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Effect of secondary copper slag as cementitious material in ultra-high performance mortar

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HIGHLIGHTS

- The increase of copper slag content enhances the workability of the fresh UHPM.
- The increasing SCS fineness is more effective for strength enhancement than QCS.
- High dosage of Glenium 51 and presence of Zn cause a delay of the cement hydration.
- The Ca ion consumption by finer copper slag is more than for coarser ones.
- The CaO-poor and SiO_2-moderate slag tends to consume limited amount of portlandite.

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ABSTRACT

This research investigates the use of copper slag as supplementary cementitious material (SCM) in ultra high performance mortar (UHPM). Two secondary slag types from a plant in Belgium were utilized as SCM and were classified as a quickly cooled granulated copper slag (QCS) and a slowly cooled broken copper slag (SCS). Both materials were ground intensively using a planetary ball mill. A low water-to-binder ratio of 0.15 was chosen for the UHPM in this study. Various mortar and cement paste samples were produced with increasing copper slag content from 0 to 20 wt% in steps of 5 wt%. Particle size distribution (PSD) and specific surface area (SSA) of the copper slag were assessed using laser diffraction and the Blaine permeability test. The pozzolanic activity of copper slag was evaluated using the Chapelle test, strength activity index (SAI) and Frattini test.

The results obtained, showed that the strength of mortars with different copper slag proportions was comparable to or even better than the control mixture at 90 days. The increased fineness of the copper slag enhances the mortar strength. Using isothermal calorimetry, it was found that the addition of copper slag slows down the hydration of the cement pastes. The rate of pozzolanic activity of copper slag depends on temperature, curing age, and particle sizes.

1. Introduction

In recent years, concrete is the most widely used construction material and it is essential for the construction of high-rise buildings, transport networks, water and energy infrastructures. Green building is a fundamental part of the concept of sustainable development which can be applied to the infrastructure sector. Since the amount of natural resources is declining due to a large consumption in the cement and concrete production and the process to produce Portland cement needs about 4000 MJ/t of cement especially for the grinding and calcination of raw materials [1] and also causes air pollution due to discharge of carbon dioxide emission, there is a motivation for using by-products which enhance the performance of the materials and which are competitive both from an environmental and an economic point of view. By-products generated by the mining industry can be problematic with regards to the environment, since these materials need large areas for storage and there is a need to protect the environment from the danger of heavy metal. However, the availability of the landfill disposal of slag is not sufficient. It would thus be good to exploit these by-products in the cement and concrete production [2].

Copper slag is a by-product, besides mill tailing, produced in the smelting process. When finely ground copper flows through a flash furnace, air and oxygen is injected to be reacted with some of the iron and sulfur to yield appropriate heat. This process generates

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the liquefied mass which is matte (copper and iron sulfides) and slag, containing pozzolanic components such as Al_2O_3, CaO, Fe_2O_3 and SiO_2 [3]. Every year, about 24.6 million tons of copper slag are produced by copper industry throughout the world [4]. In Europe, approximately 5.56 million tons of copper slag are generated by the European copper industry [4,5], and in Belgium, about 132,240 tons of secondary copper slag are produced in the recycling plant annually [6,7]. The secondary copper slag then contains elements and heavy metals which cannot be reprocessed any further and needs a large landfill for storing the slag [7]. This secondary slag can be used as a raw material for both the cement and concrete industry without loss of quality [8–10]. Within the cement and concrete industry, copper slag can be used as cementitious material or sand replacement. Looking into literature, Tixier et al. [10] and Mobasher et al. [11] investigated the effect of copper slag on the hydration of cement based materials. They replaced the cement with copper slag up to 15% by weight and added up to 1.5% of hydrated lime as an activator to accelerate the pozzolanic reactions. The highest compressive strength was achieved for 15% copper slag at 90 days of curing, which increased 48% in strength compared to control. They also concluded that the compressive strength of mortar with 15% copper slag + 1.5% lime as activator increased 100% from 30 MPa at 28 days to 61 MPa at 90 days. The effect of copper slag as cementitious material on the strength of concrete was studied by Al-Jabri et al. [12]. Results indicated that the increase of copper slag content and cement by-pass dust as activator caused a reduction in the strength of mortar compared to the reference mixture containing 100% OPC. Furthermore, mortar mixture containing 95% cement + 5% cement by-pass dust (CBPD) was the highest in strength. Al-Jabri et al. [13] continued to evaluate the mechanical properties of concrete containing copper slag and cement by-past dust as an activator. Their conclusion is that the strength of concrete containing 5% copper slag + 95% OPC was comparable to the reference mixture. Moreover, the use of copper slag as cementitious material and CBPD as activator did not further promote the concrete strength.

Arino et al. [14] investigated the response of concrete and mortar using ground copper slag under compression with axial and circumferential strain and fracture test. They concluded that concrete with ground copper slag up to 15% as a cement replacement tend to be stronger but more brittle compared to the reference. The potential use of copper slag as cementitious material in cement and mortar was also studied by Moura et al. [9]. In this study, copper slag was used in percentages of 0% and 20% for three water-to-cement ratios (i.e. 0.4, 0.5, and 0.6). Results showed that there was a slight increase in the compressive strength of concrete with copper slag for all water-to-binder ratios in comparison with the reference at 28 days of curing. This phenomenon was caused by an increasing amount of calcium silicate hydrates formed by the pozzolanic compounds from copper slag and calcium hydroxide produced during the cement hydration process, and a decreasing porosity of the cement matrix due to the finer copper slag. On the other hand, the latter was not the case for the copper slag used in De Schepper et al. [15] (Fig. 1). In this study replacement levels up to 60 wt% in steps of 10 wt% were tested and the contribution of the ground copper slag to the hydration degree of the cement paste was found negligible. De Rojas et al. [16] investigated the use of recycled copper slag as cementitious material for mortar. Their conclusion is that using 30% copper slag substitution decreases the compressive strength and flexural strength of mortar. They also found that the cumulative heat of hydration of paste containing 30% copper slag replacement determined by semi-adiabatic method was lower than that of the control mixture. Zain et al. [17] also evaluated the use of copper slag in concrete and mortar with regard to the compressive strength and stabilization/solidification of heavy metal in slag. In this study the copper slag was ground to obtain the same fineness as OPC, which is sieve 15–20% retained on the 45 μm They replaced the OPC with copper slag up to 10% by weight in steps of 2.5 wt.%. They concluded that the compressive strength of mortar decreased with an increase in copper slag content for all curing age compared to control.

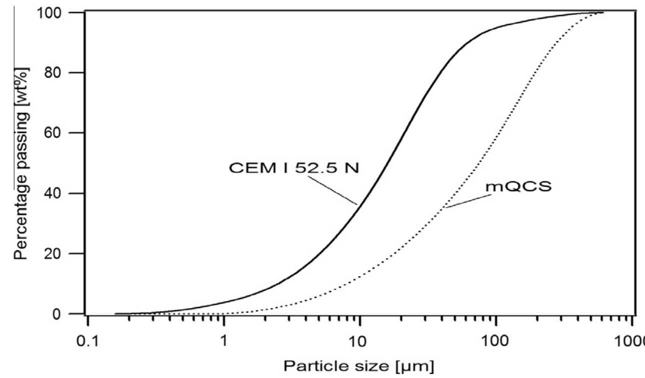

Fig. 1. Particle size distribution by laser diffraction of the quickly cooled granulated copper slag milled by a planetary ball mill (mQCS) and cement (CEM I 52.5 N) used in De Schepper et al.

In another research project, the effect of copper slag, used as a fine aggregate, on the strength of high performance concrete has been investigated [8,18]. The sand was replaced with copper slag up to 100 wt%. The conclusion was that the highest compressive strength was achieved for the mixes with up to 40–50% copper slag. This strength was comparable to that of the reference mixture. Furthermore, a positive result of copper slag used as fine aggregate replacement was seen by Al-Jabri et al. [19]. In this study, they concluded that the strength and durability of high strength concrete can be improved with the increase of copper slag content in the concrete mixture when applying constant workability as that for the control mixture [19]. Furthermore, Wu et al. [20,21] investigated the possible use of copper slag as fine aggregate on the mechanical properties of high strength concrete and reinforced concrete under vibration load. They concluded that the strength of concrete using less than 40% copper slag was comparable or better than the reference, and the dynamic response of reinforced concrete was generally increased when using up to 20% copper slag as sand replacement in comparison with the reference. In addition to fine aggregate replacement, copper slag can also be used as a coarse aggregate substitution in high performance concrete [22]. In this research, they replaced 100% limestone as coarse aggregate with copper slag. They concluded that the mechanical properties of copper slag concretes were higher than those of the limestone concretes, probably promoted by the physical properties of copper slag which created a higher bonding between copper slag aggregate and cement paste. Ambily et al. [23] investigated the use of copper slag as fine aggregate replacement for ultra high performance concrete. They concluded that there is a potential for the use of copper slag to UHPC production.

In the current research the effect of secondary copper slag as supplementary cementitious material in ultra-high performance mortar (UHPM) is evaluated. The effect of copper slag on the heat production of pastes and the pozzolanic activity of copper slag were studied.

2. Materials

2.1. Copper slag

The copper slag used in this research was a secondary slag from a Belgian recycling plant. This slag was produced by using primary