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Use of Copper Slag from Lubumbashi as Partially Replacement of Sand in the Concrete

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Abstract

Copper metallurgical slags are solid wastes resulting from the copper extraction process through pyrometallurgy. These granulated materials, dumped in the center of the city of Lubumbashi, contain certain "trace metal elements (ETM)" and/or "heavy metals" and are subjected to aerial leaching during the dry season, causing air pollution, and to leaching by rainwater, which leads to the contamination of the surrounding soil and surface water. The objective of this work was to use these slags, poor in recoverable elements (Cu, Co, Zn, Ge, and Ga), as fine aggregates for partial replacement of sand in concrete. The slags studied are of the ferrosilicate type belonging to the SiO_2-FeO-CaO (MgO-Al_2O_3) system. They are completely vitreous, and their grain size distribution ranges from 0 to 3 mm. For this study, crushed sand with a granulometric distribution similar to that of the slags was chosen. The Bolomey method was used to optimize the sand content of the concrete as well as to calculate the optimum amount of water for concrete production. Once optimized, the sand was replaced with slag at respective rates of 0%, 25%, 50%, 75%, and 100% by weight. The compressive strengths of the hardened concretes based on these slags were measured at 1, 3, 7, 14, and 28 days of curing with a W/C (Water/Cement) ratio of 0.6. Slump tests of the fresh concrete were conducted to characterize the influence of sand replacement by slag on the concrete's workability. The durability of the concrete with the optimized slag content was studied in corrosive solutions of HCl (5% wt), H_2SO_4 (3% wt), and Na_2SO_4 (1% wt). The results show the possibility of replacing crushed sand with slag up to a maximum rate of 50% by weight. The use of copper slag as sand decreases the cement's water demand and therefore increases the value of the concrete's mechanical strength. It was found that the optimum W/C ratio that allows for acceptable workability of the slag-based concrete is around 0.49. The durability study of the slag-based concretes in various corrosive solutions showed better performance of the slag-based concrete in the presence of H_2SO_4 and Na_2SO_4 solutions. Using the slag as a fine aggregate densifies the concrete structure, improves its workability by decreasing its W/C ratio, and increases its mechanical strengths while improving its resistance to corrosive environments.

Keywords

Concrete, Copper Slag, Sand Replacement, Water/Cement Ratio, Mix Design, Pouzzolanic Reaction

1. Introduction

The global usage of concrete is approximately 25 billion tonnes per year, making it one of the most commonly used construction materials [1] [2]. Its design flexibility, availability, and reasonable cost contribute to its predominance in the construction industry. It is used in both structural applications, such as buildings, bridges, roads, and dams, and non-structural applications like curbs, pipes, and drains [3]. Although its importance as a construction material remains uncontested, concrete is energy-consuming [4]. For instance, producing a cubic metre of ordinary concrete typically requires between 300 and 500 kWh of energy, used for the extraction, transportation of raw materials, cement production, mixing, and transporting the concrete. Additionally, its direct CO_2 emissions, the main greenhouse gas, are estimated to be between 200 and 500 kg per cubic metre [5]. The majority of these emissions (about 90%) come from the production of Portland cement, used as a binder in concrete, with the remainder originating from the extraction of raw materials such as clay, limestone, gypsum, aggregates, sand, etc [2] [4] [5]. Efforts are underway to develop more sustainable alternatives, like incorporating fly ash, blast furnace slag, pozzolans, and other industrial by-products to reduce the carbon footprint of concrete. Fine and coarse aggregates can occupy 55% to 80% of the volume of concrete [6]. The increasing consumption and decreasing availability of fine aggregates (sand) raise their cost and provoke serious environmental concerns with well-demonstrated consequences [7].

Various industrial activities result in the production of by-products generated in large quantities which have little or no industrial applications, leading to major challenges in managing and disposing of these wastes [4] [8]. These include blast furnace slag, fly ash, and copper metallurgical slags. The use of blast furnace slag and fly ash has been widely studied as cement admixtures or as aggregates in concrete [9] [10]. Their uses depend on their form (granulated or not), structure (crystalline or amorphous), and chemical composition (hydraulic and/or pozzolanic properties) [2] [11].

Copper slag (CS) is a by-product of the copper smelting process. For every tonne of copper produced, about 2.2 tonnes of slag are generated [8] [12]. In 2013, the global production of these slags was estimated at 24.6 million tonnes per year, a figure that has now reached 40 million tonnes per year. These materials may contain heavy metals, posing a potential environmental risk. In the Democratic Republic of Congo, more than 14 million tonnes of copper processing residues accumulated between 1924 and 1992 [2]. This accumulation is not without consequences; they contain heavy metals such as zinc (Zn), nickel (Ni), lead (Pb), cobalt (Co), copper (Cu), as well as trace metal elements like vanadium (V), manganese (Mn), chromium (Cr), titanium (Ti), arsenic (As), zirconium (Zr), molybdenum (Mo) [2] [11] [13] [14]. These metal elements can have significant effects on human health, ranging from allergies and skin irritations to neurological and respiratory disorders. Metals like lead and arsenic, which are particularly toxic and carcinogenic, affect the nervous system and various organs. While some metals, like zinc and copper, are essential in small doses, their excess can lead to health problems. Effective management and strict regulation are essential to minimise these risks [15]-[26].

The production of copper slag in the DRC is achieved by rapidly cooling with pressurised water, obtaining a solid, glassy, granulated material with a size ranging from 0 to 3 mm. Due to their amorphous structure and small size, these materials are potentially reactive. In landfills, they can be subject to dispersion, leading to leaching, which releases these metal elements, or the dispersion of fine particles by wind, which can be inhaled by neighbouring populations and carried over long distances by strong winds.

To mitigate the environmental impact of copper slags (CS), various effective management strategies are implemented worldwide. Among the most common are recycling to recover residual metals and the use of slags as raw materials in clinker manufacturing, as additives in cement and asphalt, or as aggregates in construction [4] [6]-[10] [27]-[30]. These practices reduce the need to extract new resources and stabilise heavy metals and/or metal elements within the hydrated cement matrix [31]. In this work, the use of copper slags as an aggregate in concrete was chosen, although studies on their use as an active additive in cement have been addressed.

Numerous studies on the use of copper slags as fine aggregates in concrete or mortar have shown positive results [8] [28] [32]. According to these studies, the workability of concrete improves as the proportion of slags increases [9] [28] [32]. Other research has revealed an increase in compressive strength when sand is replaced with slags, up to 50% by weight [28] [32]-[35]. However, other studies highlight a trend toward decreasing compressive strength depending on the amount of copper slag used. It has also been shown that the durability of concrete and mortar improves when copper slags are used appropriately as fine aggregates [33] [35]-[37]. These studies underline the potential for integrating copper slags into concrete, highlighting both the benefits and challenges associated with this innovative approach.

This study aims to analyse how the partial integration of copper slags from Lubumbashi (DRC) influences the mechanical properties and durability of concrete, with the goal of determining their viability and sustainability as a substitute for sand in the fabrication process.

This research seeks to analyse the impact of incorporating copper slags into concrete on its physico-mechanical properties and durability. First, we will collect data to characterise the copper slags as well as the locally used crushed sand by conducting granulometric (aggregates, sands, and slag), chemical, and physical analyses. Next, we will prepare a reference concrete using the Bolomey method to optimise parameters such as cement content, aggregates, sands, and the water/cement ratio. Then, concrete mixtures will be prepared by gradually substituting sand with 0% (control mix), 25%, 50%, 75%, and 100% slag by weight. Slump tests on fresh concrete for all these concrete mixtures were conducted for a w/c ratio of 0.55. Mechanical strength tests on hardened concrete mixes were performed at curing periods of 1, 3, 7, 14, and 28 days for the same w/c ratio.

Once the optimum sand substitution rate is determined, the influence of the w/c ratio on the slump of concrete C-CS50 as well as its mechanical properties is studied. Finally, tests were conducted to evaluate the resistance of concrete C-CS50 in aggressive environments (with 5% by weight of H_2SO_4, 5% by weight of HCl, and 1% by weight of Na_2SO_4) by measuring the mass losses and mechanical strength values after a 7-day exposure (w/c = 0.45).

By integrating copper slags in cement matrices, it is possible to reduce the environmental footprint of concrete construction while providing a waste management solution for the copper pyrometallurgical industry in the DRC. This approach contributes to a circular economy, where waste materials are converted into useful resources, reducing the need for virgin raw materials and the ecological impacts associated with their extraction and processing. This paves the way for more sustainable and ecologically responsible construction solutions.

2. Materials and Methodology

2.1. Materials

2.1.1. Cement

The cement used for this work is a Portland Cement of type CEM II/A-L 42.5 R elaborated according to the ISO 9001:2008 standard. This cement is one of the most used cements in construction industry in Lubumbashi, Democratic Republic of Congo.

2.1.2. Coarse and Fine Aggregates

Coarse and fine aggregates used in this study were taken from Roche Congo quarry near the city of Lubumbashi, DRC. Three types of coarse aggregate were used, namely 3/6, 6/12 and 12/25 (d/D; d—being the smallest dimension of aggregate and D—the biggest dimension of the aggregate). The fine aggregate used was crushed sand (0/3.15 mm). This crushed sand is mainly used in concrete mixtures in this region.

2.1.3. Copper Slag

The slag used in this work was collected from a slag dump site of a local company that processes the Lubumbashi slag heap to produce copper and cobalt. The CS is granular and amorphous in structure, blackish in color with a vitreous break. The grains of this slag are sharp-cornered. The chemical composition of this slag determined by ICP-OS (Inductively Coupled Plasma Optical Emission Spectrometry) and its X-ray diagram are provided in **Table 1** and **Figure 1**, respectively [38]. The used slag is almost entirely amorphous and presents a few peaks of ZnO which can act as a set and hardening retardater. Its chemical composition is rich in SiO_2, Fe_2O_3 and other elements such as Al, Mg and Ca.

Table 1. Chemical composition of slag [2].

	MgO	Al_2O_3	SiO_2	CaO	ZnO	V_2O_5	PbO	Cr_2O_3	MnO	FeO	Fe_2O_3	CoO	NiO	CuO	$\sum M_nO_m$ [1]
% wt	6.9	7.3	39.9	13.5	4.1	0.03	0.3	0.05	0.1	21.5	3.4	0.5	0.03	0.2	3.45

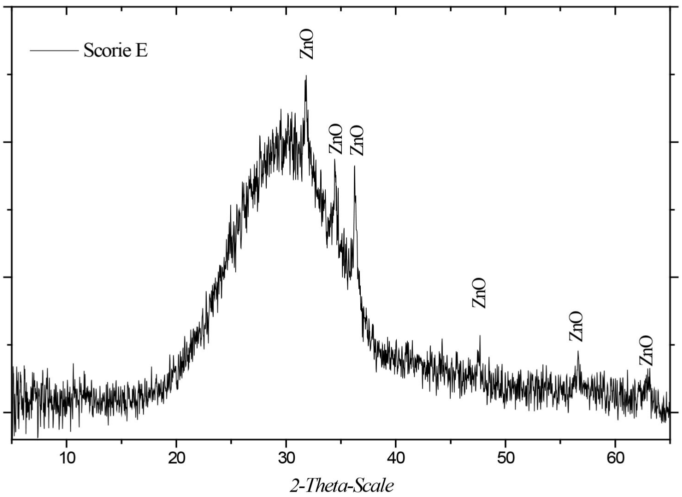

Figure 1. X-ray diagram of copper slag [2].

2.2. Methodology

In this work, all the concrete specimens formulated for the various tests were 15 × 15 × 15 cm. The concretes were made from aggregates of the following sizes: 12/25, 6/12, 3/6, 0/3.

After mixing in a concrete mixer, the concrete was poured into a 15 × 15 × 15 cm mold, and then vibrated on a shaking table for 60 seconds twice. The specimens were left in the open air, and then demolded after 24 hours. Once demolded, the specimens were stored at ±25˚C in water until the testing deadline. For each test, the average mechanical strength was obtained from the values of three specimens prepared and stored under the same conditions.

To study the influence of granulated slag on compressive strengths crushed sand were substituted by CS at a rate of 25, 50, 75 and 100% by weight. The curing times of concretes formulated at different sand and CS rates were 1, 3, 7, 14 and 28 days respectively, for a w/c ratio of ~0.55. At each sand/slag substitution rate, the Abrams cone slump of the fresh concrete was determined. This parameter was used to characterize the influence of slag on concrete workability. Based on the

[1] $\sum M_nO_m = Ga_2O_3 + SrO + ZrO_2 + K_2O + SO_3 + TiO_2 + P_2O_5$

results of the mechanical strength values and the substitution rate, the optimum value for the substitution rate of sand by CS was obtained. Based on this value, concretes containing 50% by weight of slag were made, and the E/C ratio was varied from 0.6; 0.55; 0.50 and 0.45. Based on the slump values of the fresh concrete at the Abrams cone and the mechanical strength values, it was possible to find the optimum E/C ratio value. Once the E/C value had been found, three series of three specimens of the concretes containing the optimum slag value were prepared for an E/C ratio of 0.45 and cured for 7 days. After this period, one series of 3 specimens was placed in a 5% wt. sulfuric acid solution, a second in a 5% wt. HCl solution and the last in a 1% wt. sodium sulfate solution for 7 days. The aim of this test was to characterize the resistance of concretes consisting of the optimum value of slag to aggressive solutions of mineral acids and a sulfated salt. After 7 days' exposure to these aggressive solutions, the specimens were cleaned with water, and then dried in the sun for 30 minutes. The dried specimens were then weighed, their volumes determined, and crushed to determine their mechanical strengths.

3. Experimental Study

In addition to the binder testing, several analyses were performed for each material used for this study in order to get its physical characteristics.

3.1. Physical Characteristics of Fine and Coarse Aggregates

The following tests were carried out for fine aggregates such as sand and copper slag:

- Sieve analysis in accordance with NF P 18-560 [39].
- Absolute density test in accordance with NF P 18-554 [40].
- Water absorption test in accordance with NF P 18-555 [41].
- Los Angeles abrasion test was performed for the coarse aggregate in accordance with NF P 18-573 [42].

Physical Characteristics of Copper Slag, Fine and Coarse Aggregate

Density, water absorption and Los Angeles abrasion values are shown in **Table 2**. The densities of Coarse and fine aggregate varied between 2.4 and 2.5 g/cm^3. For cement and CS, the density was 3.2 g/cm^3. As for the absorption, the sand has a relatively higher absorption rate than the other aggregate, which explains the important water demand to wet each grain of sand. Concerning CS, the water demand will be low.

Table 2. Physical properties of aggregates and cement.

	Density g/cm^3	Water absorption %	Los Angeles abrasion value
Cement	3.2	-	-
Copper slag	3.2	0.185	-
Sand 0/3	2.4	3.82	-
Gravel G3/6	2.5	1.91	-
Gravel G6/12	2.5	1.91	-
Gravel G12/25	2.4	1.91	24.3

Figure 2 shows the grading of sand and CS particle size. It is noted that their grading are similar making easier the replacement of sand by CS.

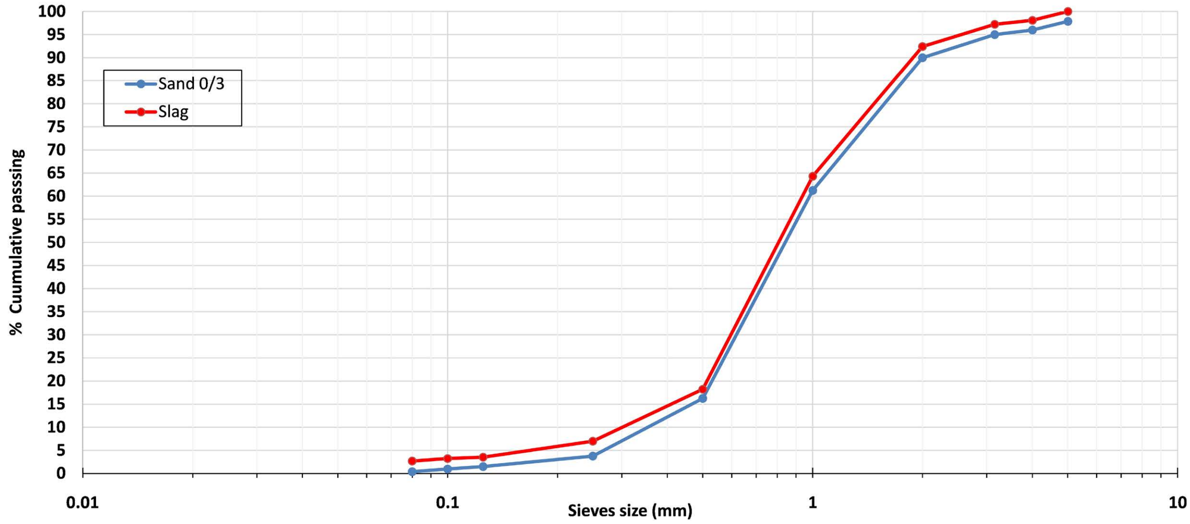

Figure 2. Particle size distribution of copper slag and sand.

3.2. Mix Design and Sample Preparations

The aim of this mix design was to determine the proportions of water, coarse and fine aggregate in one cubic meter. Bolomey's concrete design method was used [43].

Based on coarse and fine aggregate curves and reference line in green illustrated on Figure 3, the composition of a cubic meter of concrete have been calculated with cement content of 350 kg. Table 3 gives the composition of the concrete per cubic meter using Bolomey method. The fine aggregate will occupy 42% of the mass of a cubic meter. The coarse aggregate of G3/6, G6/12 and G12/25 will occupy respectively 15,5%, 31.5% and 11% of the mass of a cubic meter.

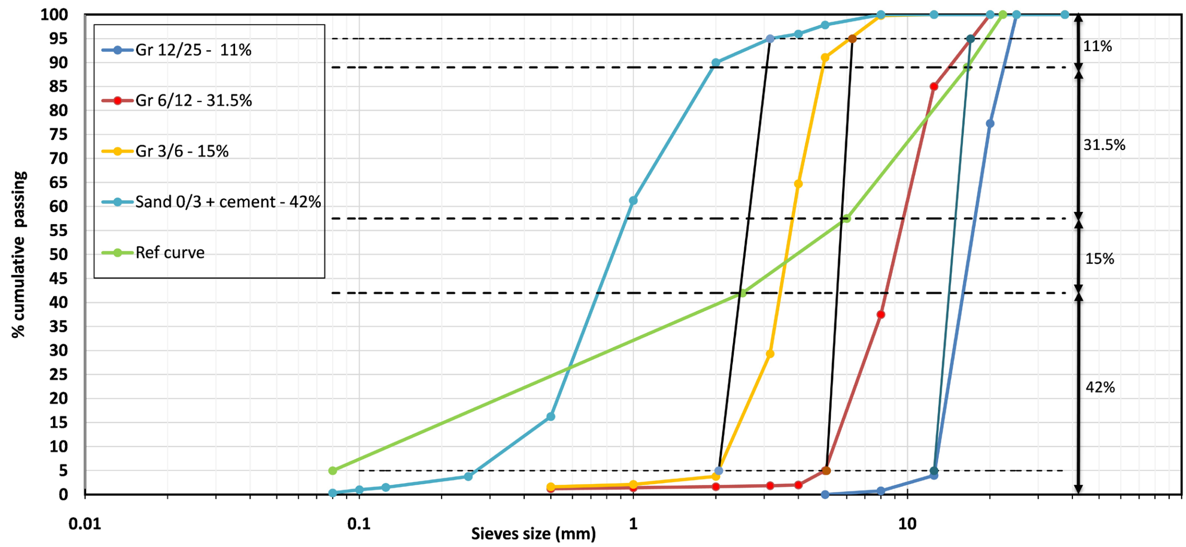

Figure 3. Particle size distribution of fine and coarse aggregate.

Table 3. Concrete composition.

Components	Components by mass (g)	Absolute density g/cm³	Volume components (cm³)	concrete in g/cm³	Percent by mass %	Component in kg
1	2	3	4	5	6	7
			2/3		2/Σ2	5 × 6/100
Cement	16	3.2	5	108.702/47.91 = 2.268~2.3 g = 2300 Kg/m³	14.71	338
Sands	26	2.4	10.83		23.92	550.16
G 3/6	15.5	2.5	6.2		14.26	327.98
G 6/12	31.5	2.5	12.6		28.98	666.54
G 12/25	11	2.4	4.58		10.12	232.76
Water	8.702	1	8.7028		8.01	184.23
Total	108.702		47.91		100	2299.61

The five concrete mixes were prepared with different percent of CS substitution starting from 0% to 100% at an increment of 25%. Control mix was designated as C-CS0 where C stands for Concrete and CS0 stand for 0% substitution with CS representing Copper Slag. The proportions of cementitious content of 350 kg/m³ and coarse aggregate were kept constant for all mixes at constant w/c ratio of 0.55.

The concrete mixtures with different proportions in percentages of copper slag used as replacement for fine aggregate (sand) were prepared in order to investigate the behavior of copper slag substitution on the compressive strength of concrete. Five concrete mixtures with different proportions of copper slag as replacement of fine aggregate were prepared. The proportions, by mass, of copper slag as a replacement of fine aggregate were as follows: 0% (control mix), 25%, 50%, 75% and 100%.

Fresh concrete of each mixture underwent slump test to measure consistency or relative ability of the concrete to flow in according with NF P 18-451 [44].

The determination of the compressive strength of concrete was obtained by casting fifteen concrete cubes samples (150 mm × 150 mm × 150 mm) for each concrete. The sample were removed from the mold after twenty-four hours and immersed in water for curing. The samples were conserved in water over period of 1, 3, 7 14 and 28 days. The Compressive Strength test was conducted in such a way that the sample was loaded under compressive stress until first crack appears. Three Sample per mixture were crushed and the mean value of the result constituted to final result for each mixture.

4. Results and Discussion

4.1. Fresh Concrete

Figure 4 shows the variation of fresh concrete slump with the rate of slag replacement. The highest slump value of 83 mm was obtained for C-CS100 whereas the lowest value of 15 mm was recorded for C-CS0. It is observed that as the rate of substitution of fine aggregate by CS increases, the workability of concrete increases. This phenomenon was observed in previous studies [28] [34] [35] [43]-[45]. The replacement of sand, a material with a high-water absorption coefficient, by CS, whose coefficient is very low, leads to an increase in the water of hydration of cement and an improvement in the workability of concrete. One of the direct consequences of this phenomenon is the increase in the reactivity of the cement and the cement-CS system. For very high sand substitution rates, the physical properties of the fresh concrete (setting time), as well as the early mechanical strengths, are likely to be negatively affected.

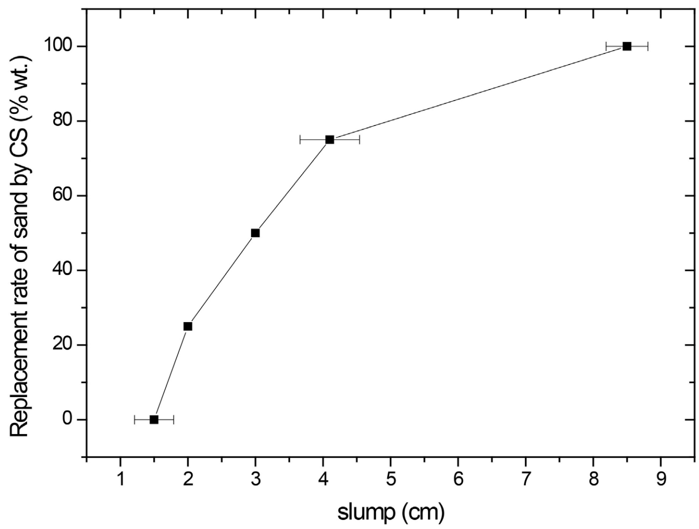

Figure 4. Slump.

4.2. Compressive Strength of CS Concrete

Figure 5 shows that, at any curing time, the compressive strength of the concrete increases with the sand substitution rate. It is also observed an increase in compressive strength from C-CS0 to C-CS50. Beyond 50% of substitution, the mechanical strength decreases. The compressive strength value of C-CS100 is 34% less than that of the control mix C-CS0 at 28th water curing day. The increase in mechanical strength with the rate of substitution of fine aggregate by CS can be attributed to the increase in the reactivity of the cement-slag system as the CS content increases. Indeed, when the CS content becomes significant in the concrete, the hydration water of the cement also increases. The calculation of excess water presented in **Table 3** indicated the increase in this hydration.

As shown in **Table 3**, the values of the mechanical resistances increase up to an excess of water of 13% in mass. Beyond that, the mechanical strength values decrease. The increase in mechanical strength up to 13% could be attributed mainly to a chemical process.

The increase of the reactivity of the cement causes an increase of the portlandite (CH) released during the hydration of the cement. The presence of a significant proportion of this compound allows the partial reaction of CS grain surfaces following a pozzolanic reaction:

$$\text{Slag}\left(\equiv \text{Si-O-S} \equiv\right) + \text{CH}\left(\text{OH-}\right) \rightarrow \text{C-S-H} \quad (1)$$

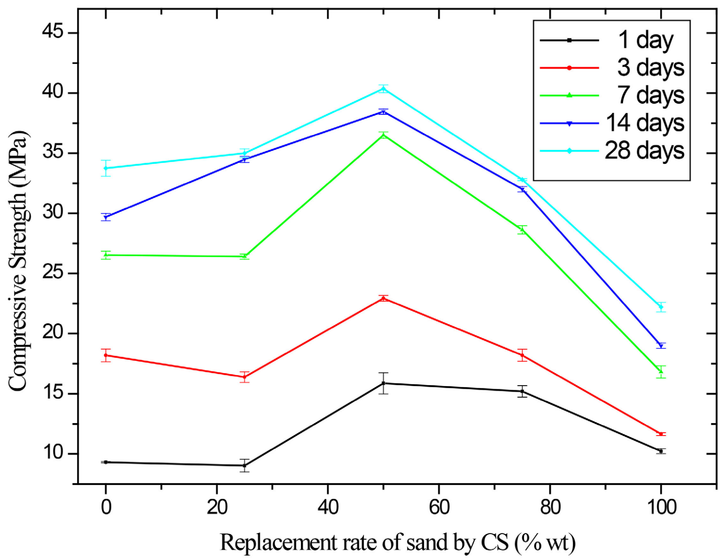

Figure 5. Mechanical strength CSC.

With this 13% excess of water, it appears that the CS grains do not release sufficient Zn^{2+} ions from their glasses to slowed down the hydration of the cement and thus negatively affect the mechanical strength property of the concrete. The increase in mechanical strength values is therefore attributed to the partial hydration of the slag grains, which provides an additional quantity of C-S-H that refines the microstructure of the concrete (porosity).

Above 13% excess water by mass, the reactivity of the cement increases considerably during the first hours of hydration, probably leading to a greater release of Zn^{2+} ions that delay the hardening of the concrete. A greater excess of water also leads to a large quantity of pores in the concrete, which decreases the mechanical strength values at all curing times.

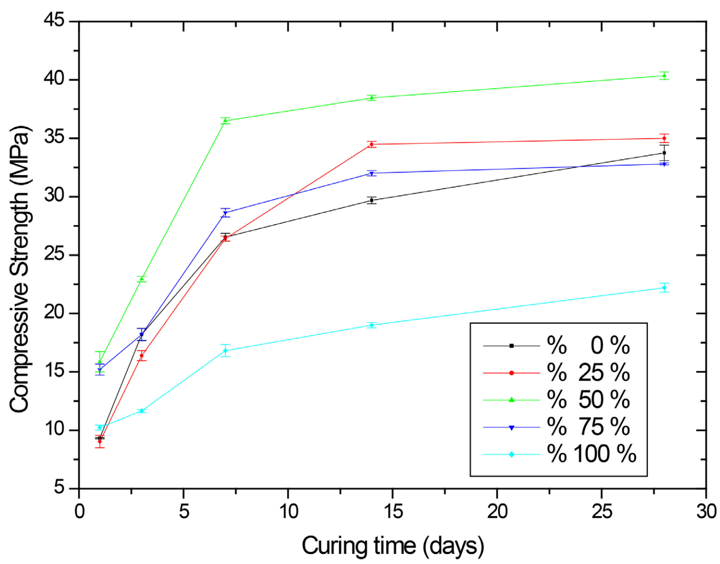

Figure 6. Evolution of the mechanical resistance to compression as a function of the cure time.

Figure 6 shows the evolution of compressive strength as function of curing time. It is observed that the mechanical strength values increase steadily with the curing time. The increase was rapid during the first 7 days of curing. Beyond 7 days, the increase in mechanical strength slowed down. The increase during the 7 curing days of hydration is due to the presence of anhydrous cement which hydrates rapidly. This implies the formation of a larger quantity of hydration phases and therefore a rapid increase in mechanical strength. After 7 days, the hydration phases densify the microstructure of the concrete. As a result, the resulting hydration reactions are controlled by diffusion reactions through the dense hydration layers of the hydration products (C-S-H).

4.3. Influence of the Water-Cement Ratio on Slump and Mechanical Strength of C-CS50 Mix

Since it was found that the mix C-CS50 (concrete made with 50% of slag replacement) showed better mechanical resistance, it was also important to check the C-CS50's w/c ratio influence. The aim is to get the optimum w/c ratio. The w/c ration ranged from 0.45 to 0.60 with an increment of 0.5.

4.3.1. Influence of Water-Cement on Workability

Figure 7 shows the influence of water-cement ration on slump. The result showed that the highest slump value of 40 mm was reached with w/c ratio of 0.60 followed by 30 mm, 15 mm and 5 mm respectively for w/c ratio of 0.55, 0.50 and 0.45.

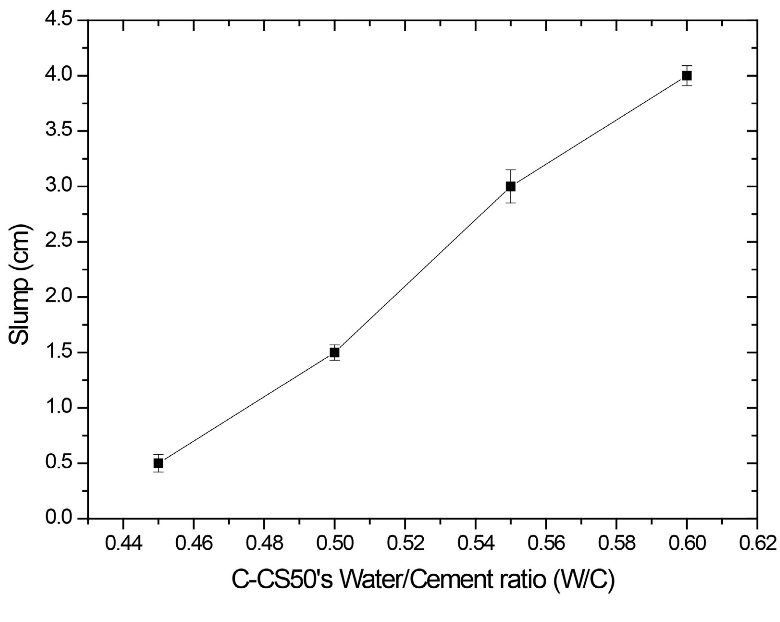

Figure 7. Influence of w/c ration on slump.

It was observed that the water content of hydration decreases caused a decrease in workability subsequently a decrease in concrete slump. This was related to the fact that by decreasing the w/c, there is a reduction of water allowing to play the role of "lubricant" between the aggregates. The plasticity was strongly reduced.

4.3.2. Influence of the Water-Cement Ratio on the Mechanical Strength of Concrete

The results in Figure 8 indicate an increase in the mechanical strength of the concrete as the w/c ratio decreases. At a w/c ratio of 0.45, the mechanical strength value reached about 43 MPa after 7 days of curing. However, with a w/c ratio of 0.60, the value obtained was 33.5 MPa at the same curing time. The increase in mechanical strength with decreasing w/c is attributed to the reduction of pore space in the concrete. Based on the value of the Abrams' cone slump test and the mechanical strength, a w/c ratio of 0.45 would be ideal for the production of a concrete of improved quality. However, the low workability may make it difficult to cast the concrete on site. Therefore, calculation must be used to determine the optimum value. Table 4 shows the calculated values of the w/c ratio for the 5 different concrete mixes.

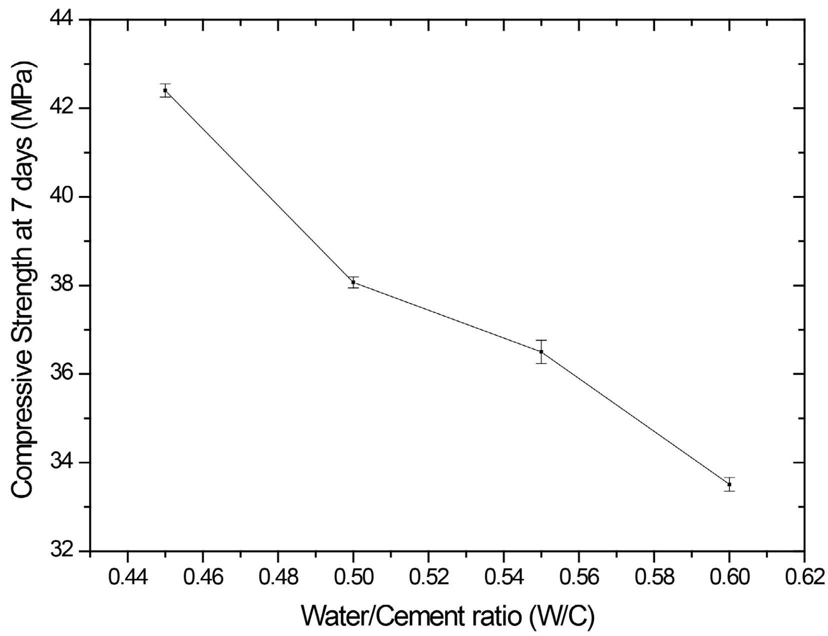

Figure 8. Influence of w/c ration on mechanical strength (7 days).

Table 4. Excess of water.

	0% CS	25% CS	50% CS	75% CS	100% CS
Excess water %	0	9.39	13.14	18.78	22.53

From Table 5, it was found that the w/c ratio of 0.49 is suitable to obtain a concrete workable and easy to cast on-site when it contains 50% substitution of fine aggregate by mass of the slag. Therefore, if reference is performed to model the relationship compressive strength versus w/c, which is represented by the exponential model: $\sigma_c = 82.217e^{(-1.496E/C)}$, the predicted mechanical strength at 7 days is only 39.5 MPa, which is a reduction of approximately 3 MPa from a w/c ratio of 0.45 to 0.49. As for the slump, using an exponential model (w/c = $0.4367e^{0.079l}$: l representing the slump) by fitting the results obtained, a value of the slump of 1.45 cm for a w/c ratio of 0.49 was found.

Table 5. Evaluation of the E/C ratio as a function of the substitution rate.

	Rate of replacement of sand by slag				
Mix	C-CS100	C-CS75	C-CS50	C-CS25	C-CS0
w/c	0.53 (0.55)	0.5	0.49	0.48	0.47

4.4. Durability

The results of durability show the values of the mass and volume loss after immersion of the concrete specimens in the solutions of 5 wt% H_2SO_4, 5 wt% HCl and 1 wt% Na_2SO_4.

4.4.1. Mass and Volume

It appears from **Figure 9** that the losses of mass and volumes of the concretes depend on the chemical solutions used to attack the concrete. In sulfuric acid, the mass loss registers an average of about 2.8%, after 7 days of immersion, or 0.4% per day. In the presence of hydrochloric acid, the mass loss corresponds to about 6%, or ~0.9% per day. As for the Na_2SO_4 solution, no mass variation was observed.

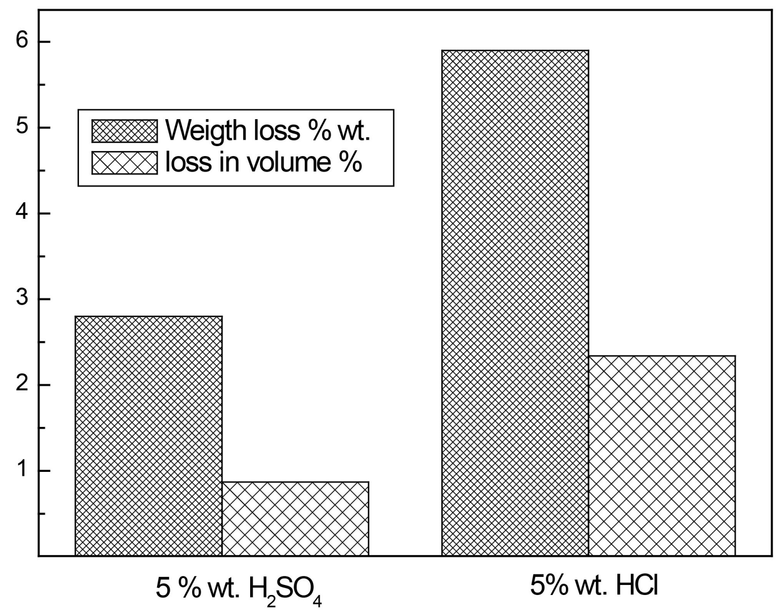

Figure 9. Mass and volume loss in % of concrete cubic specimen in H_2SO_4, HCl and Na_2SO_4 solutions.

To explain the mass variations in sulfuric and hydrochloric media, it is important to refer to the visual appearance of the specimens after their immersion in these two solutions. The photographs presented in **Figure 10** and **Figure 11** give the visual aspects of these concrete specimens.

In the case of the H_2SO_4 solution, the surface of the cube specimen is attacked.

The aggregates as well as the hardened cement paste are eaten away at the surface. A white substance is formed on the surface on the concrete specimens as shown in **Figure 10(b)** which tends to hide the visible pores of the concrete. The substance formed is probably gypsum ($CaSO_4 \cdot 2H_2O$) with a whitish color. Its formation is a combination of Ca^{2+} ions from C-S-H (also from CH) and SO_4^{2-} ions from the acid.

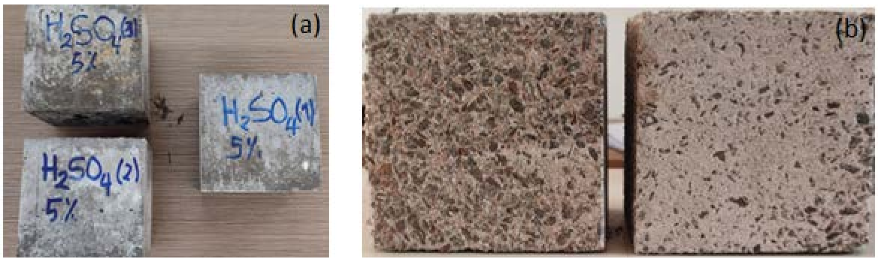

Figure 10. Cubic specimens 15 × 15 × 15 cm^3 of concrete based on 50% slag. (a) After 7 days of curing in water (b) Cubic specimens 15 × 15 × 15 cm^3 after 7 days immersion in 5% by mass of H_2SO_4.

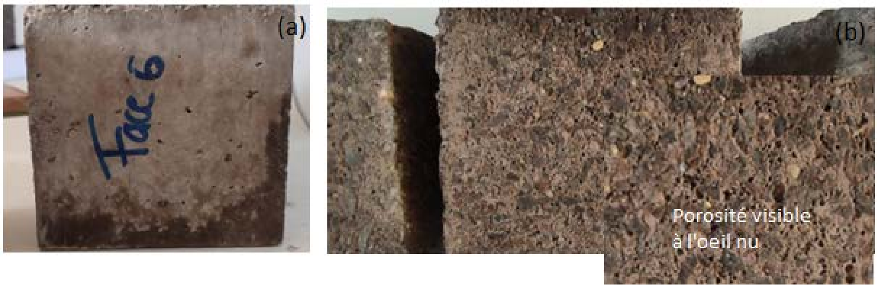

Figure 11. Cubic specimens 15 × 15 × 15 cm^3 of concrete based on 50% slag. (a) After 7 days of curing in water (b) Cubic specimens 15 × 15 × 15 cm^3 after 7 days immersion in 5% by mass of HCl.

In the presence of HCl, the surface of the concrete is also corroded without the formation of a whitish substance on its surface **Figure 11**. However, there are several pores on the surface of the concrete immersed in the HCl solution that are visible to the naked eye. This suggests the attack of the concrete in depth by the HCl solution than by the H_2SO_4 solution. The explanation is that in the presence of HCl, no insoluble salts are formed on the concrete that could prevent and/or diminish the acid attack. In the case of HCl, the solution becomes progressively saturated with Ca^{2+} ions and its attack seem to be continuous and/or not delayed. This explains a great loss of mass of the concrete in this solution.

In the presence of 1% by mass of the Na_2SO_4 solution, no change in mass or volume was recorded in **Figure 12**. In principle, when concrete is exposed to SO_4^{2-} ions, the ions attack the aluminate phases to give secondary ettringite which swells the concrete and destroys it [46]. The lack of swelling suggests that concrete containing 50 wt% slag sand is less porous at the w/c ratio of 0.45. This low porosity comes from the action of the slag on the CH which produces additional C-S-H that strongly refines the microstructure of the concrete [2].

Figure 12. Cubic test tubes 15 × 15 × 15 cm^3 of concrete based on 50% slag. Immersion of 7 days in 1% by mass of Na_2SO_4.

4.4.2. Mechanical Strength

It was found that the concrete specimens immersed in hydrochloric acid showed a lower average mechanical strength of 31.07 MPa, than the one immersed in H_2SO_4 and Na_2SO_4 solutions. The concrete immersed in solutions H_2SO_4 and Na_2SO_4 had average mechanical strength respectively around 40 MPa and 49 MPa as indicated in **Figure 13**. These different mechanical strength values are related to the recorded mass losses. For large losses, the mechanical strength is low compared to the strength at 7 days cure in lime-saturated water. In sulfuric acid, the value found is slightly lower than that of the specimen cured at 7 days in the lime-saturated solution. The attack of H_2SO_4 on the surface allows to leach the cementitious paste (and also the anhydrous cement) which plays the role of glue on a small depth of the concrete, which leads to a less resistant structure. For concrete immersed in HCl, its attack in depth and creates several large pores (voids) led to a decrease in mechanical resistance values. In Na_2SO_4 medium, the hydration processes of the anhydrous phases of the concrete and the change of microstructure of the C-S-H seem to evolve normally as in water saturated in lime. This can only be possible if the resulting concrete is less porous.

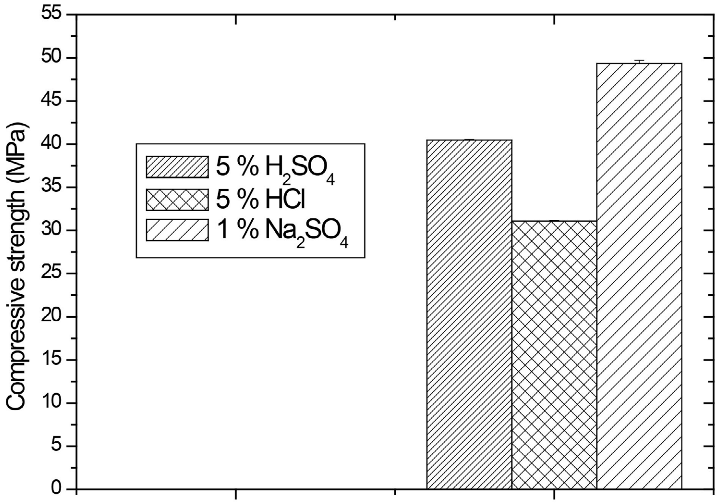

Figure 13. Evolution of the mechanical resistance in different solutions at 7 days.

5. Conclusions

In light of the experimental results obtained, it is evident that using slag as a partial substitute for sand in concrete formulation offers notable advantages in terms of workability and mechanical strength. The granulometric analysis has shown that slag can effectively replace sand without compromising the required grading, while its low water absorption coefficient enhances the workability of the concrete. The results indicate a significant improvement in mechanical strength with a slag substitution rate of up to 50%, achieving an optimum beyond which strength decreases. The beneficial effect on workability is also reflected in an increase in the slump at the Abrams cone. However, it is important to note that excessively high substitution rates can negatively affect the initial strength of the concrete. Moreover, compressive strength was slightly affected by exposure to aggressive solutions of H_2SO_4 and HCl, but not in the case of Na_2SO_4 solution. This highlights the importance of the initial configuration of materials to ensure durability.

Therefore, the concrete incorporating copper slag studied could be particularly suitable for applications where workability and mechanical strength are crucial, such as floor slabs, pavements, or certain secondary structural elements exposed to limited aggressive environments. Additionally, its potential for sustainable development could make it attractive for ecological construction projects, such as green buildings or infrastructures using recycled materials.

Regarding prospects, long-term studies on the durability of slag concrete exposed to various aggressive environments are crucial to ensure its structural viability. The exploration of new additives could also enhance the mechanical properties of the concrete. Furthermore, an economic and environmental analysis is necessary to assess the sustainable development potential of this material compared to traditional options. Finally, on-site performance tests will allow the validation of laboratory results under real conditions, thereby facilitating a wider industrial application. These efforts could lead to innovations in the production of more durable and efficient concretes.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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