Influence of intensive vacuum mixing and heat treatment on compressive strength and microstructure of reactive powder concrete incorporating secondary copper slag as supplementary cementitious material

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Highlights

- Vacuum mixing decreases the air content of RPC, and increases the density.
- The anhydrous copper slag grains play a role as filler to enhance the concrete strength.
- Heat treatment leads to activation of the hydration of binders.
- The combination between vacuum mixing and heat curing leads to a slightly lower porosity.

Abstract

In this study the effect of vacuum mixing and heat treatment on the compressive strength and microstructure of reactive powder concrete (RPC), made with secondary copper slag as partial cement replacement is investigated. The quickly cooled granulated copper slag was ground using a planetary ball mill. A low water-to-binder ratio of 0.185 was chosen. The series of concrete mixtures and cement paste samples were produced with copper slag contents from 0 to 20 wt%. The pozzolanic activity of slag was determined by the Frattini test. The performance of RPC mixed under vacuum conditions and heat-cured was compared to that of RPC mixed at atmospheric pressure without heat treatment. The porosity evolution of RPC was investigated by mercury intrusion porosimetry.

A higher workability of the fresh RPC was obtained by mixing under atmospheric pressure. The presence of copper slag in the RPC had no adverse effect on compressive strength for all treatments. The heat treatment decreases the porosity and enhances the RPC strength. Assessment of the pozzolanic activity by means of the Frattini test indicates low pozzolanic reaction of the slag after 15 days. The presence of slag in the paste tends to decrease the total heat production of the paste. The use of copper slag as cement replacement in the RPC production decreases the energy consumption and reduces the carbon footprint.

1. Introduction

Since the 1990s, Reactive Powder Concrete (RPC) has been developed as an alternative construction material to compete with steel structures. The development of this concrete can be achieved by applying the basic principles of RPC, as explained by Richard and Cheyrezy [1]. In the RPC compositions, active powders dominate as the main constituents to obtain a relatively dense and homogenous microstructure, which can increase the compressive strength to values exceeding 200 MPa [2,3]. The formation of CSH gel is determined by the hydration process of cement and active powders. However, the high amounts of cement for RPC (800–1000 kg/m³) have an adverse effect on the heat of hydration, which creates micro-cracks in the concrete and may cause shrinkage problems [4]. Besides, the production of this concrete implies high costs. Therefore, replacement of part of the cement with supplementary cementitious materials (SCM) is the key to solve these problems [5,6]. This can be proven by the findings of Wang and Zhi [7] who found that SCM (fly ash and slag) can reduce the risk...
of thermal cracking of concrete. In addition, Bouasker et al. [8] also found that replacing the cement with SCM (blast furnace slag and limestone filler) tends to delay the cracking of pastes. Furthermore, Portland cement as an ingredient of RPC requires a huge amount of energy from fossil fuels for clinker burning and grinding and non-renewable resources. Moreover, the gasses from a cement kiln also contribute to emissions of air pollutants and pose a hazard to human health. The alternative way, to protect the environment and save energy in the near future, is to utilize recycled waste material within the cement and concrete industry.

Because of the rise in global copper demand for the construction and manufacturing industry, the copper production keeps increasing. The main environmental issue associated with this industry is the production of copper slag as a waste material. Globally the estimated quantity of copper slag generated annually is 24.6 million tons [9]. In the European Union, about 4.6 million tons of secondary copper is produced by the primarily refined copper production and secondary refined production [10,11], and it is estimated that approximately 0.92 million tons slag are generated as a waste. In Belgium, copper cathodes are produced by recycling plants (Metallo-Chimique N.V., Umicore S.A., and Aurubis) (436,000 tons), which also generate about 132,240 tons of secondary copper slag annually [10–12].

Secondary copper slag is a by-product obtained during recycling of end-of-life products, using ‘old scrap’ as a raw material. In the refining furnace, this raw material, and black copper from the melting furnace is melted and oxidized by gas and oxygen [13]. During the oxidation process, sand is added as a slag builder. At the end of this stage, metal containing 99% of Cu is generated and the slag mixture is transferred to the slag furnace for the next treatment. Finally, the impure copper obtained is returned to the refining furnace and the remaining slag as secondary slag is granulated in water. This secondary slag cannot be recycled and needs a large area for storage, of which the availability is insufficient. Moreover, the impact on water quality of heavy metals and other harmful elements in this slag can be severe. One way to solve the problem regarding the environmental degradation is to upgrade this slag in concrete production. Looking into literature, copper slag was investigated by several researchers as fine or coarse aggregate replacement and cement replacement in high strength concrete (HSC) and high performance concrete (HPC) including the application for reinforced concrete [14–28]. In addition, there is limited literature available regarding ultra-high performance (UHPC). The use of copper slag as a sand replacement and cement replacement in this concrete class (UHPC and ultra-high performance mortar (UHPM)) has only been reported by Edwin et al. [12] and Ambily et al. [29]. While, there is no literature about copper slag used in reactive powder concrete (RPC), which is also one type of UHPC.

As for all materials, the microstructure of concrete is the key to its performance [30]. An improvement of the microstructure can be achieved by the mixing technology. In addition to the mixing technology, the use of reactive material and curing technology can also increase concrete performance. Heat curing technology has been used in concrete materials for over twenty years. The transformation process from amorphous C-S-H phases to crystalline C-S-H phases is faster when the concrete is subjected to heat curing [31]. However, heat and moisture curing is responsible for increasing the porosity in the cement paste [32]. In addition, Malkais and Marchand [33] found that there was a detrimental effect on compressive strength for longer curing periods when applying heat treatment on concrete with small replacement levels of fly ash. Ambily et al. [29] investigated the use of copper slag as a fine aggregate replacement for ultra-high performance concrete. They concluded that there is a potential for the use of copper slag in UHPC production under heat treatment.

In the current research, the influence of vacuum mixing and heat treatment on the compressive strength of reactive powder concrete (RPC) containing secondary copper slag as the supplementary cementitious material is evaluated. The evolution of microstructure of RPC was studied.

2. Experimental investigation

2.1. Materials

The materials used in this study were obtained from Belgian Companies. The secondary slag used in this research was quickly cooled granulated copper slag (QCS), see Fig. 1. This slag was produced by using industrial wastes from Cu such as old copper tubes, wires, scraps, cables, alloy coins, plated coins and Cu-Fe (shredded) armatures as raw materials to generate copper blister, copper anodes, and copper cathodes for industry and market [12]. Besides copper slag, an undensified silica fume was used as supplementary cementitious material (SCM). As cement, a CEM I 52.5 N HS/NA (low C3A) was used throughout all experiments. Some researchers recommend to use cement with low C3A (less than 3%) in ultra-high performance concrete (UHPC) because of a low influence on viscosity, reducing the demand for water, and a positive effect on compressive strength [34,35]. For all concrete, a quartz flour with a d50 of 12 μm was used. A quartz sand with a d50 of 0.31 mm was used for all RPC mixtures. An overview of the chemical composition of the binders is given in Table 1.

2.2. Size reduction processes

Since the copper slag obtained by the recycling plant was in granulated form, the size of this slag had to be reduced to achieve a product with a higher specific surface area (SSA). The selection of the appropriate method of grinding should be based on the physical properties of the materials. Copper slag has a hardness of 6–7 on the Mohs scale (hardness) and is mainly composed of iron silicate glass [9,36]. Therefore, there will be a high energy need to grind this material. In the grinding process, the energy is determined by the time, speed, and number of balls charged. Based on the results obtained by Edwin et al. [12], the SSA of QCS reached a value of 2533 cm2/g with the Blaine permeability test by using the dry method, long duration of grinding (5 times during 12 min at 300 rpm) and 5 balls charged in the ball mill. Since this grinding process was time-consuming and not very productive, the authors now chose a short duration grinding process (6 times during 5 min at 390 rpm) and 7 balls charged. This method reduced the grinding time with 30 min in comparison with that of the long duration method. With the increase in grinding speed and addition of two balls in this method it was expected to achieve a similar fineness as with the grinding method aforementioned. Moreover, a wet method instead of dry method was chosen as copper slag tends to be re- compacted when applying a dry method. A superplasticizer (Sika Visocrete-3095; 0.122 wt%) was added to avoid re-compaction. After the grinding process, the particle size distribution (PSD) of copper slag powder (size range from 0.1 μm to 1000 μm) was measured by laser diffraction. The particle size distribution of copper slag, cement, silica fume, and quartz flour obtained by laser diffraction is given in Fig. 2. To disperse the copper slag and cement, isopropanol was used since it does not react with it. To avoid agglomeration, the copper slag was put in a sonication bath (5 min) before the measurement. In case of silica fume, distilled water was used as dispersant. In order to obtain well de-agglomerated silica fume, this material was sonicated in two steps. At first, the solution containing silica fume and

![Fig. 1. SEM image of granulated copper slag (scale bar = 10 μm).](image-url)
Water was put in an ultrasonic bath for 5 min to de-agglomerate the particles. After this, 10% superplasticizer by weight of silica fume was added followed by sonication for 15 min prior to measurement. An overview of the parameters used to determine the PSD of the SCMs, cement, and quartz flour by laser diffraction can be seen in Table 2.

In addition to the PSD by laser diffraction, the fineness of the binders was evaluated by their specific surface area (SSA) using the Blaine air permeability test according to EN-196-6:2010.[37] To start, the pycnometer method was used to measure the density of all binders. Both the density and SSA of the binders are presented in Table 3.

### 2.3. Mixtures proportions

Table 4 describes the RPC compositions used in this research. A very low water-to-binder ratio (w/b = 0.185) was chosen in order to produce ultra high performance concrete (UHPC). In literature, it is often mentioned that a low porosity and higher strength of concrete can be achieved when applying a low water-to-binder ratio for the concrete mix.[38,39] Caijun et al.[40] noticed that the typical range of water-to-binder ratio (w/b) for UHPC is from 0.14 to 0.20. To obtain the desired workability, a polycarboxylate ether (Glenium ACE 30 con 30% Solid) was used. The Glenium ACE 30 contains a carboxylic ether polymer with long side chains and short main chains, which can combine an efficient dispersion and rapid absorption on the cement particles to obtain good workability and early high strength. These two mechanisms are not available for Glenium 51, which was used by the authors in the previous research.[12] The concrete was made with copper slag replacing the Portland cement varying between 0 and 20 wt% in steps of 5 wt%.

### 2.4. Vacuum mixing

One measure to obtain a void-free mixture is to use an intensive vacuum mixing to reduce air content. A void-free mixture contributes to an improved microstructure, strength and service life of concrete. In this research, the authors used a planetary vacuum mixing with a capacity of 5 l. The procedure of mixing is mentioned in Fig. 3[41]. In case of no-vacuum mixing (1013 mbar), the lower pressure does not apply for the entire time of mixing.

### 2.5. Heat treatment

In this research, the phase of heat curing started after 24 h of normal curing at 20 ± 2°C. The heat curing temperature raised at a speed of 0.2°C/min. This indicates that the time needed to reach the maximum temperature of 90°C from room temperature is approximately 6 h. This technique is chosen to prevent the adverse effect of heat curing, which tends to produce larger capillary pores, if a rapid increase in temperature is applied.[42,43] After removing the samples from the moulds (24 h), the heat treatment was carried out at constant temperature of 90 ± 3°C in a sealed container for two days. The specimens were positioned 2 cm above a water bath. After 48 h of heat curing, the specimens were cooled for 3 h.

<table>
<thead>
<tr>
<th>Component</th>
<th>QCS</th>
<th>CEM I 52.5 N HS/NA</th>
<th>Silica fume</th>
<th>Flour</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>7.1</td>
<td>63.7</td>
<td>0.6</td>
<td>0.02</td>
</tr>
<tr>
<td>SiO₂</td>
<td>25.9</td>
<td>20.9</td>
<td>94.2</td>
<td>99.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.9</td>
<td>3.6</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>45.3</td>
<td>5.2</td>
<td>0.5</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.8</td>
<td>0.8</td>
<td>0.7</td>
<td>n/a</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.8</td>
<td>0.2</td>
<td>1.0</td>
<td>n/a</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.2</td>
<td>0.6</td>
<td>1.1</td>
<td>0.05</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.4</td>
<td>3.0</td>
<td>0.3</td>
<td>n/a</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.8</td>
<td>n/a</td>
<td>0.1</td>
<td>n/a</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.3</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>ZnO</td>
<td>8.8</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>MnO</td>
<td>0.7</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.7</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>CuO</td>
<td>0.4</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Pb</td>
<td>0.4</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table 2

Overview of the parameters applied to determine the PSD of the different powders by laser diffraction.

<table>
<thead>
<tr>
<th>Optical parameters</th>
<th>QCS</th>
<th>Silica fume</th>
<th>Cement I 52.5 N HS/NA</th>
<th>Quartz flour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refractive index (RI) [−]</td>
<td>1.731</td>
<td>1.530</td>
<td>1.731</td>
<td>1.55</td>
</tr>
<tr>
<td>Absorption coefficient [−]</td>
<td>0.055</td>
<td>0.001</td>
<td>0.003</td>
<td>0.3</td>
</tr>
<tr>
<td>Obscuration [%]</td>
<td>10–15</td>
<td>5–10</td>
<td>5–10</td>
<td>5–10</td>
</tr>
<tr>
<td>Stirrer rate [rpm]</td>
<td>1700</td>
<td>1500</td>
<td>1500</td>
<td>1700</td>
</tr>
<tr>
<td>Dispersant RI [−]</td>
<td>1.390</td>
<td>1.390</td>
<td>1.390</td>
<td>1.390</td>
</tr>
<tr>
<td>Sonication times [minutes]</td>
<td>5</td>
<td>20</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>
Afterwards, the specimens were cured in a room at relative humidity of 95 ± 5% and temperature of 20 ± 2 °C until the time of testing. In case of no-heat treatment, the samples were demolded after 24 h and directly cured at a room temperature of 20 ± 2 °C and relative humidity of 95 ± 5% until the required age for the compressive strength test.

2.6. Workability, density and compressive strength

The workability of fresh RPC was determined using a mini slump flow according to EN 1015-3:2006 [44]. In total, thirty samples were prepared for this test (two times three per mix composition). Fifteen of the thirty samples were obtained after vacuum mixing at 100 mbar and another fifteen samples were obtained after mixing at atmospheric pressure (1013 mbar). The value of the flow is the average of the 30 samples tested per age and per treatment. In order to preserve the pore structure of the specimens, the freeze-drying method was chosen. The specimens for MIP were crushed particles with particle size between 5 and 10 mm. After putting these samples in the liquid nitrogen for 5 min, the temperature was reduced to −195 °C. Afterwards, the samples were transferred into a freeze-dryer and the temperature changed to −24 °C under vacuum condition and pressure of 0.1 Pa [45]. After four weeks, a constant mass was obtained (mass change less than 0.1% in 24 h). After the period of freeze-drying, a sample of ±1.40 g was put into a dilatometer (Thermo Scientific corporation) to start the measurement. The mercury was intruded into the specimen and extruded after reaching the maximum pressure (140 Pascal for the low pressure step and 440 Pascal for the high pressure step).

According to Mehta and Monteiro [46], the gel pores may range from 0.001 μm to 0.0045 μm. Depending on the concrete grade and water to cement ratio, the capillary voids cover the pore sizes between 0.0045 μm and 1 μm. For the concrete with a low water to binder ratio, the capillary voids may range from 0.0045 μm to 0.5 μm. For the concrete with a high water to binder ratio, the capillary voids may range from 0.0045 μm to 0.5 μm due to the discontinuous capillary pore network by C3S gel. Thus, the pore size distribution obtained is divided into three different regions: 1) gel pores ranging between 0.001 and 0.0045 μm; 2) capillary pores with pore sizes up to 0.5 μm; and 3) macropores and entrained air voids ranging from 0.5 μm to 200 μm.

2.8. Frattini test

The procedure used was based on EN-196-5:2005 [47]. The samples were prepared by mixing 20 g of binder (cement + copper slag) in 100 ml of distilled and decarbonized water in a sealed polyethylene container. The copper slag content varied from 0 wt% to 20 wt% of the binder in steps of 5 wt%. After preparation, the samples were heated in an oven at (40 ± 1) °C for 8 days and 15 days. After the first period of 8 days, the solution was filtrated using Whatman double filter paper circles with retention of <2 μm. The filtrate solution was then titrated with acid-base titration using double indicators method. The results are plotted in a chart (Ca++ vs OH−) to assess the pozzolanic activity of the copper slag. The results indicate pozzolanic activity when they are beneath the lime saturation curve [48]. Twenty samples (four per mix composition) were prepared for this test and half of them was tested after 8 days, the other half after 15 days. The value of the pozzolanic activity is the average of the titration results (in triplicate) of the measured Ca++ and OH−.

Table 3

<table>
<thead>
<tr>
<th>Materials</th>
<th>QCS</th>
<th>Cement I 52.5 N HS/NA</th>
<th>Silica fume</th>
<th>Quartz flour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>3.706</td>
<td>3.152</td>
<td>2.017</td>
<td>2.65</td>
</tr>
<tr>
<td>SSA (cm²/g)</td>
<td>Blaue permeability</td>
<td>2277</td>
<td>4955</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Laser diffraction</td>
<td>2150</td>
<td>5390</td>
<td>56200</td>
</tr>
</tbody>
</table>

Table 4

<table>
<thead>
<tr>
<th>Material Reference</th>
<th>5% CS</th>
<th>10% CS</th>
<th>15% CS</th>
<th>20% CS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 52.5 N HS/NA</td>
<td>733.0</td>
<td>671.7</td>
<td>661.7</td>
<td>625.8</td>
</tr>
<tr>
<td>Copper slag (QCS)</td>
<td>0.0</td>
<td>36.7</td>
<td>73.5</td>
<td>110.4</td>
</tr>
<tr>
<td>Silica fume (undensified)</td>
<td>230.0</td>
<td>230.3</td>
<td>230.7</td>
<td>231.0</td>
</tr>
<tr>
<td>Sand</td>
<td>1008.0</td>
<td>1009.5</td>
<td>1011.0</td>
<td>1012.5</td>
</tr>
<tr>
<td>Quartz flour</td>
<td>183.0</td>
<td>183.3</td>
<td>183.5</td>
<td>183.8</td>
</tr>
<tr>
<td>Glenium ACE 30</td>
<td>28.6</td>
<td>28.6</td>
<td>28.7</td>
<td>28.7</td>
</tr>
<tr>
<td>Water Total</td>
<td>178.1</td>
<td>178.4</td>
<td>178.6</td>
<td>178.9</td>
</tr>
<tr>
<td>Water Glenium</td>
<td>18.6</td>
<td>18.6</td>
<td>18.6</td>
<td>18.7</td>
</tr>
<tr>
<td>Water Compensated</td>
<td>159.6</td>
<td>159.7</td>
<td>160.0</td>
<td>160.2</td>
</tr>
</tbody>
</table>

![Fig. 3. Mixing Procedure.](image-url)
In addition to the assessment of pozzolanic activity of copper slag, the result for the calcium oxide concentration \( [\mathrm{CaO}] \) was compared with the theoretical maximum using the expression as shown in Eq. (1) corresponding with the lime saturation curve EN-196-5:2005 [47] and the \( [\mathrm{CaO}] \) reduction is calculated according to Eq. (2).

\[
\text{Max}(\mathrm{CaO}) = \frac{350}{10^3} \quad (1)
\]

\[
(\mathrm{CaO})_{\text{remaining}}(\%) = \frac{\text{Max}(\mathrm{CaO}) - \text{[CaO]measured}}{\text{Max}(\mathrm{CaO})} \times 100 \quad (2)
\]

### 2.9. Isothermal calorimetry

In this test, the first hydration starts when the dry materials are mixed with the water. However, the first hydration peak cannot be registered completely since the mixing occurred outside the calorimeter. This peak only amounts to a few percentage of the total heat liberated [49] and will therefore not be considered in the further analysis.

In the preparation of this experiment, the materials were kept at a temperature close to the measurement temperature to avoid significant differences between the paste and the isothermal environment. Isothermal calorimetry was carried out at 20°C on cement pastes. The cement paste compositions were made with the replacement level of copper slag ranging from 0 wt% to 20 wt% in steps of 5 wt%. The water-to-binder ratio of cement paste was 0.185. Before starting the measurement, the dry materials were poured into a small plastic container and mixed manually with a glass rod for 4 min, followed by mixing with the water and Glenium ACE 30 for 2 min. Afterwards, about 14 g of paste was injected into an ampoule using a modified syringe and transferred immediately to the calorimeter. The measurement started when the ampoule was in the channel of this calorimeter. More details about the paste composition are given in Table 5.  

### 2.10. Statistical analysis

To analyze the experimental data, the IBM SPSS Statistics version 23 was used in this study. The two-way analysis of variance (ANOVA) was used to examine the effect of copper slag replacement, vacuum mixing, heat treatment, and age on compressive strength and porosity of RPC and their interactions. The post hoc Tukey HSD (Honestly Significant Difference) method was applied. A significance level of 0.05 was chosen to reject the null hypothesis.

### 3. Results and discussions

#### 3.1. Properties of freshly mixed RPC

The results of the flow test of RPC are shown in Fig. 4. It is clear that the flow of RPC mixed under vacuum of 100 mbar is lower than that of RPC mixed under atmospheric pressure. This result indicates that the workability of fresh concrete with a lower air content decreases. This may be attributed to the increased viscosity. This finding is in contrast with the general conclusion made in most of the literature, namely the workability can be improved by decreasing the air content [35,50]. Nonetheless, it should be noted that the lower air content obtained in these studies is due to the difference in mix proportion of concrete, while the current result applies vacuum mixing to reduce the air content. In addition, Dils et al. [41] found that the development of workability for UHPC using vacuum mixing is less clear. In their research, they investigated the effect of vacuum mixing on one UHPC mixed with six different cement types. For three types of cement an increase in flowability was observed, while for another three types of cement the flowability decreased by applying vacuum mixing, which is in accordance with present results. From these results, it should be noted that further investigation should be performed to find the reasons for these variable results.

Fig. 4 also describes that the increase in copper slag content in RPC mixed under vacuum condition or at atmospheric pressure enhanced the workability of the fresh concrete. This phenomenon can be explained by the fact that copper slag is not a good water absorber [19]. When it is used as one of the components in RPC, it may even cause bleeding in concrete mixes. However, in the mixtures studied here, no bleeding was observed.

#### 3.2. Density of hardened RPC

The values of the density of hardened RPC mixed under vacuum condition and without vacuum are given in Fig. 5. In general, the density of hardened RPC mixed under vacuum condition (100 mbar) and RPC without vacuum (1013 mbar) slightly increased with rising copper slag content. Copper slag has a higher density than cement (3.706 g/cm³ vs 3.152 g/cm³), therefore a certain volume of cement is replaced by a smaller volume of copper slag. To conclude, to obtain 1 m³ of RPC more kg of constituents will be needed in the copper slag mixes.

Fig. 5 also shows that there is a 1.75% increase in average density of RPC mixed under vacuum (100 mbar) compared to RPC mixed at atmospheric pressure (1013 mbar). From this result, it can be stated that the use of vacuum mixing at 100 mbar can effectively decrease the content of air bubbles of RPC, which increases the density.

#### 3.3. Compressive strength

In Fig. 6, the compressive strength results are presented. Based on the statistical analysis (model with only main effects and two-way interactions), it was clear that heat treatment explains most of the variability, followed by the interaction of age and heat treatment and then the age. For young ages and non-heat treated specimens, also the copper slag content seems to have an important influence. In the next sections, we will focus on these aspects.

#### 3.3.1. Effect of copper slag replacement

The influence of copper slag as cement replacement on the compressive strength of RPC is shown in Fig. 6. The ANOVA result showed that the substitution of copper slag in the RPC had a significant effect on compressive strength at young ages (7 days) when vacuum mixing or heat curing was applied, resulting on a p-value <0.0001. It can be observed that the most positive effect on early strength was achieved for 5% copper slag if applying vacuum mixing and heat curing. However, without vacuum mixing and heat treatment, it can be seen from Fig. 6(d) that the strength decreased with rising copper slag content at an age of 7 days. For longer curing ages (28 and 56 days), the strength of RPC containing copper slag was comparable to or even better than the control mix-

<table>
<thead>
<tr>
<th>Table 5: Paste composition (kg/m³).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>CEM I 52.5 N NS/NA</td>
</tr>
<tr>
<td>Copper slag (QCS)</td>
</tr>
<tr>
<td>Silica fume (undensified)</td>
</tr>
<tr>
<td>Glenium ACE 30</td>
</tr>
<tr>
<td>Water Total</td>
</tr>
<tr>
<td>Water Glenium</td>
</tr>
<tr>
<td>Water Compensated</td>
</tr>
</tbody>
</table>
ture for all treatments. Replacement of cement by copper slag leads thus to a small beneficial effect on the compressive strength, as also reported by Edwin et al. [12] and De Schepper et al. [20]. To increase the effect, finer copper slag should be used. In this study, the SSA of the copper slag was only 46% (Blaine) or 40% (laser diffraction) of the SSA of the cement (Table 3). In addition to the insufficient fineness of the used copper slag, it can be assumed that the slag reaction is limited, since the Ca(OH)_2 formed by the cement reaction will perfectly bind to the highly reactive silica fume to form C-S-H gel. Furthermore, the amount of CaO in the slag itself is rather low. However, the anhydrous copper slag grains play a role as filler to enhance the concrete strength. The texture of copper slag after grinding has angular sharp edges (Fig. 1), which can improve the cohesion of the concrete matrix [18, 21, 23, 24, 28].

Based on the results of the Tukey HSD post hoc test ($\alpha = 0.05$), as tabulated in Table 6, it is shown that compressive strength is significantly different for all three different ages. In addition, samples with 5%, 10%, and 15% copper slag are significantly different (have higher strength) from samples with 0% copper slag. Samples with 20% copper slag have an in between strength, that does not significantly differ from the strength of samples with either 0% or 5% to 15% copper slag.

3.3.2. Effect of vacuum mixing

The influence of vacuum mixing on the compressive strength of RPC is also shown in Fig. 6. According to the ANOVA test, the use of vacuum mixing has a positive effect on the strength of RPC ($p$-value <0.0001). At the early days, the strength of RPC containing copper slag mixed under vacuum (100 mbar) was slightly higher than RPC containing copper slag mixed at atmospheric pressure (1013 mbar). However, the use of vacuum mixing had an adverse effect on the compressive strength of reference RPC at early ages. For a curing period of 28 days, the compressive strength of RPC mixed under vacuum (100 mbar) was comparable to the RPC at atmospheric pressure (1013 mbar) as seen in Fig. 6(c) and (d). For the longer curing age (56 days), there was a slight increase in average compressive strength of RPC mixed under vacuum (100 mbar) compared to RPC mixed at atmospheric pressure (1013 mbar). From these results, it can be stated that the effect of the vacuum technique to increase the strength of RPC is limited. This is related to the composition of reactive powder concrete. RPC is composed of fine particles, automatically reducing the porosity of this concrete and also leaving a limited amount of air voids. Therefore, when the vacuum mixing is applied, only remaining air bubbles can be removed.

3.3.3. Effect of heat curing

The result concerning the effect of heat treatment on the compressive strength of RPC is also given in Fig. 6. The use of heat treatment for RPC mixes led to a significant increase in compressive strength ($p$-value <0.0001) for all curing ages. It can be observed that at early days, the strength of RPC under heat treatment increased significantly compared to RPC without heat treatment. However, the achieved strength difference was reduced for longer curing ages since the compressive strength of RPC with heat treatment remained constant or slightly increased whereas the strength of RPC without heat treatment significantly increased with time as given in Fig. 6. Although there is no significant increase in compressive strength of RPC with heat treatment after longer curing ages, the strength remains significantly higher compared to RPC without heat treatment. These results confirm the findings of [51–53]. They noticed that there is no further strength development of UHPC with
time after heat treatment at 90 °C. This finding can easily be explained by the fact that heat treatment accelerates the hydraulic and pozzolanic reaction of binders in the early days. When heating is applied, the OH\(^-\) concentration released by the cement rises significantly to consume Ca\(^{2+}\) from pozzolanic materials. In terms of phase composition at a higher temperature, the amorphous C-S-H phases in the sample transform to crystalline C-S-H phases. When the temperature reaches 90 °C, the crystalline C-S-H transforms to tobermorite and jennite [31]. For the longer curing periods, the hydration process still continues slowly at a room temperature.

In literature it is often mentioned that heat treatment causes an adverse effect on the later age strength. Regarding this phenomenon, Heinz and Ludwig [51] noticed that this is attributed to the relaxation phenomenon due to the heat treatment. Other researchers found that in pastes cured at high temperatures, relatively dense shells of reaction products formed around the hydrating cement grains, while the outer product phase remained relatively porous as relatively little reaction product formed in this phase. Besides this non-homogeneous distribution of hydration products, there is an increase in microcracks due to the rapid temperature rise at early age and the difference in thermal expansion coefficients of the concrete ingredients [54–56]. In the current research, however, no significant negative effect of the heat treatment could be discerned up to 56 days of age.

3.3.4. Overall discussion

As mentioned previously, the individual effects such as copper slag addition, vacuum, and heat treatment have a significant contribution to compressive strength (p-value <0.0001). The results also indicate that the two-way interactions between age on the one hand and copper slag replacement, heat treatment and vacuum on the other hand, and the interaction between vacuum and heat treatment are significant in explaining the compressive strength differences.

The use of vacuum mixing can reduce the air bubbles in all mixtures, and the heat treatment speeds up the hydration of binders at the early ages. When comparing the results of all treatments for all curing ages, the use of copper slag in RPC seems beneficial as strength is comparable or even higher compared to reference mixtures. It is worth mentioning that the use of copper slag in RPC without vacuum-mixing and without heat treatment gave a negative effect on the compressive strength at young ages.

The porosity of RPC is technically decreased by the constituents of this concrete. Replacement of cement by slag cannot help further to reduce the air voids content due to the insufficient fineness and physical properties of copper slag, namely their angular shape with sharp edges, which cannot completely remove the air cavities. Nevertheless, these physical properties of the copper slag play a role to increase the compressive strength as they improve the cohesion. To minimize the porosity, vacuum mixing can be applied as this reduces the air content of the mixture and heat treatment leads to activation of the hydration of binders, generating the C-S-H gel to fill out the remaining unfilled porosity.

3.4. Development of microstructure

Mercury intrusion measurements lead to cumulative intrusion curves as presented in Fig. 7 for different types of RPC mixed under vacuum. In order to analyze the pore size distribution, three pore regions were defined (gel pores: <0.0045 μm; capillary pores: 0.0045 μm–0.50 μm; macro pores + entrained air voids: 0.50 μm–200 μm). As pores less than 0.007 μm could not be measured in our study and other techniques have to be applied to quantify

### Table 6

Post-hoc test (Tukey HSD) compressive strength results based on age and copper slag replacement of OPC; for each of the two factors, treatments indicated by the same letter are not significantly different.

<table>
<thead>
<tr>
<th>Age</th>
<th>Copper slag replacement of OPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 d</td>
<td>28 d</td>
</tr>
<tr>
<td>a</td>
<td>b</td>
</tr>
</tbody>
</table>
the gel porosity accurately. Fig. 8 only shows the capillary pores and macropores + entrained air voids.

To express the effect of heat curing, a reduction factor $R$ was defined:

$$R = \left( \frac{nA - nB}{nA} \right) \times 100$$

(3)

$R$ is the reduction in porosity (%), $n$ is the average porosity for 0 to 20% copper slag replacement, $A$ is without heat treatment, and $B$ is with heat treatment.

3.4.1. Effect of copper slag

The effect of copper slag replacement on the porosity of RPC is shown in Fig. 8. It seemed that copper slag addition had no significant contribution to porosity reduction when heat curing was applied. Only for the vacuum mixed and non-heat treated samples, the addition of copper slag reduced the porosity, especially for the 5% addition at early ages. The latter effect, however, is probably more related to the unexpected high porosity of the reference RPC at this age.

3.4.2. Effect of heat treatment

The evolution of the microstructure of RPC under heat treatment is presented in Fig. 8(a) and (b) and is compared to Fig. 8(c) and (d). It is clear that heat treatment reduces the total porosity and that the combination with vacuum mixing in addition leads to a slightly lower porosity, resulting in a $p$-value <0.0001 based on the ANOVA tests. This corresponds to the increased strength of
RPC as shown in Fig. 6(a) and (b). The reason is that the heat treatment activates the binders reaction to transform Ca(OH)$_2$ into C-S-H gel, filling some pores in hardened paste [5,57].

3.4.3. Effect of vacuum mixing in case no heat treatment is applied

Fig. 8(c) and (d) show the porosity of RPC under vacuum or non-vacuum mixing without heat treatment. The ANOVA result showed that the vacuum mixing had a significant influence on porosity reduction ($p$-value <0.0001). The total porosity, in this case, decreased in the function of curing time. It can be seen in Fig. 8(c) and (d), that the average porosity of non-heat treated RPC halved at 28 days of curing compared to 7 days of curing. Vacuum mixing does not significantly reduce the porosity of RPC. This is caused by the fact that powder ingredients of RPC automatically generate a low porosity of this concrete. From this result, it can be concluded that the contribution of vacuum mixing to the porosity reduction is limited and variable.

3.4.4. Evolution of gel pores, capillary pores, and entrained air voids

Besides reducing the total porosity, heat treatment also influences the evolution of capillary porosity, and entrained air voids. Heat treatment significantly reduced the total porosity, macropores + entrained air voids, and capillary pores for early curing days as seen through the reduction factor $R$, plotted in Fig. 9(a) and (b). This achievement also occurred for later curing ages although the effect was slightly lower compared to early curing days. It was also observed that the higher reduction in porosity was achieved for capillary pores at 7 days. From this result, it can be stated that the heat curing is effective to speed up the hydration process, resulting in lower porosity and higher strength compared to non-heat treatment.

For all mixtures, the proportion of capillary pores is similar or slightly lower to the proportion of macropores + entrained air voids for RPC under heat treatment as seen in Fig. 8(a) and (b), whereas the capillary pores proportion is higher than the macropores + entrained air voids proportion for RPC without heat treatment. It has to be remarked that pores less than 0.007 μm could not be measured in our study and other techniques have to be applied to quantitatively the gel porosity accurately.

3.5. Isothermal calorimetry

Fig. 10 shows the heat production rate in function of time for all mixes. The maximum value of the heat production rate during the second peak decreases with increasing copper slag replacement, with no significant difference between the mixes with 5%, 10% or 15% copper slag. This is due to the dilution of the clinker content in the paste and to the limited pozzolanic activity of the copper slag during the first weeks of hydration. Also the insufficient fineness of copper slag plays a role for the lower hydration heat. In literature, it is mentioned that heavy metal compounds such as Zn, Pb, and Cu may delay the setting time and hydration process.

Fig. 9. The relative reduction in porosity (total porosity, macropores + entrained air voids, capillary pores) ± standard deviation of RPC made with copper slag for different treatments: (a) Heat treatment + vacuum mixing vs non-heat treatment + vacuum mixing, (b) Heat treatment + non-vacuum mixing vs non-heat treatment + non-vacuum mixing.
of cement paste containing copper slag. Here, the difference between the pastes with up to 15% copper slag and the reference is limited. This shows that the filler effect of the copper slag is able to compensate for the reduced cement content. In comparison with earlier work of the authors [12], the superplasticizer is no longer responsible for a retardation of the hydration process of the cement. Glenium ACE 30, a new generation of polycarboxylic ether polymer superplasticizer, was used in this research, instead of Glenium 51.

The cumulative heat production is shown in Fig. 11. It is seen that the highest total heat production is achieved for the reference mixture. In the first phase of 24 h of hydration, the total heat production of pastes containing copper slag was slightly higher or similar to the reference mixture except for the 20% copper slag replacement. In the second phase after 24 h of hydration, the cumulative heat production of a paste containing copper slag was somewhat lower than that of reference mixture.

### 3.6. Frattini test

Fig. 12 shows the results obtained from the Frattini test. It is clear from the graph that the plotted data for 8 days curing were lying on or above the lime saturation isotherm, indicating that there is no reactivity. The amount of Ca ions locates in the portlandite zone. For longer curing periods (i.e. 15 days at 40 °C), all of the plotted data are located underneath but near to the saturation curve of lime, indicating low pozzolanic activity.

The pozzolanic activity for this test is determined by the consumption of the Ca ion at a second titration using Patton and Reeders indicator according to EN-196-5:2005 [47]. It is clear from Fig. 12 that all mixtures with copper slag show comparable results for the amount of Ca ions consumed at 15 days of curing. In addition, the Ca ions removal was expressed as a proportion of the theoretical maximum calculated according to Eq. (1) and shown in Fig. 13. The amount of the Ca ions removal only ranges from 6% to 10%. The result also relates to strength results of RPC using copper slag for all treatments, showing there is no significant difference in compressive strength with the reference for longer curing periods. The fact that the mix with 20% copper slag does not follow the increasing trend of Ca consumption with slag percentage, also had its repercussions on porosity and strength.

### 4. Energy consumption and carbon footprint analysis of RPC mixes

Globally the production of cement annually has reached 2.8 billion tons, and is estimated to increase about 4 billion tons per year [58]. In Belgium, about 6.4 million tons of cement is produced annually, and nearly 20% is used for infrastructures [59]. Energy
The demand in cement production is also increasing. The production of 1 metric ton of cement requires 4000 MJ [60] and also releases 833 kg CO\textsubscript{2} into the atmosphere [61]. The energy consumption for grinding granulated blast furnace slag is about 10% of the total energy consumption of cement [60]. However, the copper slag used in this study has a hardness of 6–7 on the Mohs scale (hardness) [9,36], which also needs a higher energy for grinding compared to blast furnace slag (5–6 Mohs scale, hardness) [62]. Based on the data of CO\textsubscript{2} emission and embodied energy of concrete ingredients as shown in Table 7, the energy consumption and emission reduction by partial replacement of cement by copper slag in RPC mixes can be calculated. The CO\textsubscript{2} emission and embodied energy in the process of RPC (Table 7) were assumed for a heat treatment of 48 h at 90 °C and applying vacuum mixing (lab scale process).

The energy consumption of the RPC mixes with varying replacement levels of cement by copper slag is presented in Fig. 14. It is clear that the energy consumption of RPC mixes decreased with increasing copper slag content. The total embodied energy to produce copper slag is 1.382 MJ per kg, which is about 4-fold lower than the total embodied energy to produce cement, as seen in Table 7. This is the main reason for the decreasing energy consumption in the production of RPC mixes with copper slag.

Furthermore, based on the literature data (Table 7), the quantity of CO\textsubscript{2} emissions can be obtained. In the manufacture of RPC, the use of copper slag as cement replacement seems to have a beneficial effect on air quality. This phenomenon can be seen in Fig. 14. The amount of CO\textsubscript{2} emission decreased with an increase in copper slag content for RPC mixtures. It can be observed that the lowest CO\textsubscript{2} emission (695.5 kg/m\textsuperscript{3}) was achieved for 20% copper slag replacement. It should be noted that although the use of copper slag as cement replacement of RPC gave a limited effect on compressive strength, an ecological advantage can be achieved.

Table 7

<table>
<thead>
<tr>
<th>Components</th>
<th>Embodied energy (MJ)</th>
<th>CO\textsubscript{2} emissions (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>5.5 (A)</td>
<td>0.833 (B)</td>
</tr>
<tr>
<td>Copper slag</td>
<td>1.382 (C)</td>
<td>0.411 (C)</td>
</tr>
<tr>
<td>Silica fume</td>
<td>0.036 (A)</td>
<td>0.28 (D)</td>
</tr>
<tr>
<td>Flour</td>
<td>0.85 (A)</td>
<td>0.023 (B)</td>
</tr>
<tr>
<td>Sand</td>
<td>0.08 (A)</td>
<td>0.021 (B)</td>
</tr>
<tr>
<td>Superplasticizer</td>
<td>11.5 (E)</td>
<td>0.600 (E)</td>
</tr>
<tr>
<td>Water</td>
<td>0.2 (E)</td>
<td>0.0008 (E)</td>
</tr>
<tr>
<td>Processing</td>
<td>0.247 (F)</td>
<td>0.047 (F)</td>
</tr>
</tbody>
</table>

Note: A = Aysha, et al. [63]; B = Stengel and Schiebl [61]; C = Yingshun and Jie [64]; D = King [65]; E = Mithun and Narasimhan [66]; F = Calculated in this research.

5. Conclusions

Within this paper, the influence of intensive vacuum mixing and heat treatment on compressive strength and microstructure of reactive powder concrete incorporating secondary copper slag as supplementary cementitious material was investigated. The following conclusions can be made:

(1) There was an increase in the workability with rising copper slag content, both for RPC under vacuum mixing (100 mbar) and RPC under atmospheric conditions. This can be due to the effect of the low water absorption of copper slag.

(2) By applying vacuum mixing to the mixture, the density of hardened RPC is significantly increased. Also a very small gradual increase with copper slag proportion is noticed.

(3) The use of secondary copper slag for up to 20% cement replacement in RPC has a negligible effect on the compressive strength from 28 days of age onwards. In combination with vacuum mixing and / or heat curing, an improved strength was noticed at 7 days.

(4) The use of heat treatment has a significant effect on the strength development of RPC at early days, whereas vacuum mixing has only a very limited effect on compressive strength for all curing ages. This is due to the very low amount of air voids in RPC.
(5) The addition of copper slag and application of vacuum mixing has a limited effect on the porosity reduction of RPC. However, by applying heat treatment to the mixtures, a significant reduction in total porosity, macropores + entrained air voids, and capillary pores of RPC were obtained.

(6) The increase of the copper slag proportion up to 15% has only a limited effect on the heat production of cement paste. This shows that the filler effect on the slag is able to compensate for the reduced cement content, in spite of the fineness of the slag being lower than for the cement.

(7) The results of pozzolanic activity assessed by the Frattini test show that all of the mixtures with copper slag indicate low pozzolanic activity after 15 days curing.

(8) The utilization of copper slag as cement replacement decreases the energy consumption and reduces the carbon footprint in the production of RPC.

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References


