IMPACT OF CURING METHODS ON THE STRENGTH OF COPPER SLAG CONCRETE

By

CYNTHIA MUMEKA KYALIKA

submitted in accordance with the requirements

for the degree of

MASTER OF TECHNOLOGY

in the subject

ENGINEERING: CHEMICAL

at the

UNIVERSITY OF SOUTH AFRICA

Supervisor: Prof FRANCOIS MULENGA

October 2019

DECLARATION

Name: **CYNTHIA MUMEKA KYALIKA**

Student number: **65101588**

Degree: **MTech CHEMICAL**

Exact wording of the title of the dissertation as appearing on the electronic copy submitted for examination:

IMPACT OF CURING METHODS ON THE STRENGTH OF COPPER SLAG CONCRETE

I declare that the above dissertation is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

I further declare that I submitted the dissertation to originality checking software and that it falls within the accepted requirements for originality.

I further declare that I have not previously submitted this work, or part of it, for examination at Unisa for another qualification or at any other higher education institution.

SIGNATURE DATE

DEDICATION

This work is dedicated to my beloved husband **Gaylord YAV SONY**, who is my greatest friend and my true mentor. He has not stopped supporting me and pushing me to be the best;

To my son **Jamie-Mael SONY YAV** who is my source of motivation;

And to my parents **Jean-Louis KYALIKA** and **Brigitte KYALWE**. The assiduity and discipline that you instilled in me since my youth is what gave me the ability to reach my goals. Thanks for being such wonderful persons.

ACKNOWLEDGEMENTS

I would like to take this opportunity to thank a number of people who have helped me complete my research work:

- My great supervisor, Prof. **Francois MULENGA**, for his professional guidance and mentorship;

- Mr. **Franck VAN DE WILLE**, Mr **Trevor HILLE** & Mr **Jeremy DAVEY** respectively Tenke Fungurume Mining managers for providing logistical support and the various authorizations necessary for carrying out the experimental work;

- Mr. **Charles LUMPUNGU**, Head of the Tenke Fungurume Mining Civil Engineering laboratory for his time and considerable help during the laboratory work;

- Mr. **KE LUTUMBA** for his advices and support. Thanks for being a precious elder and a friend;

- My friend Dr. **Sage NGOIE** for his smart directives.

ABSTRACT

The eco-friendly alternatives use is increasing momentum in a conscious effort towards sustainability. In this regards, the relevance and the economic value of using copper slag as a concrete aggregate are explored in this study in order to contribute towards metallurgical waste recycling. Emphasis is placed on the evaluation of the concretes strengthening prepared with copper slag contents and produced under four curing methods: water immersion, water spraying, plastic sheet covering and air-drying. In each curing case excluding for water immersion, was duplicated in indoors (i.e. in the laboratory) and outdoor exposure (so was prone to varying environmental conditions). This was specifically aimed at capturing the effects of tropical weather conditions typical of the Lualaba province in the Democratic Republic of Congo.

The control mix was designed to reach 25 MPa of compressive strength. Copper slag was successively incorporated as sand replacement at the following mass fractions: 20 %, 40 % and 60 %. Freshly mixed concrete samples were evaluated for workability. Cube specimens were cast accordingly, cured for 28 days and then tested for density and compressive strength.

Results indicated an increase in strength up to 20 % of replacement rate for all the curing methods. Further additions resulted in reduction in the strength, but the rate of reduction depended on curing conditions. The increase in strength was mainly credited to the physical properties of copper slag that could have contributed to the cohesion of the concrete matrix. It has been found that appropriate ways of curing can still achieve greater results than that of the control mix since 80 % of humidity is ensure. The two-way ANOVA test performed on the 28-days compressive strength values confirmed the significant influence of the curing methods, of copper slag content and the interaction between them. It has been found that considerable influence is attributed to copper slag content and that warm environmental conditions further extend the concrete strengthening.

Key words: concrete strengthening, cement hydration, compressive strength of concrete, concrete curing, curing methods, conventional aggregate, copper slag, copper slag concrete, statistical analysis, two-way ANOVA.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

A	:	Cross-sectional area in mm^2
AD-I	:	Air drying with inside exposure
AD-O	:	Air drying with outside exposure
ACV	:	Aggregate Crushing value
ANOVA	:	Analysis of variance
ASTM	:	American Society for Testing and Materials
A_w	:	Water absorption
C_3S	:	Tricalcium silicate
C_2S	:	Dicalcium silicate
C_3A	:	Tricalcium aluminate
C_4AF	:	Tetracalcium aluminoferrite
C&CI	:	Cement and Concrete Institute
CS0	:	Conventional concrete or control mix
CS20	:	Copper slag concrete related to 20% of replacement rate
CS40	:	Copper slag concrete related to 40% of replacement rate

CS60	:	Copper slag concrete related to 60% of replacement rate
D_{28}	:	28-day hardened density
DF	:	Degree of freedom
F_{cv}	:	F-distribution of critical values.
F_0	:	F-distribution of observed values
f_c	:	Compressive strength
f_{c28}	:	28-day compressive strength
$f_{cm}(t)$	:	Mean compressive strength at age *t* in days
H_0	:	Null hypothesis
H_1	:	Alternative hypothesis
IM	:	Immersion in water or water curing
k_1	:	Empirical constant
k_2	:	Empirical constant
M_{OD}	:	Mass of oven-dry specimen
M_{AW}	:	Mass of water that fully fills internal pores
M_{pyc+w}	:	Mass of pycnometer filled with water to calibration mark

$M_{pyc+w+sample}$	:	Mass of pycnometer filled with specimen and water to calibration mark
$M_{in\,water}$	:	Apparent mass of saturated test sample in water
M_{SSD}	:	Mass of saturated surface-dry specimen
MS	:	Mean square value
N	:	Samples number
P	:	Load at failure
PS-I	:	Plastic sheet covering with indoor exposure
PS-O	:	Plastic sheet covering with outdoor exposure
RD	:	Specific gravity
SS	:	Sum of squares of errors
S	:	Standard deviation
V_{28}	:	28-day volume
W_{28}	:	28-day cube masse
W	:	Moisture content
WS-I	:	Water spraying with indoor exposure
WS-O	:	Water spraying with outdoor exposure

$\bar{x}$	:	Mean value
ε_{ijk}	:	Random error component having normal distribution with mean 0 and variance σ^2
β_i	:	Effect of the j^{th} level of factor B
τ_i	:	Effect of the i^{th}level of factor A
μ	:	Overall mean effect
$(\tau\beta)_{ij}$	:	Effect of the interaction between factor A and factor B
ρ	:	Density
$\rho_{aggregate}$	:	Density of aggregate material

1. INTRODUCTION

1.1 BACKGROUND

Concrete can be regarded as the backbone for the development of infrastructure in many countries. Concrete is extensively used as construction material and continues to be in high demand due to its compressive strength, durability and ease of placement, and finishing (Kosmatka et al., 2003). However, the use of eco-friendly alternatives is gaining momentum in a conscious effort towards sustainability. Innovative waste recycling and recovery are being tested to mitigate the dual problem of disposal and environmental hazards.

In this respect, the suitability and economic value of copper slag have been explored for use as a component in the preparation of concrete. Copper slag is a discard of the pyrometallurgy processing of copper obtained during the matte smelting and converting process. It is a granular material rich in iron and containing various other oxides in small amount such as SiO_2, Al_2O_3 and CaO (Shi et al., 2008). It has been reported that copper slag has physical, mechanical and chemical properties comparable to that of conventional sand (Gorai et al., 2003) and that they have very pozzolanic properties due to their low CaO content. Therefore, its use as a cementitious material has been proposed under activation with NaOH (Brindha, 2011).

The inherent abrasion resistance properties make copper slag suitable for being incorporated into in concrete (Shi et al., 2008; Madheswaran et al., 2014). Despite the presence of heavy metals amounts in copper slag, leaching tests conducted under aggressive environments by various scientists indicate that these dissolved poorly to warrant concerns (Supekar, N., 2007; Shanmugananathan et al., 2008). In view of the above, there may be an opportunity to use copper slag in concrete and greatly contribute towards metallurgical waste recycling, current production being estimated at nearly forty (40) million tonnes (Prem and al., 2018; Babu and Ravitheja, 2019).

One limitation to the adoption of copper slag concrete resides in the uncertainty around the proper development of its strength in order to be structurally used. As construction material, concrete is good in resisting compressive load. Its ability to withstand compressive stress before failing is really pronounced (Perri, 2009). On top of that, the environment under which the concrete mix is prepared and cast has a great impact on the final quality of concrete. For concrete to harden properly until it reaches its required strength, curing is of critical importance to prevent or minimize the rapid loss of water by evaporation due to the exothermic reaction that takes place. Therefore, during the early age, internal moisture and temperature should be ensured (Raheem et al., 2013) and can be achieved by regularly spraying water onto the concrete. If not done properly, low hydration ensues which leads to increased number of cracks within the matrix and reduced strength of the final concrete.

It is against this background that the present research aims at assessing the compressive strength development of copper slag concrete. Different mix compositions were considered with copper slag added as sand while various curing schemes were tested. Inferential statistics was then employed to compare copper slag performance against conventional concrete. The findings reported in this dissertation are expected to find relevance in the construction industry where green low-cost concrete-based structures are in demand. Countries such as Chile, Zambia, and the Democratic Republic of Congo (DRC) may subsequently reclaim their abundant copper slag dumps and stockpiles as feedstock for the production of concrete.

1.2 PROBLEM STATEMENT AND PURPOSE OF THE STUDY

The choice of a suitable curing method for concrete processing is not a straightforward exercise. It is generally guided by carefully planned laboratory testing. To illustrate this, immersion of concrete in water has experimentally been argued to be the best curing method that would guarantee the highest strength and density (Jackson and Akomah, 2018; Usman and Isa, 2015; Safiuddin et al., 2007). This curing method has the advantage of providing enough water to cement hydration. However, in practice, concrete produced on site does not always enjoy dedicated water supply for curing (Princy and John, 2015). Even when water is readily available, weather conditions may gravely affect the quality of cured concrete (Raheem et al., 2013; Akinwumi and Gbadamosi, 2014).

Therefore, it was proposed to investigate the effects of different curing methods on the compressive strength of copper slag concrete. Copper slag has partially been added in the form of sand under different proportions. Three curing techniques were considered: immersion of concrete into running tap water, water spraying of concrete, and wrapping of concrete with a plastic sheet. The systematic study was expected to provide valuable insight into the design of medium-strength copper slag concrete.

1.3 RESEARCH QUESTIONS

The present work aimed first to examine the performance of copper slag as partial replacement of sand in concrete. Second, it was a question of identifying the most appropriate curing method for use in tropical regions. Concretes containing various proportions of copper slag was cured in variety of ways for 28-days and subjected to the tropical climate-type of the Lualaba province of the DRC. The curing methods consisted of air-curing, water immersion, water spraying, and plastic sheet wrapping to contain the moist.

The two research questions that were addressed as part of the experimental work are as follows:

- How strong and dense can concrete processed using locally-sourced copper slag be in comparison to conventional concrete?
- Do local weather conditions typical to the Lualaba province of the DRC and curing methods contribute significantly to the development of compressive strength of copper slag concrete?

To explore these questions, the physical properties of locally-source copper slag were characterised and benchmarked against conventional aggregate. Concrete mixes were then designed in such a way to ascertain the effect of gradual addition of copper slag on the workability and hardened density of concrete. Thereafter, compressive strength tests were conducted on the differently cured concrete samples. Finally, a two-way analysis of variance (ANOVA) was performed on the strength data. The research investigates the properties of copper slag concrete cured outdoors in tropical conditions typical of the Lualaba province of the DRC. The interest of this research in the Congolese context would be to demonstrate that such a concrete could well meet the demand for the development of infrastructure.

1.4 RESEARCH SCOPE

The current study is centred on an experimental work aimed at investing the effects of curing methods on the quality of copper slag concrete. Three curing methods were considered: water immersion, water spraying, and plastic sheet wrapping. The choice of the three curing methods was motivated by their widespread use and ease on-site implementation. A fourth method in which concrete was air-dried with no conventional curing was employed. The “uncured” concrete batch served the purpose of isolating the general effects of curing and local weather conditions. In each curing case except for water immersion, half of the samples were stored indoors in the laboratory while the remaining samples were stored outdoors. The latter group mimicked practical concrete production generally subjected to exposure to environmental elements. The purpose was to account for the influence of on-site weather conditions on concrete strengthening. In this regard, the experimental work was limited to studying the effects of humidity and of the ambient air temperature. The decision was primarily guided by available infrastructure for on-site testing.

Concrete mixes were prepared using sand partially replaced by copper slag in proportions of 0 %, 20 %, 40 % and 60 %. They were cured using the selected techniques: water immersion, water spraying, plastic sheet wrapping and air-drying until the testing day. Age was not investigated because of logistical limitations inherent to the Civil Engineering laboratory used for the purpose of this work. Curing was carried out over a period of 28 days only and compressive strength was measured afterwards with the understanding that concrete may reach 99 % of its mechanical strength as the improvement in strength is time dependent (Kosmatka et al., 2003; Neville, 2011). After curing, samples of copper slag concrete were subjected to compressive strength testing with corresponding data analysed later using appropriate statistical tools.

Many scientists considered the 28 days period as a reasonable time frame to characterize the concrete strength in concrete industry; so this has been incorporated in codes of practice in different countries (Kosmatka et al., 2003; Mehta et al., 2006). Another reason of this choice is related to cement hydration itself. It has been observed that after 28 days, most of the cements used to make concrete developed about 80% of their final strength (Mehta et al., 2006; Neville, 2011). Since significant hydration of the cement has already occurred at this age, therefore, the associated strength can be considered as an acceptable basis describing the final strength of the concrete. In addition, the choice of four weeks was also made so that tests and placement, fell on a working day (Neville, 2011).

In terms of the strength test itself, it should be noted the strength of any material may be determined in various modes: compression, direct and indirect tensile stress and shear stress (Perri, 2009). Concrete is acknowledged to be an excellent material under compressive loading that performs poorly under tensile loading (Kosmatka et al., 2003; Perri, 2009; Neville, 2011). As a result, this research was mainly focused on the 28-day compressive strength of the different mixtures prepared with copper slag as fine aggregate. The measurement was later used as an index of concrete quality and all other related properties.

After examining microstructure of concrete specimens with different copper slag contents, some previous investigators found that the mechanical behaviour exhibited by copper slag concretes was mainly influenced by the physical properties of copper slag (Wu et al., 2010). Others researchers found that copper slag contains low CaO and reported on its possible pozzolanic properties when activated with NaOH (Mobasher et al., 1996). Boakye (2014) investigated the chemical properties of the Katanga copper slag and found that this was not chemically a very reactive material. Hence this investigation was mainly focused on the impact of physical properties of copper slag on concrete strengthening, considering the above statements.

1.5 STRUCTURE OF THE DISSERTATION

The dissertation is organised in six chapters. The first chapter deals with the context that motivated this research, the problem addressed, the purpose and the scope. Finally, the structure of the dissertation is presented.

The second chapter reviews the fundamental aspects of concrete, which includes research published concerning the effect of different curing techniques on conventional concrete and the effect adding copper slag into concrete mix.

Chapter three describes the experimental plan, the equipment and testing rig used as well as the testing procedures followed. The data collected and underlying methodology are also presented in line with the objectives set for the research work.

Chapter four reports on the outcome of laboratory activities conducted during the experimental work described in Chapter three. First, the characterization test results physical properties obtained on copper slag, crusher sand and stone are presented. Second, the concrete properties in both fresh and hardened states are also reported.

Chapter five presents the impact of curing methods on the strengthening of concrete in which copper has partially been as added in place of conventional sand. Some discussions are provided to explain the observations made. Finally, the statistical analysis performed in order to test the simultaneous impact of adding copper slag into concrete mix and of the different schemes of curing on compressive strength data is presented.

The last chapter summarizes the important findings and their relevance. Areas for further research are also identified.

2. LITERATURE REVIEW

The great demand for concrete as a building material has led to numerous studies devoted to its final quality. Concrete strength and concrete curing are some of the topics that have been thoroughly investigated in the literature. In addition, questions pertaining to sustainable development have encouraged to the use of eco-friendly materials in concrete-making. A relevant example of this trend is the use of copper slag as the granular component of concrete.

This chapter presents the fundamentals of concrete as well as the key elements involved in the production of high-quality concrete. The associated literature survey entails an overview at the basic components of concrete, the physical and mechanical properties of concrete, the hydration reaction in concrete materials, as well as the purpose and types of curing used in concrete-making. Relevant studies are also examined to identify the extent of scientific work carried-out on the impact of different curing conditions on the concrete quality. Finally, copper slag suitability of as a granular material in concrete is examined on the basis of previous work.

2.1 FUNDAMENTALS OF CONCRETE PREPARATION

Concrete is extensively used as building material all over the world. The world consumes twice as much concrete as steel, wood, plastics, and aluminium combined (Kosmatka et al., 2003). The popularity of concrete can be ascribed to three factors: first, concrete has excellent wind and water resistance; second, concrete structural members can be easily poured to any desired shape and size; and third, the constitutive components of concrete are relatively inexpensive and can be easily obtained in many places around the world (Mehta and Monteiro, 2006).

Concrete is a composite material made up of fine and coarse aggregates embedded in binding medium made of a cement paste (ASTM C129). The cement paste is a mixture of cement powder and water. It binds the granular materials together into a compact stone as following the exothermic reaction between cement and water

Despite its compactness and density, concrete suffers from its low tensile strength compared to its compressive strength. It is also less ductile than industrial materials such as steel. This is why it is generally reinforced with steel bars so that structures can also withstand tensile stresses (Mehta and Monteiro, 2006; Kosmatka et al., 2003). However, its ability to withstand high temperature better and its slow deterioration amongst others, outweigh the above-mentioned limits. This is what puts concrete at the centre of the development of infrastructure from ancient civilization to modern civilization (Mehta and Monteiro, 2006).

Numerous types of concrete are available depending on the formulation used for the binding agent and the types of aggregates. These key components eventually determine the strength, the density, as well as the chemical and thermal resistance of the finished product. However, the choice of components for the design of the concrete mix is dictated by the intended application of the material. These various components are briefly presented in the following section as well as with the role they play in the concrete composition.

2.1.1 Concrete-making components

Concrete is made up of three basic components: cement, aggregates (gravel and sand) and water. As one of the key basic ingredients, cement is instrumental in defining the compressive strength of concrete. It acts as a "glue" that binds all other ingredients together. Alone, cement is not a binder; it develops the binding property through the hydration reaction in presence of water. Hydration is the chemical reaction through which the cement binds the aggregates together allowing concrete to set and harden (Mehta and Monteiro, 2006; Kosmatka et al., 2003; Neville et al., 2011).

There are various types of cement, but Portland cement is most often used in concrete preparation. Portland cement is basically made of two raw materials: calcareous and argillaceous materials. Calcareous materials are calcium oxide, such as limestone, chalk, or oyster shells. Argillaceous materials are a combination of silica and alumina that can be obtained from clay, shale and blast furnace slag (Mamlouk and Zaniewski, 2005). When heated to high temperature in the kiln, these ingredients form a rock-like substance called clinker. This substance is grounded into a fine powder together with a small amount of gypsum (4% to 6%), to produce the cement.

The interaction of calcareous and argillaceous materials in the kiln leads to the formation of four main chemical compounds of the cement: tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalciumaluminoferrite (C_4AF). In these shortened notations, 'C' stands for CaO; 'S' for SiO_2; 'A' for Al_2O_3 and 'F' for Fe_2O_3. These several compounds which represent 90% of cement by mass have their own hydration characteristics. In presence of water, they form different products that possess setting and hardening characteristics. So, over time, they produce a firm and hard mass (Kosmatka et al., 2003; Mamlouk and Zaniewski, 2005; Mehta and Monteiro, 2006; Neville et al., 2011).

Aggregates are the second key constituent of concrete; they are granular in nature. Materials that can be used as aggregate include sand, gravel, crushed stone or building and demolition rubble that when mixed with the binding agent, produce concrete or mortar. Aggregates are generally classified as fine and coarse. Fine aggregates consist of natural or manufactured sand particles smaller than 5 mm in size. The coarse aggregates are form of particles generally greater than 5 mm and generally between 9.5 mm and 37.5 mm. In Portland cement concrete for example, aggregates make up the bulk of the concrete mix. They represent 60 % to 75 % of the volumetric proportion of the mix which is approximately 70 % to 85 % of the weight fraction (Kosmatka et al., 2003; Mamlouk and Zaniewski, 2005).

Aggregates act as filler in the production of concrete; they reduce the amount of cement paste required in the mix. It is generally recommended to maximise the amount of aggregate for use in concrete. The reason for this is that aggregates have greater volume stability and are cheaper than cement paste (Kosmatka et al., 2003;

Mamlouk and Zaniewski, 2005). Therefore, it is understood that the properties of the aggregates used will largely influence the properties of concrete. Good quality concrete is produced with aggregates made of solid, durable and free from silts, organic matter and oils. The presence of these impurities can affect the hydration process of the cement.

Water is the last key component of concrete production; it is responsible for the hydration reaction. In this chemical reaction, cement undergoes structural change which hardens the concrete mix (Kosmatka et al., 2003). Hydration mechanism is explored in more detail in Section 2.2. Water needs to be of suitable quality so as not to harm the final properties of concrete. Almost any potable water with no pronounced taste or odour is suitable for avoiding unexpected effects on the setting time or on strength development (Goodman, 2009). This is why drives for eco-friendliness encourage the industry to resort to water sources unfit for human consumption. The specifications guiding the quality of water to be used in concrete are provided by the ASTM C1602 / C1602M standards (Neville, 2011).

Modern concrete mixtures see increased use of admixtures as the fourth component (Kosmatka et al., 2003; Mamlouk and Zaniewski, 2005; Mehta and Monteiro, 2006).The different properties of the fresh mixes and those of the finished material can be powdery or liquid. They are incorporated into the concrete mix to improve certain features that could not be achieved with ordinary concrete mixes. The common types include accelerators, air entraining agents, corrosion inhibitors, pigments, plasticizers, super plasticizers. These will not be reviewed as they are beyond the scope of the research study.

2.1.2 Key properties of concrete

Workability and compressive strength are the crucial properties of concrete respectively considered, in fresh and in hardened states. Workability is a property of freshly mixed concrete that characterises the ease with which the mix can be moulded or placed as desired, consolidated and finished (ACI, 2000). Any concrete mixture needs to be sufficiently workable to completely fill the forms and surround the reinforcement and other embedded items. Standards practices used to measure the workability usually rely on slump test which basically considers the slump of fresh concrete under its own weight. This is determined using a standard truncated metal mould filled with fresh concrete (SANS, 2006). The workability of concrete corresponds to slump value that results from the loss in height when the mould is lifted vertically.

The quality of the concrete is largely judged by its compressive strength. Indeed, concrete is a material known to take very well compressive loading. This explains why compressive strength is critical in the design and engineering of concrete structures. Heterogeneous and complex structure of concrete causes the concrete to be less resistive to tensile and flexural loading.

Concrete strength is a function of continuing cement hydration. The mechanism of this reaction is covered in detail in Section 2.2.

2.1.3 Preparation of concrete

The production of quality concrete mainly depends on the mix components. Factors related to preparation, production and quality control protocols also dictate the quality of concrete. These factors include the production and testing of raw materials, the portioning of concrete constituents to meet design requirements, the homogenisation and pouring of the mix, as well as moisture and temperature monitoring to promote strength and durability of the final concrete (Kosmatka et al., 2003).

Designing and proportioning, mixing and transporting, placement, as well as curing are acknowledged to have the greatest bearing on the final quality of concrete. Therefore, they are discussed in this section.

Concrete structures are designed and built to withstand a variety of loads while being exposed to cyclical wetting and drying, seawater, and acidic solutions amongst others (Kosmatka et al., 2003; Mehta and Monteiro, 2006; Neville et al., 2011). The objective of proper mix design is to ensure that fresh and hardened products exhibit properties dictated by the application intended for the concrete. The level of concrete strength is generally assumed based on the expected load to be carried and the environment to be exposed to (Addis and Goodman, 2009). The selected strength then dictates the choice and proportions of constituting materials for the production of concrete. So, in essence, the design and proportioning of concrete mixes is an empirical exercise, often done by trial and error. For example, cement content can be determined from the water-to-cement ratio, i.e. the weight ratio of the water to that of cement used in the preparation of a concrete mix.

The second most critical factor alluding to the preparation of concrete is mixing and transportation. Mixing is the process whereby all the components of concrete are physically stirred and combined into a homogeneous mixture. Concrete must thoroughly be mixed until it is uniform in appearance, that is, all the ingredients are evenly distributed (Kosmatka et al., 2003). Therefore, proper mixing should be such that samples taken throughout the batch essentially have the same density. After mixing, concrete must be transported to the site and placed within a reasonable time. The recommended time for the delivery and placement in mould of concrete after the addition of water to the mixture to meet the desired setting and hardening properties is 90 min as per ASTM C94 standard.

Third, three factors are successively considered: placement at the final position, consolidation and finishing. To select an appropriate placement method, it is necessary to take into account the concrete application, mix design, the size of the crew, the service environment and the economy (Kosmatka et al., 2003). Decrease in hardened strength can be caused by air trapped in the mixture. This occurs during the placement. A large part of this air can be removed by compaction, obtained by vibrating of the placed concrete. However, excessive vibration creates aggregate segregation. So, care must be taken during this process.

Once placed, concrete must sufficiently be consolidated into the shapes and around the embedded elements and reinforcements. Excess of concrete are then removed by screening the exposed surfaces. Then these are finished by floating the aggregate surface just below the surface to remove minor surface imperfections and compact the mortar to the surface.

Last, curing is the concluding factor in the production of concrete quality. Its object is to maintain a warm and wet environment for a sufficient period for the desired properties of concrete to develop. As soon as cement comes into contact with water, hydration begins, thus activating its adhesive property. This reaction continues as long as humidity and temperature conditions are favourable and when there is place for the hydration products. As the hydration continues, the concrete becomes denser and stronger. The mechanism of hydration reaction is covered in detail in the next section.

Hydration of cement causes the concrete to develop its final properties. The strength test is relatively easy compared to most other properties of concrete. For this reason, strength is generally the property specified in concrete design and quality control, and any other properties are directly related to the strength. An overview of concrete strength and associated factors of influence is covered in Section 2.3.

2.2 HYDRATION OF PORTLAND CEMENT

Hydration is the chemical reaction between the cement compounds (aluminates C_3A and silicates C_3S, C_2S) and water (H_2O). These compounds result from the combination of calcium and other components of raw materials during the burning operation in the kiln while manufacturing the cement (Kosmatka et al., 2003; Neville, 2011).

Tricalcium silicate (C_3S) and dicalcium silicate (C_2S) react with water to form calcium hydroxide $Ca(OH)_2$ and calcium silicate hydrate (C-S-H) gel which are responsible of the setting and hardening of cement paste (Soroka, 1979). In presence of gypsum, hydration of aluminate results in the formation of ettringite and monosulphate after further hydration. The following schematic represents the formation and hydration of Portland cement.

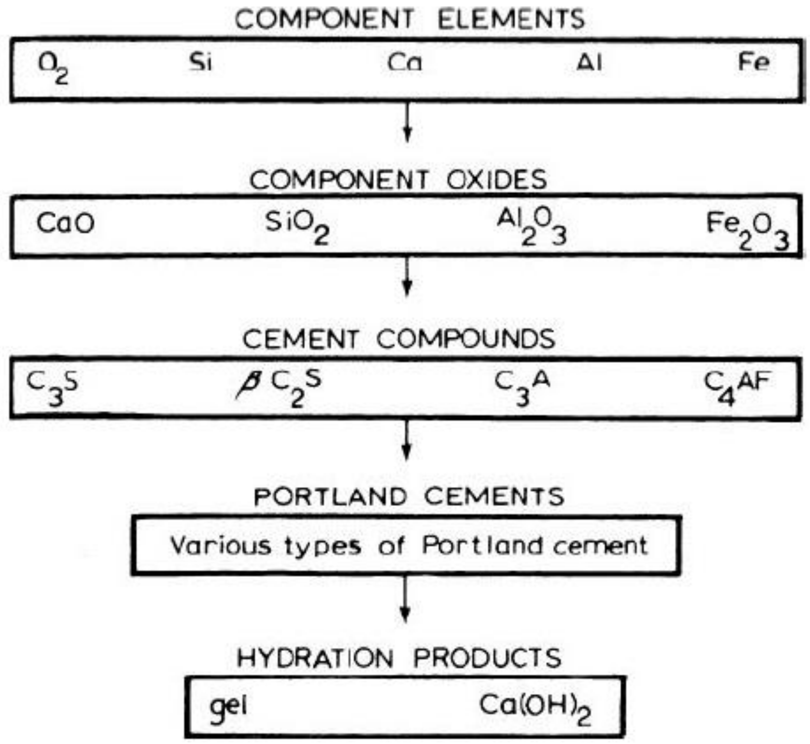

Figure 2.1 Formation and hydration of Portland cement (Neville, 2011)

The aluminates (C_3A) hydrates faster than silicates. Their reaction is immediate with large amounts of heat produced during the first few days of hydration and hardening (Soroka, 1979; Mamlouk and Zaniewski, 2005; Mehta and Monteiro, 2006). This leads to the early development of the strength characteristic of cement pastes.

Although fast, the hydration of C_3A can be slowed down by the gypsum addition. Otherwise, the concrete would be unusable for many construction applications because of its rapid hardening. The gypsum goes into solution quickly and produces sulphate ions that suppress the solubility of the aluminates (Soroka, 1979; Kosmatka et al., 2003). As result of this, aluminates balance with sulphates while hydrating. Thus, the setting time as well as the drying shrinkage are controlled.

From the calcium silicates (i.e. C_3S and C_2S) hydration, calcium hydroxide (C-S-H) and calcium silicate hydrate (or “tobermorite”) are formed. These hydrated compounds make up respectively 15 – 25% and 50% of the hydrated Portland cement mass. They greatly contribute to the primary strength and other properties of hydrated cement. C_3S hydrates more rapidly than C_2S. Its contribution is more pronounced on the final setting time and early strength gain of cement paste (Soroka, 1979; Mamlouk and Zaniewski, 2005). Besides, C_2S hydrates and hardens slowly. It contributes largely to increased strength at ages beyond a week (Mehta and Monteiro, 2006). The two calcium silicates provide therefore the driving force behind the hardening and strength development of cement. Their chemical hydration reaction may be expressed as per Equations (2.1) and (2.2).

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \tag{2.1}$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + 3CH \tag{2.2}$$

Where,'C' stands for CaO; 'S' for SiO_2; 'H' for H_2O.

Tetracalcium Aluminoferrite (C_4AF) is the fourth chemical compound resulting from the use of iron and aluminum raw materials during cement manufacture. It contributes little to the strength development but is rather the causal agent of the grey colouring of the cement. It is therefore responsible for most of the colour effects that make cement grey (Soroka, 1979; Kosmatka et al., 2002).

During the hydration reaction, different substances possessing setting and hardening characteristics are formed besides the heat is generated. Hydration reaction is essentially exothermic. The generated heat contributes to the early water loss; hence, it is recommended to cure concrete immediately after its preparation. The various types of curing are covered in the next section.

2.3 COMPRESSIVE STRENGTH OF CONCRETE

The strength of a material is its ability to withstand an applied load without failure. With regard to concrete, the strength can be defined as the unit force required to cause fracture. It is the main structural requirement that determines the capacity of concrete to support designed load without breaking thereby maintaining the stability and integrity of the structure. Strength is one of the most important properties of concrete. However, in many other practical situations, durability and permeability may be of critical. The strength is generally used as an indicator not only of the expected lifetime performance of concrete but also of its quality (Kosmatka et al., 2003; Mehta and Monteiro, 2006; Perrie, 2009; Neville et al., 2011).

2.3.1 Measure of compressive strength of concrete

The strength of a material can be determined in compressive, tensile, indirect tensile, torsion and shear modes. Concrete materials are suitable for bearing compressive load, but are weak in tension (Kosmatka et al., 2003; Mehta and Monteiro, 2006; Perrie, 2009). That is why most concrete structures are designed to take advantage of this property. Compressive strength therefore constitutes a key element in the design and the quality control of concrete structures.

Concrete can be subjected simultaneously to compressive, shear and tensile stresses. In practice, however, the uniaxial compression is the simplest and the most commonly performed test in the laboratory. It gives a direct indication of the ability of concrete to withstand compressive loads.

The 28-day compressive strength of concrete is considered to be the universal index of concrete strength (Mehta and Monteiro, 2006). It is determined by standard uniaxial compression tests on cube (SANS, 2006) or cylinder specimens (ASTM, 2014). In these standard practices, compressive strength is quantified by calculating the ratio of the maximum possible uniaxial load sustained by the specimen over the initial cross-sectional area of the specimen:

$$f_c = \frac{P}{A} \tag{2.3}$$

f_c represents the compressive strength in MPa

P is the load at failure in N

A is the cross-sectional area in mm^2

Correlations can be developed between the compressive strength of concrete to other hard-to-measure properties making it possible to infer the latter from the former (Mehta and Monteiro, 2006).

2.3.2 Factors affecting the concrete strength

Apart from the different forms of stress that can be applied to concrete, concrete strength depends on various factors linked to its porosity. These factors include the properties and proportions of the component materials of the concrete mix, the degree of compaction and the curing conditions (Mehta and Monteiro, 2006).

The water-to-cement ratio (w:c) is an indicator that has widely been used to qualify the proportion of materials making up the concrete mix. The water-to-cement ratio influences the compressive strength of concrete by extending cement hydration. Therefore, the w:c ratio plays a critical role in enabling the concrete to gain its strength. As the ratio increases, segregation occurs while voids are formed in the concrete matrix due to excess water. The formation of voids leads to increased porosity of the matrix; consequently, the resulting concrete is of lower hardened strength.

Duff A. Abrams was the first to demonstrate in 1918 that for a given set of concreting materials, the compressive strength of concrete depends solely on the water-to-cement ratio. He was subsequently able to establish a relationship between w:c and concrete strength (Neville, 2011). Commonly known as Abram's water-to-cement rule, this relationship is expressed as per Equation (2.4):

$$f_c = \frac{k_1}{k_2^{w:c}} \tag{2.4}$$

where k_1 and k_2 are empirical constants.

Figure 2.1 illustrates the significance of Equation (2.4) in that it describes the progressive weakening of the concrete matrix caused by the increase in porosity with the increase in the w:c ratio.

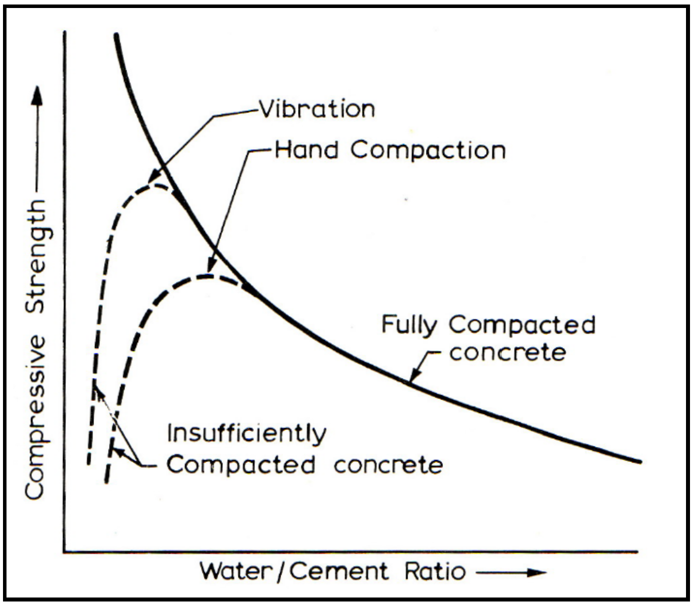

Figure 2.2 Influence of the water-to-cement (w:c) ratio on the compressive strength of concrete (Neville, 2011)

Abrams further found that for every kilogram of cement, about 0.35 kg of water is required to complete hydration reactions. However, a mix prepared at w:c = 0.35 may not be workable and may not well flow enough to be placed. Empirical observations further showed the need for additional water beyond the amount technically required for hydration. That is why practical values of w:c ratios are typically between 0.4 and 0.6 (Mehta and Monteiro, 2006; Kosmatka et al., 2003). So, since the w:c influences the concrete strength, controlling this parameter is crucial for the production of optimal quality and economical concrete.

The type of cement is also known to influence the strength of concrete by virtue of its reactivity. If the cement is not substantially reactive, the porosity will increase as there will be less hydration products to fill the pores. The reactivity of cement is dependent on the type of cement considered. Moreover, different types of cement experience different hydration rates which in turn vary with the ambient temperature. Low reactive cements can cause the volume of water in the mix to increase, and to further produce porous concrete (Soroka, 1979).

Other concrete components that impact the concrete strength are aggregates. Aggregates are incorporated into the concrete mixture to dilute the cement paste and add dimensional stability. The use of aggregates in concrete also reduce the preparation cost of concrete as they are cheaper than cement paste (Alexander and Mindess, 2005; Mamlouk and Zaniewski, 2005; Neville, 2011).

Previously, aggregates were considered as inert fillers and did not influence the concrete performance. An opposing view has become more common these days. Many investigators claim that the concrete performance is influenced by the physical, thermal and sometimes chemical properties of aggregates (Alexander and Mindess, 2005; Mamlouk and Zaniewski, 2005; Neville, 2011). The strength of concrete is related to the permanence of the bond between the cement paste and aggregates. It has been found that the chemical reactions between cement and aggregate could negatively affect the integrity of bond, such as that between high-alkali cements and reactive aggregates. However, there are some possible types of chemical superficial interaction between aggregate and the cement that concur to a more intimate and stronger union (Quinora and Fowler, 2003; Neville, 2011). The degree at which aggregate influences the concrete depends also on the strength type (Mehta and Monteiro, 2006). For example, the composition of aggregates is critical to the production of high-performance concrete than in normal strength concrete. Indeed, concrete is as strong as the aggregates found in its heterogeneous structure. But in high-strength concrete, the strength of aggregates has been found to be sometimes weaker than that of the cement paste (Mehta and Monteiro, 2006).

Besides the composition and strength of aggregates, other factors that have an influence on the strength and durability of concrete include aggregate size, mineralogy, porosity, grading, and surface texture (Alexander and Mindess, 2005).

The shape and the texture of coarse aggregates generally influence the stress causing cracks. Compared to coarse aggregate, the workability of fresh concrete, on the strength and durability of hardened concrete is more impacted by the shape and texture of fine aggregates (Quinora and Fowler, 2003). Aggregates with smooth surface tend to crack at a lower stress compared to aggregates with irregular rough surface. Aggregates with rough and angular texture, on the other hand, bond better to the cement paste. The increase in strength is therefore consequent but the associated effect of this is reduced once the chemical interaction between aggregates and cement paste is effective at later ages (Mehta and Monteiro, 2006).

Apart from the surface texture, number of aspects including the porosity and the internal bleeding, can be influenced by the maximum size of aggregates. For example, the increase in size of coarse aggregate cause the entrapped air content to decrease, thus, leading to an increase in strength.

Concrete strength can also be influenced by the maximum size of aggregates. It has been observed for example, that large aggregate particles reduce the compressive strength by having a high stress concentration when subjected to a compressive load. In addition to this, large aggregates form interfacial transition zones with more micro cracks than smaller aggregates (Quinora and Fowler, 2003; Mehta and Monteiro, 2006; Neville, 2011).

The second group of factors that influences the concrete strength is related to the degree of compaction. When concrete is cast, some air entrained can be trapped in the fresh mix. This air creates pockets in the matrix which increase the porosity of the hardened concrete. To achieve maximum density and strength, the entrained air must be expelled during compaction. If the fresh concrete is not effectively compacted, excess voids will remain, and the strength will be reduced. Hence, the degree of compaction is substantial to concrete strength (Kosmatka et al., 2003; Mehta and Monteiro, 2006).

The degree of hydration determines the porosity of a hydrated cement paste at a given w:c. Further hydration is possible when concrete is cured as the hydration of the cement compounds (C_3S and C_2S) require water to achieve maximum strength. Hence, curing conditions are also mentioned among the factors that affect the strengthening of concrete. The hydration of Portland cement compounds begins as soon as water is added. It impressively moderates when the hydration products coat the anhydrous cement grains (Mehta and Monteiro, 2006). This causes the strength value to gradually increase in time and makes the concrete strengthening time dependent. When curing is interrupted, the concrete strengthening can continue for short period and then almost stops when the vapour pressure of water in capillaries falls below 80 % of the saturation humidity. Even if the curing is resumed, the original potential strength may not be reached although the strengthening can be reactivated. The saturation conditions are conducive to a satisfactory hydration process, therefore to a satisfactory strengthening. Time and humidity are crucial variables in the hydration processes controlled by the diffusion of water. In addition, the curing temperature has effects on the rate of hydration, the rate of evaporation and the resulting drying out of the concrete, thereby on concrete strength. As for every chemical reactions, the temperature influence resumes in increasing the rate of hydration, provided that the rise in temperature does not cause drying of the cement paste (Soroka, 1979; Mehta and Monteiro, 2006). Associated with a high temperature, the increased evaporation rate delays the rate of hydration by reducing the amount of water available. Zain et al. (1999) investigated the development of compressive strength of high performance concrete exposed to medium temperature ranging from 20°C to 50°C. The researchers found that higher compressive strength developed in the range of 20°C to 35°C. Compressive strength at the temperature of 50°C was lower than that obtained at 35°C. The increase in temperature negatively influenced the degree of hydration of the cement, resulting in lower compressive strength. Similar opinion was made by Saffiudin et al. (2000).

The time-strength relationship in concrete technology generally supposes wet conditions and ordinary temperatures. At a given w:c ratio, the longer the moist curing period, the higher the quality of concrete, presuming that the hydration of anhydrous cement particles is still in progress. In thin concrete components, if the evaporation causes the water to dissipate from the pores, air-curing conditions predominate and no increase in strength over time can be expected.

Two relationships to evaluate the compressive strength with time was recommended by ACI Committee 209 and CEB-FIP Models Code (1990), respectively expressed as per Equations (2.3) and (2.4). Equation (2.5) was recommended for moist-cured concrete made with Portland cement while Equation (2.6) is applied to concrete cured at 20ºC.

$$f_{cm}(t) = f_{c28}\left(\frac{t}{4 + 0.85t}\right) \qquad (2.5)$$

$$f_{cm}(t) = exp\left[s\left(1 - \left(\frac{28}{t/t_1}\right)^{1/2}\right)\right]f_{c28} \qquad (2.6)$$

Where

$f_{cm}(t)$ is the mean compressive strength at age t in days

f_{c28} means 28-day compressive strength

s is a coefficient depending on the cement type:

s= 0.20 for high early strength cements;

s = 0.25 for normal hardening cements;

s= 0.38 for slow hardening cements.

t_1= 1 day

The impact of curing humidity on concrete strengthening can clearly be seen in Figure 2.2. The figure depicts typical strength-gain curves showing the compressive strength progression of a concrete cured by immersion for various limited curing periods.

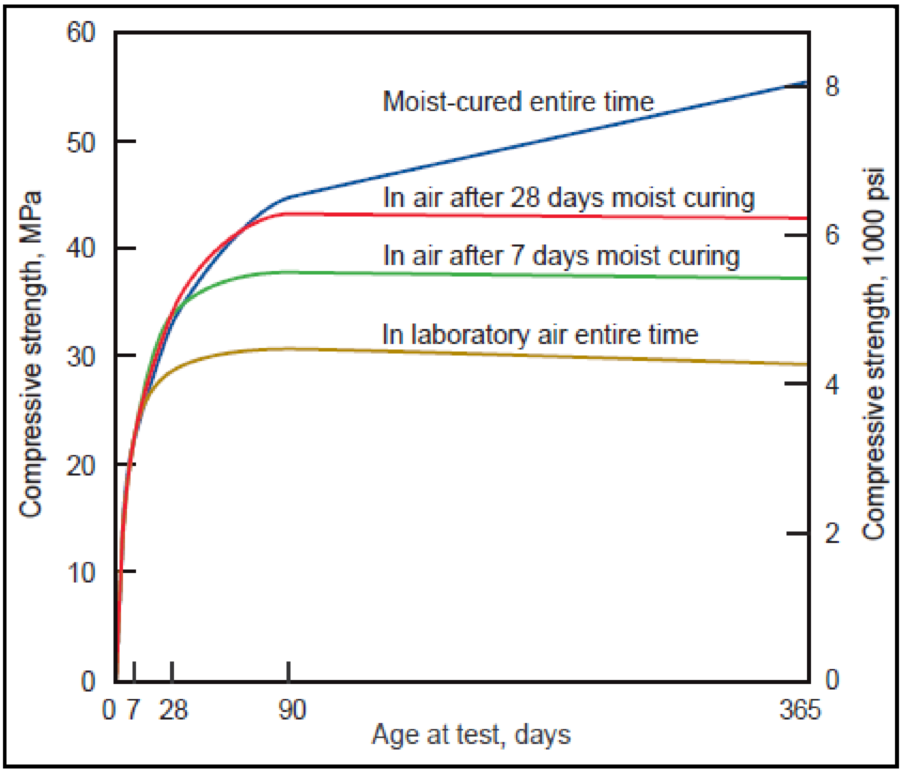

Figure 2.3 Compressive strength as a function of age for limited moist curing conditions (Kosmatka et al., 2003)

The improvement in strength is rapid at early stages (almost 28 days) but continues more slowly thereafter for an indefinite period. As previously stated in Section 1.4, the strength of concrete is traditionally characterized at 28 days in concrete technology, and some other properties of concrete are often rated at the 28-day strength. This is because considerable hydration of the cement has already occurred at this age that the 28-day characteristic strength of concrete is accepted as a standard for design and construction. As a result of this observation, at least 7 days of moist curing is generally prescribed for concrete containing ordinary Portland cement.

There are various a practical method in which curing is done. They are covered next section.

2.4 TYPES OF CONCRETE CURING

Curing is essential to produce a quality concrete. It entails the treatment of the newly placed concrete to allow it to properly harden and retain enough moisture. This limits excessive shrinkage and cracking (Jackson and Akomah, 2018). Moisture retention in the concrete after placement is essential for hydration to progress properly. At least 80% relative humidity is required (Kosmatka et al., 2003; Mehta and Monteiro, 2006; Neville, 2011; Kosmatka et al., 2011). As the hydration reaction proceeds, the resulting products gradually bind the different components to form a solid block.

Hydration encourages the reduction of porosity, thereby ensuring a fine pore size distribution in the concrete mass (Neville, 2011). However, moisture is required to activate the hydration reaction so that concrete may harden properly. If adequate moisture is not maintained, the concrete will not develop maximum strength but crack with detrimental effects on its overall quality. To avoid this, curing is required as soon as the concrete is cast.

There exist two basic ways of curing concrete: the first is to ensure constant contact between water and concrete while the second is to minimize the rapid evaporation of the mixing water from concrete by obstructing bare surface pores. A third manner, typically used for precast concrete products, entails the strengthening acceleration by additional supplies of heat and moisture to the concrete (Mamlouk and Zaniewski, 2005).

The possible curing techniques (acting either by providing additional moisture or preventing loss of moisture) are described from section 2.4.1 to section 2.4.5 (Mamlouk and Zaniewski, 2005; Kosmatka et al., 2003).

2.4.1 Water immersion

This technique, also referred to as ponding, involves the submersion of finished concrete in water. When good dam material (e.g. clay soil) is available, when water can constantly be fed and when the pond does not block future construction activities, this method is favourable.

The effectiveness of this method on the development of concrete strength continues to be explored. Its effect has been studied on conventional concrete (Princy and John, 2015, Usman and Isa, 2015), as well as on other particular concretes (Olofinnade et al., 2017; Abalaka and Okoli, 2012; James and al., 2011; Al-Jabri et al., 2009; Safiuddin and Raman, 2007). In these numerous studies, this method proved to be effective in achieving good concrete properties. Since water is always available, the contribution in improving the pore structure is important. The greater degree of cement hydration has resulted in reduced porosity. However, these results are related to concrete specimens immersed in curing tank in laboratory environment. The application of water curing in site contexts is limited only to flat surfaces such as floors and pavements, for small jobs.

2.4.2 Water sprinkling

Water sprinkling or fog curing is a curing method that entails pouring or spraying water on exposed surfaces of concrete.

After the conventional water curing, water spraying is the second method to have been explored in many studies (Usman and Isa, 2015; Raheem et al., 2013; James et al., 2011). For example, Usman and Isa (2015) have investigated its effects on compressive strength as compared the use of immersion in water, polythene sheets and sand. The results showed that water sprinkling is effective and that it approaches the performance of the water curing.

Another example is that of James (2011) who benchmarked compressive strength results of concrete specimens cured by water spraying againts water curing, wet covering and air-drying. As a result of the compression test, researchers ranked the performance of this method after immersion and wet covering. On site, the spraying method can be supplied using a system of nozzles or sprayers. It is suitable in low humidity environments. This method can help minimize the temperature of the concrete in hot weather conditions, but water requirements are higher to provide continuous spraying. Hence, water sprinkling can be expensive.

2.4.3 Wet covering

In order to maintain water on the surface of the concrete, this method uses moisture-retained material such as wet sand, burlap, cotton mats, rug and hessian. To assess the effectiveness of wet covering method, Raheem et al. (2013) considered the use of moist sand and wet burlap as moisture-retained materials to investigate the 28-days compressive strength of concrete. Other five curing techniques were also considered: air-drying, water curing, water spraying and polythene curing. Surprisingly, moist sand recorded the highest 28-day compressive strength of 30.5 MPa on concrete specimens followed by burlap curing method. The two methods aforementioned even surpassed water curing and water spraying. The researchers attributed this unusual finding to the contribution of the weather conditions that moist sand experienced. They found that the weather was essentially hot and warm during the curing period. However, concrete cube specimens presented surface discolouration making them inappropriate for use as prefabricated concrete elements since these generally require no finishing.

Another example is that of Akinwumi and Gbadamosi (2014) who investigated the use of wet rug. The use of lime water, tap water and nylon polythene sheets were also considered in the same study. Curing by wet rug covering was peformed outdoors so prone to varying weather conditions. Compressive strength results were totally different from Raheem et al. (2013). After 28 days of curing, wet rug covering gave the least compressive strength as compared to other techniques. results were close to the air-drying one. Even though water was regularly poured on the rug to keep it moist, the result shows that watering was not effective.

Therefore, the use of moisture-retained materials must be taken with great delicacy and kept moist by efficient periodic watering. This prevent early drying which can cause the material to act as a wick and absorb water from the concrete.

2.4.4 Plastic sheeting

This method consists of covering as soon as possible all exposed areas of the concrete with a plastic sheet or other impervious papers such as Kraft papers, polyethylene film, etc. without damaging the concrete finish. The plastic sheet may be black, which is suitable to cold weather, or white in hot weather, for its ability to reflect solar radiation.

The use of this technique on conventional concrete was explored by Usman and Isa (2015) and was compared to the use of immersion in water , sprinkling and sharp sand. The ranking in descending order of performance pointed this technique in the third position, after immersion in water and sprinkling.

Another example is that of Safiuddin and Raman (2007) who explored the use of plastic sheet covering on microsilica concrete. The microsilica was inserted into the concrete mix while partially replacing 10% of the cement.The investigation entailed the use of water curing and dry-curing as methods of comparison. Concrete specimens were wrapped with at least three layers poly-film to restrain moisture movement from concrete surface. After 28 days of curing, concrete specimens were tested to determine hardened properties including the compressive strength. Specimens cured by plastic sheet covering recorded strength values close to that of water curing. This was ascribed to the maintenance of moisture and to adequate vapor pressure which allowed to continue the cement hydration. The investigators concluded that it was also possible to achieve good concrete strengthening without external application of water.

2.4.5 Use of curing compounds

This curing technique entails the spraying of chemicals over the concrete surface and enables it to dry. Water is not always available to cure concrete in some areas. To overcome this limitation, progress in the construction and chemical industries have introduced the use of new compounds such as membrane curing compounds, self-curing agents, and water proofing compounds (Princy and John, 2015). Their use requires less curing protection since they settle quicker than sheets. However, they do not completely stop the evaporation of the mixing water even though they seal the concrete surface. They are widely used in developed countries.

The use of curing compounds has interested researchers such as Princy and John (2015) who investigated the application of acrylic resin based, wax based and water proofing compound on conventional concrete. The researchers found that these curing compounds were effective because they produced specimens with good strength properties, see Figure 2.3. Although water curing was the most efficient, it is the preferred option in situations where water polymerization is difficult.

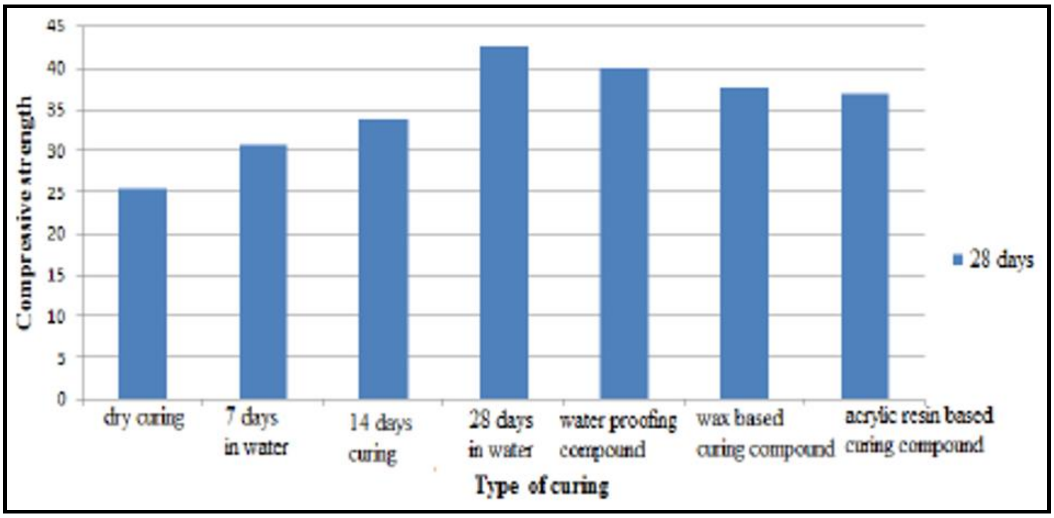

Figure 2.4 Effects of various curing techniques on the compressive strength of concrete samples (Princy and John, 2015)

In addition to the curing techniques described above, a site-specific technique such as formwork placement may be associated with the group of curing methods. It is a simple and cost-effective way to harden concrete, especially in its early stages. In the case of wooden formwork, pre-wetting is necessary to retain the moisture during the curing period.

All the curing methods mentioned above present advantages and disadvantages and their effects on the concrete strengthening differ. The choice of one method over another is based on the material availability, the method of construction and the purpose for which the hardened concrete is made. Various studies have been conducted on the impact of different curing methods on conventional concrete strengthening (Usman and Isa, 2015), on high strength concrete (Al-Jabri et al., 2009); on conventional concrete subjected tropical climate exposure (Raheem et al., 2013; Akinwumi and Gbadamosi, 2014). The idea was generally to identify the curing method best suited to a specific application. Relevant literature is reviewed in the section below.

2.4.6 Effects of curing conditions on concrete strength

There are various arguments whereby proper curing allows the concrete to reach its desired properties in hardened state. These have resulted in several efforts analysing the influence of different curing methods on the final properties of concrete. Among them, Ogah (2016) investigated the effect of curing methods on the compressive strength of concrete. The study used three curing methods, i.e.,covering with wet rug, water curing (immersion), and use of polythene sheet. Concrete specimens were prepared with 1:2:4 (cement: sand: gravel) mix proportion and were cured. Aftetward the 28-days compressive strengths were evaluated using unixial compression test. The researcher found effectively that curing was important in achieving the desired concrete strength. However, the results showed a tendency of reported strength to change with curing method. Indeed, the mean compressive strength realized from water curing was 9.8 % and 16.8 % higher than the strength gained from wet rug and polythene sheet.

More recently, Jackson and Akomah (2018) compared the compressive strength of concrete prepared with 1:2:4 mix ratio. Curing was done using the following methods: water curing method, polythene sheet wrapping, jute bags wrapping and covering with wet sand. The specimens were cured for 7, 14, 21, and 28 days and in each case the samples were tested for compressive strength. The highest compressive strength was observed for water curing at all ages while wet sand performed the worst. After water curing method, the use of jute bag yielded better compressive strength. The two researchers recommended its use on construction sites where water curing was not possible. They further recommended to water-spray the concrete surface prior to applying the covering. The purpose of doing this is to minimize early losses of water into air spaces between the concrete and the covering. It should be noted that the study was limited to the w:c ratio of 0.5 while other ratios were not investigated.

Another case is that of Usman and Isa (2015) who employed laboratory experimentation on conventional concretes. Two mix ratios were used to prepare fresh concrete, i.e., 1:2:4 and 1:3:6. Four techniques were considered to cure concrete specimens: immersion, water spraying, polythene sheeting and sharp sand. These were tested for compressive strength after 3, 7, 21 and 28 days of curing. In terms of compressive strength, the best results were recorded on specimens cured by immersion. However, the researchers argued that in practical this could be expensive on a small production scale. They proposed spraying as the closest alternative to minimize water wastage in situ.

Another interested study was that of Safiuddin et al. (2007) who additionally investigated the rate of moisture movement from concrete specimens cured under three types of curing , namely: immersion in normal tap water (water curing), wrapping with three layers of poly-film (wrapped curing), and exposure to dry air. These were used to cure concretes specimens in which microsilica was incorporated as cement replacement. A replacement rate of 10 % was used. Different hardened properties in addition to the initial surface absorption were determined after 3, 7, 14, 28 and 91 days of curing periods. The rate of moisture was also evaluated in weighing the concrete specimens after demoulding and just before testing. As result of the tests, the researchers found that the highest hardened properties and lowest level of initial surface absorption were mainly yielded by water curing at all ages. No losses of moisture from concrete surface were recorded for samples subjected to water curing. Instead, these gained some moisture from surrounding water enabling longer cement hydration which then resulted in denser and stronger structures. Concrete specimens wrapped with poly-film and those air-dried showed pronounced moisture loss while the loss was negligible in the case of poly-film covering. A very low hydration rate was also recorded for poly-film and air-drying suggesting that the escape of moisture was hindered as the surfaces of the specimens were sealed.

Additionally, Safiuddin et al. (2007) recorded a maximum loss of moisture (i.e. 50.4 g) was observed on specimens exposed to air-dry after of 28 days. This was ten times higher than that of wrapped cured specimens. No protection against the escape of moisture was put in place in this curing method. As result of this, the amount of moisture required for cement hydration was reduced. Cement hydration remained incomplete since it was stopped at a certain stage. In the case of air-drying, the reduction in hardened properties was significant along with the increase in initial surface absorption. The result of the ultrasonic pulse velocity showed that the mitigation of cement hydration increased the porosity of concrete matrix. Safiuddin et al. (2007) concluded that improper curing affects significantly the hardened properties of concrete.

Shortage of water in different parts of the world has led some researchers to compare the effectiveness of alternative curing methods against conventional water curing. One of these cases is that of Princy and John (2015) who considered the use of membrane-forming compounds. These compounds consisted of acrylic resin, wax based and water proofing compound. The investigation was made on a plain concrete prepared with a 1:1.8:3.1 mix ratio and with w:c = 0.39. They used a super plasticizer to increase the workability. Out of water curing and the use of chemical compounds, a set of specimens were allowed to dry within the ambient air in the laboratory without any form of active curing. In water curing method, concrete specimens were immersed in water during limited curing periods of 7, 14, and 28 days. The effects of other curing methods were studied for 28 days only. Compressive strength, flexural strength and split tensile strength were determined for the various curing periods. The highest mechanical properties were noted for specimens water-cured after uninterrupted 28 days. It was also found that the use wax-based curing compounds and acrylic resin curing compounds led to 99% and 96% performance respectively as compared to the conventional water curing. However, water proofing compound performed the closest to water curing that these compounds were recommended in water-scarce situations.

Further research has shown that exposure to environmental conditions may have a significant impact. Wind, air humidity, air temperature, solar activities are factors that could seriously impair or improve the properties of concrete. Raheem et al. (2013) examined the effects of curing techniques on the density and the compressive strength of concrete. Six different curing techniques were tested:

immersion in water, spraying water, polythene curing, burlap curing, moist sand curing, air curing, on the density and compressive strength of concrete. The same conditions of temperature and humidity were considered in the laboratory for all the curing methods except for moist sand covering. The latter was subjected to outside exposure, in other words, to uncontrolled environmental conditions. Doing so was aimed at accounting for the impact of weather conditions while curing the concrete. After compression tests, the highest 28-day value was observed on specimens under moist sand. Those under burlap and those air dried produced the lowest ones. The conclusion from their observation was that the recorded value could be due to the good weather conditions, as the average daily ambient temperature of 32°C was higher than that in the laboratory set at 27°C. Akinwumi and Gbadamosi (2014) conducted the same type of experiments on ordinary Portland cement concrete in a tropical region. Immersion in drinking water and lime water; covering with wet rug and with plastic sheet and air-drying were tested as curing methods for 90 days. As shown in Figure 2.4, immersion in lime water performed the most successively followed by plastic sheet covering; tap water curing method; laboratory air-drying; and wet rug covering.

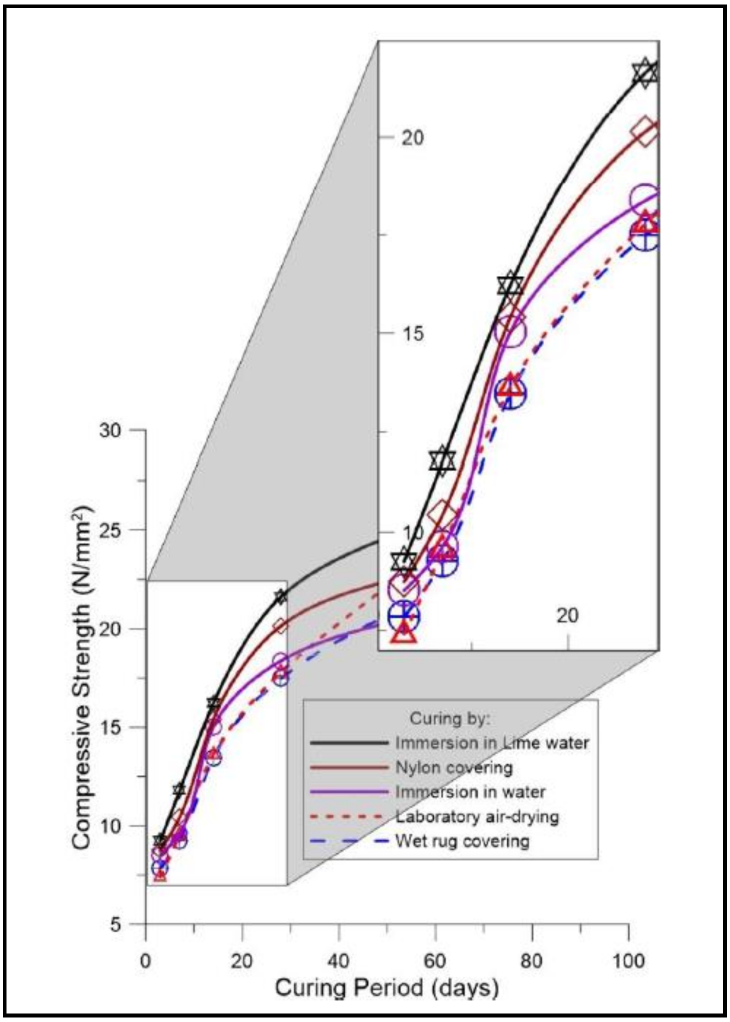

Figure 2.5 Variation of compressive strength as a function of different curing method for 28 days of curing period (Akinwumi and Gbadamosi, 2014)

Unexpectedly, concrete kept under wet rug showed lower strength than the air-dried concrete. Akinwumi and Gbadamosi (2014) argued that this might be ascribed to the varying outdoor conditions that the samples were subjected to. Indeed, for the duration of curing, the mean daily temperature and relative humidity were reported to change from 27.2°C to 30.3°C and 56 % to 83 % respectively.

Reddy (2013) focused on the influence of humidity while comparing the effect of different curing methods on concrete. Water curing, jute bags covering, single layered membrane curing, double layered membrane curing and air curing were investigated on M60 grade concrete. The curing compound used for membrane curing consisted of a white pigmented liquid parrafin based denoted C1, a wax based paraffin emulsion denoted C2 and white pigmented wax based compound denoted C3. Concrete samples were tested for compressive strength at the end of 3,7 and 28 days of curing. Spraying of chemical compounds was carried out immediately after demolding. After 5 min of application, a second coat was applied in the case of the double layered membrane curing. Water have been sprayed over jute bags once in the morning at 10 am and in the evening at 4.00 pm. The entire casting and testing procedure for the jute bags curing and air-drying was done twice, in different periods, i.e., in December and in February. The average temperatures recorded during the two months were respectively 26.53ºC and 34.8ºC while the corresponding relative humidity were 73% and 56%. The results are summarised shown in Table 2.1.

Table 2.1 28-day compressive strength for the different type of curing used by Reddy (2013)

No.	Curing type	Compressive strength in MPa
1	Water curing	66.13
2	Single coat C1	58.21
3	Double coat C1	61
4	Single coat C2	56.9
5	Double coat C2	59.86
6	Single coat C3	50.6
7	Double coat C3	58.21
8	Jute bag curing – December	61.23
9	Jute bag curing – February	51.58
10	Air curing – December	49.89
11	Air curing – February	38

In terms of the influence of humidty and ambiant temperature, Akinwumi and Gbadamosi (2014) found that the compressive strength recorded on jute bags and air curing were higher for December than that of February. Jute bags performance during December was closer to water curing.

As related to the strength gain in time, air curing during December was in comparison with jute bags curing. Warm weather could have supplied addition moisture to the cubes. This helped in gaining the strength. Air curing during February resulted in lower compressive strength of about 76.16% as compared to the one obtained for December. This shows that the influence of weather conditions cannot be ignored while curing the concrete. Air humidity and temperature are also prime factors which determines the final quality of concrete (Reddy,2013). Therefore, since climate are different all over the worlds, it necessary continuously assess the efficiency of the various curing methods in different locations.

As introduced in Chapter 1, questions about the sustainable development raise various interest and studies on the use of eco-friendly material in concrete such as copper slag. Prior to investigating the influence of curing method on such green concrete, it is necessary to assess the suitability and performance of copper slag as substitute of traditional concrete aggregates. Several researchers have studied the question. A review of the key findings is presented next.

2.5 PERFORMANCE OF COPPER SLAG CONCRETE-MAKING AGGREGATE

2.5.1 Background of copper slag

Copper slag is a black, glassy material obtained as part of the pyrometallurgy process of copper at the smelting and refining sections. Copper slag is an industrial waste commonly used in recycling, metal recovery, and manufacturing of value-added products (i.e. cutting and abrasive tools, tiles).

In 2008, a comprehensive review on the use of copper slag in cement, mortars and concrete was presented by Shi and co-workers. The researchers pointed out that a large amount of the annual production of copper slag is piled up in landfill or stocks. Chemical analysis of copper slag from various sources showed high contents in iron, silica, alumina and calcium. However, the copper content was limited from 0.5 % to 2% oxide (Gorai et al., 2002; Shi et al., 2008). The chemical properties of copper slag (chloride and sulphate contents) were found to lie within permissible limits for concrete durability (Gorai et al., 2002; Perm et al., 2018). Typical chemical compositions of copper are given in Table 2.2. These compositions differ according to the type furnace, the metallurgical process that produced them and the composition of the extracted ore.

Table 2.2 Typical chemical compositions of copper slag from different sources by mass (%)

Origin (Reference)	Components (%)							
	Al_2O_3	SiO_2	SO_3	CaO	Na_2O	MgO	K_2O	Fe_2O_3
USA (Mobasher et al., 1997)	15.6	24.7	0.28	10.9	-	1.7	-	44.8
Oman (Al Jabri et al., 2009)	2.79	33.05	1.89	6.06	0.28	1.56	0.61	53.45
Singapore (Wu et al., 2010)	2.52	31.92	1.34	1.25	1.40	1.65	0.81	59.11
Katanga, DRC (Boakye, 2014)	7.28	30.31	0.42	12.31	0.91	6.41	1.08	25.91
India (Malkhare, 2018)	0.22	25.84	0.11	0.15	0.58	-	0.23	68.29

Heavy metal leaching from copper slag has been reported to be insignificant to warrant concern (Shanmugananathan et al., 2007). This ensures the long-term stability of the copper slag. From the above, copper slag has generally been claimed non-reactive and non-hazardous. This mainly contributed to their adoption in concrete and qualified it to have a promising potential as aggregate (Gorai et al., 2002, Perm et al., 2018). Due to its low content of CaO, copper slag has been found to possess pozzolanic properties and to exhibit cementitious properties when actived with NaOH (Brindha, 2011; Boakye, 2014). Mobasher et al. (1997) found that up to 15 % by weight of copper slag can be used as a Portland cement replacement with 1.5 % of hydrated lime. Result indicated significant increase in compressive strength. Moreover, Boakye (2014) reported that the copper slag was not a very chemical reactive material without addition of sufficient quantity of lime to reach required rate of hydration and to achieve the required early-age strength.

The incorporation of copper slag into cement derived has been proposed by many researchers. The following lines cover some of the most relevant on the use of copper slag as an aggregate replacement in concrete.

2.5.2 Use of copper slag as replacement for sand

To provide an engineering base that recognize copper slag as concrete-making components, numerous other researches have been conducted all over the world. Its effects on the different mechanical and long-term properties have accordingly been investigated. The most recent work is that of Srinivas et al. (2018). The researchers investigated the effect of adding copper slag as sand on mechanical properties of M30 grade concrete. Fresh mixes were produced using 0 %, 25 %, 50 % and 75 % replacement rate. Concrete cubes were casted and cured for 7 and 28 days. Then they were tested and compared in terms of compressive strength and split tensile strength. Prior to this, slump tests were performed on the fresh mixes. The researchers found that as the percentage of copper slag increase the workability increases. As the copper slag content increase in the concrete mix, the compressive strength and split tensile strength was found to also increase up to 50%; then, start to decrease. The researchers concluded that using copper slag as concrete-making component reduces the cost of making concrete and concurs to sustainable development.

Malkare and Pujari (2018) investigated the eligibility of copper slag as sand replacement in a M25 concrete grade. In the different mixes prepared, copper slag was replacing the sand from 0 % to 100 %.Slump test were performed on the fresh concrete, then concrete specimens were casted and cured for 28 days. Different types of strength were measured in addition to ultrasonic pulse velocity (UPV). The latter was performed to examine the quality of copper slag concrete. The optimum percentage of copper slag replacing the sand was obtained at 40 % as related to the strength. A decrease in strength was observed for addition exceeding 40 %. The reduction in strength was ascribed this to the excessive free water present in the copper slag-based mixes. This caused the particles to separate leaving pores in the hardened concrete which further reduce concrete strength. When comparing the different types of strength type (i.e. compressive, split tensile and flexural), Malkare and Pujari (2018) observed that the split tensile was showing similar behaviour to the compressive strength for all mixture. The ultrasonic pulse velocity test was performed by passing a pulse of ultrasonic wave through the concrete to be tested and measuring the pulse time taken to traverse the structure. High velocities indicate good quality and material continuity, while lower velocities may indicate a concrete with many cracks and voids. Copper slag concrete recorded highest UPV of 4.62 km/s to 4.99 km/s, as compared to 4.58 km/s for the conventional concrete. This shows that the addition of copper slag certainly reduced the pores of concrete and made the concrete more compact. The optimum being at 40 % of replacement for 4.99 km/s of UPV.

As for them, Tejaswini and Priyanka (2017) focused on the behaviour of reinforced copper slag concrete. They used copper slag in substitution for fine aggregates and analysed the concrete specimens for compressive strength. Through this, an optimum percentage of 40 % was achieved for copper slag replacing conventional sand. Considering this, reinforced concrete beams were prepared with 40 % of copper slag infused in the mix. Then flexural strength test was performed. They researchers noted an increase of 48.412 % of flexural strength for the reinforced beams prepared with copper slag infused as compared to the conventional reinforced beams. They therefore recommend the use of copper slag in reinforced concrete.

Rahul et al. (2016) investigated the effect of adding copper slag into self-compacting concrete mix. The main property of this innovative concrete is that it can flow under its own weight and can completely fill the formwork. Self-compacting concrete can achieve full compaction without any form of vibration when it is placed. For the study purpose, M25 grade of concrete were prepared using

0 % to 50 % of copper slag replacing the sand. The workability was assessed through slump test; then, some specimens were casted and cured for 7 and 28 days. After that, hardened properties were evaluated such as compressive strength, split tensile strength, flexural strength. As result, the researchers found that the strength of the concrete increased with the percentage replacement of copper slag up to 40%. Further additions caused the strength to slightly decrease. They conclude that the copper slag performed similar, even better compared to natural sand concrete.

Patil and Patil (2016) were also interested on the technical feasibility of using copper slag concrete-making components. With an emphasis on permeability of the hardened concrete, they studied the mechanical behaviour of M30 grade concrete in which they replaced sand by copper slag in proportions ranging from 0 % to 100 %.A water-to-cement ratio of 0.45 was maintained while producing concretes mixes. The researchers found that the slump of concrete increased as more natural sand was replaced by copper slag. A gain in strength of 32 % was recorded for concrete containing 40 % slag compared to conventional concrete. Further addition caused the strength to reduce. Patil and Patil (2016) also generated scanning electron microscope images of the hardened concretes that was produced. Decreasing presence of voids in concrete mix containing 0 % up to 40 % of copper slag are highlighted on these images. From 60 % up to 100 %, the voids were increasing. Through the test conducting according German Code DIN-1048, they showed that the permeability decreased down to 40 % and afterwards increased from 50 % to 100 % (see Figure 2.7). Due to the increase in voids, the strength of concrete was reducing as the copper slag content increase.

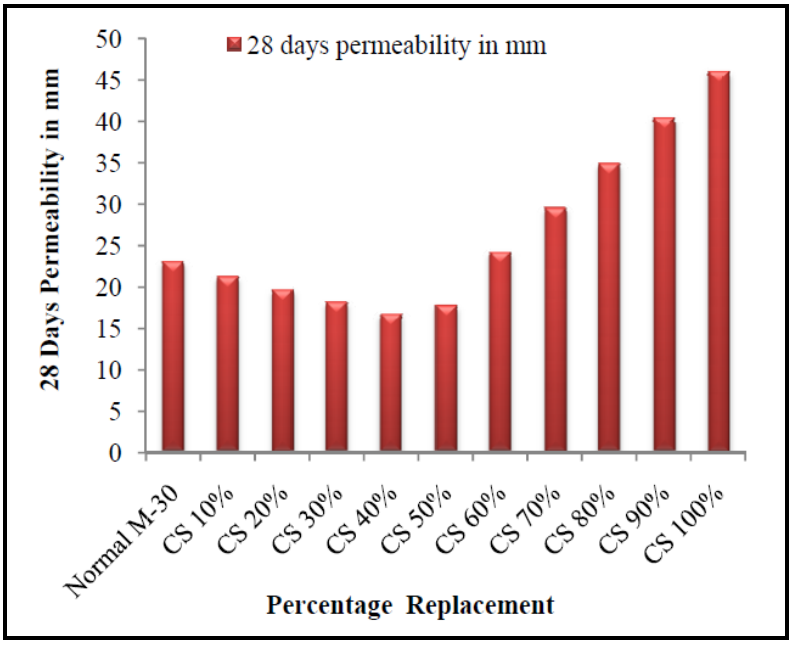

Figure 2.6 28 days permeability for different replacements of sand by copper slag (after Patil and Patil, 2016)

Out of the mechanical properties, researchers such as Brindha and Nagan (2011) investigated the corrosion and durability of such concrete. The study focused on M20 grade concrete. Copper slag was added as sand replacement in proportions ranging from 0 % to 60 %, and as cement replacement in proportions ranging from 0 % to 20 %. The slump evaluation of fresh concretes was to make sure that these would be within the design value. This was also to assess the effect of that addition on the workability. Different specimens were casted and demoulded after 24 hours. They were then cured in water and tested at room temperature for compressive strength, split tensile strength, and UPV amongst others. The results indicated an increase in the strength with respect to the fraction of copper slag added up to 40 % as sand, and up to 15 % as cement. In terms of acid resistance testing, copper slag concrete showed low resistant to H_2SO_4 solution than the conventional concrete. Additional, accelerated corrosion test were conducted to examine the corrosion properties of copper slag concrete as copper slag contains more than 50% of ferrous content. The corrosion test was first conducted on uncoated rebars, embedded in cylinder specimens of 150mm in diameter and 300 mm high. These concrete samples were subjected to alternating exposure of wetting and drying in 3.5 % NaCl solution. Regular DC power of 12V was continuously supplied throughout a 15-days corrosion period. After the corrosion period, the rod was taken out and weight to calculate the loss of weight. Hence, corrosion rate was evaluated. The test reveals higher corrosion rates for copper slag concretes as compared to the conventional concrete in all replacements. The maximum corrosion was observed on concretes made with 60 % of replacement rate. To control the corrosion rate in concrete, another test was conducted using no corrosion was observed on the rebars coated with zinc phosphate paint and for the entire replacement rate. Brindha and Nagan (2011) concluded that if the copper slag concretes are to be used in corroded environment, the reinforcement should be coated with some protective compounds.

Prior to this, many have sought to find the optimum content of copper slag as fine aggregate in high-strength concrete. Al-Jabri et al. (2009) and Wu et al. (2010) can be noted with major findings being that workability and density increase with the addition of copper slag to the concrete mixes. However, a partial substitution of the sand by copper slag was recommended in a proportion not exceeding 50 % if the improvement in mechanical properties is aimed. Further addition may cause the strength to reduce as shown in Figure 2.6.

Wu et al. (2010) attributed the strength increment observed with substitutional amounts of copper slag to the physical properties of copper slag. The researchers found on one hand, that copper slag has better compressibility than sand. This excellent compressibility of copper slag allowed to partially relieve the stress concentration if the sand is still as the dominant fine aggregate holding the concrete matrix together. On the other hand, the investigators stated that the angular sharp edges improved the cohesion of the concrete matrix.

All the aforementioned studies revealed that the workability was increased with the addition of copper slag. This finding was generally ascribed to the low water absorption property of copper slag. Copper slag is generally formed of particles with a vitreous and non-porous texture. This texture causes the free water to increase in concrete matrix with respect to the increase in copper slag content. That non-absorbed water was claimed to be acting like lubricant between the different concrete-making particles. As result, the inter-particle frictional force is reduced (Wu et al., 2010).

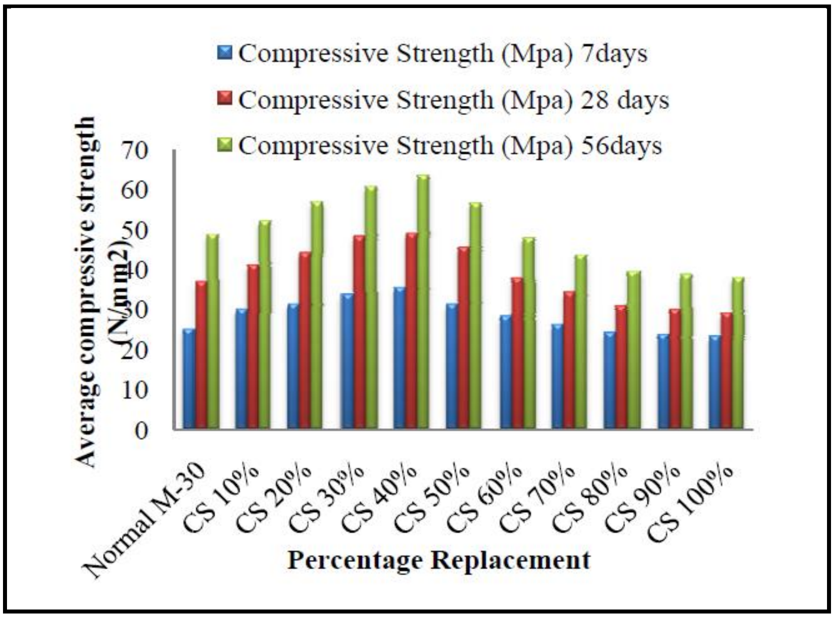

Figure 2.7 Compressive strength for different replacements of sand by copper slag (after Patil and Patil, 2016)

As related to the hardened density, an increment was observed with the increase in copper slag content. The finding was generally credited to the high specific gravity of copper slag since the weight of concrete was accordingly increased.

The non-absorbed water presents in the copper slag admixed concrete has been also pointed out as responsible of the strength reduction observed for addition copper slag exceeding 40 – 50 %. For example, Malkare and Pujari (2018) argued that the strength reduction was due to resulted pores left in the hardened concrete. Wu et al. stated that the surface texture of copper slag tends to be ‘glassy’ (smooth) that adversely affects the cohesion to concrete matrix. Moreover, due its low water absorption, copper slag leaves more excess water in the concrete. The excess water caused excessive bleeding, resulting in the formation of internal voids and capillary channels in the concrete, and eventually reduces the quality of concrete. Therefore, the strength of the concrete with lower copper slag content can be improved by the positive effect of copper slag. In this case, sand is still dominant to cohesion properties of the concrete and assisted by copper slag in abrasion resistance and compressibility.

Overall, copper slag brings considerable gain in hardened properties of concrete. In any non-aggressive environment, it can safely be used as alternate to conventionnal sand since it exhibits good durability characteristics (Brindha and Nagan, 2011).

Hence, this literature review clearly shows the benefits of using copper slag in concrete. From the arguments in Section 2.4, it is clear that different curing methods used on conventional concrete do not lead to the same outcomes. Furthermore, environmental conditions impact the development of conventional concrete strength. Investigating these factors on copper slag concrete is still topical since not well covered. That is what the proposed research is aimed at studying.

2.6 SUMMARY

Concrete is extensively used in many parts of the world. The compressive strength and the durability are commonly used to define the quality of concrete. Compressive strength, however, is the most critical property of concrete as it directly linked to the application that concrete is known for, that is, its ability to withstand compressive loads.

Various studies reviewed in this chapter have shown that curing is critical to final quality of concrete. Without any form of curing, the mixing water dries out from concrete earlier. The early evaporation of water results in low humidity within the concrete. As a consequence of this, the hydration reaction of cement gets incomplete and leads to hindered development of microstructures. For concrete to gain the required strength, the hydration of the cement must properly occur until its completion (Princy and John; 2015). To do so, fresh concrete must be immediately placed in a favorable environment which ensures constant contact between water and concrete or which alternatively prevent early losses of water. This leads to the use different techniques that present various effects on the final properties of concrete and whose choice is dictated by the site, the type of construction and the availability of the material (Reddy, 2013).

Among the curing methods reviewed, the conventional water curing (immersion or ponding) was noted to have the reputation of being the most effective method which results in high compressive strength of concrete. As the concrete is bathed in sufficient water in this method, the loss of water is prevented to the maximum, and the extent of cement hydration is maximised. This allows hydration products such as silicate and aluminate to develop and fill the pores and capillaries to the maximum. Among them, calcium silicate hydrate is the main strength-provider which also as a porosity reducer. Its hydration influences the development of microstructures. Without adequate calcium silicate hydrate, the development of dense microstructures and the refinement of structures of pores are interrupted (Safiuddin et al., 2007). So, when it comes to achieve good concrete properties, water curing seems to be the most efficient curing method.

In practical situation on sites however, water curing requires a large amount of water that is sometimes not available. Various other alternatives have been proposed such as Jute bag wrapping (Jackson and Akomah, 2018), spraying with water (Usman and Isa, 2015), poly-film wrapping (Safiuddin et al., 2007), membrane curing compounds (Princy and John, 2015). These methods generally work by reducing the moisture movement from concrete. Doing so can also increase the degree of cement hydration. And since concrete structure are not always developed in controlled temperature and humidity environments such as on site, the impact of weather conditions cannot be undermined. Indeed, several studies have reported that weather conditions can positively or negatively influence the hydration reaction. They can contribute to severely dry out the mixing water; they can also bring extra water to increase the degree of hydration. As such, weather cannot be disregarded in the curing process since it is among the prime factors that determine the final quality of concrete (Reddy, 2013).

In line with the greening of the concrete industry, copper slag has been proposed as concrete-making component by various researchers. In this literature review, copper slag has been reported to possess mechanical and chemical characteristics that qualify it for this purpose. It has also been showed that copper slag produces positive effect while bringing considerable gain in hardened properties. It makes the concrete less porous while replacing the sand in proportions not exceeding 40 – 50 %. The strength increment with substitutional amounts of copper slag was mainly attributed to the physical properties of copper slag, i.e. angular shapes edges that further improve the cohesion of the concrete matrix (Wu et al., 2010). It can be used safely in any non-aggressive environment. One limitation to the adoption of copper slag concrete resides in the uncertainty around its behaviour as related different forms of curing concrete. This is investigated in this study and reported in the remaining chapters of the dissertation.

3. EXPERIMENTAL PROGRAM AND EQUIPMENT USED

The purpose of this study was to assess the strengthening of copper slag concrete under three curing methods: water immersion, water spraying, and plastic sheet covering. In addition to this, some specimens were air-dried without curing to account for the impact of concrete curing. The influence of on-site weather conditions on concrete strengthening was also investigated.

Concrete cubes were prepared using copper slag as the granular constituent. Then samples were subjected to various curing schemes for 28 days after which their compressive strength was measured. The following steps were considered in all test cases: physical characterisation of granular materials, preparation of the concrete mix, curing and measurement of the compressive strength.

The present chapter provides relevant details about the experimental plan, the equipment and testing rig used as well as the testing procedures followed. The data collected and underlying methodology are also presented in line with the objectives set for the research work. Finally, challenges encountered during the experimental effort and their implications on future results are discussed.

3.1 MATERIALS USED IN THE PREPARATION OF CONCRETE

Concrete generally requires three entities: conventional aggregates, cement, and water. In the context of the present study, copper slag was used in the form of concrete-making components and partially substitutes for conventional aggregates. In this section, relevant technological features of the components used in the preparation of concrete are presented. The features specifically focus on the nature and the source of the concrete components.

3.1.1 Conventional aggregates

The conventional aggregates used in this study were collected from the Mofya quarry. This quarrying operation shown in Figure 3.1 is part of Tenke Fungurume Mining (TFM) in the Democratic Republic of The Congo (DRC). The locally-sourced aggregates are basically crushed dolomites. In-house characterisation indicates that the aggregates consist of micro-sandstone rock and contain around 15 – 25 % $CaCO_3$ with hardness between 3 and 5 on the Mohs scale.

Figure 3.1 Aerial view of the crushing plant at the Mofya quarry

Two types of aggregates sourced from the Mofya quarry were needed: fine aggregate or sand with particle size below 4.75 mm and coarse aggregate or stone of size larger than 19 mm (Grieve, 2009). The two fractions making up the conventional aggregates were collected from the stockpiles respectively shown in Figures 3.2 and 3.3.

Figure 3.2 Stockpile of sand at the Mofya site

Figure 3.3 Stockpile of 19 mm stone at the Mofya site

3.1.2 Copper slag

The copper slag used in this study was also directly collected on TFM site. It is a sandy-like granular material that is physically black in colour and glassy as shown in Figure 3.4. TFM uses it to spray the metals before painting them to make the surface rough and for the paint to adhere properly. This material is brought to TFM by recovering it from some old stockpiles located in the town of Kolwezi, in the Lualaba Province, DRC.

Figure 3.4 Sample of copper slag on a weighing scale

3.1.3 Binding agent

The type II Portland limestone cement illustrated in Figure 3.5 was used as binding agent for the preparation of all the concrete samples. The selected hydraulic binder is denoted CEM II A-LL 42.5 N and contains 80 – 94 % of finely ground clinker. The remainder is finely ground, and high-quality limestone and calcium added to control the setting time of concrete.

Figure 3.5 Ohorongo cement

The Portland limestone cement, i.e. CEM II A-LL 42.5 N, is designed to meet a strength class of 42.5 with normal early strength "N". The acronym "CEM" stands for cement; "LL" indicates high-quality limestone while "A" shows that the proportion of limestone by mass is between 6 % and 20 %. This type of cement was selected recommended for applications requiring high strength concrete.

3.1.4 Water

Tap water was used as the last ingredient needed in the preparation of concrete. Water from the same tap was used for concrete mixing and for curing. However, the quantities required in concrete were carefully measured using graduated cylinders and buckets.

3.2 SAMPLING PROTOCOL

The quality of results underpinning any research work is widely known to depend highly on sampling more than even the testing itself. Sampling must be performed carefully in order to ensure the production of representative lot fractions.

As far as this research is concerned, a protocol was devised for the collection of similar aggregate fractions from the bulk material. This entailed the following steps followed for both the sand and the stone: on-site collection of two lots of fine and coarse aggregates respectively from the stockpiles in Figures 3.2 and 3.3, splitting of coarse aggregates, and quartering of fine aggregates and copper slag.

The sampling routine followed on-site and in TFM's Civil Engineering laboratory is covered in detail in the subsequent sections. The idea was to prepare ingredients that would guarantee the production of concrete cubes of similar quality.

3.2.1 On-site collection of lots of aggregates

Large batches of fine and coarse aggregates were constituted from stockpiles in accordance with ASTM Practice D75. The two lots were later stored in the laboratory.

On-site collection was done in such a way that the effect of segregation of the integrity of the two lots of aggregates was minimised. Basically, shovels were used to collect three increments from each stockpile. The first increment was taken from the top tier of the stockpile, the second from the mid-section, and the last from the base. All three increments were constituted by randomly collecting shovelfuls of material all around the stockpile. Figure 3.6 exemplifies some of the 25 kg bags making up the lot of coarse aggregates. In the end, ten (10) bags of stone, six (6) bags of sand, and six (6) bags of copper slag were transported to the laboratory.

Figure 3.6 Samples collected on site

The bagged bulk samples finally obtained from the two stockpiles were to be portioned in small-sized samples characterisation in accordance with ASTM Practice C-702. The protocol of portioning entailed the splitting of coarse aggregates and the quartering of fine aggregates, i.e. sand and copper slag. The two techniques used for bulk lot portioning are presented in the next two sections.

3.2.2 Splitting of coarse aggregates

The protocol followed for splitting coarse aggregates in compliance with ASTM Practice C-702 is summarised hereafter. First, 25 kg bag of stone was arbitrarily selected for reduction to a representative 3 kg sample. Next, a fraction of the bag content was poured onto a receiving pan; this was then poured into a Jones riffle as shown Figure 3.7. The splitter discharged the aggregates as two fractions of approximately equal mass into two chutes. The process was repeated until the content of the bag was emptied into the Jones riffle. One of the two fractions collected from the riffle chutes was further split through the riffle. The cycle was repeated with the product from one of the two receptacles as many times as necessary until a 3000 g sample was readied for laboratory characterisation.

Figure 3.7 Jones riffle used for the splitting of coarse aggregates

3.2.3 Quartering of sand and copper slag

Quartering is a sampling technique that is more appropriate for finely-grained materials. In this work, the technique was used to prepare samples of both sand and copper slag. The same standard, i.e. ASTM Practice C-702, used for splitting of coarse aggregates also applied here.

In terms of the protocol, 10 kg of bulk sample of sand was to be reduced to a representative 500 g sample for later characterisation. The same routine was followed also in the handling of copper slag.

The initial bulk sample was placed on a clean levelled surface and homogenised by mixing it over with a shovel three times. The bulk sample was then shovelled into a conical shape by piling each shovelful on top of the preceding one. The pile was flattened by pressing down its apex with the shovel and divided into four equal quarters with a trowel as shown in Figure 3.8. Two non-consecutive quarters of fine materials were then selected and recombined for further quartering. The process was repeated until the desired 500 g sample was obtained for laboratory characterisation.

Figure 3.8 Illustration of sand quartering

3.3 CHARACTERISATION OF GRANULAR MATERIALS

Granular materials are essential components to the preparation of concrete. Also known as aggregates, their purpose is to stabilise concrete and limit the need for expensive cementitious materials to a small fraction thereby cutting down on preparation costs. For this to effectively happen, granular materials must be of adequate particle size distribution so that a cheap, malleable, workable, dense and coherent concrete is produced. It follows that the characterisation of granular materials is important as critical properties are determined for the proper design of a concrete mix. The properties include, on the one hand, size, shape and compacted bulk density for stone, and on the other, fineness modulus for sand (Addis and Goodman, 2009).

In this work, the following tests and properties were considered on stone, sand, and copper slag: particle size analysis, specific gravity, water absorption, bulk density, and moisture content. In addition to this, aggregate crushing value (*ACV)* testing was conducted on coarse aggregates to determine its strength. Details of the associated laboratory procedures are provided in the subsequent headings.

3.3.1 Particle size analysis

The particle size distribution of a granular material is conventionally measured by standard sieving. Once performed, the particle size distribution obtained is used to extract three basic properties of the material: grading, dust content, and fineness modulus. Grading refers to the particle size distribution in the aggregate material. The latter corresponds to the percentage of the material passing through each sieve. Dust content refers to the mass fraction of material passing 75 µm. Fineness modulus refers to the fineness or the coarseness of the aggregate. It is a dimensionless parameter describing the average particle size of the aggregate.

The execution of the particle size analysis is presented in this section while the properties of the material are determined later in the next chapter. Figure 3.9 is a snapshot of the equipment that was used for particle size analysis.

Figure 3.9 Shaker with a stack of sieves during particle size analysis

From the onset, samples of mass 3000 g for stone and 1000 g for sand or copper slag were prepared for sieving by splitting and quartering (refer to Section 3.2). Each sample was oven-dried at 105˚C ± 5˚C for 24 h to eliminate any trace of moisture. As shown in Figure 3.9, a set of sieves of openings in a ratio-2 geometric sequence was stacked from the coarsest down to the finest. The nest of sieves was placed on a vibrating shaker while the initially oven-dried sample of granular material was poured from the top sieve. The stack was covered with a lid and shaken for 10 min for stone and 15 min for sand and copper slag. Then, the mass of material retained of each sieve was carefully poured into a pan and weighed on a scale. Sieves of size between 37.5 and 0.150 mm arranged in a ratio-2 geometric sequence as per standard ASTM C125 were used. This was to make the later determination of the fineness modulus easy. Conversely, sieves between 25 mm and 0.075 mm were arranged in line with standard ASTM C136 so that dust content could be inferred. Mass retained on each sieve following the above sieve sequence was finally recorded on a gradation analysis sheet for later use.

3.3.2 Determination of density and specific gravity

Density and specific density were measured in line with standards ASTM C127 for coarse aggregate and ASTM C128 for fine aggregate and copper slag.

As for the ASTM C127 test method, 3000 g of coarse aggregate was allowed to dry in an oven at 105˚C for 24 h; then, weighed and soaked in water for 24 h. after this period, the test sample was removed from water. The sample was then rolled in a large absorbent cloth to completely remove all visible films of water. Thereafter, it was weighed to determine its mass in the saturated surface-dry condition. After that, test sample, in saturated-surface-dry state,was placed in a container, and weighed now in water to determine its apparent mass in water. Using the mass values thus obtained, and Equation (3.1), it was then possible to calculate the specific gravity (RD) and the density (ρ):

$$\begin{cases} RD = \dfrac{M_{OD}}{M_{OD} - M_{in\,water}} \\ \rho_{aggregate} = 997.5\ (\text{or}\,1000) \times RD \end{cases} \qquad \textbf{(3.1)}$$

where M_{OD} represents the mass of oven-dry test sample in air (g)

$M_{in\,water}$ represents the apparent mass of saturated test sample in water (g)

$\rho_{aggregate}$ represents the density of the aggregate (kg/m^3)

As for the ASTM C128 test method, each test was carried out by using two graduated pycnometers of different volumes (ranging between 925 cm^3 and 950 cm^3 generally). It consisted of taking 600 g sample of sand or copper slag, drying it in oven at 105˚C for 24 h and weighing it. Afterwards, the dry sample was placed into a pycnometer and water was filled in sufficient quantity to properly immerse the dry material. After that, the pycnometer was rolled, invert and agitated to release and eliminate the air bubbles and then left to rest for 24 h. After this period, further water was added up to the calibrated capacity of the pycnometer and the total mass of the pycnometer containing the sample and water was determined. At the end, the sample was removed from it, the remaining mass (the pycnometer filled with water up to calibrated capacity) was determined.

Density and specific gravity were calculated for the mass values was obtained as per Equation (3.2):

$$\begin{cases} RD = \dfrac{M_{OD}}{M_{pyc+w} + M_{OD} - M_{pyc+w+sample}} \\ \rho_{aggregate} = 997.5\ (\text{or}\,1000) \times RD \end{cases} \tag{3.2}$$

where M_{OD} is the mass of oven-dry specimen (g)

M_{pyc+w} is the mass of pycnometer filled with water to calibration mark (g)

$M_{pyc+w+sample}$ is the mass of pycnometer filled with specimen and water to calibration mark (g).

3.3.3 Water absorption

Absorption is the ability of an aggregate to suck up water into its porous spaces; it helps control the quality of concrete. High values indicate non-durable material.

The test was performed as follows: 1 kg sample of stone, sand or copper slag was soaked in water for 24 h. Then, water was dried from the surface particles to determine the mass of saturated surface-dry test sample. This was done by using a blow dryer for copper slag and sand (ASTM C128) and an absorbent cloth for coarse aggregate (ASTM C127). Water absorption was then determined as per Equation (3.3):

$$A_W = \frac{M_{AW}}{M_{OD}} \times 100\% = \frac{M_{SSD} - M_{OD}}{M_{OD}} \times 100\% \quad \textbf{(3.3)}$$

where M_{OD} represents the mass of oven-dry specimen (g)

M_{SSD} represents the mass of saturated surface-dry specimen (g)

M_{AW} represents the mass of water that fully fills internal pores (g).

3.3.4 Bulk density

The compacted bulk density (*CBD*) was determined for each type of granular material in accordance with the ASTM C29 standard. This test method was carried out using apparatus like scale, tamping rod, scoop and a cylindrical metal measure of height approximately equal to the diameter provided with handles.

The starting point was to prepare 15 kg of material that was oven-dried at 105˚C for 24 h. The weight of the cylindrical measure was determined using the scale and its volume was recorded. Aggregates were then filled in the cylinder in three equal layers. Before adding a layer, the previous one had to be compacted with 25 blows using the tamping rod to make it compact. The last layer had to overflow. After that, the aggregates surface was levelled with a straightedge and the weight of the whole (the measure plus its content) was determined.

For reproducibility, the routine described above was repeated five times and the values were recorded each time. The compacted bulk density (kg/m^3) value was then calculated as per Equation (3.4):

$$CBD = \frac{C - A}{B} \quad \textbf{(3.4)}$$

where A represents the weight of the measuring cylinder

B represents the volume of the measuring cylinder

C represents the weight of the measuring cylinder filled with aggregate.

3.3.5 Aggregate crushing value test

Aggregate crushing value test is a method commonly used to assess the aggregate strength. The aggregate crushing value (*ACV*) represents a useful index that shows the overall quality of the aggregate.

The associated test consists in measuring the crushing strength of the broken rock. The test methodology was done in accordance with BS 812:110 and BS 812-11 standards. It entailed the oven-drying of 3 kg of aggregates at 105˚C for 24 h followed by sieving. Aggregates passing 12.5 mm and retained on the 9.5 mm sieve were selected as the test sample and weighed. The selected sample was then poured in a crushing cylinder (see Figure 3.10) in three equal layers which had to be compacted with 25 blows before adding the next one.

Figure 3.10 Aggregate in crushing cylinder

At the end of this, the cylinder content was covered with a base plate then placed in the compression machine. A 400 kN load which has to be reached in almost 10 min was applied to crush the aggregate (see Figure 3.11).

Figure 3.11 Crushing cylinder placed in compression machine

After that, the crushed material was carefully removed from the crushing cylinder and sieved through a 2.36 mm sieve as shown in Figure 3.12. The passing fraction was then weighed.

Figure 3.12 Crushed sample and 2.36 mm passing

The *ACV* was finally computed as per Equation (3.5):

$$ACV = \frac{M_b}{M_a} \times 100\% \quad \textbf{(3.5)}$$

where M_a represents the original mass before crushing

M_b represents the mass of material passing 2.36 mm sieve.

3.3.6 Moisture content

Moisture content was determined following the ASTM C566-13 standard. Indeed, a representative sample (3000 g of stone, 500 g of sand or copper slag) was placed into a clean dry container and weighed to determine the apparent mass of sample (a). Then, the container was oven-dried at 105˚C for 24 h. After that, the container was cooled down and its content weighed again so as to determine the mass of the dry sample (b). Moisture content (in %) was finally calculated as per Equation (3.6):

$$W = \frac{a-b}{b} \times 100\% \qquad \textbf{(3.6)}$$

3.4 PREPARATION OF THE CONCRETE MIX

Concrete mixes were designed in this study following the method advocated by the Cement and Concrete Institute or C&CI (Addis and Goodman, 2009). The adoption of the method was primarily motivated by the availability of all the required materials features such as: the fineness modulus, the bulk density and specific gravity. Steps presented in the subsequent sections are taken in the mix design process and consist in specifying the desired concrete characteristics and properties; characterize the different components (cement, sand and stone); then after properly proportion them.

3.4.1 Specification of concrete characteristics and properties

The purpose of this section is to specify the desired strength and slump of concrete. For investigation purpose, a 25 MPa concrete strength was chosen as the specified strength.

The target strength to be considered in the design process is usually equal to the specified strength plus an allowance to account for variations in materials, variations in methods of mixing, transporting, and placing the concrete; and variations in making, curing, and testing concrete specimens (Kosmatka et al., 2003). As related to the aim of the present study, this has not been taken into account. The specified strength of 25 MPa was simply considered as the target strength.

To allow for manual compaction, an approximate slump range of 75 – 150 mm is recommended by C&CI (Addis and Goodman, 2009).

Using Figure 3.13, water-to-cement ratio (*w*:*c*) was determined to be 0.60 for a 25 MPa non-air-entrained concrete.

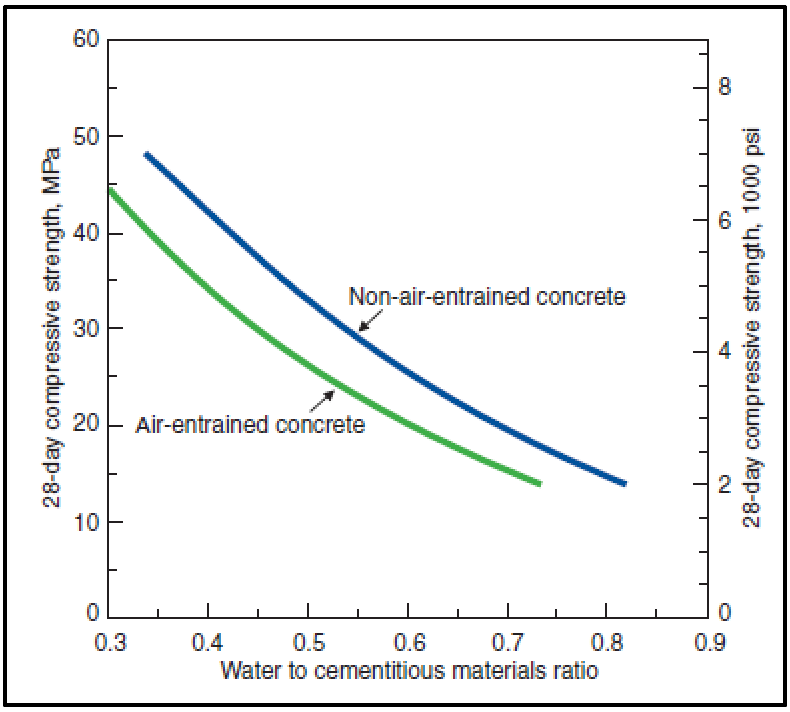

Figure 3.13 Approximate relationship between compressive strength to cementitious materials ratio for concrete using 19 – 25 mm nominal maximum size coarse aggregate (Kosmatka et al., 2003)

3.4.2 Characterisation of materials

This was the goal of tests previously conducted and exposed on Section 3.3. The essential characteristics retained on granular materials are listed in Table 3.1.

Table 3.1 Essential characteristics of concrete ingredients

Ingredients	Characteristics
Cement	Type: CEM II 42.5N *RD*: 3.14
Stone	Size: 19 mm *CBD*: 1510 kg/m^3 *RD*: 2.66
Sand	Type: washed crusher sand *RD*: 2.75 *FM:* 2.58

3.4.3 Proportioning of materials

This action involved the estimation of the required water, the calculation of cement content and the calculation of aggregate content.

Water requirements depend on particle shape and surface texture of sand, stone size, required slump, and cementitious materials. By using the average values in Table 3.2, the water requirement was estimated at 205 l/m^3. The choice of this value was done with the understanding that the sand is of good quality as it is washed at the Mofya quarry after crushing.

Table 3.2 Water requirements of concrete mixes using 19 mm stone, for 75 mm slump (Addis and Goodman, 2009)

Sand quality	**Water content, *l*/m^3**	
	Natural	**Crusher**
Very poor	240	235
Poor	225	225
Average	210	215
Good	195	205
Excellent	180	195

For the calculation of cement content, the following was done per Equation (3.7):

$$M_c = \frac{\text{Water content}}{w:c} = \frac{205}{0.6} = 342 \quad \textbf{(3.7)}$$

Rounded to the closest multiple of 50, M_c = 350 kg/m^3.

For the calculation of aggregates content, the fractional contents of stone and sand needed to be determined. The stone was calculated as per the Equation (3.8) advocated by the C&CI:

$$M_a = CBD\left(K - 0.1\,FM\right) \quad \textbf{(3.8)}$$

Where *CBD* is the stone bulk density given in Table 3.1 and *K* is factor that depends on the maximum size of stone and the workability of the concrete.

Guidelines on applicable values of *K* for various conditions of slump size and compaction techniques are provided in Table 3.3.

Table 3.3 Values of *K* for determining stone content (Addis and Goodman, 2009)

Approximate slump range, mm	Placing requirement	*K* values for 19 mm stone
75 – 150	Hand compaction	0.94
25 – 100	Moderate vibration	1.00
0 – 25	Heavy vibration	1.08
60 – 125	Pumped	0.86
25 – 50	Concrete roads	-

Based on the conditions prevailing in this research, K = 0.94 was selected as the most appropriate value. FM is sand fineness modulus, given in Table 3.1 so that based on Equation (3.8), stone content is M_a = 1030 kg/m^3.

The sand content was calculated, assuming full compaction of the concrete, from the fact that volume of concrete is equal to the sum of absolute volumes of cement, sand, stone and water. Thus, ignoring air content, for 1 m^3 concrete:

$$1 = \frac{M_c}{RD_c \times 1000} + \frac{M_a}{RD_a \times 1000} + \frac{M_s}{RD_s \times 1000} + \frac{M_w}{RD_w \times 1000} \qquad \textbf{(3.9)}$$

The sand content can now be solved for and determined to be M_s = 815 kg/m^3.

From all the above computations, estimated mass proportions per cubic meter are: 350 kg of cement, 815 kg of sand, 1030 kg of stone, and 205 *l* of water.

3.4.4 Make and assess a trial mix

With the estimated contents, 0.025 m^3 trial mixes were prepared. Using an electric concrete mixer, cement, sand and stone were first stirred together, and then water was gradually added.

The stone content and the cohesiveness of the fresh concrete obtained were assessed through the slump test (see Section 3.6). Then, cube specimens were cast, immersed in a curing tank for crushing at 7 and 28 days, to check the strengthening.

In total, three trial mixes TMCS1, TMCS2 and TMCS3 were successively prepared and corrected. Stone, sand and water contents were adjusted to obtain the ideal mix meeting the specified requirements.

Base on the outcome of previous activities, proportions shown in Table 3.4 reflect the mix designs retained for investigation purposes.

Table 3.4 Concrete mix design

Mix ID	**Replacement rate**	**Constituents for 1 m^3 of concrete**				
		Water, *l*	**Cement, kg**	**19 mm stone, kg**	**Crusher sand, kg**	**Copper slag, kg**
CS0	0 %	228	350	1100	700	0
CS20	20 %	228	350	1100	560	140
CS40	40 %	228	350	1100	420	280
CS60	60 %	228	350	1100	280	420

CS0 stands for a concrete mix design not containing copper slag depicts the design fixed after corrections on trial mixes (see section 3.4.4.) to achieve 25 MPa of compressive strength. From it, sand has successively been replaced partially with copper slag in proportions of 20 %, 40 % and 60 %. Thus, other three (3) concrete combinations were prepared: CS20, CS40, and CS60.

3.5 MIXING PROCEDURE

Granular materials were assumed to be in *ad* (air-dry) state as they were stored in a dry space in the laboratory. Thus, before mixing them, moisture contents (see Section 3.3.6) were determined in order to adjust the amount of aggregate and water required.

Using the mix designs listed in Table 3.4., appropriate content of concrete constituents was weighed as illustrated in Figure 3.14. Granular materials tossed into the mixer; and then, the cement and water were added and mixed until a consistent and homogenous mix was obtained. As shown in Table 3.4, constant proportions of cement and water were used for all design. In other words, a water-to-cement ratio of 0.65 was used for all the batches.

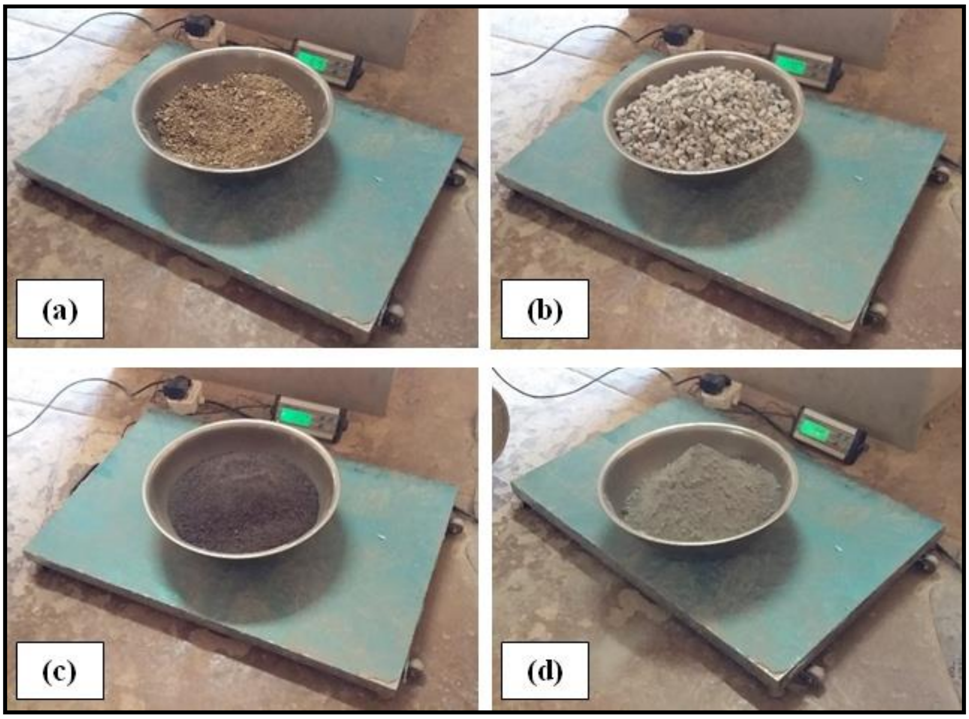

Figure 3.14 Weighing of concrete constituents: (a) crusher sand; (b) 19mm stone; (c) Copper slag; and (d) Type II Portland limestone cement

3.6 SLUMP TEST

Slump test was done in accordance with SANS 5862-1:2006 to assess the effect of adding copper slag on the workability of concrete. The test basically measures the slump of fresh concrete under its own weight.

To start, the cone mould and the base plate were damped and placed on a levelled surface. Afterwards, the mould was maintained with feet above the base plate and then fresh concrete was filled in approximately three equal layers which had to be tamped 25 times using a tamping rod. When full, the top surface was levelled by rolling the tamping rod across the top edge of the mould. After carefully removed the mould, the resulting slump was measured as shown in Figure 3.15.

Figure 3.15 Slump test

3.7 SPECIMENS CURING

After slump tests, the fresh concrete was poured in two compacted layers into 150 x 150 x 150 mm steel cube moulds. The cubes were shaken by hand to prevent segregation. Twenty-four hours after casting, the concrete cubes were removed from the moulds and labelled appropriately in terms of the curing method to be used and the production date (Figure 3.16(c)).

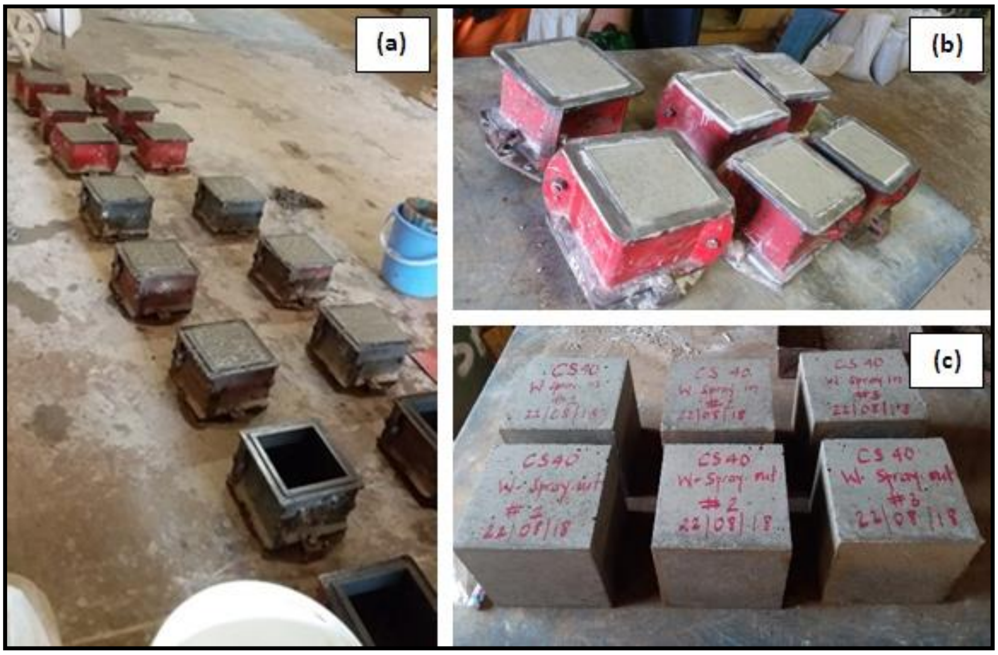

Figure 3.16 (a) Casting, (b) de-moulding and (c) labelling of concrete cubes

Six specimens were prepared per mix type (i.e. 0 %, 20 %, 40 % and 60 % copper slag substitution) so that 24 samples were available per curing method (see Table 3.5).

Table 3.5 Specimen number that was casted

No.	Curing method	Mix ID	Cube samples
1	Immersion in water	CS0	6
		CS20	6
		CS40	6
		CS60	6
2	Indoor water spraying	CS0	6
		CS20	6
		CS40	6
		CS60	6
3	Outdoor water spraying	CS0	6
		CS20	6
		CS40	6
		CS60	6
4	Indoor plastic sheet	CS0	6
		CS20	6
		CS40	6
		CS60	6
5	Outdoor plastic sheet	CS0	6
		CS20	6
		CS40	6
		CS60	6
6	Indoor air drying	CS0	6
		CS20	6
		CS40	6
		CS60	6
7	Outdoor air drying	CS0	6
		CS20	6
		CS40	6
		CS60	6

The cubes were cured using the designated curing method: immersion in water, water spraying, air-drying, and covering with plastic sheet. Half of the samples were stored indoors in the laboratory at ±20˚C of temperature while the remaining half was stored outdoor. The purpose of doing this was to account for the influence of on-site weather conditions on concrete strengthening for each curing method (apart from immersion).

Curing process of each method is described in following sub-sections.

3.7.1 Immersion in water

Using a curing tank, specimens were immersed under tap water in the laboratory for 28 days (Figure 3.17).

Figure 3.17 Curing tank holding concrete cubes immersed in water

The curing tank was equipped with a temperature controller to maintain temperature between 20˚C and 24˚C. After 28 days of curing, cubes were removed from the water and left to dry at room temperature.

3.7.2 Water spraying

This method consisted in watering cube specimens using a watering can, every morning around 7 a.m. – 8 a.m. and evening after 5 p.m., for 28 days. The spraying was done until cubes became completely wet as shown in Figure 3.18.

Figure 3.18 Water spraying of concrete cubes under two different conditions: (top) indoors and (bottom) outdoors

3.7.3 Plastic sheet covering

For this method, every concrete cube was wrapped with four layers of a clear plastic sheet as shown in Figure 3.19. The cubes were then subjected to inside or outside exposure for 28 days (see Figure 3.20).

Figure 3.19 Actual plastic sheet covering of concrete cubes

Figure 3.20 Plastic sheeting of concrete cubes under two different conditions: (top) indoors and (bottom) outdoors

3.7.4 Air curing

In this method, the concrete cubes were allowed to dry in open air with no other form of curing.

Figure 3.21 Curing of concrete cubes at ambient temperature under two different conditions: (top) indoors and (bottom) outdoors

3.8 COMPRESSIVE STRENGTH AND HARDENED DENSITY

After curing cubes for 28 days, concrete samples were collected for further testing. First they were weighed as shown in Figure 3.22 and then their masses recorded on a datasheet. Using the 28-day volume (V_{28}) of each specimen, the hardened density D_{28} (in g/cm^3) was calculated as follows:

$$D_{28} = \frac{W_{28}}{V_{28}} \quad \textbf{(3.11)}$$

Where W_{28} represents the 28-day cube masse

After that, in accordance with SANS 5863:2006 cube specimens were placed under the compression machine at a loading rate of 350 kN/min until breakage was observed. At the end of the compression cycle, the load (P) was recorded, and the compressive strength f_{c28} (in MPa) was determined as follows:

$$C_{28} = \frac{P}{S} \qquad \textbf{(3.12)}$$

Where S is the cube face area on which the load was applied.

Figure 3.22 Weighing of concrete cubes

3.9 CHALLENGES ENCOUNTERED

The “sand” produced at the Mofya quarry contains particles of size 9.5 mm (see Figure 3.23) that should normally fall into stone grading. As such, the lot of Mofya sand had to be sieved in order to screen out all particles coarser than size 4.75 mm. The laborious task enabled to produce the desired fine aggregate or sand of particle size less than 4.75 mm.

Figure 3.23 Samples of crusher sand (top) before and (bottom) after sieving through a 4.75 mm sieve

Fortunately, the availability of proper equipment and qualified staff on the TFM site made the effort easy to carry out.

4. CHARACTERISATION OF THE LOCALLY-SOURCED COPPER SLAG CONCRETE

The experimental work described in Chapter 3 consisted in first characterizing all the raw materials in order to extract critical properties necessary to properly design the concrete mix; then, the preparation of the concrete mixes followed. By using the mix designs retained for investigation purposes (CS0, CS20, CS40 and CS60), concrete cubes were prepared, subjected to various curing schemes and then crushed to measure their compressive strength after 28 days.

This chapter presents on the results of physical characterization tests conducted on copper slag, crusher sand and stone. Concrete properties in both fresh and hardened states are also reported. Slumps values and the 28-day compressive strength are presented in terms of the seven curing method used: immersion in water (IM), indoor water spraying (WS-I), indoor covering with plastic sheet (PS-I), indoor air-drying (AD-I), outdoor water spraying (WS-O), outdoor covering with plastic sheet (PS-O) and outdoor air-drying (AD-O).

A raw data was collected on six replicates of cube specimens per curing method and on each mix type. Resulted average values and standard deviations were calculated. Thus, outcomes of the impact of the different curing techniques used on compressive strength are reported.

4.1 GRANULAR MATERIALS CHARACTERIZATION

The following tests were considered on stone, sand, and copper slag: particle size analysis, specific gravity, water absorption, bulk density, and moisture content. In addition to this, aggregate crushing value (*ACV)* testing was conducted on coarse aggregates to determine its strength. Results of the associated laboratory procedures are provided in the subsequent headings.

4.1.1 Particle size analysis

Particle size analysis has been used to understand the particle size distribution and the fineness modulus of granular materials. Thus, Table 4.1 presents the percentages of mass fraction passing on each sieve after the sieving procedure, reported as gradation distribution.

Table 4.1 Aggregate gradations

Sieve size (mm)	Mass fraction passing (%)		
	Copper slag	**Crusher sand**	**19 mm stone**
25	-	-	100
19	-	-	99
9.5	-	-	7.0
4.75	100	100	2.0
2.36	66	100	2.0
1.18	21	67	-
0.6	8	40	-
0.3	3	23	-
0.15	1	14	-
0.075	0	11	-

The grading curves plotted from Table 4.1 results are reported in Figure 4.1.

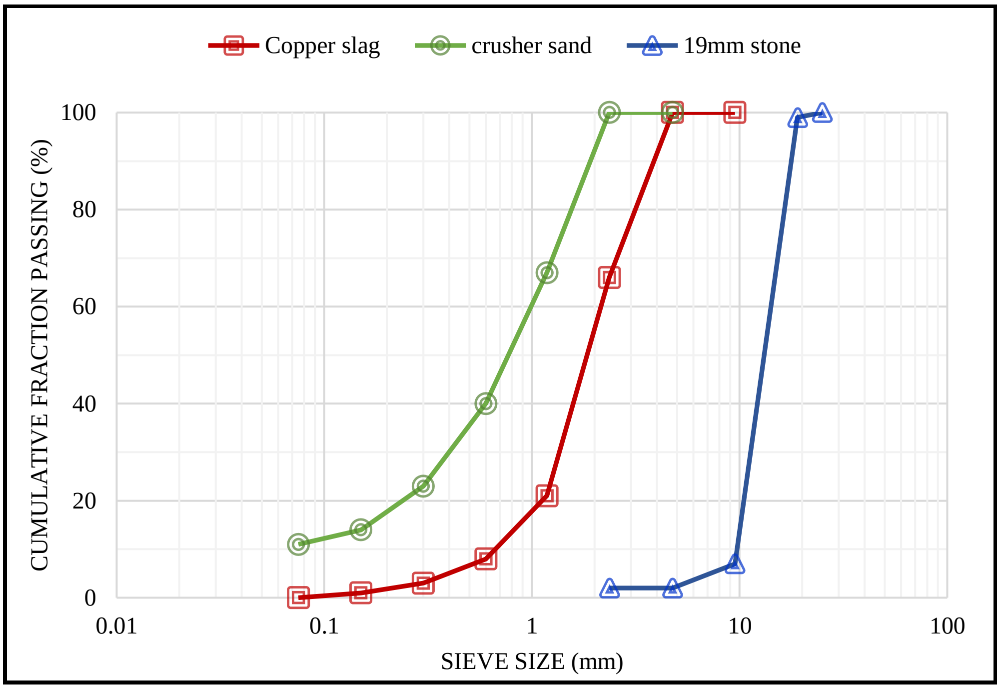

Figure 4.1 Grading curves of granular materials

The results show that copper slag contains granular particles ranging from 4.75 mm to 0.15 mm in size; crusher sand from 2.36 mm to 0.075 mm and stone from 19 mm to 2.36 mm. That is, copper slag contains coarser particles than the sand used in this study. Moreover, values in Table 4.1 show a significant dust content within the crusher sand; namely, 11 % of mass fraction of crusher sand passing 0.075 mm sieve size.

Regarding grading curves, it can visually be seen from Figure 4.2 that copper slag and crusher sand are continuously graded while stone is uniformly pretty graded. Indeed, Table 4.1. shows that stone consists of predominantly one particle sizes since 99 % of its particles have passed through 25 mm sieve size and 7 % through 19 mm. That, the nominal size of Mofya stone is 19 mm showed by 92 % of retained. Copper slag and crusher sand, as for them, contains particles across a wide range of sizes.

Table 4.2 reports on fineness modulus (FM) calculated from Table 4.1 results.

Table 4.2 Fineness modulus values

Sieve size (mm)	Cumulative mass fraction retained (%)		
	Copper slag	**Crusher sand**	**19 mm stone**
19	-	-	1.2
9.5	-	-	92.9
4.75	-	-	97.6
2.36	34.2	0	97.7
1.18	78.9	33.2	97.7
0.6	91.7	59.5	97.8
0.3	96.5	76.7	97.8
0.15	98.6	89	97.9
FM	**4.00**	**2.58**	**6.81**

Ranking in descending order of fineness modulus result in 19 mm stone, copper slag and finally crusher sand. Thus, crusher sand is the finest material of the three granular materials used in this investigation with a fineness modulus of 2.58 which classifies it as medium-fine.

4.1.2 Specific gravity and compacted bulk density

Specific gravity (*RD*) was determined in accordance with ASTM C127 for coarse aggregate and ASTM C128 for fine aggregate and copper slag, while the compacted bulk density (*CBD*) was determined for each type of granular material in accordance with the ASTM C29 standard. Results of the associated laboratory procedures are summarized in Table 4.3.

Table 4.3 Specific gravity, compacted bulk density and water absorption of copper slag, sand and stone

Properties	Aggregate type		
	Copper slag	Crusher sand	19 mm stone
Specific gravity *(RD)*	2.72	2.75	2.66
Compacted bulk density *(CBD)*	1.45	1.60	1.51
Aggregate crushing value (*ACV*)	-	-	21.43 %

From Table 4.3, it comes out that copper slag possesses a specific gravity of 2.72 g/cm^3 reasonably similar to that of crusher (2.75 g/cm^3). Moreover, copper slag showed the lowest compacted bulk density compared to Crusher sand. This depicts the presence of high void content within copper slag particles than crusher sand.

4.1.3 Water absorption and moisture contents results

In this investigation, the water absorption was determined in accordance with ASTM C127 for stone and ASTM C128 for crusher sand and copper slag; while the moisture contents were determined following the ASTM C566-13 standard for both stone, crusher sand and copper slag.

The water absorption was measured at 0.0 % for copper slag, compared to 5 % for crusher sand and 1.15 % for stone. As the water absorption coefficient describes the permeability of a granular material, it can be said that copper slag mixtures would not require more mixing water than those based on sand since no amount of water would be lost through absorption. However, for mixtures based on more sand, it would be necessary to additionally admix a quantity equivalent to that absorbed to maintain the workability.

The moisture content was determined whenever the need to produce a concrete mixture arose. As a result of this, the recorded values differed depending on the moisture conditions of the collection source as well as the storage environment. These ranged from 0.2 % to 1.4 % for crusher sand and from 0.1 % to 1.8 % for 19 mm stone. Copper slag, on the other hand, recorded 0.0 % moisture.

4.2 ENVIRONMENTAL CURING CONDITIONS

Exposure to environmental conditions could have a significant impact through the action air humidity and ambient temperature. These factors can impact the hydration process of the concrete positively by bringing more water or negatively by severely drying out the water. They are among the prime factors which determine the final quality of concrete (Reddy, 2013).

Environmental conditions usually vary except in controlled environments. This experiment was conduct from October 2018 to May 2019. Throughout the different 28-day curing periods, TFM and its surroundings were in the rainy season. The mean daily temperature and daily relative humidity were measured using the local weather stations and recorded. These ranged from 18°C to 25.22°C and 30.64 % to 100 % respectively.

4.3 CONCRETES CHARACTERISATION

4.3.1 Workability

Seven batches, devoted to each curing method were prepared per mix type namely CS0, CS20, CS40 and CS60.The workability was assessed immediately after producing fresh mixes. The measurement based on the slump test method described in Section 3.6. Results of workability of various sets of concrete are summarized in Table 4.4, following each of the curing methods.

Table 4.4 Recorded slump values in mm

Curing method	CS0	CS20	CS40	CS60
IM	115	117	118	119
WS-I	120	125	115	115
PS-I	115	118	110	117
AD-I	110	117	115	114
WS-O	115	117	117	117
PS-O	118	120	115	115
AD-O	115	117	110	115
Mean	**115**	**119**	**114**	**116**
Standard deviation	**2.9**	**2.8**	**2.9**	**1.6**

IM stands for water immersion curing, WS for water-spraying, PS for plastic sheet covering, and AD for Air drying. O and I stand respectively for outdoor and indoor exposures. It can be seen that the measured slump ranged between 110 mm and 118 mm for the conventional mix (i.e. CS0); and for the copper slag mixes (i.e. CS20, CS40 and CS60), they respectively ranged between 117 mm and 125 mm; 110 mm and 118 mm; 114 mm and 119 mm. All in all, they ranged between 110 mm and 125 mm which indicate that they effectively fall under the standard required values of 75 mm to 150 mm based on the mix design specified in Section 3.4.1.

4.3.2 Hardened properties of concrete

Six (6) cubes were prepared per mix type: 0 %, 20 %, 40 % and 60 % copper slag substitution. And in total, 24 samples were available per curing method. These cubes was cured using the designated curing method: immersion in water (IM), indoor water spraying (WS-I), indoor air-drying (AD-I), indoor plastic sheet wrapping (PS-I), outdoor water spraying (WS-O), outdoor air-drying (AD-O), and outdoor plastic sheet wrapping (PS-O). Half of the samples were stored indoors in the laboratory at ±20˚C of temperature while the remaining half was stored outdoor (so was prone to varying environmental conditions). The purpose of doing this was to account for the influence of on-site weather conditions on concrete strengthening for each curing method (except for immersion). After curing for 28-days periods, concrete samples were first weighed in order to calculate their hardened density D_{28} has expressed in Section 3.8. Then, the compressive strength was measured using a compression machine and reported as an average of the six samples per mix type. The following lines report on the results recorded on the densities of the cubes samples.

The value recorded on hardened density measurement are reported in appendix A. It apparent from the recorded data that all the mixes produced concrete cubes with hardened densities ranging from 2290 kg/m^3 to 2440 kg/m^3 with the average being 2371 kg/m^3.These can be classified as normal weight concrete as their densities values lies with the range of 2200 kg/m^3 to 2500 kg/m^3 specified as density of normal weight concrete (Neville, 2011).

As shown in Table 4.5, the measured density was reported on an average of the six samples per mix type. The standard deviation is also listed along for each curing method.

Table 4.5 Average hardened densities (× 1000 kg/m^3) for different curing methods

No.	Curing method	CS0	CS20	CS40	CS60	Standard deviation
1	**IM**	2.373	2.418	2.412	2.408	0.021
2	**WS-I**	2.312	2.367	2.348	2.343	0.025
3	**PS-I**	2.345	2.368	2.378	2.383	0.019
4	**AD-I**	2.320	2.350	2.353	2.353	0.022
5	**WS-O**	2.365	2.365	2.398	2.393	0.019
6	**PS-O**	2.368	2.383	2.412	2.408	0.022
7	**AD-O**	2.360	2.358	2.373	2.375	0.013

Copper slag concretes admixed (CS20, CS40, and CS60) produced highest mean densities ranging from 2330 kg/m³ to 2430kg/m³ while that consisted of only conventional aggregates (CS0), produced the lowest ones (2290 kg/m³ to 2390kg/m³).

Table 4.6 Increase in density compared with conventional concrete (CS0)

Curing method	Relative increase			
	CS0	CS20	CS40	CS60
IM	-	2%	2%	1%
WS-I	-	2%	1%	1%
PS-I	-	1%	1%	2%
AD-I	-	1%	1%	1%
WS-O	-	0%	1%	1%
PS-O	-	1%	2%	2%
AD-O	-	0%	1%	1%

Table 4.7 highlights the fact that there is an increase in density with the increase of copper slag content. This is obvious for the copper slag admixed concretes (CS20, CS40, and CS60) specimens cured for IM; PS-O; AD-O; WS-I; PS-I and AD-I.

By analysing Figure 4.2 depicting the different density evolution curves of density as a function of mix type, it came out that for WS-O and AD-O cases, CS0 and CS20 densities were similar.

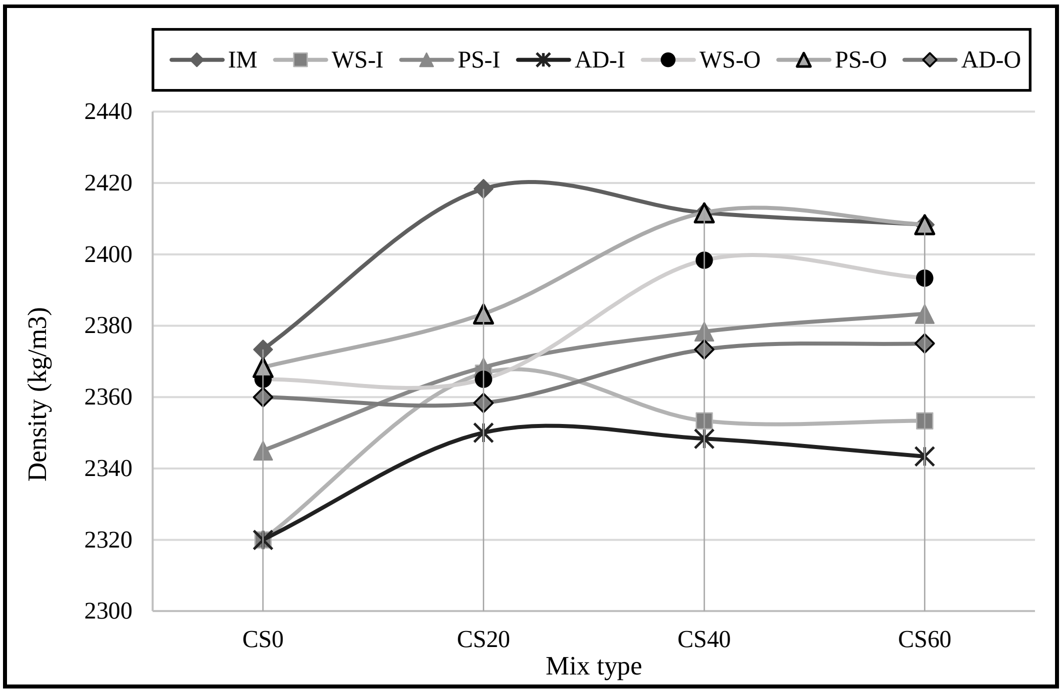

Figure 4.2 Hardened density as a function of mix type for variety of curing conditions

In terms of density results, the ranking in descending order of curing method performance is as follows: IM; PS-O; WS-O; PS-I; AD-O; WS-I; AD-I. Mostly, IM method performed better for all the mix types. It was closely followed by PS-O. AD-I method was last one. Surprisingly for CS20, WS-I came in the fourth position. This indicates that the CS20 mixture was cured under the period of the high daily temperature was and low relative humidity. So, outdoor conditions were prone to rapid evaporation. But in general, the exposure to environmental conditions has produced highest values of densities than indoor ones.

As related to the results obtained around the compressive strength tests, the measured value on all the concrete specimens subjected to the seven (7) curing methods are presented in appendix B.

The results of the 28-day average compressive strengths are reported in Table 4.7 for each six (6) replicates of each mixture and for each curing method. The standard deviations are also listed along.

Table 4.7 28-days mean compressive strengths of concrete specimens

Curing method	Compressive Strength (MPa)				Standard deviation
	CS0	CS20	CS40	CS60	
IM	25.6	27.0	26.5	23.4	**1.6**
WS-I	22.9	26.2	25.1	22.7	**2.1**
PS-I	23.8	26.9	25.4	22.7	**2.1**
AD-I	22.7	23.4	21.8	20.6	**1.5**
WS-O	23.5	29.3	26.5	23.2	**2.9**
PS-O	25.0	30.9	26.0	23.1	**3.5**
AD-O	22.6	24.6	20.8	19.8	**2.1**

From Table 4.7, the following observations are drawn:

- On CS0, IM curing method performed the highest mean compressive strength of 25.6 MPa while the least one of 22.6 MPa was by AD-O;
- On CS20, PS-O yielded the highest compressive strength of 30.9 MPa while the least one of 23.4 MPa was by AD-I;
- On CS40, IM and WS-O produced the highest mean compressive strength of 26.5 MPa while the least one of 20.8 MPa was by AD-O;
- And finally, on CS60, IM gave the highest mean compressive strength of 23.4 MPa while the least one of 19.8 MPa was by AD-O.

This is clear when look at Figure 4.3 which graphically summarizes Table 4.9.

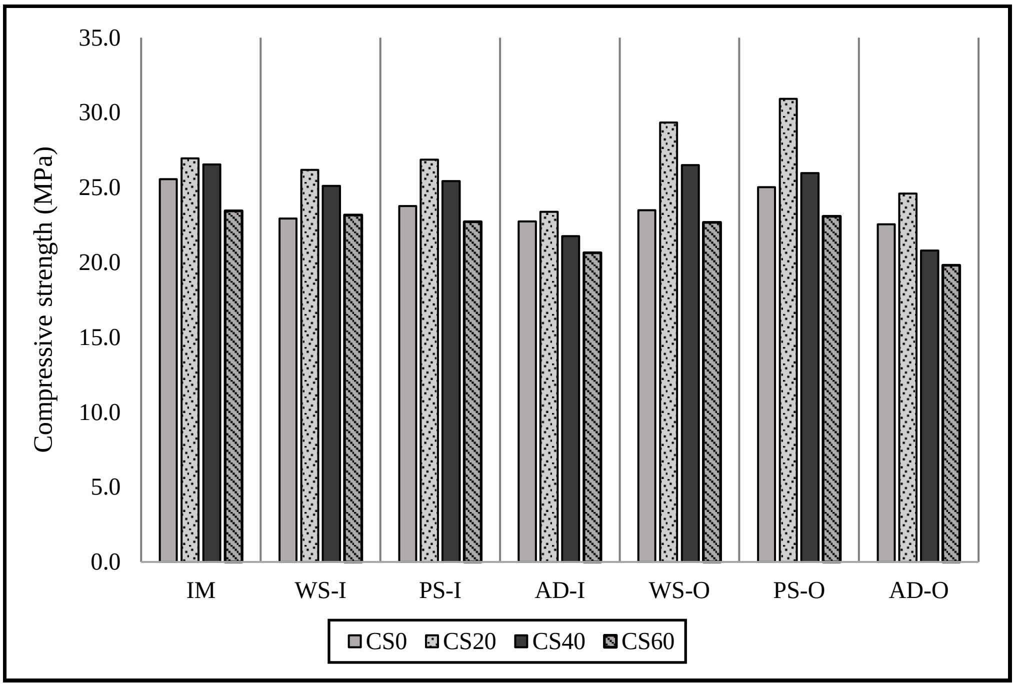

Figure 4.3 Bar chart of mean compressive strength after 28 days as a function of mix type and curing methods

All in all, the highest mean compressive value was observed on CS20 mix type cured by plastic sheet covering with outdoor exposure while the least one was observed on CS60 allowed to dry, again, in environmental exposure.

The positive effect of incorporating copper slag into concrete mix is clearly shown when looking at Figure 4.3 trends. These correspond to an increasing profile up to 20 % replacement of copper slag for all the seven curing techniques. The decreasing profile is showing up for further addition of copper slag. So, there is a compressive strength gain of which the progression is quite similar for all the curing methods used.

Increase in compressive strength with the copper slag content and for the seven curing techniques successively applied on the studied mixes are summarized in Table 4.8 as compared to the conventional concrete CS0.

Table 4.8 Increase in compressive strength relative to conventional concrete (CS0)

	CS20	**CS40**	**CS60**
IM	5%	4%	-8%
WS-I	14%	10%	-1%
PS-I	13%	7%	-4%
AD-I	3%	-4%	-9%
WS-O	25%	13%	-1%
PS-O	24%	4%	-8%
AD-O	9%	-8%	-12%

From Table 4.8, the following observations can be made:

- For IM, PS-I, WS-I, WS-O and PS-O curing methods, CS20 and CS40 copper slag concrete produced high strength values as compared to CS0, while CS60 has gone down;
- For AD-I and AD-O, the increase was only observed for CS20 while CS40 and CS60 went down.

It can therefore be said that the increase in compressive strength with the copper slag content goes up for proportions not exceeding 40 %.

Otherwise, the comparison of the different compressive strengths recorded on specimens cured by immersion with the six others remaining result in Table 4.9. From this table, it can be seen that the IM curing method performed better in 75 % of cases, except for CS20. AD-O worked the least also in 75 % of cases, except for CS20. PS-O curing method came in second position followed by WS-O.

Table 4.9 Increase in compressive strength in comparison with immersion curing method

	WS-I	PS-I	AD-I	WS-O	PS-O	AD-O
CS0	-10%	-7%	-11%	-8%	-2%	-12%
CS20	-3%	0%	-13%	9%	15%	-9%
CS40	-5%	-4%	-18%	0%	-2%	-22%
CS60	-3%	-3%	-12%	-1%	-2%	-16%

When comparing these results following exposure conditions (outdoor and indoor) on the other hand, it can be noted that outdoor-cured specimens had greater values, so exposure to environmental conditions had mostly a positive impact; this is obvious when looking at Figure 4.3. Indeed, most of the peaks are located on the right side, which corresponds to outdoors exposure. Outdoors conditions have performed better than indoor ones in most of the cases, except for air-drying method for which AD-O gave the least values on CS0, CS40 and CS60. The copper slag concrete behaviour in relation to curing methods can be graphically expressed as in Figures 4.4 and 4.5 respectively for indoor and outdoor exposures. Even separately compared to IM curing method, indoors curing method performed the least, while some of the outdoors surpassed IM curing results.

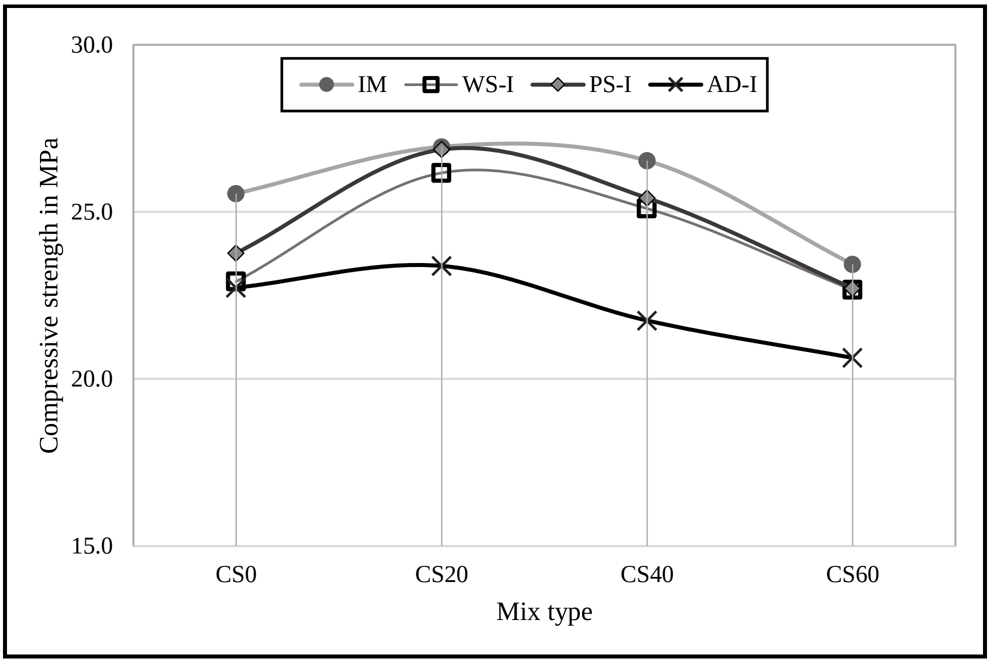

Figure 4.4 28-day compressive strength as a function of mix type for immersion and indoors curing method

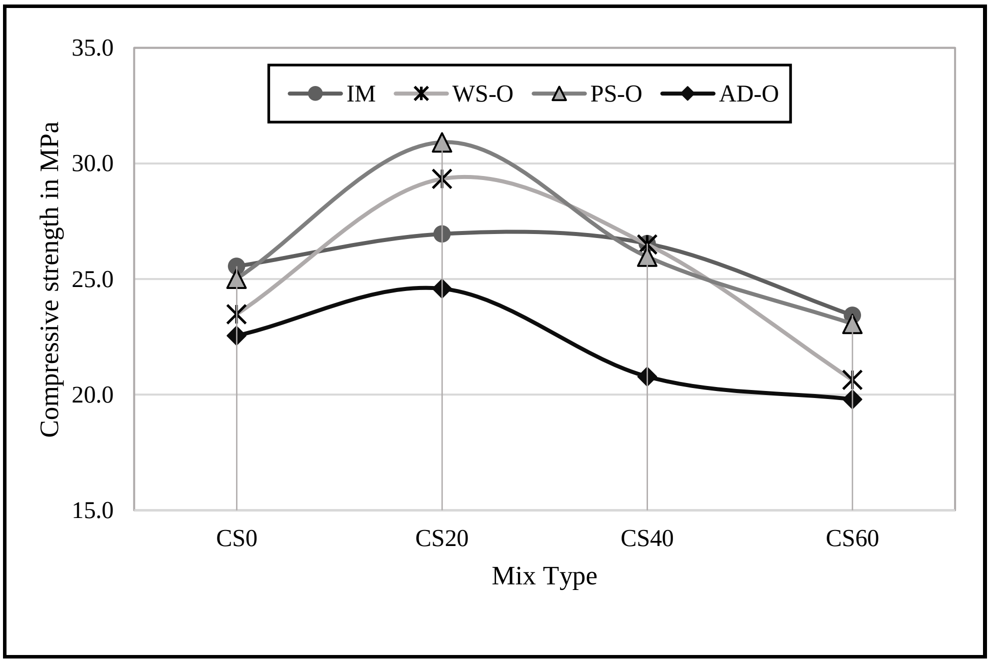

Figure 4.5 28-day compressive strength as a function of mix type for immersion and outdoors curing method

Furthermore, the ranking of the curing method in descending order of mean compressive strength values for all the mixes can be expressed as following for the two exposure conditions:

Table 4.10 Descending order of curing methods relative to the mean compressive strength values

	Indoor exposure	**Outdoor exposure**
1	PS-I	PS-O
2	WS-I	WS-O
3	AD-I	AD-O

On each mix type, the highest values of compressive strength were successively recorded by PS-O for CS20 mix type, by WS-O for CS40 mix type and by WS-O for CS60 mix type.

4.4 SUMMARISED FINDINGS

The work carried out has clearly demonstrated the influence of the selected curing methods and weather conditions on the compressive strength of copper slag concrete. It was observed that immersion in water was the first method for 75 % of mix cases, except for CS20. After IM method, PS-O followed by WS-O curing methods gave greater results. Then after, curing method conduct in indoors conditions came. In general, exposure to environmental conditions had a positive contribution on the compressive strength development although AD-O worked the least also for 75 % of mix cases, i.e. CS0, CS40 and CS60.

It is important to note that this work was a long-term effort for about seven months and ranging from material collection to the crushing of concrete cubes. It was a winding path strewed with pitfalls such as the replica of CS0 and CS20 mix samples, i.e., the casting of extra eighty-four concrete cubes, besides logistical organisation (materials and manpower) surrounding it. The disqualification of the previous samples was due to a clumsy manoeuvre by a laboratory technician who had crushed the samples directly covered with plastic sheets. This distorted the results. Thus, the experimental work was longer than expected due to additional 28 days (corresponding to curing periods) of waiting.

4.5 CONCLUDING REMARKS

This study was focused on only un-reinforced concrete samples. Curing was only considered up to 28 days without investigating other curing ages results because of logistical limitations inherent to laboratory and of the limited time frame.

The outdoor exposure to which this study refers only to the tropical rainy season prevalent in Lualaba province of the DRC. It would have been interesting to also investigate outcomes during the dry season when the relative humidity is essentially low.

Four mix types of concrete were considered. First, CS0 mix was made of essentially conventional aggregates, i.e. crusher sand and 19 mm stone. Then, CS20, CS40 and CS60 mixes resulted from the partial replacement of sand by copper slag in proportions of 20 %, 40 % and 60 % respectively. After being casted, hundred and sixty-eight (168) concrete cubes were available for each selected curing method. A total of 168 compressive strength values have been recorded after crushing them.

The experimental results plotted clearly showed the dependence of compressive strength of concrete to the various copper slag content and to the seven curing method applied. For further confirmation regarding these observations, two-way ANOVA test for the repeated measurements need to be performed such as conclusions can be drawn regarding the effect of one another. This is covered in the next chapter.

5. DISCUSSION OF RESULTS

In this study, the stated problem was to highlight and understand the physical and mechanical behaviour of concrete in which copper slag was used as sand substitute and cured in different ways. Emphasis was placed mainly on the physical properties of copper slag, on workability of the fresh mixes, the hardened density and the compressive strength as properties of interest. From the experimental work carried out and described in Chapter 3, different observations were drawn first on the freshly mixed concretes and then on hardened concretes. In line with the literature reviewed in Chapter 2, the various arguments that try to explain these observations are presented in this chapter. The effect of copper slag addition on fresh and hardened concrete are first discussed; then the different observations made on the workability, on the hardened density and on the compressive strength of concrete are analysed. Finally, explanations on the impact of the different curing methods on copper slag concrete are presented.

The two-way analysis of variance (ANOVA) test was also performed on compressive strength data in order to simultaneously test the effects of the different curing methods and the copper slag content into the concrete mix; and to determine the level of interaction between them. Overall, the two-way ANOVA test was performed for four (4) concrete types (CS0, CS20, CS40 and CS60) cured under seven (7) environments for 28 days.

5.1 USE OF COPPER SLAG AS CONCRETE-MAKING AGGREGATE

5.1.1 Effect of copper slag addition on fresh mixes

Aggregates are one of the factors that influence the concrete strengthening. They generally make up 60 % to 70 % of the concrete volume and can impact the properties of the freshly mixed concrete and those of the hardened concrete (Kosmatka et al., 2002; Neville, 2011).

In this study, seven batches, devoted to each curing method were prepared per mix type i.e.CS0, CS20, CS40 and CS60 as reported in Table 4.4. The gathered data indicate that slump values ranged between 110 mm and 125 mm. Mean values were found to vary between 114 mm and 119 mm with associated scatter plot against single-point value as shown in Figure 5.1. The figure presents the measured slumps as a function of the mix type following the intended curing methods.

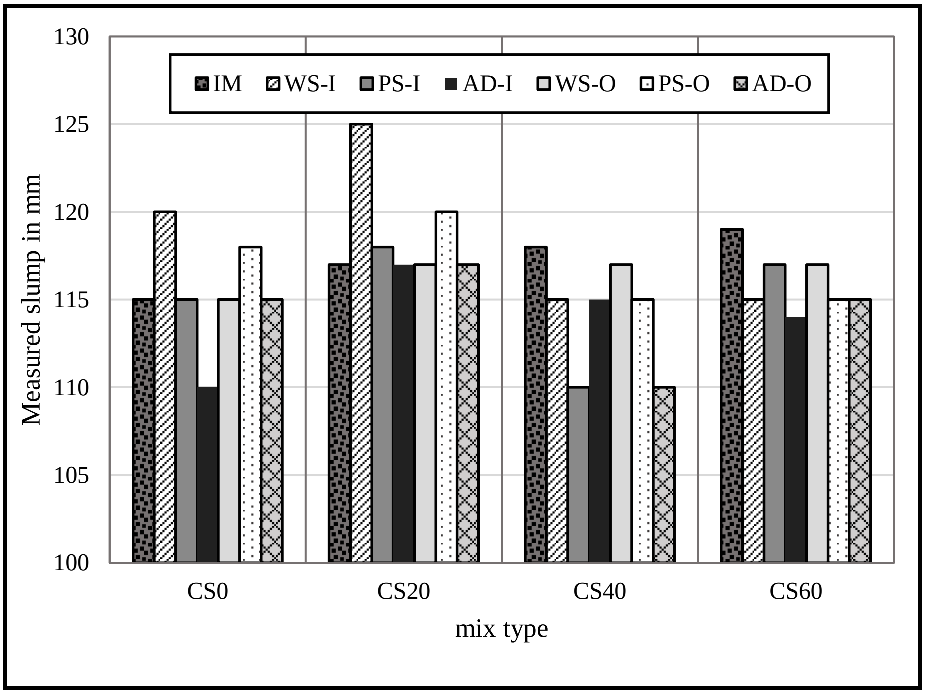

Figure 5.1 Workability as a function of mix type

Variations within the different slump measurements are clearly highlighted on Figure 5.1. The standard deviations computed on each set of mixes (i.e. CS0, CS20, CS40 and CS60) indicate large amount of variation within CS0, CS20, and CS40 mixes – set (i.e. 2.9 mm of standard deviation), and a low one for CS60 (i.e. 1.6 mm of standard deviation). Furthermore, it shows that measurement is likely to vary when they are repeated. The variability in the measurement could have been due to human action within the process that cannot be perfectly replicate, hence the presence of some outliers.

The remarkable finding which emerges from the above is that the workability is fairly similar, despite the increasing addition of copper slag. This is in contrast with some published studies which have found that as a granular material, copper slag improved the workability of the freshly mixed concrete (Malkare and Pujari, 2018;

Tejaswini and Priyanka, 2017; Rahul and Rasl, 2016; Madheswaran et al., 2014, Wei Wu et al., 2010; Al-Jabri et al., 2009). The following paragraph outlines possible explanation to this result.

After characterization tests, the water absorption measured on granular material was 5 %, 1.15 % and 0 % respectively for sand, gravel and copper slag. The moisture content test showed various water contents in the stone and the sand depending on the moisture conditions of the storage environment (see Section 4.1.3), while the copper slag was found to be effectively dry. In order to respond precisely to the water requirements of the mix design proposed in Table 4.4, the weight of the aggregate and water batch had to be adjusted before mixing with cement. The adjustment consisted of deducting the amount of water that was supposed to be free moisture in aggregates (the quantity related to the moisture contents) while that supposed to be absorbed was added. In addition, the aggregate pull weights were also adjusted by an additional amount corresponding to moisture contents. As a result of this, the workability was fairly maintained within the same level of 114 mm to 119 mm, hence the similarity.

This is an important finding to understand the impact of free water within granular material (see Section 2.1.1.). If the moisture contents and the water absorption had not been taken into account to adjust the mixing water, perhaps the observation could have been similar to that of previous researchers. To confirm that, other sets of fresh mixes could have been produced without the adjustment process described above. But to stay focused on the research questions (and also limited by the time frame), this has not been investigated here. Future research is needed in order to clarify this observation.

5.1.2 Effect of copper slag on hardened properties of concrete

The freshly mixed concretes were prepared with different copper slag content ranging from 0 % to 60 %. Concrete specimens were casted and cured under seven different schemes until the testing day. After that, these were weighed to measure the hardened density before crushing them for compression test after 28 days of curing. The seven curing conditions consisted mainly of water immersion (IM), water spraying (WS), plastic sheet covering (PS), and air-drying (AD); duplicated in indoor (I) and outdoor exposure (O), except for water immersion.

The first question in this study aimed to determine the density and strength of concrete prepared using locally-sourced copper slag compared to conventional concrete. Following lines discuss the various observations related to the hardened density and the compressive strength results.

As related to the gathered results on the hardened density, the following can be mentioned.

The measured hardened density values for all the seven curing conditions have been reported in Table 4.5. These indicated an increase in hardened density relative to the copper slag content into the concrete mixes. However, this increase stopped at 20 % of replacement rate, then the density starts to decrease for specimens cured by IM, WS-I, and AD-I. Conversely, it stopped at 40 % of replacement rate for specimens cured by PS-I, PS-O, WS-O and AD-O.

The important finding was that incorporating copper slag as fine aggregate into the concrete mixes produced denser concretes; however the improvement rate was dependent upon the curing method used. As seen in Table 4.7, 2 % of increase was yielded by most of the curing method as compared to the conventional concrete (CS0).

A similar observation was made by Malkhare and Pujari (2018). These researchers ascribed the finding to the high specific gravity of the copper slag they used (3.15) as compared to sand. Surprisingly, outcomes related to this experiment was the same even though the locally-sourced copper slag had lower specific gravity of 2.72 compared to that of the crusher sand, i.e. 2.75. Copper slag concretes admixed (CS20, CS40, and CS60) produced highest mean densities ranging from 2330 kg/m^3 to 2430 kg/m^3 while that consisted of only conventional aggregates (CS0), produced the lowest ones (2290 kg/m^3 to 2390 kg/m^3).

It seems possible that the reduction in density observed on CS0 specimens is mainly due to the significant dust content in crusher sand. Indeed, the particle analysis conduct on granular material indicated dust content of 11 % within the sand compared to 0 % for copper slag. This significant content may due to the comminution of limestone gravels that produced the sand. The incidence of high dust content in concrete-making aggregate is to hinder the bond to cement by forming coating similar to that of clay (Kosmatka et al., 2003; Neville et al., 2011). I t can therefore be said that in the copper slag concretes (CS20, CS40 and CS60), the binder acted effectively without interference with the dust.

Another possible explanation can be attributed to the effect of surface texture of copper slag particles. The physical characterization work that was performed showed that locally-sourced copper slag was essentially made of coarse particles than of the crusher sand. Fineness modules (FM) of 4 and 2.58 were respectively computed for copper slag and the sand. The angular sharp edges of copper slag particles have contributed to a greater bond with the cement paste, resulting in a better compactness and cohesion, thereby in a stronger concrete matrix (Wu et al., 2010; Brindha, 2011). Hence copper slag concretes (CS20, CS40 and CS60) showed greater hardened density compared to the conventional concrete in which the copper slag was not-existent.

The following lines deal with discussions related to the findings on compressive strength of copper slag concrete.

The measured compressive strength reported in Table 0.2 (see Appendices) indicate increases in compressive strength for addition of granulated copper slag up to 20 %. Conversely, however, a decrease in strength has been observed for further additions. However, using an adequate curing method can still give better result up to 40 % addition compared to the conventional concrete.

The increase in compressive strength could be credited to the rough nature of copper slag particles which caused increase in bulk material stability. This resulted in a better interlocking and bonding effect with the cement paste, thus allowing greater strengthening. Other previous researchers have pointed out that high densities of copper slag are also responsible for increasing the strength of concrete (Malkare and Pujari, 2018; Tejaswini and Priyanka, 2017; Patil and Patil, 2016; Rahul and Rasl, 2016; Madheswaran et al. 2014; Wei Wu et al., 2010; Al-Jabri et al., 2009). These investigations were mainly carried out under the conditions of ASTM and IS standards and found optimal replacement rates ranging from 40 % to 50 %. Patil and Patil (2016) for example used a copper slag of 3.30 density but a sand of 2.65. In this study, however, the locally produced copper slag had a density of 2.72, lower but close to 2.75 crushed sand (see Table 4.3).

The results of this research work further suggest that the glassy surface texture of copper slag could have contributed to the reduction in strength recorded for mixtures of concretes prepared with high contents of copper slag (beyond 20 %). In a similar study, Boakye (2014) determined the glass content of copper slag using the Rietveld X-ray diffraction method (XRD). The copper slag used in the study was a same locally-sourced material also coming from the former province of Katanga, in the DRC. The test result indicated a glass content of 99.3 %. High glass content significantly reduces the compressive strength. In fact, the glassy nature negatively affects the friction property between the particles of copper slag (Gorai, 2002). As a result, bonding to the cement paste was reduced in the concrete matrix and microscopic voids were formed. The concrete strengthening is consequently reduced (Adaway and Wang, 2015), as by similarity with the effect of glass waste in concrete (Otunyo and Tornwini, 2016).

Moreover, due to its glassy surface texture and to low absorption capacity (see Section 3.3), copper slag is unable to absorb and hold all of the mixing water. So, the more copper slag is added to a concrete mix, the more the free water content can be, as non-absorbed. Previous researchers reported that the excess water caused excessive bleeding, resulting in the formation of internal voids and capillary channels in the concrete, and eventually reduces the quality of concrete (Al-Jabri, 2009; Wu et al., 2010; Brindha, 2011; Boakye, 2014; Malkare and Pujari, 2018).

These findings put a little more emphasis on the influence of the physical properties of the copper slag as fine aggregate on the concrete strengthening. However, it is increasingly claimed nowadays that aggregates could have certain chemical properties that could have a positive or negative impact on the integrity of the bonding to the cement paste (Quinora and Fowler, 2003; Alexander and Mindess, 2005; Mamlouk and Zaniewski, 2005; Neville, 2011). After examining the microstructure of concrete samples with different contents of copper slag, Wu et al. 2010 observed that the physical properties of copper slag were mainly responsible for increasing or decreasing in strength. Since copper slag was only considered in its granular form in the present study, no significant impact could therefore be expected with regard to chemical properties. Chemical analyses by Boakye (2014) indicated that copper slag was not a very reactive material. Further analyses are necessary to understand the impact that can physicochemical properties of copper slag can have of concrete.

As part of the research objectives, the second question addressed in this study was to understand the contribution of the selected curing methods and the local weather conditions typical to Lualaba in the DRC on the strength development. Thereby, it is presented in subsequent section the arguments that try to explain the different findings on the 28-days compressive strength as related to the impact of the curing method and weather conditions.

5.2 EFFECT OF THE DIFFERENT CURING SCHEMES ON THE STRENGTH OF COPPER SLAG CONCRETE

This research work entailed the use of seven curing methods namely water immersion (IM), water spraying (WS), plastic sheet covering (PS), and air-drying (AD); duplicated in indoor (I) and outdoor exposure (O), except for water immersion). Their effects on the compressive strength of concretes containing various proportions of copper slag were investigated and presented in Figure 4.3. The results indicated first that concrete specimens immersed in tap water (IM) yielded higher compressive strengths, except for CS20 specimens. Second, the highest compressive strength of 30.9 MPa was recorded for CS20 concrete mix, cured by PS-O curing method. Third, the close performance of WS-O to PS-O. Fourth and last, the worst performance of AD-O compared to others. The purpose on this section is to discuss the aforementioned findings.

As presented above, the compression test results first indicated that the conventional water curing (IM) was the most effective compared to the six others. Similar results were obtained by previous researchers (Jackson and Akomah, 2018; Olofinnade et al., 2017; Gokul et al., 2016; James et al., 2011; Saffiudin et al.,2007). In addition, this method recorded the highest performance rate on the four types of mixtures, with the exception of CS20 (see Table 4.11). The probable reason is that sufficient humidity has been maintained in this method to ensure the continuous hydration of the cement and therefore a continuous strength gain. Similar opinions were also made by Zain et al., (1999); Saffiudin et al. (2007); Abalaka and Okoli (2013) and Jackson and Akomah, (2018). No loss of moisture movement could have been possible on the surface of the samples as they were continuously submerged (Saffiudin et al., 2007) and 100 % humidity was ensured (Raheem et al., 2013). The continuous hydration of the cement therefore promoted the growth of calcium silicate hydrate gels (CSH), which are the main strength-providers (Neville, 2011; Abalaka and Okoli, 2013; Usman and Issa, 2015).

Second, it is reported that PS-O curing method performed closely to IM curing method and produced the highest compressive strength on CS20 (see figure 4.5). Through this result, the possibility of ensuring a good strength gain without external water supply is confirmed. Similar opinion were made by Zain et al. (1999); Saffiudin and Ysof (2000) as well as Saffiudin et al. (2007). In this study, PS curing method was implemented by applying impervious layers of plastic sheet to contain the moisture on concrete specimens (see Section 3.7.3). The reported performance on PS curing method indicates that the external surfaces of the concrete specimens were tightly sealed and the loss of water by evaporation was minimized although some water losses are possible by doing this (Saffiudin et al., 2007). The trapped water provided the moisture required to continue hydration and increase the compressive strength. The plastic sheets acted effectively against the moisture movement.

As can also be seen in Figure 4.5, the performance of the WS-O curing method ranked practically after that of PS-O; and the second highest compressive strength of 29.3 MPa, was recorded by this method on CS20. This outcome indicates that with spraying curing method, sufficient hydration products, i.e. CSH gels, have had time to develop, fill the pores and produce a dense microstructure (Saffiudin et al., 2007). Good concrete strengthening is possible without continuous curing with water. Spraying can therefore be considered as a close alternative to immersion, providing the moisture required to maintain an environment conducive to continuous hydration. A similar opinion was expressed by Usman and Isa (2015).

Moreover, the compressive strength results indicate increases of 15 % and 9 % was respectively recorded on PS-O and WS-O as compared to IM curing method. PS-O as well as WS-O curing were carried out in the natural atmosphere so as to correspond to the in-situ conditions. This experiment was conduct from October 2018 to May 2019. Due to a clumsy manoeuvre by a laboratory technician who had crushed the samples directly covered with plastic sheets, CS0 and CS20 mix samples, i.e., the casting of extra eighty-four concrete cubes, were replicated. Throughout the different 28-day curing periods, TFM and its surroundings were in the rainy season. The mean daily temperature and daily relative humidity were measured using the local weather stations and recorded. The replica of CS20 cube specimens were specifically cured in April 2019. During this period, the mean daily temperature and daily relative humidity ranged from 29.88°C to 33.22°C and 50 % to 89.42 % respectively. The previous mixtures were cured in a period of which the mean daily temperature and daily relative humidity ranged from 18.75°C to 23.73°C and 68.84 % to 99.9 % respectively. This indicates that the CS20 outdoor atmosphere were essentially hot and less wet compared to the previous curing period. Thereby, the greater performance of PS-O and WS-O on CS20 can be attributed to the influence of weather conditions by the simultaneous action of high relative humidity and air temperatures.

By extension, when also comparing the impact of the curing method after the exposure conditions (outdoor and indoor), a positive impact of weather conditions was noted on the concrete strengthening, since outdoor-cured specimens have most of the high compressive strengths compared to indoor ones. However, in the specific case of air drying, serious losses in compressive strength were recorded on AD-O compared to AD-I and the other curing methods (see Table 4.9). As shown in Table 5.1, a summary of different standard deviations computed on different compressive strengths performed by each curing method and for each mix type is presented.

Table 5.1 Standard deviations computed on different compressive strengths in relation with the different curing method

Curing method	Standard deviation (MPa)
IM	**1.6**
WS-I	**2.1**
PS-I	**2.1**
AD-I	**1.5**
WS-O	**2.9**
PS-O	**3.5**
AD-O	**2.1**

When examining theses values, one can see that outdoors curing method (WS-O, PS-O and AD-O) recorded the highest values compared to indoor ones (WS-I, PS-I and AD-I). This confirms the fact that those methods were prone to much variability that could have effectively come from the temperature and humidity gradients in the ambient air.

With regard to the action of humidity, it can be said that the recorded outdoor relative humidity contributed to strengthen the maintenance of moister environments. The moist environment further minimized water losses by evaporation in the case of IM and PS curing methods while providing additional amount of water to the water spraying curing method. The additional moisture kept the concrete saturated as possible. Hence, the originally water-filled space in the fresh cement paste were filled to the desired extent by the products of cement hydration (Abalaka et al., 2013).

Regarding the temperature influence, previous researchers have reported that temperature accelerates the rate of hydration which leads to the development of compressive strength (Soroka, 1993; Saffiudin and Ysof, 2000; Mamlouk and Zaniewski, 2005). Some of them indicated that a high temperature could enhance the rate of evaporation, further reduce the amount of water and delay the rate of hydration. However, combined with an effective curing method such as IM, PS and WS, moderately high temperatures (around 35°C) still have positive effects on concrete strengthening up to a certain stage.

The worst performance of air-drying curing method may be due to the inability of the concrete to have adequate access to external water replacing water lost by evaporation (Olofinnade et al., 2017). For AD-O curing method, the influence of the temperature rise was more pronounced thus promoting the rapid evaporation of water (Zain et al., 1999; Saffiudin and Ysof, 2000). The drying of the concrete specimens was therefore more significant due to the high temperature (up to 32ºC at times) despite the presence of moisture. As a result, the hydration process could have been stopped before the pores were blocked by adequate calcium silicate hydrate (Zain et al., 1999; Saffiudin and Ysof, 2000; Safiuddin and Raman, 2007). The strength gain was seriously hindered due to the lack of sufficient capillary water suitable for the continuity of hydration process (Hayri and Baradan, 2011).

In accordance with the foregoing, it can therefore be assumed that without proper curing, early elevated temperatures can reinforce the rapid loss of water, resulting in decreased strength.

5.3 STATISTICAL ANALYSIS OF RESULTS

The experimental results plotted in Figures 4.3 – 4.5 clearly showed the dependence of compressive strength of concrete to the various copper slag content and to the seven curing method applied. For further confirmation regarding these observations, two-way ANOVA test is proposed in this section as statistical analysis of the repeated measurements in order to:

- simultaneously test the effects of the different curing methods and of the copper slag content on the compressive strength;
- and to determine the level of interaction between them.

5.3.1 Statistical analysis of compressive strength results

As presented in Appendix B, Table 0.2, 168 compressive strengths values were recorded as a result of the compression test on concrete specimens. These come from the 168 concrete specimens that were subjected to different combinations of curing method and mix type. Per curing method, six duplicates of concrete specimens were produced. All in all, 28 combinations of mix type (four) and curing method (seven) were performed. Forty-two (42) compressive values were recorded per mix type. These repeats did not produce exactly the same result. These were varying. This is what the next section is devoted to describing and understanding using the two-way ANOVA test of the obtained dataset.

5.3.2 Statistical parameters of the tested compressive strength

Table 5.2 summarises the statistical parameters coming from Table 4.8 dataset. It is reported the general minimum and maximum values, the overall mean value and the standard deviation obtained 42 data group relative to each mix type.

Table 5.2 Statistical parameters for compressive strength

Statistical parameter		CS0	CS20	CS40	CS60
Samples number	***n***	42	42	42	42
Minimum value	***min***	18.8	23	19.7	17.5
Maximum value	***max***	26.5	34.6	28.2	24.2
Mean value	$\bar{x}$	23.72	24.55	24.58	22.21
Standard deviation	***s***	1.61	3.05	2.46	1.51

It can be seen from Table 5.2 that the standard deviation for compressive strength of CS20 specimens is higher than that of other mixes. This finding indicates a large amount of variation in CS20 group; with the recorded values ranged from 23 MPa to 34.6 MPa.

The explanation to this can be attributed to variabilities in weather conditions (e.g. temperature and relative humidity). CS20 specimens were essentially cured over the April month. In the typical tropical climate of Lualaba in the DRC, this period is characterized by a decrease in rainfall as tending towards the end of the rainy season, with some long dry periods. Over the curing period the rainfall record ranged from 0.0 mm to 55.6 mm. Hence, CS20 concrete specimens were greatly influenced by temperature and moisture gradients within the ambient air.

5.3.3 Frequency distribution of the compressive strength

According to what it is known as Sturge's guideline, the ideal number N of class intervals for a frequency distribution can be approximated by (Triola, 2015):

$$N = 1 + \frac{\log n}{\log 2} \qquad \textbf{(5.1)}$$

Where n is the number of the data values.

Considering the 168 data values reported in Table 0.2 of Appendix B, 10 class intervals of compressive strength have been drawn in order to numerically (see Table 5.3) and visually (see Figure 5.2) understand the frequency distribution.

Table 5.3 Frequency distribution descriptive of the compressive strength data

No.	Class interval	Frequency	Percent fraction
1	$16.5 \leq x < 18.5$	2	1.2
2	$18.5 \leq x < 20.5$	7	4.2
3	$20.5 \leq x < 22.5$	29	17.3
4	$22.5 \leq x < 24.5$	56	33.3

5	24.5 ≤x< 26.5	42	25.0
6	26.5 ≤x< 28.5	20	11.9
7	28.5 ≤x< 30.5	7	4.2
8	30.5 ≤x< 32.5	3	1.8
9	32.5 ≤x< 34.5	1	0.6
10	34.5 ≤x< 35.5	1	0.6

It can be concluded that almost 74 concrete samples reached the target strength of 25 MPa specified for the mix design, a success rate of only 44 %.

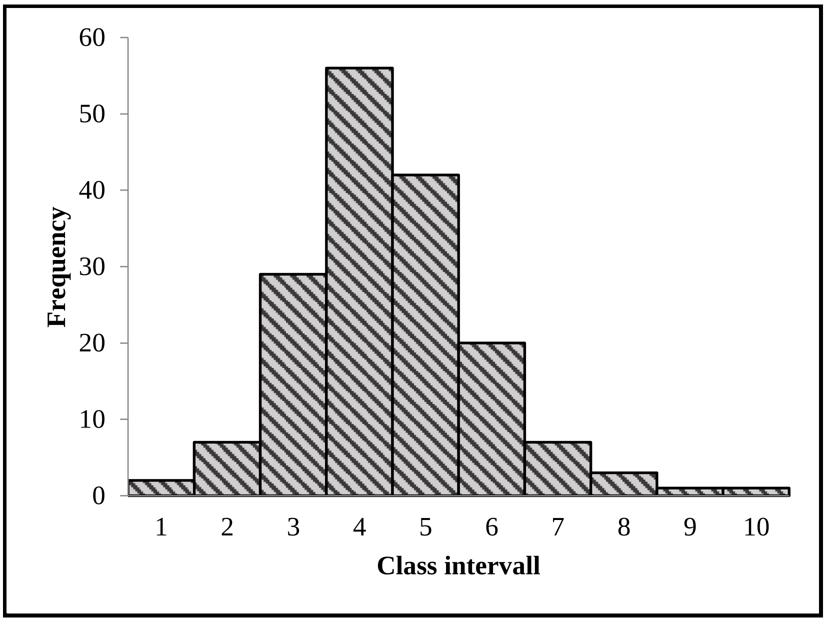

Figure 5.2 Histogram of the frequency distribution in Table 5.3

From Figure 5.2, it can also be visually seen that the frequency distribution shows a positive bell-shaped curve skewed. This indicates that the mode, the median, and the mean do not match. As related to dataset of the recorded compressive strength their respective values that were computed are 22.8 MPa; respectively 23.95 MPa; and 24.3 MPa.

5.3.4 Two-way analysis of variance

The analysis involved two set of **treatments** or **factors**: factor A stands for curing methods and factor B for mix type which describe the copper slag content. There were **a = 7 labels** of factor A (IM, WS-I, PS-I, AD-I, WS-O, PS-O, and AD-O) and **b = 4 labels** of factor B (CS0, CS20, CS40 and CS60). The experiment has **n = 6** replicates, and each replicate contained all **ab = 7 x 4 = 28** treatment combinations. Thus, there was **abn = 168** observations.

The 28-day compressive strength value, as the observation is described by the linear statistical model:

$$y_{ijk} = \mu + \tau_i + \beta_i + (\tau\beta)_{ij} + \varepsilon_{ijk} \qquad \text{With} \begin{cases} 1 \leq i \leq a \\ 1 \leq j \leq b \\ 1 \leq k \leq c \end{cases} \qquad \textbf{(5.2)}$$

Where:

- μ is the overall mean effect
- τ_i, the effect of the ithlevel of factor A
- β_i, the effect of the jth level of factor B
- $(\tau\beta)_{ij}$, the effect of the interaction between factor A and factor B
- ε_{ijk} is the random error component having normal distribution with mean 0 and variance σ^2

The hypothesis made for the test was as follows:

$H_0: \tau_1 = \tau_2 = \cdots = \tau_a = 0$ (No main effect of curing method)

$$H_1: \text{at least one } \tau_i \neq 0$$

$H_0: \beta_1 = \beta_2 = \cdots = \beta_a = 0$ (No main effect of mix type)

$$H_1: \text{at least one } \beta_i \neq 0$$

$H_0: (\tau\beta)_{11} = (\tau\beta)_{12} = \cdots = (\tau\beta)_{ab} = 0$ (No interaction)

H_1: at least one $(\tau\beta)_{ij} \neq 0$

Where H_0 and H_1 represent respectively the null and the alternative hypothesis. The ANOVA test was performed at 5 % confidence level using an electronic spreadsheet set in Microsoft® Excel®.

Table 5.3 summarises the ANOVA test performed on Table 4.8 results. *SS* stands for sum of square, *DF* for degree of freedom, *MS* for mean square value, F_0 and F_{cv} for respectively F-distribution of observed values and of critical values.

Table 5.4 Two-way ANOVA test on 28-day compressive strength values

Source of variation	*SS*	*DF*	*MS*	F_0	F_{cv}
Curing method	425.8690	6	70.978175	36.639	0.999
Copper slag content	481.0949	3	160.36498	82.780	0.985
Interaction	132.9005	18	7.3833598	3.811	1.000
Error	271.2150	140	1.93725		
Total	1311.0795	167	7.8507752		

Based on the above, it can be concluded that all the hypothesis of the averages being equal (H_0) are rejected since all F_{cv} are less than F_0:

1. For curing method effect:

$$F_0 = 36.639 > F_{cv} = F(0.05; 6; 140) = 0.999$$

2. For copper slag content:

$$F_0 = 82.780 > F_{cv} = F(0.05; 3; 140) = 0.985$$

3. For the interaction:

$$F_0 = 3.811 > F_{cv} = F(0.05; 18; 140) = 1.000$$

5.4 DISCUSSIONS OF THE FINDINGS

As statistical analysis, the two-way ANOVA test was performed on repeated measurements of compressive strength in order to:

- simultaneously test the effects of the different curing methods and of the copper slag content on the compressive strength;
- and to determine the level of interaction between them.

The level on significance has been set at 0.05. As result, all the null hypothesis of the averages being equal (H_0) were rejected since all F_{cv} are less than $F_{0.}$The effect of curing methods, of copper slag content and the interaction between them were found to be statistically significant.

The response to the 28-day compressive strength was found to be effectively impacted by the aforementioned factors and by the interaction between them. However, one can see that F_0 values indicate that copper slag content exerted the greatest influence since having the greatest value as compared the curing methods. And as previously mentioned, copper slag caused the compressive strength to increase for additions up to 20 % of replacement rate. Further additions caused reduction in strength, but the reduction rate depended on the curing techniques used. For IM, PS-I, WS-I, WS-O and PS-O curing methods, CS20 and CS40 copper slag concrete stayed higher; then, CS0 strength value, while CS60 went down. For AD-I and AD-O, the increase was only observed for CS20 as compared to CS0, while CS40 and CS60 went down.

Here, the ANOVA results confirmed the impact of the simultaneous effect of curing method and of copper slag content on the compressive strength. Figure 5.3 tries to illustrate this by presenting the mean 28-day compressive strengths as a function of curing method for the four mix types.

Figure 5.3 shows that the three curves plotted on each copper slag concrete (CS20, CS40, and CS60) have almost similar without intersection. This indicates that the simultaneous action of curing methods and copper slag content on the compressive strength is not of significant level (Montgomery and Runger, 2014).

In addition, Figure 5.3.Indicates that lowest points of the different curves are located on AD-I and AD-O. The influence of curing method is clearly visible at these points. The weak values recorded may be due to the lack of any form of curing. This caused the loss of water and affected the hydration process. It has previously been mentioned that during the hydration process, some resulting products gradually bind the different concrete-making components to form a solid block. It can be said that the absence of any form of curing resulted in porous and weak concretes.

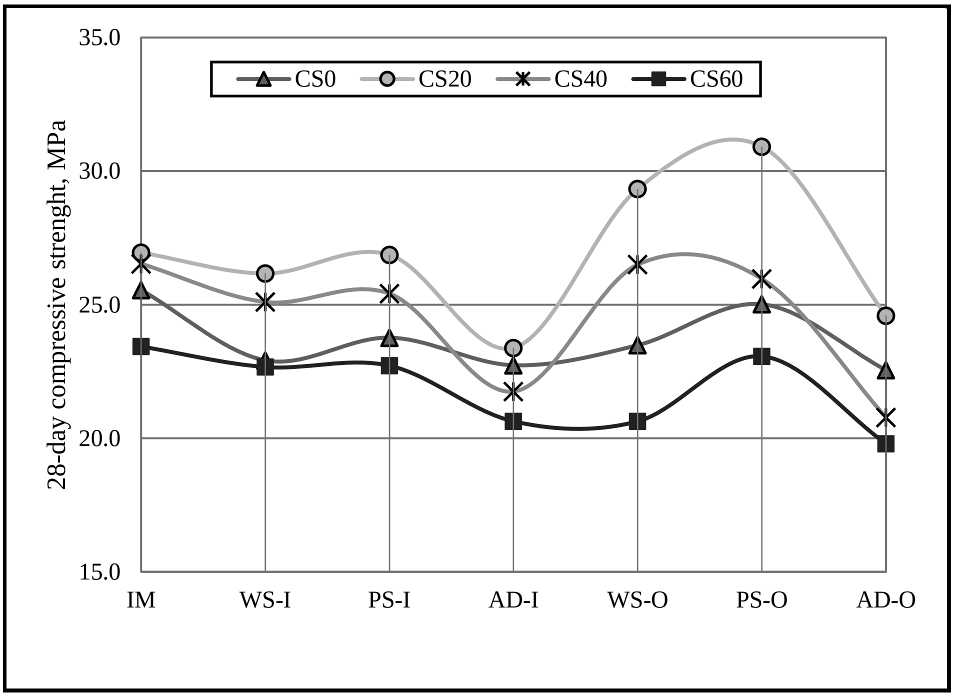

Figure 5.3 Mean compressive strength after 28 days as a function of curing method for the four mix types

Another important observation on Figure 5.3 is that WS-O, PS-O and AD-O are very scattered as compared to IM, WS-I, PS-I, AD-I. This is due to the additional influence of warm weather conditions these benefited from. However, laboratory - cured specimens are less scattered as being performed in an environment of same conditions of temperature and humidity.

The large response recorded by CS20 on the PS-O curing method, indicate the greater performance of PS-O as compared to the others.

5.5 SUMMARIZED FINDINGS

This chapter presented the various discussions related to outcomes of the experimental work described in Chapter 3.

The similarities observed in the workability of the different mixes were attributed the water adjustment that occurred before mixing the different concrete components. This adjustment was related to the moisture content and water absorption properties of the various granular materials.

As related to the hardened density, copper slag addition has been found to produce denser concretes compared to that produced with only natural aggregate.

The compressive strength was found to increase for additions up to 20 % of replacement rate. Further additions have resulted in a decrease in strength but the reduction rate was related to the curing techniques used. Inadequate curing such as air-drying cause severe reductions. The increase in strength was credited to the rough nature of copper slag particles which caused increase in bulk material stability. This results further in a better interlocking effect and bonding with the cement paste, thus allowed the greater strengthening.

As related to the reduction observed for further additions of copper slag, the results from this study suggest that the glassy and smooth texture of copper slag particles could have been the cause. As the sand decreased in the mixture, the copper slag content increased and as well as the proportion of the smooth particles in it. As result to this, the bond to the cement paste was reduced and microscopic voids were formed. So, density and compressive strength was affected and reduced accordingly.

The various discussions related to the impact of different curing methods are summarized in the following paragraphs.

The greater performance of water curing (IM) as compared to the six others was attributed to the fact that the continuously immersed specimens have benefited from the maintenance of a warm and moist environment. This allowed for a smooth progress of the cement hydration until its completion.

With environment exposure, it has been additionally found that the concrete strengthening is influenced depending on whether the atmosphere is hot or cold, dry or wet. Warm and wet weather conditions contribute to the extension of cement hydration, thereby to better concrete strengthening.

This case of the greater performance of PS-O curing method on CS20 specimens was also ascribed to the varying weather conditions that were essential warm and hot. This was in addition to the fact that the plastic sheet had been assumed to have strongly sealed the concrete surfaces thus, preventing the loss of the mixing water. The trapped water on the concrete surface was re-absorbed; thereby the hydration of cement continued properly leading to better hardening of the concrete.

Finally, the two-way ANOVA test performed on the 28-days compressive strength values confirmed the significant influence of the curing methods, of copper slag content and the interaction between them. However, it was found that the copper slag content exerted a considerable influence.

6. CONCLUSION AND RECOMMENDATIONS

6.1 INTRODUCTION

The main goal of the current study was to assess the performance of copper slag as concrete-making granular. Copper slag was successively incorporated as sand replacement in concrete at the following mass fractions: 20 %, 40 % and 60 %. Then, the concrete strengthening of related cubes cured under various ways was investigated. The impact of weather conditions typical to Lualaba province of the DRC on was also studied. In terms of weather conditions, relative humidity and ambient temperature were specifically considered.

Prior to incorporate copper slag into the concrete mix, physical characteristics such as grading, fineness modulus, water absorption, relative density and moisture content were evaluated as a comparison the conventional sand.

A mix to reach 25 MPa of compressive strength was first designed and then copper slag mixes were prepared. Cubes specimens were casted and cured for 28 days. The curing methods consisted of air-curing, immersion in water, water spraying, and plastic sheet covering. In each curing case excluding for immersion in water, half of the samples were stored indoors (i.e. in the laboratory) at ±20˚C while the remaining half was stored outdoor (so was prone to varying environmental conditions). Afterwards, cube specimens were crushed to measure their compressive strength.

The main findings are summarized here along with the related discussions.

6.2 COPPER SLAG AS CONCRETE-MAKING AGGREGATE

The locally-sourced copper slag has been found to possess properties that make it suitable for concrete production. In terms of the characterization test, the following findings were noted:

- The particle size conducted to compare the particle size distribution and fineness of copper slag and of conventional aggregates showed that copper slag contains coarser particles than of sand. A significant dust content of 11 % was found within the crusher sand.

- The specific gravity test showed that copper slag had a lower specific gravity of 2.72, compared to 2.75 for sand.

- The measured water absorption was at 0.0 % for copper slag, compared to 5 % for crusher sand. This suggest that, copper slag mixtures would not require more mixing water than those based on sand since no amount of water would be lost through absorption.

- According to the moisture conditions of the collection source as well as the storage environment, the measured moisture contents ranged respectively from 0.2 % to 1.4 % for crusher sand, compared to 0.0 % for copper slag.

As previously mentioned, copper slag was successively incorporated as sand replacement at mass fractions ranging from 20 % to 60 %. The slump test on the freshly mixed concrete indicated that, despite the addition of copper slag into concrete mix, the workability was fairly maintained within the same level of 114 mm to 119 mm. This observation was attributed the water adjustment that occurred before mixing the different concrete components. This adjustment was related to the moisture content and water absorption properties of the various granular materials. It consisted of deducting the amount of water that was supposed to be free moisture in aggregates (as related to the moisture contents) while that supposed to be absorbed was extracted.

After investigating fresh state properties, the hardened density and the compressive strength were measured after 28 days of curing.

The results of the hardened density indicated that concretes incorporating copper slag (CS20, CS40, and CS60) produced dense concretes than those consisted of only conventional aggregates (CS0). This observation was made despite the fact the locally-sourced copper slag had lower specific gravity of 2.72 compared to that of the crusher sand (2.75) used.

The possible explanation to this was that, the angular sharp edges that copper slag particles are made of could have contributed to a greater bond to the cement paste, resulting in a better compactness and so in a stronger concrete matrix. Additionally, the significant dust content in crusher sand was assumed to hinder the bond to cement by forming coating similar to that of clay. Hence copper slag performed better than crusher sand.

As related to the compressive strength development, the optimum percentage of replacing fine aggregate with copper slag was identified to be 20 % for all the curing methods. For further additions exceeding 20 %, the compressive strength starts to decrease but the rate of reduction was depended upon the curing methods.

Finally, the two-way ANOVA test performed on the 28-days compressive strength values confirmed the significant influence of the curing methods, of copper slag content and the interaction between them. However, it was found that the copper slag content exerted a considerable influence.

The explanation to the increase in strength was that was ascribed to the angular shapes edges that copper slag particles are made of. This contributed to a better interlocking effect and bonding with the cement paste. Adversely, the glassy nature of copper slag particles was assumed to cause the strength reduction observed for further additions of copper slag. So, as the copper slag content increases in the concrete mix, the proportion of the smooth and glassy surface was increasing as well. As result, the adhesion between the copper slag particles and the cement paste was reduced and microscopic voids were formed creating points of low strength.

6.3 APPROPRIATE CURING METHODS FOR COPPER SLAG CONCRETE

The investigation further showed that despite the reduction in compressive strength, the values recorded for 40 % replacement rate remained above that of CS0, except for air- drying curing methods (i.e. AD-I and AD-O). The current study suggests that compressive strength losses recorded on these methods may be due to early losses of the mixing caused by the lack of proper curing. As the water evaporated earlier, the hydration process was slowed down or even halted. The strength gain was then hindered due to the lack of sufficient capillary water suitable to properly fill the pore and capillaries to the maximum. There was not enough water to develop the hydration products that are the strength providers.

As related to the performance of the selected curing methods, the use of the conventional water curing (IM) was found to be more effective than the six others since it recorded the highest performance rate on the four mix types (75 %). This finding was attributed the abundant presence of water that allowed for the cement hydration to progress continuously until its completion. This means that the immersed specimens have benefited from a continuous maintenance of a warm and moist environment. The latter favoured the development of hydration products.

Another important finding was that the highest compressive strength was achieved by CS20 specimens out-door cured using plastic sheet (PS-O) and water spraying (WS-O). The increase was about 15 % and 9 % respectively, as compared to CS0. It has been found that outdoor atmosphere was essentially hot and wet during the curing period. The mean daily temperature and daily relative humidity ranged from 29.88°C to 33.22°C and 50 % to 89.42 % respectively. Hence the weather conditions had greatly contributed to the extension the cement hydration, thereby to a good concrete strengthening.

Finally, the current study answered to the second research question. In addition to the curing methods, this question interrogated the contribution of the local weather conditions typical to Lualaba province of the DRC to the concrete strengthening. The various results of outdoor-cured specimens indicated highest strength values as compared to the indoor-cured ones. One exceptional case was that of AD-O curing method who worked the least. It has been observed that in this method, the warm temperatures, that went up to 32ºC at times on the weather, concurred to dry the concrete severely despite the moisture presence. Therefore, the strength providers did not have time to develop properly and to form hard and solid masses.

6.4 GENERAL SUMMARY

As general finding, this study indicates that copper slag is suitable as concrete-making aggregate. Additions exceeding 20 % replacement rate can adversely affects the concrete strengthening. However, using an appropriate curing method can still give better result as compared to the conventional concrete. Exposure to warm and moist weather conditions contributes positively to the strength development since adequate curing is ensured.

The present study confirms previous findings on the use of copper slag as fine aggregate and demonstrates that the addition of copper slag into concrete mix can therefore ‘add value’. This finding may be an incentive for the construction sector. Doing so meets the requirements of sustainable development and has a benefit for the environment by reducing such waste disposal.

6.5 RECOMMENDATIONS FOR FUTURE WORK

Through the current experiment, much information regarding the effect of different curing conditions on the strength of copper slag concrete were generated. Nonetheless, a number of concerns could not be addressed due to time frame and logistical limitations.

First, the impact of chemical properties of copper slag used as fine aggregate in concrete; including the impact of the curing methods on other mechanical properties such as flexural and tensile strength of concrete can be mentioned. Various trials should accordingly assess the durability of such concrete cured in various ways.

Further experimental investigations are needed to account for the variations of the rate of moisture movement from copper slag concrete specimens cured under various ways.

The current study has only examined the strengthening in the wet season of a tropical climate typical to the Lualaba province in the DRC. Another experimental work can be performed taking into account exposure to the dry season of the same climate. It would also be interesting to investigate the impact of latter term curing period (beyond 28 days) to assess later strength development.

These are some of additional investigations that need to be addressed in order to enrich the engineering base that would enable the use of copper slag as a sand replacement in concrete.

REFERENCES

Abalaka, A.E., Okoli, O.G., 2012. Effects of curing condition on high strength concrete. Journal of Civil Engineering and Construction, vol. 3, no. 10, pp. 273 – 279

ACI, 2000. Cement and concrete terminology. ACI 116R-00. American Concrete Institute, Detroit

Adaway, M., Wang, Y., 2015. Recycled glass as partial replacement for fine aggregate in structural concrete – Effects on compressive strength. Electronic Journal of Structural Engineering, vol. 14, no. 1, pp. 116 – 122

Addis, B., Goodman, J., 2009. Concrete mix design. In: G. Owens (Ed.), Fulton's Concrete Technology, 9th Edition. Cement and Concrete Technology, pp. 219 – 228, Midrand

Akinwumi, I., Gbadamosi, Z., 2014. Effects of curing condition and curing period on the compressive strength development of plain concrete. International Journal of Civil and Environmental Research, vol. 1, no. 2, pp. 83 – 99

Al-Jabri, K-S., Hisada, M., Salem K., Al-Oraimi, Abdullah H., Al-Saidy, 2009. Copper slag as sand replacement for high performance concrete. Cement and Concrete composites, vol. 31, pp. 483 – 488

Alexander, M. and Mindess, S., 2005. Introduction. In: Aggregate in concrete, 1st Edition, New York, pp. 1 – 15

Akinwumi, I., Gbadamosi, Z., 2014. Effects of curing condition and curing period on the compressive strength development of plain concrete. International Journal of Civil and Environmental Research, vol. 1, no. 2, pp. 83 – 99

ASTM, 1997. Standard test method for total evaporable moisture content of aggregate by drying, ASTM C566-97.ASTM specification. American Society for Testing and Materials, Philadelphia

ASTM, 1997. Standard test method for bulk density (“unit weight”) and voids in aggregate, ASTM C29/C29M-17a.ASTM specification. American Society for Testing and Materials, Philadelphia

ASTM, 1998. Standard practice for reducing samples of aggregate to testing size, ASTM C702.ASTM specification. American Society for Testing and Materials, Philadelphia

ASTM, 1999. Standard specification for concrete aggregates, ASTM C33.ASTM specification. American Society for Testing and Materials, Philadelphia

ASTM, 1999. Standard practice for sampling aggregates, ASTM D75. ASTM specification. American Society for Testing and Materials, Philadelphia

ASTM, 2001. Standard test method for density, relative density and absorption of coarse aggregate, ASTM C127-01.ASTM specification. American Society for Testing and Materials, Philadelphia

ASTM, 2001. Standard test method for density, relative density and absorption of fine aggregate, ASTM C128-01.ASTM specification. American Society for Testing and Materials, Philadelphia

ASTM, 2001. Standard test for sieve analysis of fine and coarse aggregate, ASTM C136-01.ASTM specification. American Society for Testing and Materials, Philadelphia

ASTM, 2003. Standard practice for sampling aggregates, ASTM D75-03. ASTM specification. American Society for Testing and Materials, Philadelphia

ASTM, 2009. Standard specification for ready-mixed concrete, ASTM C94/C94M. ASTM specification. American Society for Testing and Materials, Philadelphia

ASTM, 2014. Standard test method for compressive strength of cylindrical concrete specimens, ASTM C36/C39M-14. ASTM specification. American Society for Testing and Materials, Philadelphia

Babu, K.M., Ravitheja, A. 2019. Effect of copper slag as fine replacement in high strength concrete. Materials Today: Proceedings, vol. 19, Part 2. pp. 409 – 414

Binaya, P., Seshadri, S., Srinivaso, R., 2014. An experimental investigation on optimum usage of copper slag as fine aggregate in copper slag admixed concrete. International Journal of Current Engineering and Technology, vol. 4, no. 5, pp. 3646 – 3648

Boakye, D.M., 2014. Durability and strength assessment of copper slag concrete. MSc dissertation, University of Witwatersrand, Johannesburg, South Africa

Brindha, D., Nagan, S., 2011. Durability studies on copper slag admixed concrete. Asian Journal of Civil Engineering (Building and Housing), vol. 12, no. 5, pp. 563 – 578

Brinda, D., 2011. Experimental investigation on effective replacement of cement and fine aggregate by copper slag and its application to reduce seismic earth pressure. PhD Thesis, Anna University

Gokul, T., Arun, M., Arunachalam, N., 2016. Effects of different types of curing on strength of concrete. International Journal of Innovative Research in Science, Engineering and Technology, vol. 5, no. 2, pp. 1643 – 1649

Gorai, G., Jana, R.K., 2003. Characteristics and utilisation of copper slag-a review, resources. Conservation and Recycling, vol. 39, no. 4, pp. 299 – 313

Goodman, J., 2009. Mixing water. In: G. Owens (Ed.), Fulton’s Concrete Technology, 9th Edition. Cement and Concrete Technology, pp. 25 – 61, Midrand, South Africa

Grieve, G., 2009. Aggregates for concrete. In: G. Owens (Ed.), Fulton’s Concrete Technology, 9th Edition. Cement and Concrete Technology, pp. 25 – 61, Midrand, South Africa

Hayri, U., Baradan, B., 2011. The effect of curing temperature and relative humidity on the strength development of Portland cement mortar. Scientific Research and Essays, vol. 6, no. 12, pp. 2504 – 2511

Husain, A., Ahmad, J., Mujeeb, A., Ahmed, R., 2016. Effects of temperature on concrete. International Journal of Advanced Research in Science and Engineering, vol. 5, no. 3, pp. 33 – 42

Jackson, E.N., Akomah, B.B., 2018. Comparative analysis of the strength of concrete with different curing methods in Ghana. International Journal of Engineering and Science, vol. 7, no. 9, pp. 39 – 44

James, T., Malachi, A., Gadzama E.W., Anametemok, A., 2011. Effect of curing methods on the compressive strength of concrete. Nigerian Journal of Technology, vol. 30, no. 3, pp. 14 – 20

Kosmatka, S., Kerkoff, B., Panaresse, W., 2002. Design and control of concrete mixtures. 14th Edition. Portland Cement Association (Eds.), Illinois, United States of America

Kosmatka, S., Wilson, M. L., 2011. Design and control of concrete mixtures. 15th Edition. Portland Cement Association (Eds.), Illinois, United States of America

Lalla, J.R.F., Mwasha, A., 2014. Investigating the compressive strengths of Guanapo recycled aggregate concrete as compared to that of its waste material. West Indian Journal of Engineering, vol. 36, no. 2, pp. 12 – 15

Madhavi, D.-T.-C., 2014. Copper slag in concrete as a replacement material. International Journal of Civil Engineering and Technology, vol. 5, no. 3, pp. 327 – 332

Madhavi, T.C., Kumar, S.A., 2016. Experimental investigations on compressive strength of copper slag in concrete. ARPN Journal of Engineering and Applied Sciences, vol. 11, no. 9, pp. 5983 – 5985

Madheswaran, C.K., Ambily, P.S., Dattatreya, J.K., 2014. Studies on use of copper slag as replacement material for river sand in building constructions. Journal of the Institution of Engineers (India): Series A, vol. 95, no. 3, pp. 169 – 177

Malkhare, S.S., Pujari, A.B., 2018. To study the performance of copper slag as partial or full replacement to fine aggregates in concrete. International Journal of Research and Review, vol. 5, no. 5, pp. 102 – 109

Mamlouk, M.S., Zaniewski, J.P., 2005. Materials for civil and construction engineers, 2nd Edition. Pearson, Prentice Hall

Mehta, P.K., Monteiro, P.J.M., 2006. Concrete: Microstructure, Properties, and Materials. 3rd Edition. McGraw-Hill, New York

Mobasher, B., Devaguptapu, A.M., 1996. Effect of copper slag on the hydration of blended cementitious mixtures. Proceedings of the ASCE Materials Engineering Conference, Materials for the New Millennium; pp. 1677 – 1686

Montgomery, D.C., Runger, G.C., 2014. Applied statistics and probability for engineers, 6th Edition. Wiley, United States of America

Neville, A.M., 2011. Properties of concrete, 5thEdition. s.l.: Pearson

Ogah, O., 2016. Effect of curing methods on the compressive strength of concrete. International Journal of Advanced Trends in Computer Science and Engineering, vol. 5, no. 7, pp. 17160 – 17171

Olofinnade, O.M., Edel, A.N., Ndambuki, J.M., Olukannil, D.O., 2017. Effects of different curing methods on the strength development of concrete containing waste glass as substitute for natural aggregates. Covenant Journal of Engineering Technology, vol. 1, no. 1, pp. 1 – 17

Otunyo, A.W., Torwini, G.L., 2016. Effect of waste glass as partial replacement for coarse aggregate in concrete. European International Journal of Science and Technology, vol. 5, no. 9, pp. 89 – 97

Patil, M.V., Patil, Y.D., 2016. Effects of copper slag as sand replacement in concrete. International Journal of Engineering and Technology, vol. 8, no. 2, pp. 1172 – 1181

Perri, B., 2009. Strength of hardened concrete. In: G. Owens (Eds.), Fulton's Concrete Technology, 9th Edition, South Africa, pp. 97 – 110

Prem, P.R., Verma, M., Ambily, P.S., 2018. Sustainable cleaner production of concrete with higher volume copper slag. Journal of Cleaner Production, vol. 193, pp. 43 – 58

Princy, K.P, John, E., 2015. Study on the effectiveness of various curing methods on the properties of concrete. International Journal of Engineering and Technology, vol. 4, no. 11, pp. 213 – 216

Quinora, P.N., Fowler, D.W., 2003. The effect of aggregates characteristics on the performance of Portland cement concrete. Report ICAR 104-IF. International Center for aggregates research. Austin, United States of America

Rasheed, S.R., 2017. Effect of curing temperature and conditions on compressive strength of concrete containing supplementary pouzzolanic materials. Journal of Engineering and Sustainable Development, vol. 21, no. 1, pp. 1 – 10

Raheem, A.A., Soyingbe, A.A., Emenike, A.J., 2013. Effect of curing methods on density and compressive strength of concrete. International Journal of Applied Science and Technology, vol. 3, no. 4, pp. 55 – 64

Rahul, S., Rasl M.R., Vadivel, S., Kanchana, S., 2016. Experimental study on properties and effects of copper slag in self compacting concrete. International Journal of Science Technology and Engineering, vol. 2, no. 12, pp. 455 – 460

Safiuddin, M., Raman, S.N., 2007. Effect of different curing methods on the properties of microsilica concrete. Australian Journal of Basic and Applied Sciences, vol. 1, no. 2, pp. 87 – 95

SANS, 2006. Concrete tests – consistence of freshly mixed concrete – slump test, SANS 5862-1:2006. South African Bureau of Standards, Pretoria

SANS, 2006. Concrete tests – compressive strength of hardened concrete, SANS 5863:2006. South African Bureau of Standards, Pretoria

Shanmugananathan, P., Lakshmipathiraj, P., Srikanth, S., Nachiappan A.L., Sumathy, A., 2008. Toxicity characterization and long-term stability studies on copper slag from the ISASMELT process. Resources, Conservation and Recycling, vol. 52, pp. 601 – 611

Shi, C., Meyer, C., Behnood, A., 2008. Utilization of copper slag in cement and concrete. Resources, Conservation and Recycling, vol. 52, pp. 1115 – 1120

Soroka, I., 1979. Setting and hardening. In: Portland Cement Paste and Concrete, 1st Edition, pp. 28 – 45

Srinivas, Ch., Naveen Kumar, V., Vinod, E., 2018. Experimental study of copper slag on mechanical properties of concrete. International Journal of Applied Engineering Research, vol. 13, no. 7, pp. 5328 – 5331

Supekar, N., 2007. Utilisation of copper slag for cement manufacture construction. Management and Review, Sterlite Industries (I) Ltd, Tuticorin

Tejaswini, M.L., Priyanka, N., 2017. Study on properties of concrete containing copper slag as a partial replacement of fine aggregate. International Journal of Advances in Scientific Research and Engineering (IJASRE), vol. 3, no. 1, pp. 292 – 298

Triola, M.F., 2015. Essentials of statistics, 5th Edition. Pearson, New York

Usman, N., Isa, M.N., 2015. Curing methods and their effects on the strength of concrete. Journal of Engineering Research and Applications, vol. 5, no. 7, pp. 107 – 110

Wu, W., Zhang, W., Ma, G., 2010. Optimum content of copper slag as fine aggregate in high strength of concrete. Materials and Design, vol. 3, pp. 2818 – 2883

Zain, M.F.M, Safiuddin, M., Mohamed, I.A.A., 1999. Influence of different curing methods on the compressive strength and modulus elasticity of high performance concrete. Proceedings of the Sixth International Conference on Concrete Engineering and Technology, pp. 13 – 25

Zain, M.F.M, Safiuddin, M., Yusof, K.M., 2000. Influence of different curing conditions on strength and durability of high-performance concrete. Proceedings on the Fourth ACI International Conference on Repair, Rehabilitation and Maintenance, ACI SP-193, American Concrete Institute, Farmington Hills, Michigna, USA, pp. 276 – 291

APPENDICES

This section presents raw data collected after density (see appendix A) and compressive strength measurement (see appendix B)

APPENDIX A

Table 0.1 28-day hardened density (× 1000 kg/m^3) for different curing methods

Curing method	CS0						CS20						CS40						CS60					
	#1	#2	#3	#4	#5	#6	#1	#2	#3	#4	#5	#6	#1	#2	#3	#4	#5	#6	#1	#2	#3	#4	#5	#6
IM	2.37	2.37	2.36	2.37	2.39	2.38	2.44	2.41	2.42	2.42	2.40	2.42	2.42	2.40	2.42	2.41	2.42	2.40	2.39	2.40	2.40	2.42	2.42	2.42
WS-I	2.30	2.29	2.34	2.32	2.34	2.33	2.38	2.39	2.35	2.34	2.36	2.33	2.36	2.37	2.33	2.35	2.36	2.35	2.36	2.34	2.38	2.37	2.33	2.34
PS-I	2.35	2.33	2.36	2.33	2.35	2.35	2.37	2.36	2.35	2.39	2.37	2.37	2.37	2.39	2.36	2.40	2.38	2.37	2.38	2.40	2.38	2.38	2.39	2.37
AD-I	2.30	2.29	2.34	2.32	2.34	2.33	2.36	2.35	2.38	2.34	2.34	2.33	2.33	2.38	2.34	2.36	2.34	2.34	2.36	2.34	2.36	2.33	2.33	2.34
WS-O	2.35	2.39	2.35	2.35	2.38	2.37	2.36	2.37	2.37	2.35	2.37	2.37	2.39	2.40	2.39	2.41	2.40	2.40	2.39	2.40	2.41	2.38	2.40	2.38
PS-O	2.37	2.36	2.35	2.38	2.37	2.38	2.36	2.38	2.38	2.39	2.40	2.40	2.41	2.41	2.40	2.42	2.43	2.40	2.40	2.41	2.42	2.40	2.43	2.39
AD-O	2.37	2.34	2.37	2.34	2.36	2.38	2.37	2.35	2.35	2.35	2.36	2.37	2.38	2.37	2.37	2.37	2.38	2.37	2.38	2.38	2.37	2.36	2.39	2.37

Appendix B

Table 0.2 28-day recorded compressive strengths (MPa)

Curing method	CS0						CS20						CS40						CS60					
	#1	#2	#3	#4	#5	#6	#1	#2	#3	#4	#5	#6	#1	#2	#3	#4	#5	#6	#1	#2	#3	#4	#5	#6
IM	26.5	25.8	25.1	25.6	24.9	25.4	25.1	25.8	26.5	27.1	29.0	28.2	26.2	27.0	26.3	27.4	26.0	26.3	23.2	22.8	24.2	23.6	23.5	23.3
WS-I	22.8	19.9	23.6	23.2	24.3	23.7	27.8	28.7	28.3	23.7	25.4	23.1	24.5	26.0	24.5	24.8	25.5	25.3	23.1	23.0	24.0	23.8	22.6	22.5
PS-I	23.2	23.7	24.7	24.4	22.1	24.5	28.1	28.3	29.7	25.9	26.2	23.0	24.4	24.0	26.2	27.2	25.0	25.7	22.3	23.0	22.8	22.8	22.6	22.8
AD-I	18.8	23.4	24.6	22.9	23.0	23.7	23.4	23.5	23.5	23.1	23.1	23.7	21.7	21.3	21.8	22.3	21.4	22.0	20.6	21.3	21.7	21.6	20.2	18.4
WS-O	23.9	24.9	22.3	24.6	21.6	23.6	32.0	27.4	28.8	29.8	26.0	32.0	26.5	26.1	26.2	26.9	26.3	27.0	22.1	23.1	23.1	24.0	21.5	22.2
PS-O	24.7	25.7	25.1	25.3	23.9	25.4	34.6	30.1	29.7	26.7	32.9	31.5	24.6	28.2	21.0	27.6	26.6	27.8	22.3	22.8	23.3	23.3	23.4	23.3
AD-O	21.4	21.2	22.7	21.8	24.2	24.0	25.5	25.0	23.4	24.6	24.8	24.2	19.7	21.3	20.6	20.5	21.3	21.3	20.1	20.6	17.5	19.9	20.5	20.2