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Copper slag waste as a supplementary cementing material to concrete

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Summary The use of industrial solid waste to concrete production is environmentally friendly because it contributes to reducing the consumption of natural resources, the pollution concrete production generates and the power it consumes. This paper presents the results of a study on the use of copper slag as pozzolanic supplementary cementing material for use in concrete. Initially, the chemical and mineralogical characteristics of the copper slag were determined. After this, concrete batches were made with copper slag additions of 20% (relative to the cement weight) and a set properties were investigated, i.e., specific gravity, compressive strength, splitting-tensile, absorption, absorption rate by capillary suction and carbonation. The results pointed out that there is a potential for the use of copper slag as a supplementary cementing material to concrete production. The concrete batches with copper slag addition presented greater mechanical and durability performance.

Introduction

In recent years, technological progress, industrial development, population growth, and the resulting increase in consumption of natural resources have caused a disorderly use of nonrenewable resources, increased power consumption, as well as the generation of large volumes of urban and industrial waste. Consequently, negative environmental impacts such as the depletion of the ozone layer, the greenhouse effect, and water spring pollution are increasingly harming the humankind. The construction activity causes great damage to the environment due to the consumption of large volumes of natural resources and power and by the large volumes of waste it generates. However, this industry is also characterized by a high potential to use recycled waste in construction materials. Thus, many research activities have been carried out with the purpose of using waste as a pozzolanic supplementary cementing material for the production of cement-based materials to be used in construction.

The three most necessary metals in the world are steel, aluminum and copper. Copper production activities result in significant amounts of slag during the process for transforming raw material into finished goods. Nearly 13 million tons are generated worldwide. An average of 230 thousand tons is generated annually in Brazil, which needs too much landfill space for storing the copper slag. Using copper slag as raw material in the construction industry appears to be an alternative to minimize this problem. Some studies were carried out using grained copper slag as fine aggregate [1–3] and fine powder copper slag for partial replacement of cement [4]. There are no studies available about the copper slag effect on concrete durability. This paper presents the study of the effect of copper slag has as a supplementary cementing material in concrete, mechanical and durability properties of concrete containing copper slag at 20% replacement levels were compared with control concrete (without copper slag).

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Materials and methods

Copper slag

Copper slag grains have a fineness modulus of 3.4. In order to use copper slag as a mineral admixture it was necessary to carry out an experimental study associating grinding time, average diameter and pozzolanic activity assessed in mortars [5]. Based on this study, it was verified that 60 min was the optimal grinding time in horizontal ball mills to achieve an average diameter of 27.2 μm. The copper slag presented a pozzolanic activity index of 87% according to specification requirements of ASTM 618 °C [6] for Portland cement mineral additives. Copper slag has a specific gravity of 3.87 g/cm^3. Its chemical composition is showed in Table 1. Figure 1 shows the X-ray diffraction and Fig. 2 shows secondary electron scanning electronic microscopy. The results obtained from the copper slag micrography demonstrate that the material's grains are originally spherical, with a smooth and nonporous surface. The X-ray diffraction results indicated the presence of fayalite and magnetite. Some high peak frequencies were observed, which suggests a basically crystalline structure.

The results obtained through leaching and solubility tests [5] (based on the NBR 10005 [7] and NBR 10006 [8] standards) revealed that no substance deemed as toxic was leached or soluble above the limits set by the NBR 10004 [9] standard. Therefore, the use of copper slag as a construction raw material neither imposes risks to the humankind nor to the environment. Because of that, it can be used as a construction raw material.

Cement and aggregates

Standard Portland cement was used (ASTM Type I) in the experiments. The aggregates used in both concrete mixtures were river quartz sand, with specific gravity of 2.624 kg/dm^3 and fineness of 2.45, and basaltic coarse aggregate, with a typical maximum size of 25 mm. Tap water supplied by the local water supply company was used on the mixtures.

Concrete production using copper slag

Preliminary studies on the use of copper slag to produce mortars were used to assess the best copper slag admixture content for concrete production. The literature about the topic suggests that the 20% rate shows the highest performance [5].

The IPT/EPUSP [10] methodology was used for concrete mix design. Ranges were determined considering three different water/cement ratios (0.40, 0.50 and 0.60) for control mix and copper slag concrete. The concrete batches were identified as REF (control mixture) and COB 20% (mixture with 20% of cement addition, by weight). Therefore, six mixes were produced namely: REF40 and COB20%-40, REF50 and COB20%-50, REF60 and COB20%-60 with water/cement ratios 0.40, 0.50 and 0.60, respectively. The mix proportions (by weight) from both concrete types are shown in Table 2.

A concrete mixer was used to mix all materials during 5 min. The concrete workability, measured by slump test, set in ASTM C 143 [11], was fixed at 70 ± 10 mm.

Four 100 by 200 mm cylinder specimens were molded to evaluate each property studied (i.e., specific gravity, compressive strength, splitting-tensile, absorption, absorption rate by capillary suction and carbonation). The specimens were removed from their molds 24 h after the molding process and were kept in a moist room at a temperature of 23 ± 2 °C and relative humidity of 95 ± 5% until the test age. After 28-day aging, specific gravity, axial compressive strength and splitting tensile strength were assessed, according to ASTM C 642 [12], ASTM C 39/C39M [13] and ASTM C 496 [14] respectively. Experimental data were statistically treated using the analysis of variance (ANOVA) technique. The two-way ANOVA for repeated measurements was used to assess: the effect of copper slag addition in concretes; the water/cement ratio of test specimens on their compressive strength, splitting tensile strength and the interaction of these factors.

In addition to investigating the mechanical performance of the specimens, some durability properties, i.e., absorption rate by capillary suction, absorption and depth of carbonation, were also evaluated.

Table 1 Chemical composition of the copper slag

Chemical Component	SiO_2	Fe_2O_3	Fe_3O_4	CaO	MgO	Al_2O_3	Na_2O	K_2O	CuO	ZnO
COB	26.0	55.0	7.0	2.0	2.7	3.3	1.1	0.6	1.4	0.9

COB—Copper slag

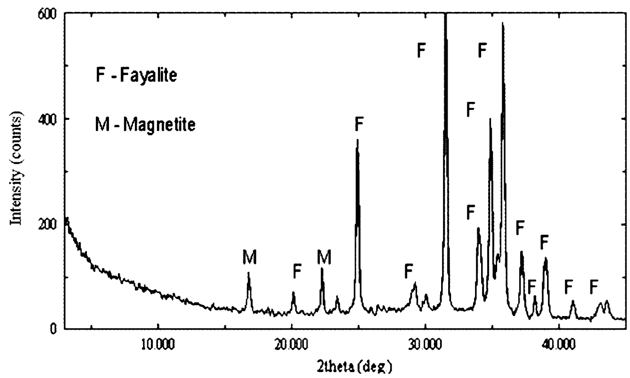

Fig. 1 X-ray diffraction of the copper slag sample

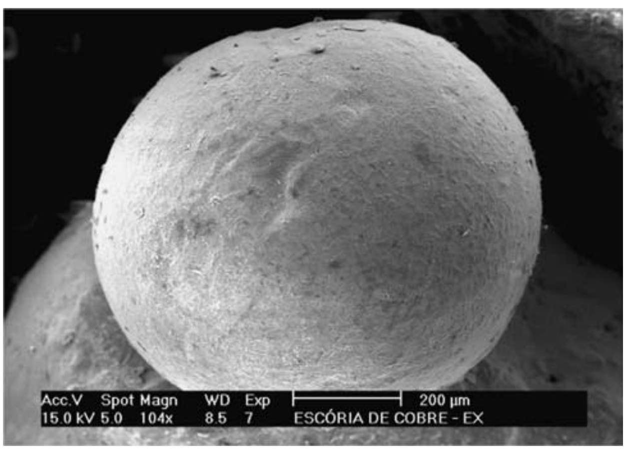

Fig. 2 SEM by secondary electron of the copper slag grain (5000× amplification)

Capillary water suction was determined based on the test developed by Kelham [15] and adapted by Gopalan [16]. The rate of absorption water by capillary suction ($g/h^{1/2}$) is calculated adjusting the slope of a straight line, based on the charts of the gain of mass versus the square root of time [17]. The absorption test for concrete specimens is prescribed by ASTM C 642 [12]. Finally, the depth of carbonation was assessed by an accelerated test. The accelerated carbonation test was carried out in a controlled concentration chamber, at 5% of CO_2 concentration, under acclimatized conditions (relative humidity of 68 ± 2% and temperature of 21 ± 2 °C). Two (10 × 10 × 15) cm^3 prismatic specimens were tested for each mixture proportion. After removing the molds, the concrete specimens were wrapped in a plastic film to prevent any contact with the environment and they were cured for 7 days in a moist room. Subsequently to the referred aging, the specimens were weighted and placed in a weathering chamber to reach the balanced humidity of the acclimatized room, based on the regular weightings until reaching a constant mass. On every test date (180, 210 and 240 days) the concrete specimens were taken out from the carbonation chamber and crushed. Afterwards, the freshly broken surface of concrete was treated with a solution of phenolphthalein in diluted alcohol. Free calcium hydroxide colored pink while the carbonation portion remained uncolored when the broken surfaces were treated with the aforementioned solution. The extent of carbonation was measured after 20 min. Four measurements were made for each specimen, from each side of the broken prism, with a 0.5 mm approximation. For each sample the thickness of carbonation sample was the average value of the referred four measurements.

Results and discussion

Mechanical properties

Table 2 shows the results of density, compressive strength and splitting tensile strength from the control and the copper slag concrete.

The density of hardened concrete increased with the addition of copper slag because the residue shows higher specific gravity than the Portland cement. An increase of 2.4% was observed for the COB20%-50 concrete when compared to the REF50.

The ANOVA test showed that both the copper slag addition and the water/cement (w/c) ratio had a significant effect on compressive strength and splitting tensile strength resulting on a p-value < 0.00001. It was

Table 2 Unitary mixture proportion (by weight) of concrete mixes

MIX	Unitary mixture proportion (by weight)				Copper slag
	Cement	Fine aggregate	Coarse aggregate	Water/cement	
REF40	1	1.36	1.46	0.40	–
REF50	1	2.04	3.16	0.50	–
REF60	1	2.72	3.87	0.60	–
COB20%-40	1	1.36	1.46	0.40	0.2
COB20%-50	1	2.04	3.16	0.50	0.2
COB20%-60	1	2.72	3.87	0.60	0.2

REF01—Control mixture (without copper slag)

COB 20%—20% copper slag concrete

Table 3 Density, compressive strength (CS), splitting tensile strength (STS), absorption rate by capillary suction, absorption, and the mean depth of the carbonation front of the concrete mixes

Mix	Density (kg/dm^3)	CS—C.V. (MPa) (%)	STS—C.V. (MPa) (%)	Absorption rate (g/cm^2 h$^{1/2}$)	Absorption (%)	Carbonation		
						Mean thickness (mm)		
						180 days	210 days	240 days
REF40	2.52	38.70 (4.31)	3.90 (6.78)	5.08	3.98	0.0	0.0	0.0
REF50	2.48	28.10 (2.96)	3.23 (6.44)	8.44	4.43	0.0	1.0	5.0
REF60	2.46	22.00 (1.82)	2.95 (7.10)	13.30	5.20	9.0	17.5	21.0
COB20%-40	2.58	39.60 (1.54)	4.40 (4.55)	4.62	3.82	0.0	0.0	0.0
COB20%-50	2.54	34.80 (6.08)	3.80 (5.26)	7.46	4.23	0.0	0.0	1.0
COB20%-60	2.49	28.70 (3.51)	3.20 (6.25)	10.09	4.50	0.0	7.5	13.5

C.V.—Coefficient of variation (%)

observed an interaction between copper slag addition and w/c ratio with a p-value < 0.00001. Yet, a different behavior was observed to splitting tensile strength, which shows a p-value equal to 0.19957 for the interaction between copper slag addition and w/c ratio.

The concrete compressive strength increased with the use of copper slag admixture. The increasing rate of compressive strength is higher for high w/c ratios than for low ones. It was observed that for w/c = 0.40, w/c = 0.5 and w/c = 0.6 the increasing rate of copper slag concrete compressive strength is respectively 2.3%, 23.8% and 30.4% at 28 days. Accordingly, splitting tensile strength increased with copper slag admixture to all w/c ratios. Nevertheless, the increasing rate of tensile strength was lower than the rate of compressive strength, and it was higher to low w/c ratios. The increase in splitting tensile strength was about 17.6% for the 0.40 w/c ratio, whereas for the 0.60 w/c ratio it was about 8.5%.

Copper slag concrete showed an enhanced mechanical performance because two main factors: (i) the chemical reaction between copper slag and calcium hydroxide, that was up to the amount of products of hydration, basically calcium silicate hydrate; (ii) the filler effect of copper slag grains. These small particles have a beneficial effect on matrix and interface zone densification, which provides porosity reduction and improve concrete performance.

Durability properties

Table 3 shows the results of the absorption rate by capillary suction, absorption, and carbonation depth test. All copper slag concrete batches have shown a reduction on absorption (linked to total porosity) and absorption rate by capillary suction.

It was observed that the absorption reduction was 13.5% for COB20%-60. Similarly, the absorption rate by capillary suction on COB20%-60 showed the same behavior. In this case, the absorption rate by capillary suction was 24.1% lower for COB20%-60 when compare to REF60. The copper slag concrete presented a decrease in porosity. It is related to filler and pozzolanic effect activity that fills copper slag concrete microstructure space promoting reduction and discontinuity of capillary pores and packing matrix. These features contributed to pore refinement by increasing the amount of smaller pores and decreasing the amount of the bigger ones.

Carbonation depth was assessed at 240 days of exposure to 5% of CO_2 concentration. Table 3 presents the results obtained from this test. Copper slag concrete had a decrease in advancing carbonation front, 80% and 35.7% for 0.50 and 0.60 w/c ratios, respectively. These suggest that copper slag concrete has a lower diffusivity of CO_2 because of the denser structure of the hardened copper slag cement paste when compared to ordinary Portland cement.

Conclusions

This paper has demonstrated the suitability of copper slag as a supplementary cementing material for use in concrete production. The following conclusions may be drawn from this study:

- The addition of copper slag to concrete results in an increase on the concrete's axial compressive and splitting tensile strengths;
- It was observed that a decrease in the absorption rate by capillary suction, absorption and carbonation depth in the copper slag concrete tested improved its durability.

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