an industrial vibropress at 50 Hz for 3 s. The carbonation chamber at Masterbloc was used at atmospheric pressure, with commercial CO$_2$, with a purity of 70%. Note that the temperature and relative humidity were not actively controlled. The carbonation duration was set to 48 h. Various characterization tests, including compressive strength, capillary water absorption coefficient, and dry density were carried out [40–42].
3. Results and Discussions

3.1. RCA Results

Table 4 shows the measured parameters of the original and the carbonated RCA samples. The water absorption of the RCA decreases after carbonation, making the aggregates more resistant to disintegration by freeze–thaw cycles. The Los Angeles abrasion coefficient decreases, and there is no increase in water-soluble sulfate after carbonation. The total carbon (TC) content increases by about 0.9%, equaling a storage of 32 kg CO₂/ton RCA (or 17 kg CO₂/m³ concrete in case of 50% replacement of the RCA). Carbonation for longer than 24 h does not further decrease the water absorption of the RCA, although the TC content seems to increase further. However, the TC content strongly depends on the amounts of (primary) limestone aggregates in the sample.

Table 4. Measured parameters for the RCA samples (carbonated and not carbonated).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>RCA Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original</td>
</tr>
<tr>
<td>Water absorption after 24 h (%) (duplicates)</td>
<td>3.9 ± 0.4</td>
</tr>
<tr>
<td>Los Angeles abrasion coefficient</td>
<td>34</td>
</tr>
<tr>
<td>Disintegration after freeze–thaw cycles (%)</td>
<td>7.2</td>
</tr>
<tr>
<td>Total carbon content (%)</td>
<td>2.74</td>
</tr>
<tr>
<td>Water soluble sulfate (%)</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 5 shows the measured properties of the freshly produced concrete. Since the RCAs were pre-saturated before their use in the concrete mixture, the concrete samples with the cRCA do not show a higher workability than the mixture with RCA. A significant reduction in the workability is visible for the concrete produced with 100% RCA (carbonated); the slump of the freshly produced concrete drops to 60 mm.

Table 5. Properties of the freshly produced concrete.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concrete Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ref. 30% RCA 50% RCA 30% cRCA 50% cRCA 70% cRCA 100% cRCA</td>
</tr>
<tr>
<td>Air content (%)</td>
<td>1.4 1.5 1.5 1.5 1.5 1.4 1.5</td>
</tr>
<tr>
<td>Slump (mm)</td>
<td>110 110 120 90 100 90 60</td>
</tr>
</tbody>
</table>

The concrete made with cRCA shows a higher compressive strength than the concrete made with the same amount of RCA (Figure 7); a denser concrete is also produced with cRCA (Figure 8). Concrete with similar strength as the reference concrete can be produced with 50% replacement of the coarse aggregates with cRCA.

The effect of the use of different CO₂ concentrations was investigated (Figure 9). After 24 h of carbonation, the RCA displays no significant differences in water absorption after carbonation at 20% or 30% CO₂. This indicates that the carbonation process can be performed with the use of exhaust or flue gases, for instance from cement manufacturing. When using exhaust or flue gases, however, the influence of other components in these gases (such as acids, SOx, NOx, and the high moisture content) on the carbonation behavior and final product quality needs to be investigated.
Figure 7. Compressive strength (28 days) of the produced concrete samples.

![Compressive strength (MPa) diagram](image1.png)

Figure 8. Apparent density of the produced concrete samples after 28 days.

![Apparent density (kg/m³) diagram](image2.png)

Figure 9. Water absorption value after carbonation at different CO₂ concentrations (24 h, 60 °C).

![Water absorption (%) diagram](image3.png)
3.2. RCF Results

The RCF is mainly composed of quartz (40%), amorphous C-S-H (30%), calcite (22%), and minor quantities of portlandite (2.6%), orthoclase (2.4%), and albite (1.8%). The C-S-H and portlandite are the minerals that can be easily carbonated. The mineralogy of the Carbinox is mainly dominated by merwinite, bredigite, cuspidine, $\gamma$-C2S, and amorphous phases. The minerals that are prone to carbonation are merwinite (18%), bredigite (18%), $\gamma$-C2S (15%), cuspidine (12%), and $\beta$-C2S (3%) [38].

The total carbon (TC) of the Carbinox and RCF were, respectively, 0.32% ± 0.02% and 3.52% ± 0.03% which translates to a CO$_2$ content of 1.17% ± 0.07% and 12.90% ± 0.09%, respectively. In addition, the Carbinox and RCF were milled to an average particle size (d50) of approximately 10 microns and then pressed into a cylinder 2 cm diameter using a hydraulic press at 150 kg/cm$^2$. The amount of material was adjusted to reach a height of 4 cm. The two compacted materials (Carbinox and RCF) were then carbonated separately at 80 °C, 20 bars, 100% RH, and 100% CO$_2$, for 72 h, giving a TC value of, respectively, 5.56% ± 0.03% and 4.28% ± 0.02%, which, in this study, is considered the maximum TC value that the materials can reach. Using the law of mixtures, the theoretical maximum TC value of each mixture was estimated and compared to the experimental results obtained.

Table 6, the TC values are translated into a CO$_2$ content, and these CO$_2$ contents are used to calculate the CO$_2$ uptake realized during carbonation. Based on the CO$_2$ uptake, the density of the carbonation products, and the average density of the material before carbonation, a corresponding volume increase was calculated. The calculated solid volume increase shows the higher volume increase that can be realized by carbonating steel slag (Carbinox) in comparison to RCF. The literature data indicate that the carbonation of cement paste can result in a 13% volume increase [43]. As cement only makes up about 15% of concrete and about 30% of the RCF, this can give a volume increase of about 3.9%, which is in line with the calculated value (Table 6). In the steel slag (Carbinox), several minerals are present that can be carbonated and give rise to a significant volume increase [44], which is also shown by the carbonation data and calculations presented in Table 6.

Table 6. Initial and final (maximum) CO$_2$ contents of the materials, and the calculated weight and volume gain based on the CO$_2$ uptake of the materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Initial CO$_2$</th>
<th>Final (Max) CO$_2$</th>
<th>CO$_2$ Uptake</th>
<th>Volume Increase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbinox</td>
<td>1.2 ± 0.1</td>
<td>20.4 ± 0.1</td>
<td>24.1</td>
<td>27.6</td>
</tr>
<tr>
<td>RCF</td>
<td>12.9 ± 0.1</td>
<td>15.7 ± 0.1</td>
<td>3.3</td>
<td>3.2</td>
</tr>
</tbody>
</table>

The ultrasonic pulse velocity (UPV) and flexural strength results of the vibropressed carbonated prisms of the mixes with different moisture contents (MC) from the lab-phase examination are shown in Figures 10 and 11. The compressive strength results based on cubes cut from the carbonated prisms after flexural strength testing are shown in Figure 12. Overall, as the content of the Carbinox increases from 5% in the Mix 1 series to 15% in the Mix 2 series, and 25% in the Mix 3 series; the UPV, flexural strength, and compressive strength increase.

Figure 13 shows the CO$_2$ content of the Mix 1 series and Mix 3 series for different moisture contents of the prisms. In the case of the Mix 1 series, and more systematically the Mix 3 series, higher moisture contents led to lower CO$_2$ uptakes, although the differences are small.

In the Mix 1 series, an increase in the moisture content did not have a significant effect on the UPV and the flexural strength values. However, as the moisture content increased, the compressive strength decreased. This can be explained by the fact that, in the Mix 1 series (5% Carbinox and 95% RCF), not enough fines were present to fill the space between the particles of the RCF, and thus, the packing density was low. This is corroborated by Figure 14, where the microstructure of Mix 1/95/5/MC12% is shown. Another important
observation was that, due to the limited number of fines in the mixture, the mixtures with 12 and 13% moisture content were too wet, making vibropressing impractical, as shown in Figure 15.

In the Mix 2 series, the Carbinox content was increased to 15%; this resulted in a higher content of fines than in the Mix 1 series, which led to better packing and a decrease in the overall porosity. In the Mix 2 series, there is a continuous increase in UPV, flexural strength, and compressive strength as the MC increases from 6.5% to 12%. The 6.75% MC was not enough to efficiently remove the air between the particles, and that is why the properties at this MC are not as good as the Mix 1 series. At an MC of 8.75%, the positive impact of the increased MC can be seen, and it seems that this positive impact continues up to an MC of 12%. However, like in the Mix 1 series, an MC higher than 10% showed excessive wetness, making vibropressing impractical for making the prisms, even though the mechanical properties are improved.

![Figure 10. Ultrasonic pulse velocity (UPV) of the vibropressed prisms of the lab phase with different moisture contents (MC) after carbonation.](image)

![Figure 11. Flexural strength of the vibropressed prisms of the lab phase with different moisture contents (MC) after carbonation.](image)
In the Mix 3 series, the Carbinox content was increased to 25%, which resulted in a higher content of fines than in the other two mixes, which led to better packing and a decrease in the overall porosity (Figure 16). This is corroborated by Figure 17 where the microstructure of Mix 3/75/25/MC12% is shown. However, there is a turning point for the improvement in the mechanical properties of the Mix 3 series between an MC of 12% and 13%. This is most likely due to excessive wetness as mentioned also in the case of the Mix 1 series and Mix 2 series. In the case of the Mix 3 series, it can be clearly seen that the porosity after carbonation decreases (Figure 16). For an MC of 13%, this decrease is less significant than for the moisture contents of 10% and 12%.

![Figure 12. Compressive strength of the vibropressed prisms of the lab phase with different moisture contents (MC) after carbonation.](image)

![Figure 13. CO₂ content of the vibropressed prisms of the lab phase with different moisture contents (MC) after carbonation. The Mix 2 series samples were not available for TC measurements. The legend “Initial” is the CO₂ content of the mixture before carbonation.](image)
In addition to the physical parameters, such as particle size distribution and the packing density of mixtures, that have a direct impact on the mechanical properties, the minerals and amorphous phases in the RCF and Carbinox powders, which are carbonatable, will also affect the porosity and microstructure, and, thus, the mechanical properties of the carbonated prisms. The microstructure of the carbonated prisms made in the Mix 1 series and the Mix 3 series with an initial MC of 12% were analyzed by SEM. SEM images of these mixes are shown in Figures 14 and 17, respectively. The carbonation of RCF mainly affects the C-S-H of the cement paste and results in the formation of calcite and decalcified C-S-H.

The carbonation of steel slag (Carbinox) results in the carbonation of calcium-containing silicates such as γ and β-C2S, merwinite (Ca₃Mg(SiO₄)₂), bredigite (Ca₁₄Mg₂(SiO₄)₆), and cuspidine (Ca₄(Si₂O₇)(F,OH)₂) (e.g., [38,45,46]). The carbonation of these silicates may result in a more significant increase in the solid volume content. For γ-C2S, Mu et al. 2018 demonstrated a volume increase of 74% after complete carbonation [44]. The carbonation
of these crystalline silicates may lead to a significant reduction of the initial porosity, while this may not be the case during the carbonation of cement paste.

Figure 16. Initial and final porosity of the vibropressed prisms after carbonation of the Mix 1 series and Mix 3 series with different moisture contents (MC).

Figure 17. SEM-BSE image of Mix 3/75/25/MC12%. Field of view is approximately 12 mm (A) top of the block, (B) bottom of the block. The larger light-grey particles are limestone aggregates from the recycled concrete.

Based on the results of the lab-phase examination on the prism samples, in the next phase of the research, zero-cement hollow blocks were made with 85% RCF—15% Carboxin with an initial moisture content of 10% and 11% (Mix 2/85/15/MC10% and Mix 2/85/15/MC11%), and with 75% RCF—25% Carboxin and 10% initial moisture content (Mix 3/75/25/MC10%). Table 7 summarizes the results obtained for UPV, compressive strength, and TC measurements, and the calculated CO₂ uptake. Note that in the case of the Mix 3 series, only 10% moisture content was considered since, by decreasing the RCF content from 85% to 75%, less water was needed for the compaction, since the BET value of RCF is approximately 1.8 times larger than the Carboxin, as reported in Section 2.2. At 11% MC for the Mix 3 series, there was a challenge to reach the appropriate height and remove the monolith from the vibropress intact, and, thus, it was not considered further. In the Mix 2 series, 11% MC gave better results in terms of UPV and compressive strength through better compaction. A higher TC content suggests a higher carbonation degree of the 11% MC compared to the 10% moisture content. Using the law of mixtures, and considering TC values of 5.56% ± 0.03% and 4.28% ± 0.02% for when Carboxin and the
RCF are fully carbonated (see Section 2.2), the theoretical TC value of the Mix 2 series can be estimated to be 4.47% (16.4% CO₂). In all three mixes, the maximum TC that was calculated based on the law of mixtures was lower than the actual measured TC values (Table 7). This probably indicates that the conditions for carbonation of the RCF used in Section 2.2 were not optimal, or the mix of both allows for higher CO₂ uptakes.

Table 7. Summary of the results obtained for lab phase after carbonation: making of hollow blocks at a laboratory scale for the Mix 2 series with MC of 10 and 11% and Mix 3/75/25/MC10%. The calculated max. CO₂ content was obtained from the law of mixtures and the Section 2.2 results for the Carbinox and the RCF.

<table>
<thead>
<tr>
<th></th>
<th>UPV</th>
<th>Compressive Strength</th>
<th>Initial CO₂ Content</th>
<th>Final CO₂ Content</th>
<th>Calculated Max. CO₂ Content</th>
<th>Calculated CO₂ Uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>m/s</td>
<td>MPa</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>kg/ton</td>
</tr>
<tr>
<td>Mix 2/85/15/MC10%</td>
<td>2150 ± 70</td>
<td>7.4 ± 0.4</td>
<td>12.3</td>
<td>17.6 ± 0.2</td>
<td>15.9</td>
<td>64</td>
</tr>
<tr>
<td>Mix 2/85/15/MC11%</td>
<td>2550 ± 70</td>
<td>9.3 ± 0.6</td>
<td>11.1</td>
<td>18.1 ± 0.2</td>
<td>16.4</td>
<td>85</td>
</tr>
<tr>
<td>Mix 3/75/25/MC10%</td>
<td>3000 ± 60</td>
<td>15.4 ± 0.0</td>
<td>10.0</td>
<td>18.7 ± 0.1</td>
<td>16.9</td>
<td>107</td>
</tr>
</tbody>
</table>

Although the mechanical properties and the TC value of Mix 2/85/15/MC11% are higher than Mix 2/85/15/MC10%, the porosity estimated from each mixture after carbonation is comparable. This could be because the helium density measurement was carried out on a small portion of each hollow block after the compressive strength test. Note that the results shown are based on two hollow blocks made for each mixture.

In the case of Mix 3/75/25/MC10%, a higher UPV and compressive strength were obtained compared to the Mix 2 series. This is due to a combination of better compaction because of the increase of the fines content from the Carbinox, filling the space between the RCF grains and the carbonation of the Carbinox. Mix 3/75/25/MC10%’s TC value reached 5.10%; note that the theoretical TC value at which Mix 3/75/25/MC10% is fully carbonated was estimated to be 4.60%. The porosity estimated for Mix 3/75/25/MC10% with 10% moisture content was also lower than that for Mix 2/85/15/MC10% with the same 10% moisture content.

Based on the results of Phase 1 and Phase 2, there is a significant decrease in the compressive strength values from prism to hollow blocks, which is due to a significant increase in porosity in the hollow blocks, since the TC values are comparable. This shows that, as the size (specifically the height) of the sample increases, the efficiency to reach similar strength for the same mixture and the same moisture content decreases significantly if the vibropressing steps remain the same.

In the third stage of the research, Mix 3/75/25/MC11% was considered for upscaling. The decision to use 11% MC instead of 10% MC was made based on an initial trial carried out on the industrial scale showing that Mix 3/75/25/MC10% was dry and Mix 3/75/25/MC11% showed a good consistency. In this stage, 25% of the Carbinox was used, although the laboratory scale results on hollow blocks suggested that 15% Carbinox would suffice, reaching the minimum compressive strength required (5 MPa). The main reason for this approach was threefold: (1) the dimensions of the upscaling hollow block differed from the ones made on a laboratory scale; (2) the industrial vibropress was used in one step unlike the laboratory research which was done in 3 steps; and (3) the RCF was aged for several months before the industrial trial, which could have impacted the carbonation of the blocks and, thus, the compressive strength since the major component of the block was the RCF. That is why, to ensure the pilot-scale production of the two-ton demonstration material goes smoothly, Mix 3/75/25/MC11% was considered. From the two-ton carbonated products, two specimens were selected, following EN 722, for analysis and certification of the produced hollow blocks.
Table 8 summarizes a selection of these tests. The average compressive strength based on 10 samples was evaluated to be $6.4 \pm 0.2$ MPa, which satisfies the minimum requirement of class $f_5$ ($f_b \geq 5$ N/mm²), in which the hollow blocks were intended to be used. The average gross dry density ($1828 \pm 4$ kg/m³) falls into the volume mass class of $\rho_1.9$ ($1600$ kg/m³ to $1900$ kg/m³) [47]. The capillary water-absorption coefficient was determined to be $12.4 \pm 0.5$ g/(m²s); according to the provisions of EN 771-3, the water absorption capacity becomes a required parameter when the blocks are used as decorative exterior masonry stones ($\leq 6.0$ g/(m²s) or as an exterior masonry stone ($\leq 8.0$ g/(m²s)). The hollow blocks made will be used in neither the former nor the latter applications but as an interior separation wall.

Table 8. Selection of test results after carbonation carried out by Geos, an independent control laboratory, for certification of the produced hollow blocks.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard/Norm</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive strength (MPa)</td>
<td>[47]</td>
<td>$6.4 \pm 0.2$</td>
</tr>
<tr>
<td>Capillary water absorption (g/(m²s))</td>
<td>[41]</td>
<td>$12.4 \pm 0.5$</td>
</tr>
<tr>
<td>Gross dry density (kg/m³)</td>
<td>[42]</td>
<td>$1828 \pm 4$</td>
</tr>
<tr>
<td>Net dry density (kg/m³)</td>
<td>[42]</td>
<td>$1488 \pm 4$</td>
</tr>
</tbody>
</table>

4. Conclusions

Mineral carbonation is a promising technology to enhance the use of recycled concrete aggregates and concrete fines in products with added value and, at the same time, to reduce CO₂ emissions by converting CO₂ gas (e.g., from exhaust or flue gases) into stable carbonates in the produced construction materials.

4.1. RCA Conclusion

This manuscript shows the results of the pilot-scale upgrading of RCA by carbonation. The characteristics of the RCA, which were obtained from a high-quality concrete fraction consisting of concrete columns and beams, are improved (decrease in water absorption, increase in resistance to abrasion, or disintegration caused by freeze-thaw cycles), as is the concrete produced with the carbonated RCA. Concrete with the same compressive strength as the reference concrete can be produced with a 50% replacement of the coarse aggregates with carbonated RCA. The carbonation process leads to a carbon storage of $32$ kg CO₂/ton RCA.

The research further shows that the carbonation process can be performed at atmospheric pressure and low CO₂ concentrations, as low as 10% CO₂. This would allow for the direct use of exhaust or flue gases, for instance from cement manufacturing.

Since a strong water-absorption reduction can also be achieved from RCA with low initial water absorption, it will be important to define the target water-absorption value for RCA for certain replacement levels and certain concrete types and investigate the most cost-effective ways to achieve these targets (selective demolition, carbonation, and new crushing technologies.

4.2. RCF Conclusion

Hollow blocks were made with a mixture of 75% recycled concrete fines (0–4 mm) and 25% stainless steel slag (Carbinox) without any cement. The carbonation of the hollow blocks resulted in a CO₂ uptake of approximately $100$ kg CO₂/ton of product. After carbonation, these blocks had an average compressive strength of $15.4$ MPa at the lab scale and $6.4 \pm 0.2$ MPa at pilot production. They comply with the minimum compressive strength of $5$ MPa needed for hollow blocks that can be used as non-bearing separation walls.

It has been shown that the compaction of the mixtures before carbonation is of strong importance to achieve higher strengths. Further research has to be conducted on how to
achieve optimal compaction and the influence of different interaction parameters (particle size distribution, water content, and vibropress settings).

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