PROPERTIES OF CONCRETE CONTAINING WASTE COPPER SLAG AS A FINE AGGREGATE REPLACEMENT

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ABSTRACT

Copper slag is a voluminous waste material obtained during the manufacturing of copper (matte smelting process). To obtain one tonne of clear copper approximately 2.2-3 million tonnes of copper slag are produced. The disposal of this waste becomes a concern for environmental protection agencies and governments; thus possible alternatives to the disposal of this material are needed. Some researchers suggested copper slag as a potential suitable candidate for the partial or full replacement of aggregate in concrete. To date a limited research has been performed on this topic in particular as types of copper slag vary according to the cooling process used and so is the experimental evidence reported for the resulting concrete containing each of these types of slag.

The presented research performed a laboratory study on CEM-I concrete mixes, containing water-cooled copper slag waste material as a partial to full replacement of fine concrete aggregate. A series of tests were then performed at two different water to cement ratios to investigate the influence of copper slag content on salient concrete properties including workability, cube compressive strength, tensile splitting strength, static modulus of elasticity in compression, flexural strength and surface water absorption.

Water-cooled copper slag was found to have variable effects on the resulting concrete properties, depending on the sand replacement level and water to cement ratio; however most mixes with copper slag gave concrete with adequate properties, with the optimal sand replacements by water-cooled copper slag overall being in the region of 30-60%. Based on the results water-cooled copper slag can be considered to be a suitable candidate for the partial replacement of fine aggregate in concrete. This shows promise for developing an additional viable solution to tackle the issue of copper slag waste.

Keywords: industrial solid waste management; copper slag aggregate; concrete properties

1. Introduction

Copper slag (CS) is a waste material widely obtained from the industrial sector in the manufacturing of copper during the matte smelting process. When copper liquid settles down in the smelter due to its higher density, the smears of copper slag remaining on the surface (also in liquid form) are removed and cooled. Slow air-cooling creates a hard and crystalline product while fast cooling in water produces amorphous, glassy granulates (Shi *et al*. 2008). It is estimated that 14.98 million tons of copper are produced every year (Shanmuganathan *et al*. 2008), and that to obtain 1 ton of clear copper 2.2-3 million tons of copper slag are produced (Shi *et al*. 2008). Thus utilization and disposal of this waste material becomes a concern for environmental protection agencies and governments. Due to the increasing problem, studies on this material showed many possibilities of how it could be reused or recycled. At present copper slag is predominantly used for the recovery of metal or employed as an abrasive material and for abrasive and cutting tools, railway ballast, tiles, glass and roofing granules (Gorai *et al*, 2003). Some researchers also considered copper slag as a good candidate for the replacement of aggregates in concrete and probably also as cement replacement due to its physical and chemical properties (Gorai *et al*, 2003). In addition copper slag has been excluded from the listed hazardous waste category of the United States Environmental

Protection Agency as well as the United Nations (UN) Basel Convention on the Transboundary Movement of Hazardous Waste and its Disposal (De Britto and Saikia, 2013). Further studies confirmed that the heavy metals present in the slag are stable and are not likely to dissolve significantly even through repetitive leaching under acid rain in a natural environment, and that the highest concentration of all the elements is far below the prescribed limits in USEPA 40CFR Part 261(Shanmuganathan *et al*. 2008).Thus there would be no serious concerns regarding the leaching of toxic elements if copper slag was used in large-scale construction. This is promising, as concrete is the most widely used material in construction after water, thus providing an ideal opportunity for the recycling of waste materials in large quantities. However compared to other waste materials suggested as concrete aggregate, copper slag appears to be less well researched. Some limited studies were performed but these are not sufficient to give confidence in the industrial scale use of this material. In addition either air cooled or water-cooled copper slag were studied by researchers as concrete aggregates (either fine or coarse) further reducing the amount of the available experimental evidence for each type of slag and aggregate respectively. In general aggregate properties influence the freshly mixed and hardened concrete properties. Concrete aggregate must be clean and free of objectionable materials, which can affect the bonding of the cement paste to the aggregate or be corrosive to metal reinforcement. It must be strong, hard and durable, uniformly graded and falling within certain upper and lower bounds of grading. For a material to be considered as aggregate for concrete production, the minimum requirements of workability, strength and durability of the resulting concrete should also be met. Further studies are thus required to assess whether concrete with copper slag would satisfy these requirements. To address this research need, a comprehensive experimental programme was set out to study salient properties of concrete with water cooled copper slag used as concrete sand replacement. The experimental procedures and main results are described in this paper.

2. Experimental procedure, material and mixes

For this study water-cooled copper slag was supplied by ScanGrit (brand name ScanGrit Iron Silicate Grade 5 i.e. of particle size ranging 0.2 mm-2.5 mm). According to the supplier's description it is an inert synthetic mineral manufactured by granulation in water of the slag arising from unique fumed copper smelting processes. It is an iron silicate with trace metals bound in an amorphous glass in the form of complex silicates and oxides and contains no free silica. Its detailed chemical composition according to the supplier is presented in Table 1. Other physico-chemical characteristics as determined in the supplier's datasheet are shown in Table 2. A main observation from Table 1 is that the copper slag has a much higher specific gravity than the natural mineral aggregate (uniform river sand) whose specific gravity tested during this research by the pycnometer method was found to be 2.65. This could cause some segregation in the concrete mixes containing both types of aggregate.

The particle size distribution of the copper slag compared to the river sand aggregate used in the mixes was determined using the dry sieving test (see Fig 1). It can be seen that the two materials had a very similar grading, with D_{90} of 1.2 and 1.6 for the copper slag and sand respectively, D_{50} of 0.47 and 0.54 for the copper slag and sand respectively and D_{10} of 0.22 for both materials, a coefficient of uniformity of 2.91 and 2.51 for the slag and sand respectively, and a fineness modulus of 2.97 for the slag versus 2.98 for the sand. This confirms the suitability of the slag for use as fine concrete aggregate from the point of view of gradation.

Concrete was made with a mix design of 1:1.5:3 (1 part cement; 1.5 parts sand and 3 parts coarse aggregate). The cement used was CEM I Portland cement strength class 52,5N obtained from Hanson – UK (brand name: Castle High Strength 52,5). The mix design was according to BS 5328: Part 1 guidelines for RC40 (BSI, 1997). Copper slag was used at increasing percentages per total sand mass to replace regular concrete sand. Mixes without copper slag were also made to serve as control mixes. The dry materials comprising cement, sand (or copper slag) and coarse aggregate were well mixed before the water was gradually included. Two different sets of mixes were made with water/cement (w/c) ratio of 0.55 and 0.45 respectively. For consistent comparisons when assessing the effect of the copper slag on the different concrete properties, the w/c ratio was kept constant when the sand was partly or fully replaced by copper slag (i.e. w/c of 0.55 and 0.45 respectively for the two sets of mixes). The workability of all fresh mixes was then assessed using the slump test. Specimens to be used for hardened concrete properties were then cast in moulds and compacted using a vibrating table. The compacted specimens were demoulded 24 hours after casting and placed in a steel tub of water, to cure at a minimum temperature of 20^{o}C for the required curing time. A number of tests on the hardened mixes were then performed, including cube compressive strength (100mm cubes), splitting tensile strength, surface water absorption characteristics, static modulus of elasticity of cylinders in compression and flexural strength test. The results of each test are shown in the following sections.

Table 1: Chemical composition of the copper slag used in this study

Chemical Composition	**%**
SiO_2	33.0 - 38.0
FeO	43.0 - 55.0
Al_2O_3	3.0 - 7.0
CaO	1.0 - 4.0
MgO	1.0 - 2.0
Na_2O	0.1 - 0.5
K_2O	0.1 - 0.5
Cu	0.5 - 0.7
Mn	0.2 - 0.4
TiO_2	0.1 - 0.25
Pb	0.01 - 0.20
Zn	1.0 - 2.0
S	0.5 - 1.0
Cr (III)	0.1 - 0.24
Cr (VI)	nil
Free Silica	< 1.0

Table 2: Physico-chemical characteristics of the copper slag used in this study

Physical state	Solid, angular
Colour	Black, glassy
Odour	None
Specific gravity	3.3 kg/dm^3
Bulk density	1.7 kg/dm^3
Hardness	7 – 8 Mohs
Conductivity of aqueous extract	<15 mS m^{-1}
Chloride content	<15 ppm

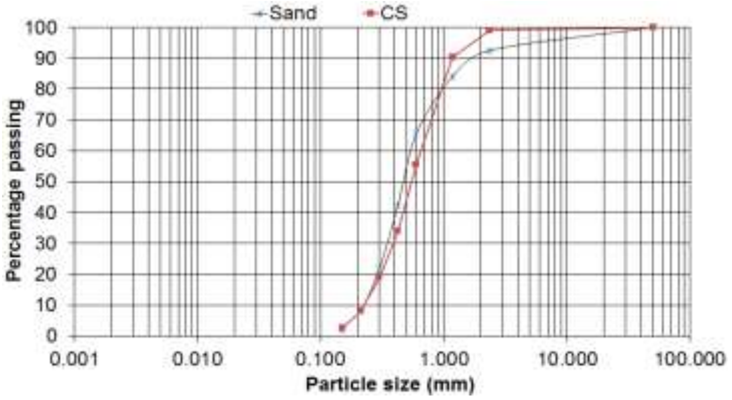


Figure 1: Particle size distribution of copper slag compared to the sand used in the tests

3. Experimental results

3.1. Slump test

As mentioned above, a possible anticipated difficulty when using aggregate other than that recommended for concrete could be the effect on the workability of the fresh concrete. Slump tests were performed according to BS EN 12350-2:2000 (BSI, 2000a) to assess concrete workability. Figure 2 presents results of the slump tests for each copper slag percentage for the two different w/c ratios used. These showed that all 0:55 w/c mixes had very high slump and hence workability. However in most cases the slumps of mixes including copper slag were similar or lower to those of the control mixes, against the original assumptions made that the lower water retention of the copper slag aggregate would cause higher slumps than those of the control mixes. In fact in two instances the copper slag mixes showed lower slumps than the control mix, however without a particular pattern concerning the decreasing or increasing sand replacement. Namely the 30% and then 100% showed the same, lower slumps compared to the control mix, whereas all other mixes with sand replacements between 30 and 100% showed lower or higher values of slump without any particular trend. Interestingly these two copper slag percentages of 30% and 100% showed consistently the same and comparatively much lower slumps in both the 0.55 and 0.45 w/c ratios but it is difficult to explain why this happened consistently for these two particular copper slag percentages. It is possible that slumps were affected to some extent by some segregation and bleeding of the mixes which were variable according to the w/c and copper slag content.

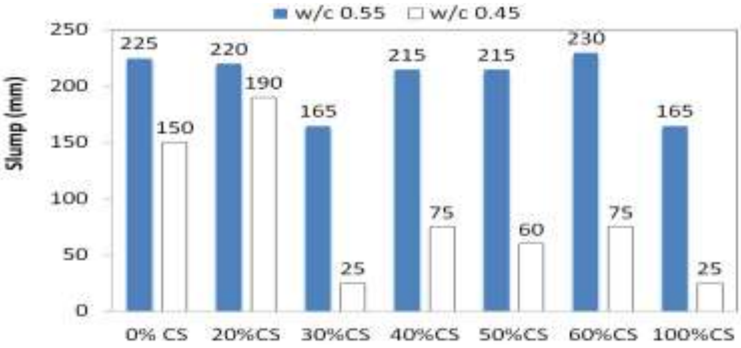
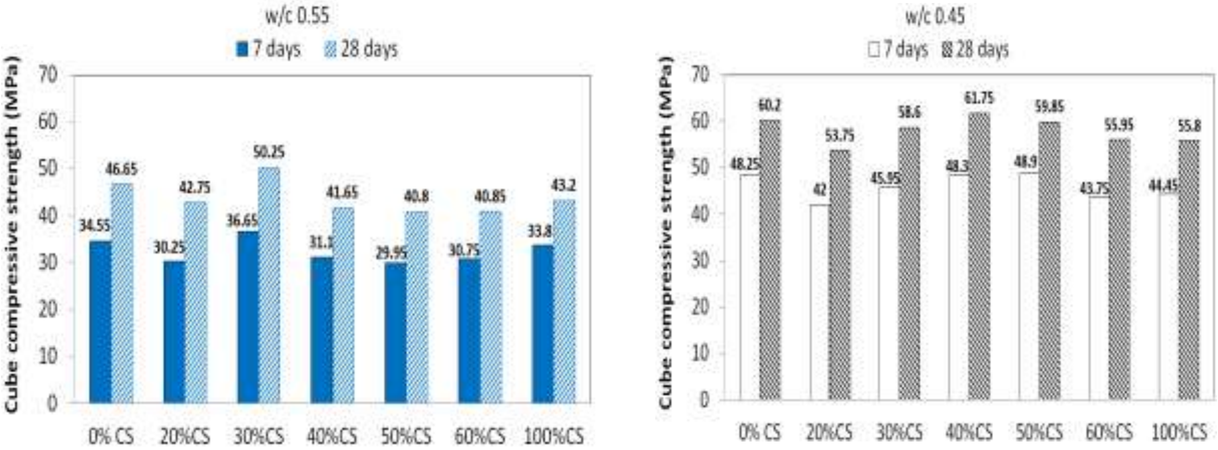


Figure 2: Slump test results

3.2. Cube compressive strength tests

These were performed in a Zwick Roell ToniPACT II 2000kN compression test plant according to BS EN 12390-3:2002 (BSI, 2002). Figures 3 (a) and (b) show the average cube compressive strengths for 7 and 28 days of curing for mixes with w/c=0.55 and w/c 0.45 respectively.



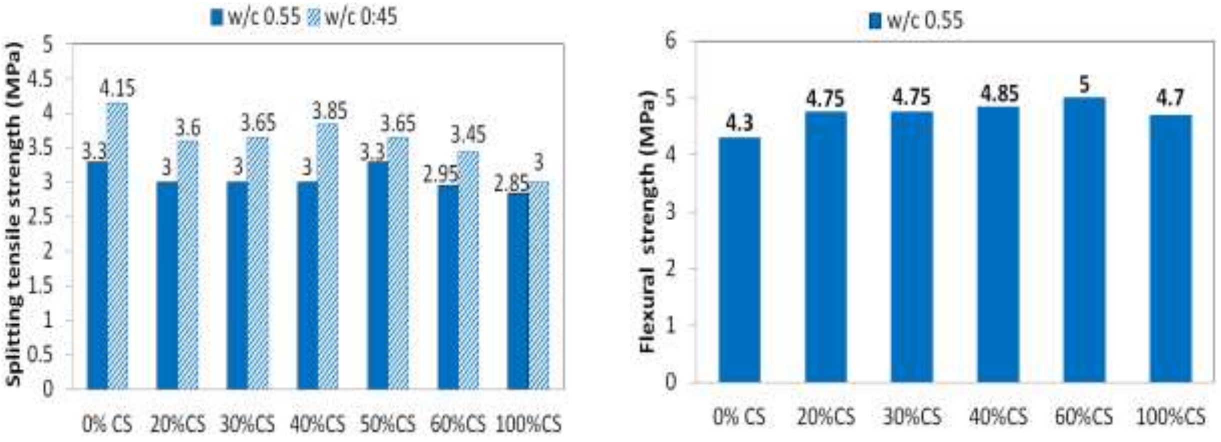
(a) (b)

Figure 3: 7 and 28-day curing compressive strengths of mixes: (a) w/c=0.55; (b) w/c=0.45

Both Figures 3(a) and (b) show that compressive strengths of the mixes with copper slag are generally lower than those of the control mix with one exception for each w/c ratio (for both w/c rations the 30% copper slag mixes consistently have higher strengths than the control mix). Although of lower strength than the control mix (with the exception of the 30% copper slag mix), the strengths of the mixes with the lower w/c ratio are generally closer to those of control mix for all copper slag percentages. The smaller differences in strengths with respect to the control mixes of 0.45 w/c ratio, especially at 28 days curing, could be due to a usual variability in the concrete batches around a mean value, rather than showing any significant trends. This implies that with the selection of appropriate w/c ratios, the sand can be successfully replaced by copper slag in concrete.

3.3. Tensile strength tests

The tensile strength of mixes was determined based on two indirect testing methods: (a) the tensile splitting strength of 150 mm diameter and 300 mm height cylinders tested according to BS EN 12390-6:2009 (BSI, 2009b) using the Zwick Roell ToniPACT II 2000kN compression test plant (b) the flexural strength, also known as Modulus of Rupture (MoR), determined from two-point flexural strength tests on selected mix beams of 500mm length and a section of 100mm x100mm according to BS EN 12390-5:2009 (BSI, 2009c). This test concerns strength in tension of a beam or slab and shows when cracking will develop upon bending. It is therefore relevant for structures such as highway and airfield pavements loaded in bending and hence designed on the basis of the flexural strength of concrete. The splitting tensile strength results are consistent with the compressive strength results (i.e. generally lower or in one case equal strength values are noted) except that in this case the 30% copper slag mixes also showed a lower strength than the control mix, as opposed to compressive strength results. The values of the splitting tensile strength were about 7% of the value of the respective compressive strengths as was the case in the control mix. Conversely, a clear increase in the modulus of rupture (MoR), was observed in all copper slag mixes in comparison to the control mix.



(a) (b)

Figure 4: Indirect tensile strength tests: (a) splitting tensile strength; (b) Flexural strength

3.4. Static modulus of elasticity

The static modulus of elasticity E_c was determined on 28-day cured cylinders with w/c 0:55, according to BS 1881-121:1983 (BSI, 1983). This is a property crucial to the long-term serviceability of concrete. The E_c values of cylinders with various percentages of copper slag, shown in Fig. 5 had the same or higher modulus of elasticity than the control mix, with one exception only (but even then, the E_c was close to that of the control mix), which gives further confidence in the use of this aggregate in concrete.

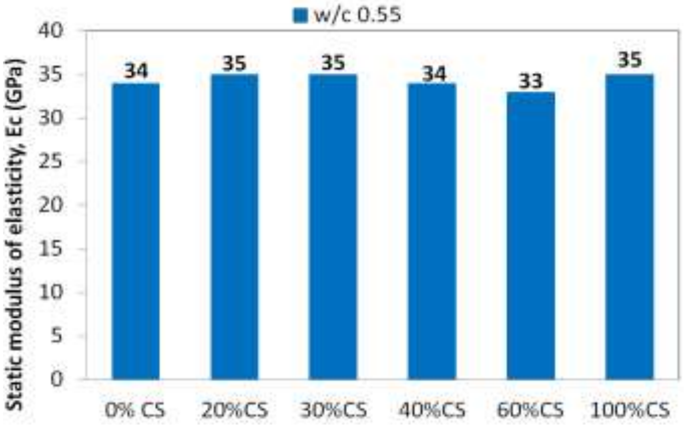


Figure 5: Static modulus of elasticity of 28 day-cured beams (w/c: 0.55)

3.5. Surface water absorption tests

The test was performed on 72h oven-dried 100 mm^3 concrete cubes (cured for 28 days), which were subsequently left to cool in a dry air-tight vessel for 24 h. The cubes were then completely immersed in water for 30 min. Surface moisture absorption was calculated as the increase in the mass of the cube upon immersion, expressed as a percentage of the mass of the dry cube. The average absorption results of duplicate specimens are shown in Figure 6. It can be seen that all mixes with copper slag had a slightly increased water absorption compared to the control mixes, with the exception of one mix for each w/c ratio (30 and 40% slag respectively for the 0.55 and 0.45 w/c ratio) which had the same water absorption as the respective control mix. A possible explanation for this is that as the copper slag is not hydrophilic some water voids are formed around the copper slag aggregates which increase the porosity of the mix; this then leads to an increased absorption when the dried concrete is subsequently re-immersed in water. It should be noted however that despite the slight increase in water absorption all mixes maintained low water absorptions of 3% or less.

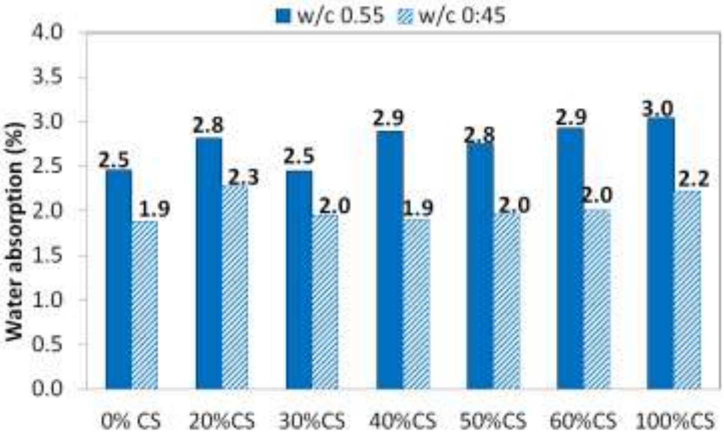


Figure 6: Water absorption of 28-day cured cubes

4. Conclusions

From the results it was shown that overall, mixes with the tested copper slag percentages had workability, strengths and moduli of elasticity comparable to those of normal concrete. Based on these findings it can therefore be concluded that this type of aggregate can be used as a substitute for natural sand, as none of the recorded properties appeared to present any significant changes with respect to the control mixes with natural concrete sand. An area that would need further investigation is possible effects linked to corrosion of metal reinforcement due to the iron oxide content of this aggregate. Other long-term durability data of concrete with this aggregate would also be necessary to produce this material at an industrial scale with confidence. Eventually, as for any other cases where unconventional materials are suggested for use in concrete, the viability of using this aggregate in concrete will depend on local economics, i.e. cost, availability of the material in sufficiently large quantities and availability and costs of similar natural aggregates in the respective regions where concrete production plants operate. Nonetheless with the depletion of the natural aggregates the use of suitable alternative aggregates based on waste materials should be encouraged as a potentially more sustainable option overall.

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