

UTILIZATION OF COPPER SLAG AS A CEMENTITIOUS MATERIAL IN REACTIVE POWDER CONCRETE

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ABSTRACT: This research studies the use of copper slag from a plant in Belgium as a cementitious material in reactive powder concrete (RPC). The quickly cooled granulated copper slag (QCS) was ground intensively using a planetary ball mill. A low water-to-binder ratio of 0.18 was chosen for the RPC in this study. Various concrete and cement paste samples were produced with increasing copper slag contents 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, respectively. The results obtained, showed that the strength of RPC with different copper slag proportions was similar to or better than the control mixture at 90 days. The presence of copper slag in the paste tends to decrease the total heat production of the paste. The pozzolanic reactivity of QCS determined by the Chapelle test was found to be low.

Keywords : *Copper slag, Reactive Powder Concrete, Compressive Strength, Hydration, Pozzolanic Reactivity*

CONTEXT

In recent decades, concrete has grown to be the most popular material for infrastructure projects due to its relative low cost in production and treatment. However, Portland cement as ingredient of concrete requires a huge amount of energy from fossil fuels and non-renewable resources and for clinker burning and grinding. Moreover, the toxic gases from a cement kiln also contribute to emissions of air pollutants and pose a hazard for human health. The alternative way, to protect the environment and saving energy in the near future, is to utilize recycled waste material within the cement and concrete industry.

The use of industrial by-products as cement replacing material is very popular. Typical by-products that are already widely used are e.g. fly-ash and blast-furnace slag. Copper slag is one of the by-product materials from the copper smelting. In Belgium, about three million tons of slag are produced by the copper industry every year (Flanders Cleantech Association, 2012). In Europe, approximately 40 million tonnes of slag were generated by the European metal industry according to Euroslag data in 2004 (Böhmer et al. 2008). Since this material needs a large area for landfilling, of which the availability is insufficient, and to avoid problems related to the leaching of heavy metal and other harmful elements, it would be interesting to upgrade these 'waste' products in high-value applications. Moreover, the amount of natural resources is declining due to a large consumption in the cement and concrete production. A possible breakthrough can thus be sought in exploiting by-products within cement and concrete production.

Reactive powder concrete (RPC) is classified as an ultra-high performance concrete (UHPC) (Zenati et al. 2009) which has a compressive strength of 200 MPa when applying heat curing and up to 800 MPa when using steel aggregate (Richard 1995). In the RPC compositions, active powders dominate as the main constituents to obtain a relatively dense and homogenous microstructure (Yu et al. 2014), (Zang et al. 2008), (Yasici et al. 2013).

Looking into literature, many researchers have investigated the use of copper slag as cementitious material in high performance concrete. Hydrated lime can be used as activator in high performance concrete since it accelerates the pozzolanic reaction. The highest compressive strength is achieved for 15% copper slag and 1.5% lime at 90 days of curing, which is twice as high compared to the strength at 28 days (Mobasher et al. 1996) and (Tixier et al. 1997). The effect of copper slag as cement replacement in concrete and cement by-pass dust as activator is limited to the compressive strength (Al-Jabri et al. 2002). The positive effect of copper slag on the strength of concrete and mortar is caused by an increasing amount of calcium silicate hydrates formed by the pozzolanic reaction of copper slag and calcium hydroxide from cement during the hydration process (Moura et al. 2007). Opposite results were obtained by De Schepper et al. (2014) when using the copper slag as cement replacement up to 60 wt% in steps of 10 wt%. They found that the effect of copper slag on the hydration process was minor. Copper slag was used in ultra-high performance

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concrete as fine aggregate by Ambily et al. (2014). Their conclusion is that the copper slag has a promising future in the production of UHPFRC.

This paper presents the study of the effect of copper slag as cementitious material in reactive powder concrete. This study is a continuation of previous studies which focus on ultra high performance mortar (Edwin et al. 2015). The author used Glenium ACE 30 as superplasticizer in the current study since Glenium 51 previously delayed the setting time of the mortar.

MATERIALS AND METHODS

Materials

The secondary slag used in this research was quickly cooled granulated copper slag (QCS) from a Belgian recycling plant. This slag was produced by using waste materials such as copper wires, dust from tin production, old television and radiators from cars as raw materials to generate copper, lead, tin and nickel.

Besides copper slag, an undensified silica fume (type 940U, Elkem) was used as SCM. As cement, a CEM I 52.5 N-HS/NA (low C₃A) was used throughout all experiments. An overview of the chemical composition of the binders is given in Table 1.

Table 1. Chemical composition of the applied binders reactive fine aggregate determined by XRF analysis [wt%]

Material	QCS	Cement	Silica fume	Flour (M400)
CaO	7.1	63.7	0.6	0.02
SiO ₂	25.9	20.9	94.2	99.5
Al ₂ O ₃	5.9	3.6	1.0	0.2
Fe ₂ O ₃	45.5	5.2	0.5	0.03
MgO	0.8	0.8	0.7	-
Na ₂ O	0.8	0.2	1.0	-
K ₂ O	0.2	0.6	1.1	0.05
SO ₃	0.4	3.0	0.3	-

Table 2 depicts 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). To obtain the desired workability, a polycarboxylate ether (Glenium ACE 30 con 35% S) was used. The concrete was made with copper slag contents varying between 0 and 20 wt% in steps of 5 wt%. For all concretes, a flour (type M400, Sibelco) with a d₅₀ of 12 µm was used.

Table 2. Composition of the RPC mixtures with copper slag

Material	Reference	5% CS	10% CS	15% CS	20% CS
CEM I 52.5 N HS/NA	(g) 960	912	864	816	768
Copper slag	(g) 0	48	96	144	192
Silica fume (940 U)	(g) 301	301	301	301	301
Sand M31	(g) 1320	1320	1320	1320	1320
Flour M400	(g) 240	240	240	240	240
Glenium ACE	(g) 37	37	37	37	37
Water Total	(g) 233	233	233	233	233
Water Glenium	(g) 24	24	24	24	24
Water Compensated	(g) 209	209	209	209	209

Methods

Grinding process

Before using the copper slag as cementitious material, QCS was intensively ground using a planetary ball mill. The copper slag was ground at 390 rpm for 6 times 5 minutes. To avoid agglomeration of the slag upon grinding, a superplasticizer (Sika Viscocrete-3095x; 0.122 wt%) was added

The particle size distribution of the copper slag obtained by laser diffraction is given in Figure 1. To disperse the materials, isopropanol was used since it does not react with copper slag. To avoid agglomeration, the copper slag was put in a sonication bath (5 min) before the measurement. An overview of the parameters used to determine the PSD of the SCMs by laser diffraction can be seen in table 3.

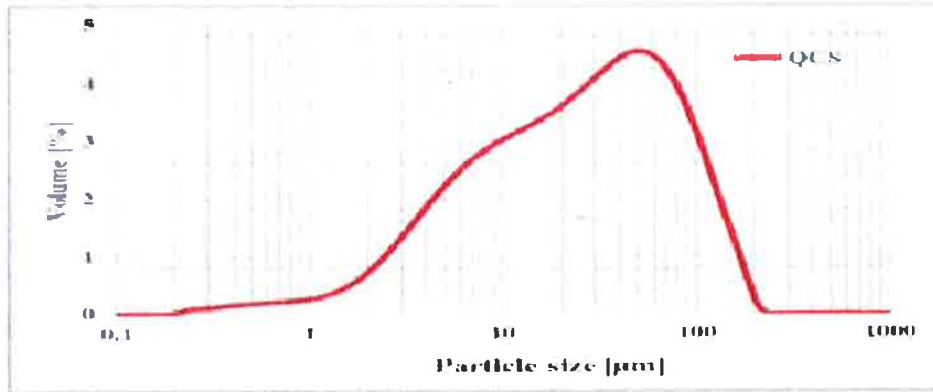


Figure 1 : Particle size distribution of copper slag.

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. 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 4.

Table 3. Overview of the parameters applied to determine the PSD of the different SCMs by laser diffraction

Optical parameters	Copper slag	Silica fume
Refractive index (RI)	1.731	1.53
Absorption coefficient	0.055	0.001
Obscuration [%]	10 - 20	5 - 10
Stirrer rate [rpm]	1700	1500
Dispersant RI	1.390	1.390
Sonication times [minutes]	5	15

Table 4. Density and SSA of the different binders

Materials	QCS	CEM I	SF
Density (g/cm ³)	3.761	3.152	2.017
SSA (cm ² /g) :			
Blaine permeability	2533	4955	-
Laser diffraction	2610	-	56200

Mixing Procedure

A mixer with two speeds (140 and 285 rpm) was used. First dry powder materials were inserted and mixing was started at low speed (140 rpm) for about two minutes. Afterwards, water and superplasticizer were dosed and mixed for about 1.5 minutes at 140 rpm. The highest speed (285 rpm) was then started for about 6 minutes in order to obtain a homogeneous mixture. Finally, normal speed was applied for about 2 minutes to obtain an optimal workability.

Compressive strength testing

After curing in a room at relative humidity of $95 \pm 5\%$, the specimens were tested to evaluate the compressive strength according to NBN EN 196-1 (2005) at the age of 7, 28, 56, and 90 days.

Isothermal Calorimetry

Isothermal calorimetry was carried out at 20°C on cement pastes that were mixed manually using a small container. After 4 minutes of dry mixing, the water and Glenium ACE 30 were added and mixing continued for another 2 minutes. Afterwards, around 14 g of paste was injected into an ampoule using a modified syringe. The water-to-binder ratio of the cement pastes was 0.185. Similar to the RPC, the cement pastes were made with an increasing copper slag content from 0 wt% to 20 wt% in steps of 5 wt%. More details about the paste composition are given in Table 5.

Table 5. Paste composition.

Material	Reference	5% CS	10% CS	15% CS	20% CS
CEM I 52.5 N HS/NA	(g) 25.00	23.75	22.50	21.25	20.00
Copper slag	(g) 0.00	1.25	2.50	3.75	5.00
Silica fume (940U)	(g) 7.84	7.84	7.84	7.84	7.84
Glenium ACE 35% solid	(g) 0.97	0.97	0.97	0.97	0.97
Water Total	(g) 6.08	6.08	6.08	6.08	6.08
Water Glenium	(g) 0.63	0.63	0.63	0.63	0.63

Water Compensated	(g)	5.45	5.45	5.45	5.45	5.45
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Chapelle test.

To evaluate the pozzolanic activity of copper slag, the Chapelle test was performed according to NF P 18-513. In this test, 2 g of pozzolan and 1 g of CaO were inserted into an Erlenmeyer. In order to obtain decarbonized water, 250 ml of distilled water was boiled in a heater to remove the CO₂. The agitation system was started using a magnetic stirrer to create a circular motion in order to obtain a homogeneous material after mixing. During agitation, the material was boiled at constant temperature (90 °C) during 16 hours to facilitate the reaction of the solid particles and the liquid. The test reflected positive if there is no evaporation throughout the heating process. A smooth condenser column with circulating water was installed to create a cooling system to prevent evaporation. A reference mixture was prepared using the same method by mixing 1 g of CaO and 250 ml of distilled and decarbonized water. After cooling at room temperature, the solution was mixed with 60 g of sucrose and shaken for about 15 min using a magnetic stirrer in order to extract non reacted calcium hydroxide. After filtering, the solution was titrated using 0.1M HCl with phenolphthalein as indicator instead of methyl orange. This test is considered positive if CaO is consumed by the pozzolan.

RESULTS AND DISCUSSIONS

Figure 2 describes the effect of copper slag replacement on the compressive strength of RPC at 7, 28, 56 and 90 days. In general, the strength of RPC at 7 days decreases with rising copper slag substitution in the concrete mixture. The strength increase for RPC with CS between 7 and 28 days was similar as for the reference mortar. However, for longer curing periods the strengths of mixtures with 10% CS and 20% CS were higher than those of the reference mixtures. Although the strength development of the 5% CS mixture was delayed at early ages, it was higher than that of the reference specimens at 90 days. The highest compressive strength (165 MPa) was achieved for 10% copper slag at 90 days of curing, which increased about 7% compared to the control specimens. The lowest RPC strength at 90 days (150 MPa) was obtained for 15% copper slag replacement. Nevertheless, the strength of this mix remained stable between 28 and 90 days as well as for the control mixture as seen in figure 2. Generally it can be stated that the use of the finely ground copper slag for up to 20% cement replacement will have no or a positive effect on the strength of RPC.

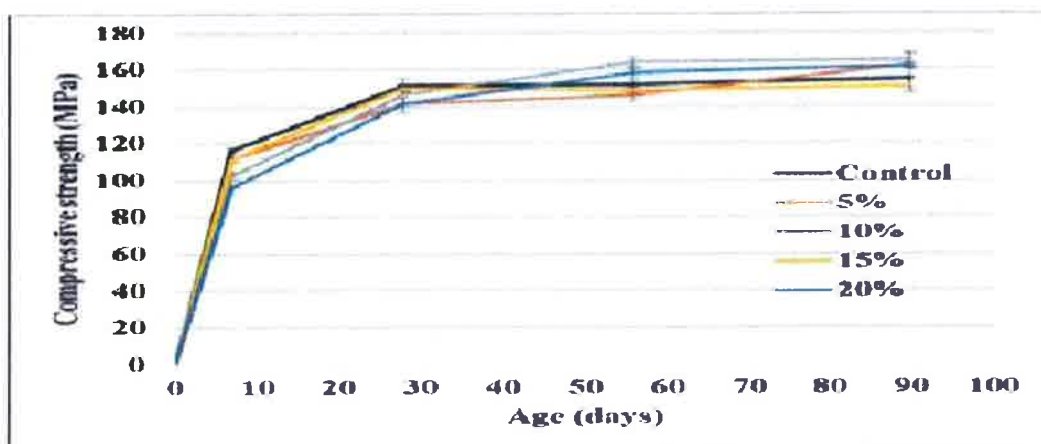


Figure 2 : RPC compressive strength results (error bars represent standard errors)

Figure 3 shows the process of the heat production 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, and comes later in time. Furthermore, the maximum heat production rates for pastes containing copper slag are lower compared to the reference. This phenomenon is probably caused by heavy metals present in the copper slag [Zain et al. 2004]. This can be 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 heavy metal compounds such as Zn, Pb, and Cu may play a role in the delay of the setting time and hydration process of the cement paste containing copper slag. In comparison with earlier work of the authors (Edwin et al. 2015), 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 in Edwin et al. 2015).

The cumulative heat production is shown in Figure 4. It is seen that the highest total heat production is achieved for the reference. In addition, in this study, an increase of the copper slag amount did not further promote the increase of total heat production of the paste. This is in line with the discussion presented above.

In this study, the concentration of CaO consumed by 2 g of copper slag was lower than for the reference. These test results indicate the non-reactivity of the copper slag with CaO to produce calcium silicate hydrates, giving an explanation for the obtained lower hydration heats in figure 3 and 4. The slightly higher strength results obtained are probably related to an improved microstructure. In subsequent research it will be studied whether the reactivity can be improved by obtaining higher fineness.

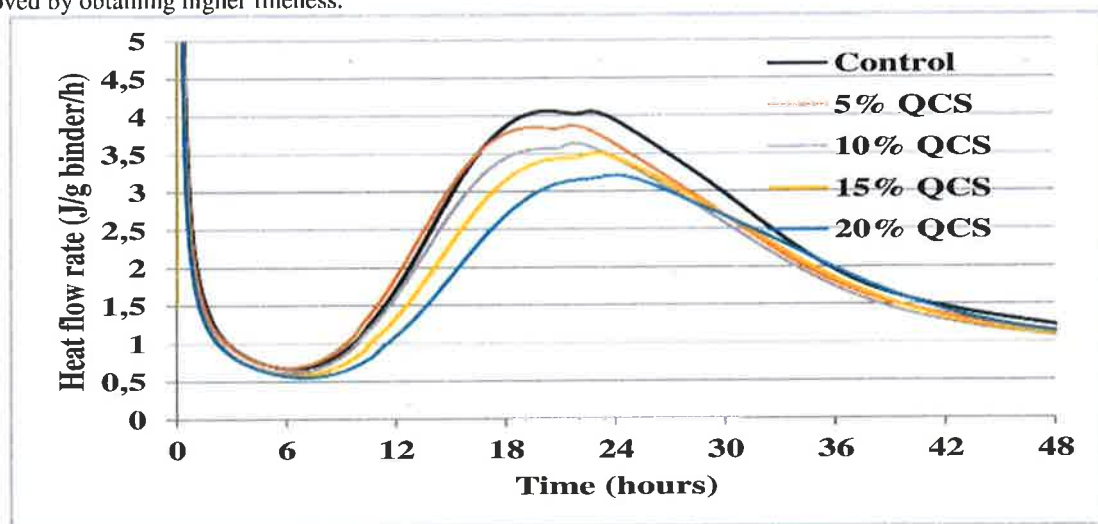


Figure 3. Influence of copper slag addition on the binder hydration

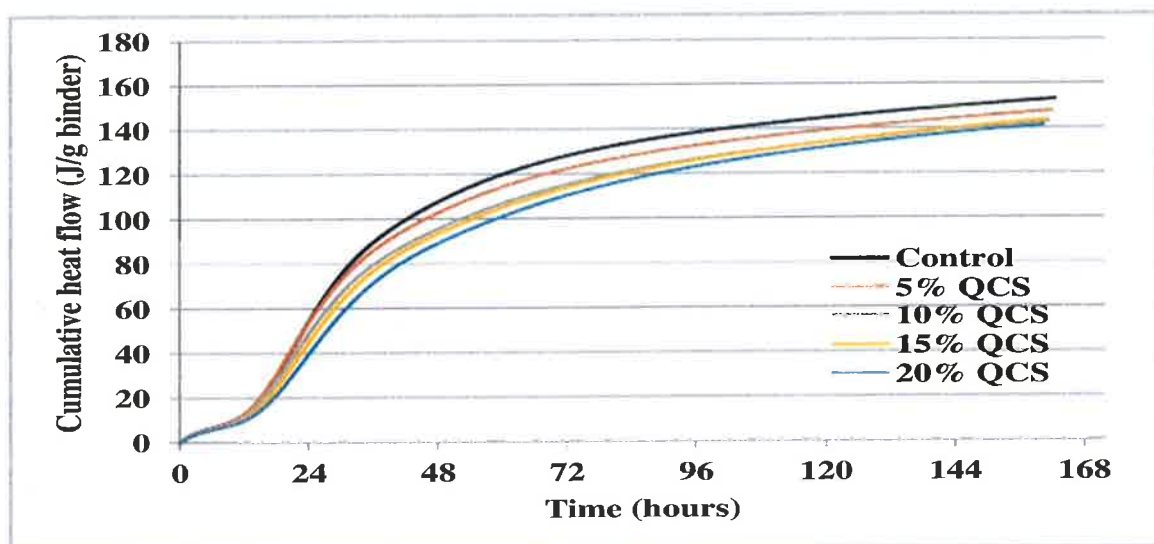


Figure 4: Total heat production for pastes with copper slag

CONCLUSIONS

Within this paper the utilization of quickly cooled copper slag (QCS) as cementitious material in Reactive Powder Concrete (RPC) was investigated. The following conclusions can be made:

1. The use of copper slag as cement replacement up to 20% has no adverse effects on the compressive strength. For some replacement levels minimal strength increases at later ages were observed. The presence of copper slag in the cement paste decreases both the maximum of the heat production rate and the total heat production after 7 days.
2. The copper slag used in this research is not reactive with CaO (Chapelle test) and is thus not considered to be pozzolanic. This explains the effects of copper slag on the heat production of the cement paste. The minimal effect on the compressive strength is probably related to an improved microstructure in the presence of copper slag.

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