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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.

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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/m^3) 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

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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, Maltais 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 C_3A) was used throughout all experiments. Some researchers recommend to use cement with low C_3A (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 d_{50} of 12 μm was used. A quartz sand with a d_{50} 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 cm^2/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 Viscocrete-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

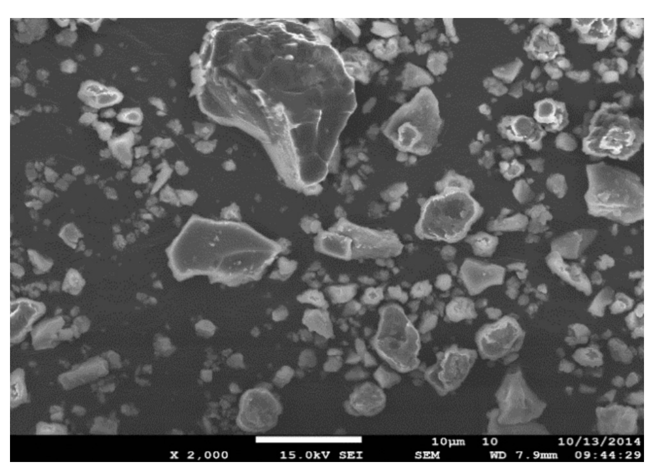

Fig. 1. SEM image of granulated copper slag (scale bar = 10 μm).