Properties of Cement Based Materials Containing Copper Tailings

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ABSTRACT

Increasing demands for copper and copper allied products have made the processing of low grade ores with high volume waste output unavoidable. Presently, billions of tons of copper tailings can be found in major copper producing countries. This study explored the possibility of using these copper tailings either as a cement replacement or additive material in pastes, mortars and concretes of 0.65, 0.57 and 0.50 w/b ratios. Fresh properties of mixtures such as paste consistencies and setting times, mortar yield stresses and flow losses, and concrete slumps were studied. The mechanical properties investigated were compressive strength, flexural strength, splitting tensile strength and abrasion resistance. The durability properties evaluated were autoclave and sulfate expansions, acid and chloride penetration resistance, rapid chloride permeability, accelerated corrosion and half-cell potential (HCP) tests. Finally, visual inspection of reinforcements after corrosion tests, toxicity characteristic leaching (TCLP) test and cost analysis were also performed.

Results showed that dry copper tailings affect mixture consistency negatively. However, the use of pre-wetted tailings reduced this drawback. Compared to mortar and concrete mixtures containing copper tailings as a cement replacement material, enhanced mechanical strengths much better than those of the control samples were obtained from mixtures containing copper tailings as an additive. Improved durability properties were also observed in mixtures containing copper tailings. Leaching of toxic metals from concretes were below the US Code of Federal Regulations (CFR) limits. Considering all these test results and cost analyses, the use of pre-wetted tailings at 5% addition level by mass of cement seemed to be the best reuse approach.

Keywords: Copper tailings, environment, pastes, mortars, concretes, mechanical strength, sulfate and acid attack, chloride penetration, accelerated corrosion, leaching.

ÖZ

Gittikçe artan bakır kullanımı nedeni ile üretim sırasında oldukça fazla atık ortaya çıkmaktadır. Günümüzde çeşitli ülkelerde bu üretimden dolayı milyarlarca ton atık malzeme olduğu bilinmektedir. Bu çalışmada bu atık malzemenin su/çimento oranları 0,65, 0,57 ve 0,50 olan betonda ve harçta çimento ile ikamesinin veya çimentoya eklenmesinin olasılıkları araştırılmıştır. Karışımların priz zamanı, akışkanlığı, basınç dayanımı, çekme dayanımı, basmada yarma dayanımı, ve aşınma dayanımı ölçülmüştür. Karışımların dayanıklılığını belirlemek için ise otoclav, sülfata karşı dayanıklılık, asit ve klor dayanıklılığı, hızlı klor geçirgenliği, hızlandırılmış korozyon ve korozyon potansiyeli ölçülmüştür. En son olarak ise demir donatı korozyon durumu, TCLP sızması ve ekonomik analiz yapılmıştır.

Sonuçlara bakıldığı zaman bakır madeni atıklarının betonun ve harçların kıvamını olumsuz yönde etkilediği görülmektedir. Fakat, önceden ıslatılmış olan bakır madeni atıklarında bu olumsuzluğun ortadan kalktığı görülmüştür. İkame edilerek kullanılan bakır madeni atıklarının çimentoya eklenerek yapılan karışımlara nazaran daha iyi mekanik dayanımlar verdiği görülmüştür. Dayanıklılık sonuçlarına bakıldığında ise bakır madeni atıklarının %5 oranında eklendiği karışımların çok daha iyi olduğu görülmüştür. TCLP deney sonuçlarına bakıldığı zaman en kötü şartlarda bile sızdırmanın insan hayatına ve çevreye zarar verecek düzeyde olmadığı görülmüştür.

Anahtar Kelimeler: Bakır madeni atıkları, çevre, pasta, harç, beton, mekanik dayanım, sülfat ve asit dayanımı, klor penetrasyou, hızlandırılmış korozyon ve sızdırma.

To the greatest Bookmaker: the source of the glue that held the pages of my life together, throughout the duration of this study. Your name is GOD.

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LIST OF ABBREVIATIONS

AMD	Acid mine drainage
ASTM	American Society for Testing and Materials
BSI	British Standards Institution
CCA	Crushed concrete aggregate
CFR	Code of Federal Regulation
CKD	Clinker kiln dust
CMC	Cyprus Mining Corporation
GGBS	Ground granulated blast furnace slag
Ha	Hectare
HC	Handling cost
HCP	half-cell potential
HPC	High performance concrete
HSC	High strength concrete
IC	Internal curing
ICSG	International Copper Study Group
LWA	Lightweight aggregate
NWA	Normal weight aggregate
OPC	Ordinary Portland cement
PFA	Pulverized fuel ash
PW	Pre-wet

SAP	Super-absorbent polymer
TCLP	Toxicity characteristic leaching procedure
US EPA	United States Environmental Protection Agency

Chapter 1

INTRODUCTION

1.1 General

Presently, achieving an environmentally-friendly community through effective waste recycling and sustainability in construction are key issues across the world. Thus far, utilization of some categories of industrial by-products in concrete production seems to be providing satisfactory solution to these concerns. In fact, several research studies have comprehensively shown that industrial waste materials like silica fume, coal fly ash, and ground granulated blast furnace slag (GGBFS) can be used in producing durable concretes. However, the growing quantities of waste being generated by the ongoing rapid industrialization across the world, dwindling landfill sites, clamor for a reduction in energy consumption and CO_2 emissions at cement plants makes it imperative that more industrial wastes should be explored for utilization in concrete production.

In the olden days, countries such as Cyprus bordering the Mediterranean have been recorded among the major sources of copper. Copper has been a very useful material since ancient times due to its availability, durability, conductivity and aesthetic properties. From being used for weapon and tool making in the past, the needs for copper and copper alloy products have grown in building construction, industrial machinery, transportation, general consumer products, telecommunication, electrical and electronic products. Furthermore, as a new innovation in information and communication technologies, "copper chip" allows microprocessors to operate at higher speeds with less energy; hence, increased production of copper in the coming years is definite. The International Copper Study Group (2010) estimated that between 1900 and 2009, annual use of copper increased from less than 500 hundred thousand to over 18 million metric tons. Thus, despite the billions of tons of already existing waste deposits at abandoned and still operating copper processing facilities, several billion tons of additional waste material will inevitably be produced in the incoming years. Presently, a small proportion of available copper waste is utilized in making abrasive materials, roofing granules, tiles and road base construction while the rest is disposed off at landfills.

Between 1914 and 1974, Cyprus Mining Corporation (CMC) operated a copper processing plant at the Lefke-Xeros area in the Northern part of the Island and according to Gokcekus et al. (2003), the primary operations at this plant included ore crushing, acid leaching, flotation for both copper and pyrite ores, and production of cement copper. This decades of mineral exploration produced huge deposits of waste material that were disposed around the processing plant. It is estimated that the piles of tailing deposits at the abandoned facility contain approximately 2.5 million tons of waste material (Yukselen, 2002). This waste material has constituted a serious environmental problem in the area, contaminating soil, underground water and the nearby Mediterranean Sea. Studies by Yukselen (2002) confirmed that the soil around the smelting facility and water from the adjoining Mediterranean Sea contain high concentrations of heavy metals and this anomaly was clearly associated with the tailings disposed at the site. Hence, to forestall further pollution of the area, immediate decontamination process should be initiated. However, conventional remediation methods are time consuming and very costly (Gonzalez & Gonzalez-Chavez, 2006). Outright evacuation of these tailing deposits and remediation of contaminated soil would be ideal. However, this may be infeasible given the size of the contaminated area and the cost implication (Boisson et al., 1999). Hence, cement stabilization of heavy metals in the copper tailings seem attractive since there are many inherent benefits in utilizing this material as a constituent in cement based materials. Research breakthroughs and validations through the promulgation of standards and guidelines for copper tailings blended cement mixtures will certainly create a new window of opportunity in the construction industry across the world. The gains will be unquantifiable; economically, environmentally and in terms of sustainability of concrete infrastructures.

This thesis presents a reclamation option that will not only eliminate future environmental contamination, it also has a high potential for large volume reuse of these tailings by the local construction industry. Hence, this study explored the possibility of using copper tailings as a potential ingredient in cement based materials by considering fresh, hardened, durability and leaching properties of pastes, mortars and concretes incorporating it at four different cement substitution levels. Similarly, the possibility of using these tailings as cement additive at three addition levels was also investigated. Details of findings were presented and conclusions drawn on how these findings will affect the environmental and socioeconomic well being of the inhabitants of Lefke-Xeros area and Northern Cyprus in general.

1.2 Objectives of the Research

The objectives of this thesis are:

1. To determine the physical and chemical properties of copper tailings used in this study.

2. To evaluate and compare the performance of cement based mixtures containing copper tailings either as a cement replacement material or as an additive.

3. To determine the impact of copper tailings on fresh and hardened properties of pastes, mortars and concretes such as consistency, setting time, compressive strength, splitting tensile strength, flexural strength, abrasion and impact resistance, water absorption and porosity, sulfate resistance, chloride resistance and reinforcement corrosion.

4. To check the possibility of enhancing mixture properties through the use of pre-wetted tailings.

5. To investigate the level of stabilization and immobilization of heavy metal ions in concretes containing copper tailings using the (TCLP) test procedure.

6. To investigate the cost efficiency of using copper tailings as a cementitious material in mortar and concrete. Furthermore, the impacts of tailings reuse on the environmental and socioeconomic well being of the inhabitants of Lefke-Xeros area and Northern Cyprus in general were also evaluated.

7. Finally, considering all the test results, an ideal utilization method and usage level for copper tailings in cement based materials shall be determined.

1.3 Work Done

In order to achieve the objectives earlier outlined, the following activities were undertaken:

1. To be abreast of the state-of-the-art regarding copper processing waste utilization in cement mixtures, a variety of scientific articles and books were reviewed. This was further supplemented by attending lectures and conferences.

2. Environmental impacts of copper tailings deposits found at Lefke-Xeros area of Cyprus were analyzed and possible uses for this waste material in the construction industry were discussed.

3. Through material characterization tests, physical and chemical properties of copper tailings such as particle size distribution, specific gravity, fineness, water absorption, oxides and heavy metal content were determined.

4. Experiments to determine the effect of copper tailings on mortar and concrete mixtures rheology, consistency, setting time, compressive strength, splitting tensile strength, flexural strength, abrasion resistance, water absorption and porosity, sulphate resistance, chloride resistance and reinforcement corrosion were performed.

5. To confirm the actual effect of copper tailings on reinforcement corrosion, concrete samples were split after corrosion tests and visually inspected.

6. TCLP tests were performed using deionized water and acetic acid as leaching solutions in order to determine the degree of immobilization of heavy metal ions contained in concrete mixtures containing copper tailings.

7. Optimization of mixtures containing copper tailings was undertaken using pre-wetted tailings. The effect of pre-wetted tailings on rheology, consistency, setting time, compressive strength, splitting tensile strength, flexural strength, water absorption and porosity, sulphate resistance, chloride resistance and corrosion were investigated.

8. The material cost estimates of concrete mixtures were determined using the local prices of construction materials in North Cyprus. Similarly, the environmental and socioeconomic benefits that will accrue to Lefke-Xeros area residents and the Government were discussed.

9. Interactions between copper tailing content, consistency, mechanical strength, heavy metal leachability, durability properties, and cost benefits were harnessed in suggesting the best utilization option and optimum copper tailings usage level in mixtures.

1.4 Achievements

1. In-depth review of scientific articles yielded the background information, knowledge and hypothesis required to embark on this study. Hence, the experiments were tailored accordingly and results analyzed properly.

2. Findings indicate that these copper tailings have caused severe soil contamination, ground water and Mediterranean Sea pollution at Lefke-Xeros area of Cyprus. Furthermore, this is equally an international environmental issue since the Mediterranean Sea cuts across many countries.

3. Copper tailings consist of porous and coarse particles. It has poor fineness, high acidity and heavy metal content.

4. Results from fresh properties tests showed that copper tailings affect rheology, consistency, and setting time of mixtures negatively. Copper tailings led to an increase in yield stress of mortar mixtures. It equally caused decreases in flow spread, and this became more pronounced as tailings content of mixtures increased. However, pre-wetting of the tailings before use improved rheological and consistency properties of mixtures significantly.

5. Concrete compressive, flexural and tensile strengths comparable to those of the control specimens were obtained, especially at 5% cement substitution level. However, the use of these tailings as a cement additive produced mortars and

concretes with more enhanced mechanical strengths compared to those of control mixtures.

6. Improved durability properties were observed in mixtures containing copper tailings, and the best performances were recorded in mixtures containing copper tailings as an additive.

7. With the exception of 5% cement replacement level, addition of copper tailings to concretes prolonged corrosion initiation time. Similarly, while HCP measurement showed that the corrosion status of all samples could not be predicted, visual inspections revealed the absence of deteriorations in reinforcements.

8. Leachate concentrations obtained from the TCLP leaching tests were significantly lower than the US CFR limits. Hence, there is a strong potential for the use of these tailings as a cement substitution or additive material in cement based mixtures.

9. Compared to the control mixtures, mortars containing copper tailings either as a cement replacement or additive material were more cost efficient. Similar trend was observed in concretes containing copper tailings as an additive, and this will become more significant on the long-term.

10. Successful utilization of these copper tailings will bring substantial environmental and socioeconomic benefits to local communities.

1.5 Guide to Thesis

The thesis contains the following chapters:

Chapter 1, the introduction contains a short background identifying the aim and scope of the thesis. It also describes the research method and thesis outline.

Chapter 2 discusses the generation of copper processing wastes. It highlights the environmental impacts of copper tailings in Lefke-Xeros area of Cyprus. Furthermore, different potential ways of utilizing these tailings as construction materials were equally presented.

Chapter 3 reviews fresh and hardened properties of mortars and concretes incorporating copper processing wastes, especially copper slag. Leaching behaviors of toxic metals in cement based mixtures were also discussed.

Chapter 4 discusses the enhancement of fresh, mechanical and durability properties of mortars and concretes through internal curing (pre-wetting).

Chapter 5 presents the experimental set up, explaining the materials and mixtures used. Furthermore, details of specimens and testing procedures were also highlighted.

Chapter 6 deals with results and discussions of the tests performed during the study. Analyses of findings were equally presented.

Chapter 7 presents the conclusions drawn from each of the tests performed. Furthermore, recommendations for future research studies were also given.

Chapter 2

ENVIRONMENTAL IMPACTS AND POTENTIAL REUSES OF COPPER TAILINGS

2.1 Introduction

Copper extraction and purification consist of a series of processes such as ore mining, crushing, milling, flotation, roasting, smelting, electro-refining, etc. First, copper-bearing ores containing 1-2% copper is extracted by mining, then, ore crushing, powdering and conversion to slurry by milling is performed. Using water and other chemicals, cycles of froth flotation is usually carried out to separate waste rock (tailings) from copper concentrate. Thereafter, copper concentrate is further processed to produce pure copper.

2.2 Types of Copper Processing Wastes

2.2.1 Copper Slag

Smelting in a furnace removes more impurities from dry copper concentrate converting it into a molten mass (matte), with iron-silicate glass (slag) on top. The slag is skimmed off for crushing, grinding, flotation and re-smelting. The molten matte is then processed in a converter to form blister copper of 98.5-99.5% copper content. The blister copper is finally purified by casting into anode and is electro-refined. There are two types of copper slag; air cooled copper slag which is black in color, glassy with a low water absorption capacity and water cooled molten slag which is amorphous, granulated with higher water absorption. Nowadays, copper slag is stored in impoundment facilities.

2.2.2 Copper Tailings

At the end of the froth flotation process, tailings are usually pumped to ponds to undergo sedimentation and dewatering. This process is repeated until a tailing pond is filled up and appropriately covered with impermeable top layer. Alternatively, after being dewatered, solid tailings are then disposed off in impoundment facilities such as earthen dams, open pits and valleys. In the olden days, indiscriminate discharge of untreated tailings around processing sites is a common occurrence. Similarly, there are instances where slurries bearing tailings were discharged directly into water bodies. Tailings consist of finely ground rock particles which contain residual ore metals and toxic processing chemicals. Hence, copper tailings are usually toxic.

2.3 Environmental Impacts of Copper Tailings

According to Bridge (2000), for every 1 ton of copper produced; about 196.5 tons of solid and liquid tailings are produced. This estimate was fine-tuned to 128 tons of solid copper tailings for every 1 ton of copper extracted by (Gordon, 2002). The massive waste generation going on in the copper industry, was highlighted by Boger (2009) when he submitted that about 230,000 tons of dry copper tailings is produced daily at the Escondida copper mine in Chile. Thus, in major copper producing countries of the world such as Chile, United States, Peru, China, Indonesia etc, huge deposits containing billions of tons of copper tailings abound. Given the increasing world population, and the wide application of copper and copper allied products in electrical, telecommunication and construction industry, the high demand for copper is expected to continue. Hence, to satisfy this growing demand, even low grade ores with high waste volume output will be processed. Therefore, despite the billions of tons of already existing waste deposits all over the world, several billion tons of additional waste material will inevitably be produced in the incoming years.

The main problem of mine wastes containing sulfide is uncontrolled exposure to weathering (Dold, 2008). This is because acid mine drainage (AMD) which has been associated with severe environmental contamination is made to occur. In the presence of oxygen and water, iron sulfide (FeS_2) contained in tailings is oxidized to cause AMD. Studies by Singer and Stumm (1970) showed that the chemical reactions associated with the generation of AMD can be generalized as shown below:

$$2FeS_{2\,(S)} + 7O_{2\,(g)} + 2H_2O_{(l)} = 2Fe^{2+}_{(aq)} + 4SO^{2-}_{4(aq)} + 4H^{+}_{(aq)} \quad (1)$$

$$4Fe^{2+}_{(aq)} + O_{2\,(g)} + 4H^{+}_{(aq)} = 4Fe^{3+}_{(aq)} + 2H_2O_{(l)} \quad (2)$$

$$4Fe^{3+}_{(aq)} + 12H_2O_{(l)} = 2Fe(OH)_{3\,(S)} + 12H^{+}_{(aq)} \quad (3)$$

$$FeS_{2\,(S)} + 14Fe^{3+}_{(aq)} + 8H_2O_{(l)} = 15Fe^{2+}_{(aq)} + 2SO^{2-}_{4(aq)} + 16H^{+}_{(aq)} \quad (4)$$

In equation 1, iron sulfide (FeS_2) contained in tailings is oxidized, producing ferrous ion (Fe^{2+}), sulfate ion (SO_4^{2-}) and hydrogen ion (H^+). In equation 2, Fe^{2+} is further oxidized to form ferric ion (Fe^{3+}). Thereafter, Fe^{3+} may hydrolyze in water to form yellow precipitate of Iron (III) hydroxide ($Fe(OH)_3$) or it may act as an oxidant in equation 4, producing additional Fe^{2+} and acid. Through surface runoff, precipitates and other heavy metal ions soluble in acid are then released into the soil, surface and subsurface waters thereby contaminating the environment.

Several studies have shown the severe impacts of copper tailings and AMD on the environment. High metal and acid concentrations in water obtained close to abandoned copper mines and mine wastes in Southern Tuscany, Italy was observed by (Benvenuti et al., 1997). In a related study, Salonen et al. (2005) investigated the impact of un-remediated mining areas on the environment, and they discovered that even after 50 years of the closure of the Orijărvi Mine, southwest Finland. Lake Orijărvi water still contains high concentrations of heavy metals which suggest that contamination through AMD is still ongoing. Studies by Brooks et al. (2005) showed that macro/meso fauna and flora were completely absent in lakes and ponds adjacent to the Karabash copper smelter, southern Ural Mountains of Russia which directly receive contaminated waters. Findings by Andrade et al. (2006) suggests that the discharge of tons of untreated tailings from the El Salvador mine, into the sea, made the Chañaral coastline in north of Santiago, Chile to be significantly copper contaminated. Similarly, Ntengwe & Maseka (2006) observed high concentrations of zinc and nickel in water and sediment soils in streams located near the Chambishi copper mine, in Zambia. Severe heavy metal contamination of soil within the vicinity of the Dabaoshan Mine, Southern China, was also observed by Zhou et al. (2007), and they attributed this occurrence to tailings and AMD.

Over the years, severe environmental impacts and loss of lives have also been associated with copper tailings dam failures. According to Grimalt et al. (1999), approximately 2 million m^3 of mud containing heavy metals were spread over 4286 ha of land and surface water during the 1998 Aznalcollar tailings pond failure in Spain. Similarly, Destouni (2005) suggested that about 1.6 million m^3 of tailings impoundment water was released to surrounding waterways during the year 2000 Aitik copper tailings dam failure in Sweden. Lungu (2008) reported that the 2006, tailings spillage at the Nchanga copper processing plant, Zambia, released high concentrations of heavy metals into the nearby surface water, thereby contaminating the local source of water supply. Loss of lives has also been recorded during severe tailings dam failures. The deaths of 54 people during the 1928 Barahona copper tailings dam failure in Chile was reported by (Harder & Stewart, 1996). Likewise, Barrerra et al. (2011) were of the opinion that about 300 lives were also lost in Chile, during the 1965, El Cobre dam failure. The deaths of 89 persons during the 1970 Mufulira copper tailings dam collapse in Zambia was also highlighted by (Blight & Fourie, 2005). Hence, given these aforementioned menaces associated with the disposal of copper processing wastes, devising methods for the utilization of these by-products as valuable and useful materials in cement based mixtures is necessary.

In Cyprus, for more than six decades, Cyprus Mining Corporation (CMC) operated three mines; Skouriotissa, Mavrovouni and Apliki mines near the Lefke-Xeros area of the Island. Sulfide ores from these mines were transported to the treatment plant situated near the coast of Xeros for mineral processing. The main mineral produced was copper while gold was the secondary product. Decades of mineral exploration and processing produced huge deposits of toxic waste materials disposed across the area. Waste deposits at the abandoned processing site contain about 2.5 million tons of copper tailings which have led to air, soil and water pollution (Yukselen, 2002). Some research studies have revealed ongoing severe environmental pollution in the Lefke-Xeros area.

Presently, successful closure of mine operations and decontamination processes usually involve huge financial outlay. The disclosure by Cherry (2008) that in the early 1990s, the Kennecott Utah Copper company spent more than $350 million in tailings removal and land remediation efforts at the hundred-year-old open-pit copper mine in Salt Lake City, underscores the high cost of remediation projects. Similarly, Dold (2008) submitted that the costs for remediation of mine wastes in the United States and Canada are estimated to be between 1 and 2 billion United States dollars per year. However, the costs incurred in carrying out remediation works are only but a small percentage of the total expenditure, since the actual cost of environmental impacts are difficult to quantify. This is because it bequeaths the generations yet unborn a huge environmental burden at an inestimable cost. The environmental impacts of copper tailings in Lefke-Xeros area of Cyprus is presented in subsequent paragraphs. Possible recycling approaches for this waste material were also discussed.

2. 3.1 Description of the Abandoned Copper Processing Site Area in Cyprus

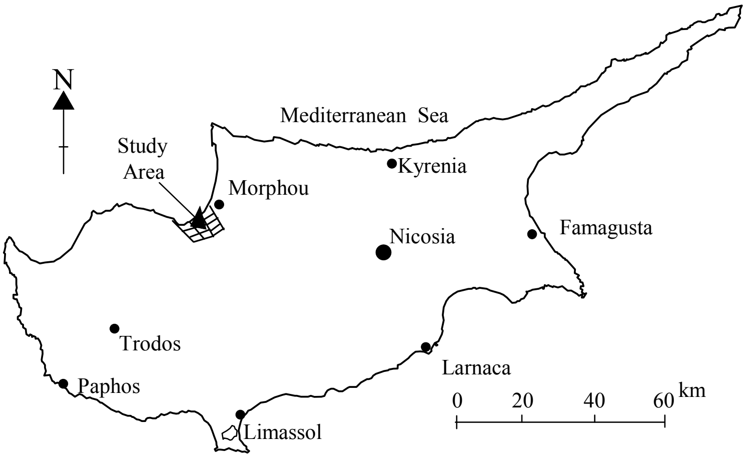


Figure 2.1. Map of Cyprus Showing the Location of the Abandoned Processing Site

The abandoned copper processing site area (Figure 2.1) which is located northwest of Cyprus consists of two villages, Lefke and Xeros. The distance from Lefke (lat.35°08′38″N, long. 32°51′2″E) to Xeros (lat.35°08′30″N, long. 32°50′0″E) is about 3.8 km. Lefke-Xeros neighborhood is an amalgam of coastline and low-lying mountains. The region is well known for its very green landscape, agriculture, citrus fruits cultivation and environmental devastation caused by copper mining and processing activities. The abandoned copper processing facility and waste deposits are bordered on the east by the Lefke River and on the west by the Xeros River and an earth irrigation dam. The Lefke and Xeros Rivers originate mainly from surface runoff from the Troodos Mountains and they are seasonal.

The climate of Lefke-Xeros area, like the rest of Cyprus is semi-arid of the Mediterranean type. This is a typically hot and dry summer starting from early June, with increasing temperature as the summer is progressing. The winters are relatively mild, and rainfall is usually observed from November till April. Temperature and rainfall distribution depends on altitude and most of the precipitation over the area is distributed locally with respect to proximity to the sea. More annual rainfall is usually recorded in the Troodos Mountains (close to the study area) and the Kyrenia Range than in the Mesaoria lowland. The average annual rainfall in Cyprus is about 500 mm with an average of 300–400 mm in the central plain to nearly 1200 mm at the summit of the Troodos Mountains (Elkiran & Ergil, 2006).

Cyprus is composed of four geological zones; the Troodos Ophiolite Complex, the Circum-Troodos Sedimentary Succession, the Mamonia Terrane and the Kyrenia Range. The Troodos Ophiolite Complex dominates the topography of the central part of the island, serving as the country's major deposit of aquifers, copper and other minerals bearing sulfide ores. The Circum-Troodos Sedimentary Succession covers the area between the Kyrenia Range and Troodos Ophiolite Complex as well as the southern part of the island. It is the main source of bentonitic clays, melange, marls, chalks, cherts, limestones, calcarenites, clastic sediments etc. which are useful construction materials. The Mamonia Terrane on the other hand is located to the west of the Troodos, a blend of igneous, sedimentary and metamorphic rocks. The Kyrenia Range comprises sedimentary originated hills and mountains running from west to east along the north coast of the country.

2.3.1.1 Air Pollution

Air pollution due to dust particles and gaseous pollutants has been associated with mining and processing operations across the world. The absence of vegetation, aids the dispersion of particles, sulfur dioxide (SO_2) and other metals emitted from oxidizing copper tailings. These air-borne particles and gas have adverse effect on humans, animals, vegetation, climate, materials and structures. The transportation of pollutants over long distances has the potential to affect other localities in Cyprus too. The inhalation of these wind dispersed, heavy metal laden tailings particles and emitted SO_2 gas constitute a serious source of health hazards for local dwellers. While the young and the elderly are particularly vulnerable, people already indisposed with one sickness or the other, stand the risk of having their ailments aggravated. There is an absence of comprehensive studies and data on health problems in the study area. However, this does not preclude the existence of diseases associated with pollution among residents. Bleaching of leaves by SO_2 gas and the deposition of particles on plant leaves which reduce access to CO_2 and sunlight required for photosynthesis; cause stunted growth and reduced crop yield. Reduced crop productivity in the study area was reported by (Stone, 2001).

2.3.1.2 Soil Pollution

A soil polluted from mining and smelter processes usually contains harmful chemical substances, toxic heavy metals, high acidity, low organic matter and nutrients. These compositions, make the soil inimical to biodiversity, and predispose it as a pathway for surface and subsurface water contamination. In the study area, wind deposited particles, floatation tanks, chemicals, plant equipment, ore fragments, waste ponds seepages and tailings deposits are major sources of soil contaminants. Figure 2.2 shows one of the abandoned and uncovered 23 tailings ponds which form artificial lakes during the wet season. Seepages and runoff from these lakes are a source of serious soil, surface and subsurface water pollution.

Figure 2.2. Artificial Lake formed by One of the Tailings Ponds

Studies by Yukselen and Alpaslan (2001) on soil samples taken from the abandoned processing facility site showed that the soil contained high concentrations of heavy metals and was also of very low pH. The mean metal contents of soil samples were 510.0 mg/kg for Cu, 153.0 mg/kg for Pb and 15.3 mg/kg for Fe. Similar studies by Altinbaş et al. (2001) on soil samples taken from the gardens of local residents close to the processing facility equally revealed high metal contents. The mean metal concentrations were 504.0 mg/kg for Cu, 45.0 mg/kg for Pb and 6.10 mg/kg for Fe. Comparisons of the maximum concentrations of some metals in these two aforementioned studies suggest that the pollution of the garden soils may have originated from contaminants dispersed by wind/water erosion from the processing facility.

2.3.1.3 Surface and Subsurface Water Contamination

In Cyprus, like most other island countries, potable water is relatively scarce. The water problem is especially critical since precipitation, which is an important source of replenishment for the groundwater, has been declining for years. According to Elkiran and Ergil (2006), water shortage in Cyprus began in the 1960s and it has persisted. As a water conservation measure, a 4 million m^3 Xeros earth dam was constructed by the government to impound water from the Morphou Aquifer for irrigation purposes. Some wells which were meant to serve as domestic source of water supplies are equally located close to the dam. However, studies have shown that these water bodies near the study area are contaminated. Contamination of the Mediterranean Sea by copper tailings disposed at the site was reported by (Yukselen, 2002). Similar opinion was expressed by Gokcekus et al. (2003), attributing the contaminations to AMD. Figure 2.3 shows the flow of AMD from the processing site towards the sea. On the other hand, Figure 2.4 highlights the contamination of the Mediterranean Sea by surface runoff from the processing site during the rainy season. In a more recent study, Gökmen and Taşer (2007) reported that the concentrations of copper and manganese in the Xeros dam were far above regulatory limits. Hence, to safeguard public health, the use of the dam and other wells close to it had to be abandoned.

Figure 2.3. Acid Mine Drainage (AMD) Flow Towards the Sea

Figure 2.4. Contamination of the Mediterranean Sea

2.3.1.4 Land, Vegetation and Landscape Destruction

Lefke-Xeros area is one of the most beautiful regions in Cyprus, with lush green vegetation, fertile agricultural land and abundant supply of citrus fruits. The blending of the vast green scenery and orange-colored citrus fruits groves creates a kaleidoscopic landscape that is visually alluring. Moreover, during the mining era, the study area was a bustling industrial center with well planned residential quarters and green areas set aside for recreational purposes. However, decades of mining and ore processing operations have caused a severe impairment of land and landscape within the area. According to Cohen (2002), the land area suspected to have been contaminated covers about 2000 hectares, of which 156.6 hectares of land was appropriated by the abandoned copper processing facility, and 84.1 hectares by tailings ponds and tailings deposits. Land is a very scarce resource in Cyprus, hence, it is a huge loss that these hectares of land, which could have been used for agriculture or other purposes has been desolate for years.

The large expanse of land without vegetative cover shown in Figure 2.5 is the area on which the processing facility is located. The complete absence of vegetation observed, is traceable to factors such as high soil acidity, heavy metal contamination and lack of required soil nutrients for plant growth. Mine wastes often contain excessive concentrations of metals that are toxic to plants, and hence these wastes are often devoid of vegetation (Wong, 2003). Healthy and aesthetically appealing surroundings enhance the quality of life experienced in a community. However, obtrusive and unsightly heaps of tailings shown in Figure 2.6, some of which are more than 9 m in height dot and distort the Lefke-Xeros landscape. Similarly, the usually beautiful seascape associated with the Lefke beach has been destroyed through soil erosion, sediment deposition and sea pollution. These despoiled natural sceneries are difficult to recreate.

Figure 2.5. Derelict Land within the Abandoned Copper Processing Site

Figure 2.6. Typical Tailings Deposit at the Site

2.4 Potential Applications of Copper Tailings in Construction

2.4.1 Tiles and Glass-ceramic Products

Tiles and ceramic products are used for a variety of purposes in the construction industry. Hence, there is a significant potential for the use of copper tailings to manufacture these products. The blending of copper tailings with other raw materials in the production of unglazed tiles was investigated by (Marghussian & Maghsoodipoor, 1999). They reported that tiles containing 40% copper tailings fired at 1025°C for 1 h presented good mechanical and acid resistance properties. Similarly, Çoruh et al. (2006) observed that copper flotation waste vitrified at 850°C for 2 h, formed glass–ceramic products with very good chemical durability. However, the high energy consumption cost associated with these prospects may negate the inherent benefits.

2.4.2 Bricks

Copper tailings could also be reused in brick production. Several studies have investigated the possibility of using copper tailings in the manufacture of bricks with significant successes. Copper tailings could be used in producing good quality fired bricks at a firing temperature of 950°C (Pappu et al., 2007). Similarly, Fang et al. (2011), investigated the use of copper tailings having SiO_2 content of 35% as river sand replacement material in the manufacture of autoclaved sand–lime brick. They suggested that there is a strong potential for this, provided the tailings content of mixture did not exceed 50% and the correct proportions of river sand and sand powder have been added to increase SiO_2 content. By activating low-silicon tailings with slag and fly ash, Feng-qing et al. (2009) produced load-bearing bricks with ideal mechanical strength and durability properties using the autoclaved process. However, the very low SiO_2 content and high specific gravity of some copper tailings, which invariably will lead to the manufacture of very heavy bricks are the main drawbacks of this application method.

2.4.3 Cement Production

Portland cement is a fine powder produced from the pre-grinding of calcareous materials such as clay and limestone, heating and re-grinding of formed clinker. During the pre-grinding and mixing stage of raw materials, iron ore powder is usually blended to regulate the final iron oxide content of cement. Hence, copper tailings which contain high percentage of iron (III) oxide (Fe_2O_3) can be used as an ingredient in cement clinker production. Studies by Alp et al. (2008) showed that mortar samples containing cement produced with copper waste clinker has mechanical performance similar to that of conventional CEM I cement. They further averred that the leaching of heavy metals from these mortar samples were below regulatory limits. In a related study, the effect of waste materials containing Cu on the formation of clinker minerals was investigated by Ma et al. (2010), and they observed that at an appropriate quantity, these wastes lower clinker burning temperature and improve clinker hydration.

Thus far, the possibility of using copper tailings as a mortar and concrete making material in the construction industry is yet to be addressed. Therefore, recycling of copper tailings as a source of Fe in cement clinker production and as a cement replacement or additive material in mortar and concrete, will not only reduce waste and environmental contamination, it will also enhance sustainability in natural resources usage.

Chapter 3

PROPERTIES OF MORTARS AND CONCRETES CONTAINING COPPER PROCESSING WASTES

3.1 Introduction

Some past studies evaluated the use of copper slag as a cementitious material in cement mixtures. The attempt to use copper slag as a cement replacement or supplement material was as a result of its moderate silicon (IV) oxide (SiO_2) content. More recently, research efforts have been channeled towards achieving higher volume of usage for copper slag in concrete. Hence, few studies on the use of copper slag as a sand replacement material in concrete are available. However, thus far, no study exists on the possible use of the more abundant copper tailings as a mortar or concrete making material. Therefore, this chapter will review the various properties of cement mixtures containing copper slag, with a view of making future comparison with experimental results on the behavior of mixtures containing copper tailings.

3.2 Fresh Properties

3.2.1 Consistency

Research studies have shown that the incorporation of copper slag in concrete improves concrete workability. This behavior is traceable to the low water absorption (0.13-0.15%) recorded in literature for copper slag by Shi et al. (2008) and its smooth glassy texture. Zain et al. (2004) suggested that the slightly lower water demand compared to that of the control mixtures they observed in pastes prepared with 10% partial substitution of cement with copper slag was as a result of the nonporous slag particles. Similarly, Al-Jabri et al. (2009a) observed reduced water demand in high strength concrete mixtures prepared using copper slag as a replacement material for fine aggregate. According to Wu et al. (2010a), the smooth glassy texture and low water absorption of copper slag improves concrete slump tremendously when it is used as a substitute for fine aggregate.

3.2.2 Setting Time

Delayed setting time of mixtures containing copper slag has been reported by various researchers. Mobasher et al. (1996) observed moderate delay in setting time of cement pastes containing copper slag. However, in a related study, Ayano and Sakata (2000) reported severe delayed setting time in cement mixtures containing copper slag. Hence, the effects of copper slag on the setting time of mixtures depend on its specific properties, especially the chemical constituents. The precipitation of Cu, Pb and Zn compounds, such as the oxides and hydroxides in cement mixtures have been shown by Diet et al. (1998) and Olmo et al. (2001), to interfere with the cement hydration process, thereby delaying setting time. Zain et al. (2004) attributed the delayed setting time of cement pastes they observed to the presence of Cu, Pb and Zn compounds in copper slag. This postulation was further supported by the assertion by Hashem et al. (2011) that the presence of Cu (II) ions retard cement hydration

3.3 Hardened Properties

3.3.1 Mechanical Strength

Some research studies have shown that copper slag as a concrete making material can improve mechanical properties of concrete. As a cement replacement material, Tixier et al. (1997) observed a strength increase in mortars containing copper slag and they attributed this occurrence to capillary porosity reduction by the copper slag grains. Similar studies performed by Moura et al. (1999) with 10% by weight of cement replaced by copper slag suggested that at 91 days, concrete with copper slag had lower compressive strength compared to concrete without copper slag. This reduction in compressive strength suggests that a limit exist for a beneficial use of copper slag as a cement replacement. This was further clarified by Al-Jabri et al. (2006) when they stated that at low water/binder ratios of 0.5 and 0.6, the use of 5% copper slag instead of Portland cement would yield a marginally lower but similar performance as the control mixture. In order to increase the use of copper slag as a cementitious material in concrete, other approaches were equally explored. Using 1.5% hydrated lime activation; Mobasher et al. (1996) achieved increased compressive strength and reduced porosity for concrete specimen with 15% by weight of cement replaced with copper slag. Arino and Mobasher (1999) also observed that as long as rapid strength gain is not a major design constraint, ground copper slag at 10% cement replacement level competed favorably with the strength of control specimens. Moreover, rather than replacement with copper slag, Moura et al. (2007) employed copper slag as an additive in concrete and they observed increased mechanical strength, reduced porosity and carbonation for concrete samples.

The use of copper slag as aggregates in concrete and the associated mechanical properties have also been investigated by researchers. Hwang and Laiw (1989) investigated the use of copper slag as fine aggregate replacement in mortar and concrete and they were of the opinion that below 80% replacement level, higher compressive strengths were recorded for mortars while 60% sand substitution yielded a much better performance in concrete specimens. Al-Jabri et al. (2009a) investigated the effect of copper slag as sand replacement on the properties of high performance concrete (HPC) and they recommended that 40% by weight substitution can yield a very workable HPC with good properties. This assertion was also confirmed by Wu et al. (2010a) when they concluded that less than 40% copper slag as sand replacement can achieve a high strength concrete that is comparable or with superior performance to that of the control mix, beyond which however its behaviors decreased significantly. Further research by Al-Jabri et al. (2009b) revealed a more than 20% improvement in the compressive strength of HSC with 100% copper slag substitution for sand in comparison with the control mix at the same workability. Khanzadi and Behnood (2009) reported that the use of copper slag aggregates compared to limestone coarse aggregates resulted in an increase in compressive and tensile strength of HSC. To underscore the growing awareness about the need to understand the behavior of concrete under dynamic loading, Wu et al. (2010b) investigated the dynamic compressive strength of concrete containing copper slag as a replacement for sand and they were of the opinion that strength was generally improved with substitution of copper slag up to 20%, compared with the control concrete, beyond which it reduced.

3.3.2 Durability Properties

Circumstances such as acid and sulfate attack, chloride penetration and reinforcement corrosion can lead to severe deterioration of concrete. Several studies to find solutions and measures to counteract the problem of poor durability performance of concrete have been conducted, and significant successes achieved through the use of various supplementary cementitious materials in concrete. Research by Polder and Peelen (2002) suggested that concrete containing blast furnace slag, fly ash or both has superior resistance to chloride penetration and corrosion activity. Similar studies by Smith et al. (2004) not only confirmed that fly ash, slag cement and microsilica increase concrete durability, they were also of the opinion that ternary mix design utilizing these three cementitious materials will produce concrete of very high resistivity. Thus, it is expected that copper slag will have similar effect on concrete durability. However, less information exists on the durability properties of concretes containing copper slag. Evaluation of some durability properties of concrete containing copper slag as aggregates showed that these mixtures displayed no significant sulfate induced deterioration and the rate of carbonation was minimal compared to those of the control specimens (Hwang and Laiw, 1989; Ayano and Sakata, 2000). Research findings by Al-Jabri et al. (2009b) also showed that at adequate consistency, high strength concrete mixtures containing copper slag as a partial substitute for sand recorded reduced water absorption. Similarly, Najimi et al. (2011) were also of the opinion that the resistance to sulfate attack of concrete samples containing copper slag was better than those of the control samples.

3.3.3 Leaching Behavior

Concerns about the fate of toxic metals contained in copper processing wastes have also been expressed. However, various studies have shown that heavy metals can be effectively stabilized and solidified in cement-based materials. Park (2000) investigated the stabilization of heavy metals in OPC, clinker kiln dust (CKD) modified OPC, and quick setting agent (QSA) modified OPC. He observed lower leaching of heavy metals in the blended mixtures. Studies by Lin et al. (2003) showed that at a w/c of 0.38, leaching of heavy metals from mortar samples with 10 to 40% cement substitution by MSWI fly ash slag were below the United States Environmental Protection Agency (US EPA) regulatory standard for hazardous substances. Giergiczny and Krol (2008) showed that OPC, fly ash and GGBFS blended mortar mixtures can successfully immobilize heavy metals. Shi and Kan (2009) submitted that the leaching of heavy metals from cement paste samples containing MSWI fly ash was below the Chinese regulatory limits. Choi et al. (2009) observed effective immobilization of heavy metals in mortars containing tungsten tailings, especially in mixtures containing binary blend of the waste and GGBFS.

It has been shown that copper slag has high concentration of heavy metals. However, immobilization of heavy metals in copper slag blended concretes is another research area with scanty information. Zain et al. (2004) investigated the leaching of Cu, Ni, Pb, and Zn from mortar samples incorporating ground copper slag up to 10% cement replacement. The results indicated that the leaching of heavy metal ions from the cement matrix was low and did not exceed the Malaysian Environmental Quality Act. Alp et al. (2008) reported that the leaching of heavy metals from mortar samples produced with copper slag clinker cement were below regulatory limits. Mesci et al. (2009) studied the effect of using copper flotation waste and clinoptilolite, a naturally occurring crystalline aluminosilicate mineral as a partial substitute for cement. Results indicated that at 12.5% replacement level, leaching of copper from the various cement mixtures did not exceed the regulatory limits. Related studies by Çoruh and Ergun (2006) and Hashem et al. (2011) have also shown that heavy metals contained in copper slag can be effectively immobilized in cement mixtures.

From the foregoing, it is obvious that mortars and concretes containing copper slag have desirable attributes which enhance its acceptability in the construction industry. However, copper tailings which are more abundant are yet to receive close scrutiny from concrete researchers. Many gaps such as fresh, hardened, durability and leachability properties of cement mixtures containing these tailings need to be addressed. Such studies become more imperative, given the assertion by ICSG that millions of tons of copper and copper processing wastes will definitely be produced in the coming years as world population increases and the needs for copper and copper allied products in high technology applications grow.

Chapter 4

INTERNAL CURING AS A MEANS OF ENHANCING THE PROPERTIES OF CEMENT MIXTURES

4.1 Introduction

Over the years, various approaches have been established as means of improving fresh and hardened properties of concretes. The use of supplementary cementitious materials such as silica fume, coal fly ash, ground granulated blast furnace slag (GGBFS) to improve concrete properties is well established. Partial substitution of cement with some of these aforementioned supplementary materials has led to the production of concretes of very high strength and performance. However, these high strength concretes (HSC) which are usually produced at low w/b ratios, have been shown to be prone to incomplete cement paste hydration, self-desiccation and shrinkage problems. Hence, in an effort to overcome these drawbacks, an alternative approach which harnessed material property such as the porosity of aggregates in optimizing concrete performance has been explored. The principal aims of internal curing (IC) are the provision of additional water required by hydrating cement paste and the reduction of self-desiccation. The idea of using saturated fine lightweight aggregates (LWA) as agents of internal curing in HSC was proposed by (Philleo, 1991). A diagrammatic representation of the process of internal curing is shown in Figure 4.1.

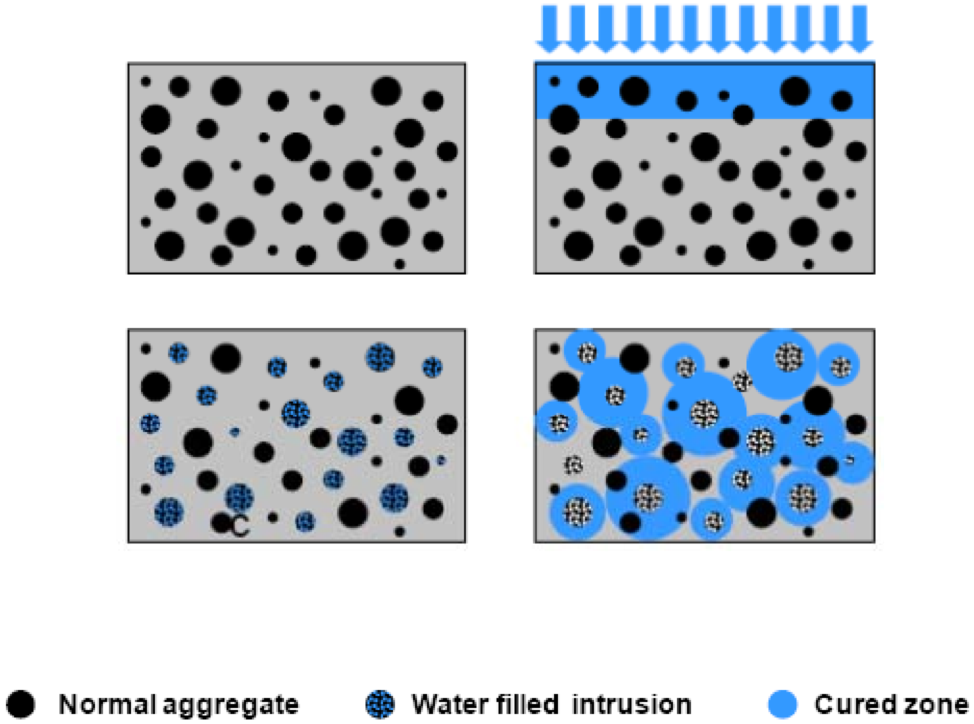


Figure 4.1. Diagrammatic Representation of Internal Curing (Bentz and Weiss, 2011)

4.2 Current Trends in Internal Curing

Artificial LWA are processed natural materials and industrial by-products such as expanded clay, expanded shale, expanded slate, expanded glass, foamed slag, sintered pulverized fuel ash etc., while pumice and scoria are examples of unprocessed natural LWA. Several studies have utilized artificial saturated LWA as internal curing agents in mortars and concretes. Computer simulation results by Bentz and Snyder (1999) suggest that the self-desiccation and autogenous shrinkage of HPC could be best minimized by using well dispersed saturated fine LWA particles. van Breugel and Lura (2000) suggested that the use of saturated smaller sized LWAs is very effective in reducing autogenous shrinkage in HPC because they are more homogenously distributed. These observations were affirmed by Hoff (2002), who stated that saturated large sized LWA are not as effective as the smaller sized LWA in enhancing paste hydration.

The water absorption and retention capacity of dry granulated materials known as super-absorbent polymers (SAP) were originally utilized in the diaper manufacturing industry. Presently, it has been applied in different areas, one of which is concrete research. Jensen and Hansen (2001) pioneered the concept of SAP as a means of decreasing self-desiccation in HPC. However, in a supplementary study, Jensen and Hansen (2002) suggested that separation of particles during mixing, change of setting time and rheology are potential drawbacks with SAP utilization. The high cost of these materials constitutes another hindrance to its usage. Mohr et al. (2005) proposed the use of pre-wetted wood derived powders and fibers as internal curing agents in cement based materials while Kim and Bentz (2008) investigated the use of saturated crushed returned fine aggregates. The frontier of internal curing in concrete was further extended by Suzuki et al. (2009) when they studied the effect of pre-saturated porous ceramic waste coarse aggregates on autogenous shrinkage and strength.

4.3 Benefits of Internal Curing

4.3.1 Shrinkage

The volume change in concrete known as shrinkage is an issue of great concern in the construction industry, since it affects the strength and durability properties of constructed facilities. There are various types of volume changes in concrete; autogenous, plastic, drying and carbonation shrinkage. Concrete researchers have shown that internal curing of cement mixtures reduces autogeneous and plastic shrinkage at early age. At later ages, it also minimizes self-desiccation and other associated shrinkage problems. Kohno et al. (1999) were of the opinion that the use of saturated coarse sized LWA reduces autogenous shrinkage of concrete. Bentur et al. (2001) observed the absence of autogenous shrinkage in HSC concrete samples containing saturated LWA as partial replacement for normal weight aggregate (NWA). Similarly, Jensen and Hansen (2002) noticed that internal curing of mixtures eliminated autogeneous shrinkage problems in pastes. Kim and Bentz (2008) recorded significant reduction in the autogeneous shrinkage of blended mortar mixtures containing saturated fine CCA and LWA. Similar observation was made by Suzuki et al. (2009) in HPC mixtures containing pre-saturated porous ceramic waste coarse aggregates. Henkensiefken et al. (2009) reported reduced autogeneous shrinkage, drying shrinkage and extended cracking time in mortar specimens with internal curing. The enhanced resistance to shrinkage of internally cured mixtures was traceable to the ready availability of water in pre-wetted LWA to maintain saturation of the cement paste, thereby reducing plastic, autogenous, and drying shrinkage (Bentz & Weiss, 2011).

4.3.2 Mechanical Strength

The effect of saturated LWA on concrete strength varies, it may increase or decrease mechanical strength. Some of the factors which may affect the strength of internally cured concretes are test age, material type, size, surface texture, mixture proportion, modulus of elasticity and volume fraction in mixture. Generally, the strength of internally cured cement mixture may be lower at early age. Thereafter, it improves at later ages. Bentz and Weiss (2011) suggested that increased hydration of internally cured mixtures could enhance concrete strength and modulus of elasticity. However, they also mentioned that the lower strength of LWA compared to the NWA being replaced, and increased air voids induced by internal curing agent like SAP may cause a reduction in concrete strength. Increased strengths in sealed and internally cured mortar mixtures were observed by (Bentz, 2007). Similarly, Suzuki et al. (2009) did not detect any decrease in compressive strength in HPC mixtures containing pre-saturated porous ceramic waste coarse aggregates. Conversely, studies by Mohr et al. (2005) highlighted decrease in compressive strength in mixtures containing pre-wetted wood derived powders and fibers. However, to guide against the possibility of excessive strength reduction in internally cured mixtures. Álvaro and Mauricio (2011) suggested that the use of natural LWA such as pumice with highly interconnected porosity could provide excellent internal curing with minimum reduction in strength.

4.3.3 Microstructure Related Properties

Increased hydration of cement paste improves concrete microstructure, reduce pore interconnectivity and this ultimately boosts concrete durability significantly. Bentz and Stutzman (2008) observed that high performance blended cement mortars with internal curing has less unhydrated cement particles compared to those of the control samples. Hence, these specimens have denser microstructure which reduces its permeability to deleterious substances. Henkensiefken et al. (2009) observed denser microstructure, reduced water absorption and electrical conductivity in mortar mixtures containing saturated LWA. Similarly, Bentz (2009) reported reduced chloride penetration depths in internally cured mortar samples compared to those of the control samples.

4.4 Future Applications of Internal Curing

From the foregoing discussion, it seems that internal curing of cement binders is an innovation that deserves further scrutiny since it clearly has positive influence on durability properties. Hence, the behavior of mixtures containing other types of saturated porous materials should be studied. Research studies by Suzuki et al. (2009) have already shown that there is a strong potential for the use of porous waste materials as internal curing agents in concrete. Hence, the impacts of other pre-wetted wastes such as copper tailings on concrete properties are worth investigating.

Chapter 5

EXPERIMENTAL STUDY

5.1 Introduction

The binders used in the preparation of paste, mortar and concrete mixtures were Portland slag cement CEM III/A (Class 32.5N) and copper tailings. The aggregates used in the mortar and concrete mixtures were ASTM C 778 (ASTM, 2006) standard sand and crushed limestone rock (fine and coarse) aggregates, respectively. High grade natural gypsum was also used to prepare some mortar samples for sulfate expansion test. For the pastes, the fresh properties investigated were consistency and setting time, while autoclave expansion test was the only hardened property test performed. Flow spread and yield stress were the mortar fresh properties determined while the hardened properties evaluated were potential sulfate expansion test, compressive strength, flexural strength, abrasion and impact resistance, water absorption, acid resistance and chloride penetration tests. Similarly, these concrete properties were investigated; slump, compressive strength, flexural strength, splitting tensile strength, abrasion and impact resistance, water absorption, acid resistance, rapid chloride permeability, chloride penetration, accelerated corrosion and half-cell potential tests.

5.2 Materials

5.2.1 Cement and Copper Tailings

The well preserved Portland slag cement batch used during the mixture preparation stage of this study was supplied by Bogaz Endustri Madencilik (BEM) cement factory. The copper tailings, which were stored in air-tight containers, were obtained at various depths from deposits at an abandoned processing facility at Lefke, Cyprus. Equal quantities of tailings from each container, sufficient to produce a well blended sample for the tests were mixed thoroughly, air dried and sieved with a 600 μm sieve before usage. Figure 5.1 shows a sample of these copper tailings.

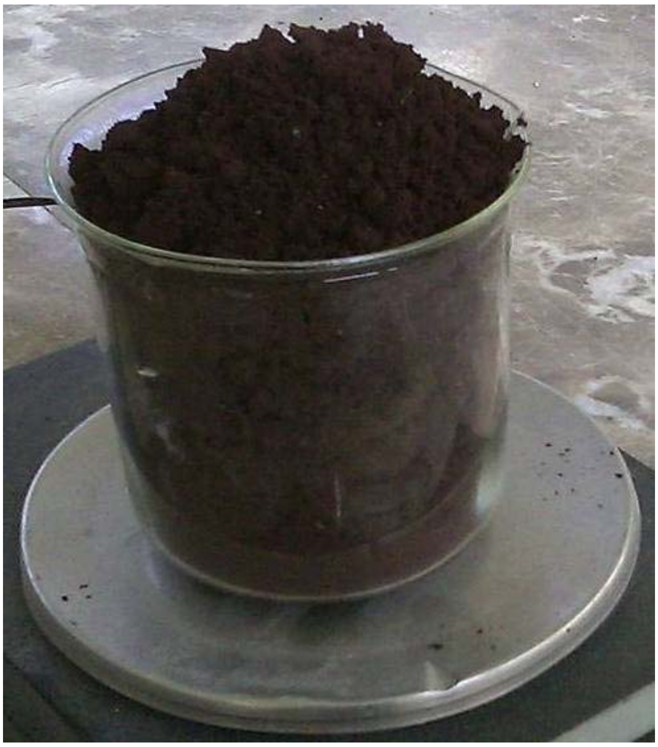


Figure 5.1. Typical Copper Tailings Sample

5.2.1.1 Physical and Chemical Properties of Copper Tailings

Physical properties, such as the specific gravity of copper tailings, were determined according to the ASTM C 188 (ASTM, 2009) specification. The specific surface areas were obtained using ASTM C 204 (ASTM, 2007) and Blaine's air permeability apparatus. The particle size distribution of copper tailings was also determined using sieve analysis and a hydrometer method. Finally, oxide and heavy metal content of tailings were determined according to TS EN 196-2 (2002) and EPA 6020 A (1998) specifications.

The specific gravity of the copper tailings was 4.29 and this high specific gravity was attributed to the high concentration of iron (III) oxide (Fe_2O_3) in it. Similarly, the concentrations of toxic metals in these tailings are high. The water absorption property of these tailings (13.8%) was much higher than the 0.13-0.55% reported by Shi et al. (2008) in literature for copper slag. It is suspected that prolonged exposure to weathering might have also contributed to the increased porosity of the tailings. Moreover, contact with water and oxygen, imparted the chemical characteristics of these tailings through the oxidization of iron sulfide (FeS_2) contained therein to aqueous acid. Thus, these copper tailings are acidic with a mean pH value of 3.2, and this enhances the mobilization of heavy metals. The particle size distribution curve of the copper tailings is shown in Figure 5.2. The curve indicated that about 50% of the tailing particles were finer than 0.1 mm. Some physical and chemical properties of copper tailings are also shown in Table 5.1.

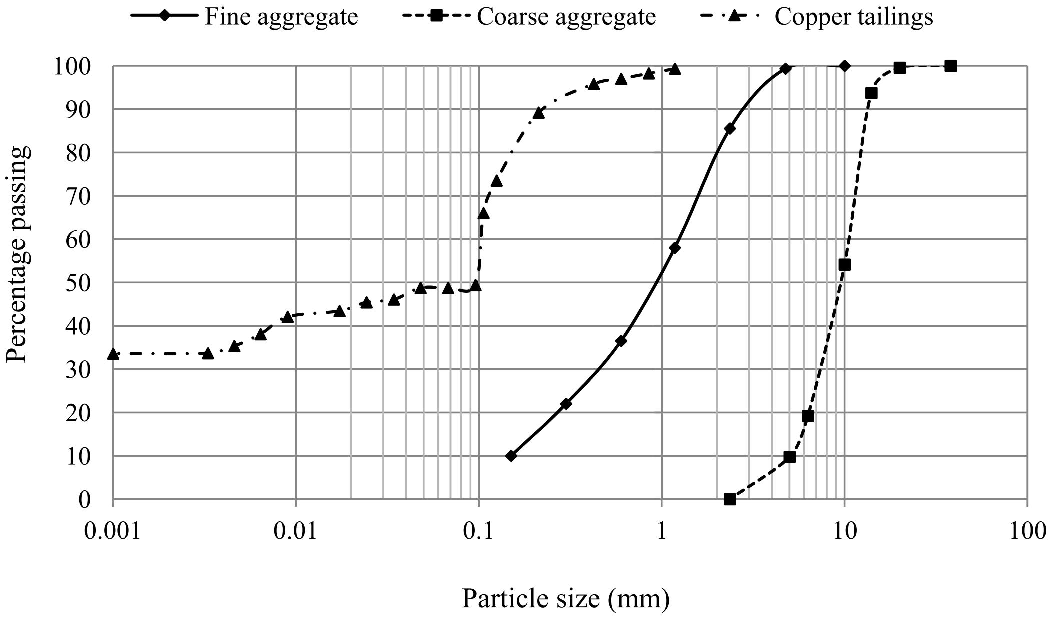


Figure 5.2. Particle Size Distribution of Aggregates and Copper Tailings

Table 5.1 Chemical and physical properties of cement and copper tailings.

Component	CEM III A	Copper tailing
Chemical composition (%)		
SiO_2	29.15	11.20
Al_2O_3	7.34	-
Fe_2O_3	2.42	85.30
CaO	50.04	-
MgO	3.99	-
SO_3	1.97	-
Cl	0.01	-
Loss on ignition	1.65	-
Insoluble residue	0.27	-
pH	-	3.2
Heavy metal content (mg/kg)		
Cu	-	2284
Zn	-	402
Pb	-	60
Cr	-	12
Cd	-	0.86
Physical properties		
Specific gravity	2.96	4.29
Blaine finenesse (cm^2/g)	3440	537
Absorption (%)	-	13.82

5.2.2 Gypsum

The ASTM C 452 (ASTM, 2010) specified high grade natural gypsum was used for the preparation of mortars. Chemical properties of the gypsum are shown in Table 5.2.

5.2.3 Aggregates

Two coarse aggregate sizes were used; 10 mm and 14 mm. The specific gravities of fine and coarse aggregates were 2.7 and 2.54, respectively. The water absorption of the aggregates was 0.6%. The particles size distribution curves of the aggregates are shown in Figure 5.2

Table 5.2 Chemical and mineral composition of gypsum.

Component	Gypsum
Chemical composition (%)	
CaO	39.00
MgO	0.24
SO_3	53.92
Combined water	5.02
Insoluble residue	0.40
Undetermined matter	0.75
Chemical composition (%)	
$CaSO_4.2H_2O$	24.0
$CaSO_4$ (Anhydride)	72.70
SiO_2 + insoluble residue	0.40
$CaCO_3$	2.20
$MgCO_3$	0.50

5.2.4 Water

For the preparation of paste, mortar and concrete mixtures, potable tap water was used. However, for the preparation of various chemical reagents used in the tests, de-ionized water was used.

5.2.5 Hydrochloric Acid (HCl)

To prepare dilute aqueous acid solution for reinforcement pickling and acid resistance tests, concentrated HCl solution with the following properties was used. The fuming, density and pH were 37%, 1.19 g/cm^{3}and less than -1.0, respectively.

5.2.6 Sodium Chloride (NaCl) and Sodium Hydroxide (NaOH)

For the chloride penetration and permeability tests, laboratory grade NaCl powder and NaOH pellets of high purity were used to prepare aqueous solutions. The molar mass and density of NaCl powder were 58.4 g/mol and 2.17 g/cm^3, respectively. Similarly, the molar mass, density and pH of NaOH pellets were 40.0 g/mol, 2.13 g/cm^3 and 14.0, respectively.

5.2.7 Sodium Sulfate (Na_2SO_4)

For the sulfate resistance tests, laboratory grade Na_2SO_4 powder of high purity was used to prepare aqueous solutions. The molar mass, density and pH of Na_2SO_4 powder were 142.04 g/mol, 2.70 g/cm^3 and 7.0, respectively.

5.3 Mixture Details

The water-to-binder (w/b) ratios utilized for the pastes were dependent on the findings from the consistency tests while a standard w/b ratio of 0.485 was used for mortar mixtures. Table 5.3 and Table 5.4 show the material proportions of paste and mortar mixtures, respectively. For the concretes, 3 w/b ratios of 0.65, 0.57 and 0.50 determined according to Building Research Establishment (BRE, 1992) guidelines were used in mixture design. Details of concrete mixture proportions are shown in Table 5.5. For mixtures whereby copper tailings were used as partial substitute for cement by mass, replacement levels of 0%, 5%, 10% and 15% were used. These mixtures were identified according to cement replacement levels as C0 for 0%, C5 for 5%, C5-PW for 5%

replacement with pre-wetted tailings, C10 for 10% and C15 for 15%. Similarly, for mixtures incorporating copper tailings as a cement additive by mass, the names of the mixtures were C5A for 5%, C5A-PW for 5% addition level with pre-wetted tailings and C10A for 10%.

Table 5.3 Paste mixture proportions

Test	**Materials**	**Mixtures (g)**							
		C0	**C5**	**C5-PW**	**C10**	**C15**	**C5A**	**C5A-PW**	**C10A**
Consistency	Cement	400	380	380	360	340	400	400	400
	Tailings	0	20	20	40	60	20	20	40
Autoclave	Cement	650	618	618	585	553	650	650	650
	Tailings	0	32	32	65	97	32	32	65

Table 5.4 Mortar mixture proportions

Mixture type	Mix name	Tailings (% by mass)	W/B ratio	Quantities (g)			
				Water	Cement	Tailings	Fine
Cement replacement	C0	0	0.485	242	500	0	1375
	C5	5	0.485	242	475	25	1375
	C5-PW	5	0.485	242	475	25	1375
	C10	10	0.485	242	450	50	1375
	C15	15	0.485	242	425	75	1375
Cement additive	C5A	5	0.485	242	500	25	1375
	C5A-PW	5	0.485	242	500	25	1375
	C10A	10	0.485	242	500	50	1375

Table 5.5 Concrete mixture proportions

Mixture type	Mix name	Tailings (% by mass)	W/B ratio	Quantities (kg)				
				Water	Cement	Tailings	Fine	Coarse
Cement replacement	C0	0	0.50	225	450	0	818	887
	C5	5	0.50	225	428	22	818	887
	C5-PW	5	0.50	225	428	22	818	887
	C10	10	0.50	225	405	45	818	887
	C15	15	0.50	225	383	67	818	887
	C0	0	0.57	225	395	0	810	950
	C5	5	0.57	225	375	20	810	950
	C5-PW	5	0.57	225	375	20	810	950
	C10	10	0.57	225	355	40	810	950
	C15	15	0.57	225	335	60	810	950
	C0	0	0.65	225	346	0	923	886
	C5	5	0.65	225	329	17	923	886
	C5-PW	5	0.65	225	329	17	923	886
	C10	10	0.65	225	311	35	923	886
	C15	15	0.65	225	294	52	923	886
Cement additive								
	C5A	5	0.50	225	450	22	818	887
	C5A-PW	5	0.50	225	450	22	818	887
	C10A	10	0.50	225	450	45	818	887
	C5A	5	0.57	225	395	20	810	950
	C5A-PW	5	0.57	225	395	20	810	950
	C10A	10	0.57	225	395	40	810	950
	C5A	5	0.65	225	346	17	923	886
	C5A-PW	5	0.65	225	346	17	923	886
	C10A	10	0.65	225	346	35	923	886

5.4 Mixing and Casting

First, cement and copper tailings were pre-mixed dry, then pastes were mixed according to the specifications of BS EN 196-3 (2005) while mortars were prepared in accordance to ASTM C 305 (2008) guidelines. For concrete mixtures, the order of material placement in the drum mixer was; coarse aggregates, fine aggregates, cement, copper tailings and water. To ensure homogeneous blending of concrete constituents, mixing was done for five minutes. On completion of the casting operations, specimens were kept in the curing room for 24 h before they were then de-molded and left in the room at a temperature of 23.0 ± 2.0°C and humidity of 85 ± 5% until the time of testing.

5.5 Fresh Property Measurements

5.5.1 Fresh Property Measurements

5.5.1.1 Paste Consistency and Setting Time

Using the BS EN 196-3 (2005) specification, water demands and setting times of cement pastes incorporating different percentages of copper tailings were evaluated.

5.5.1.2 Mortar Yield Stress and Flow

The yield stress of each mortar mixture at specific time intervals were measured according to the suggestions of (Nguyen and Boger, 1985), using a Brookfield Soft Solid Rheometer having a V30–15 vane rotating at 0.2 rpm for 5 min. The dimensions of the cup containing samples during the tests were 65 mm x 80 mm. The first yield stress measurement was taken 5 min after mixing operation commenced. Thereafter, subsequent measurements were taken after 30 min, 60 min, 90 min and 120 min of mixing. The flow spread of mortar mixtures were also determined after 5 min, 30 min, 60 min, 90 and 120 min of mixing, using ASTM C 1437 (2007) guidelines. All measurements were taken at a temperature of 20±2°C with relative humidity varying from 70 to 80% and the results presented were average of three measurements. Figure 5.3 shows the Brookfield Rheometer used in the experiment.

Figure 5.3. Brookfield Rheometer

5.5.2 Hardened Property Measurements

5.5.2.1 Mechanical Strength

5.5.2.1.1 Compressive and Flexural Strengths of Mortars

The compressive strengths of mixtures were determined using ASTM C109 (2008) guidelines. Similarly, the flexural strengths of mixtures were determined using ASTM C 348 (ASTM 2008) guidelines. For each mixture, twelve 50 mm cubes and twelve 40 mm x 40 mm x 160 mm prisms were cast for the determination of compressive and flexural strengths at 3 days, 7 days, 28 days and 90 days.

5.5.2.1.2 Compressive Strength of Concrete

The compressive strength of concrete mixtures were determined using the BS EN 12390-3 (2009) guidelines. For each mixture, twelve 150 mm cubes were used for the compressive strength tests at 3 days, 7 days, 28 days and 90 days.

5.5.2.1.3 Flexural Strength of Concrete

Using six 100 mm x 100 mm x 500 mm prisms from each mixture, the flexural strengths of concrete mixtures were determined according to ASTM C 293 (2008) guidelines at 28 days and 90 days.

5.5.2.1.4 Splitting Tensile Strength of Concrete

Similarly, six 100 mm x 200 mm cylindrical samples from each mixture were used for splitting tensile strength tests according to ASTM C 496 (2004) specification at 28 days and 90 days.

5.5.2.1.5 Modified Abrasion and Impact Resistance of Mortars and Concretes

The abrasion and impact resistance of mortar and concrete mixtures was evaluated using the Los Angeles abrasion apparatus, according to the ASTM C 535 (2009) specification. For each mortar mixture, twelve 50 mm cubic mortar samples were used for the tests, while for the concrete mixtures, twelve 50 mm cubic concrete specimens sawn from the flexural strength prisms were used for the tests. However, instead of the standard 1000 revolutions, test specimens in conjunction with twelve 50 mm diameter steel balls were subjected to 500 rotations and the mass loss was determined after every 100 revolution.

5.5.2.2 Durability Properties

5.5.2.2.1 Autoclave Expansion

The impact of copper tailings on CaO, or MgO, or both, induced delayed expansion of pastes was investigated in accordance with the ASTM C 151 (2009) specification. For each mixture, two 25 mm x 25 mm x 285 mm prisms were tested for autoclave expansion. Figure 5.4 shows the autoclave expansion test apparatus.

Figure 5.4. Autoclave Expansion Test Apparatus

5.5.2.2.2 Water Absorption and Volume of Permeable Voids in Mortars

Using three 50 mm cubic specimens from each mixture, volume of absorbed water and permeable void were determined according to ASTM C 642 (2006) specification. The rates of water absorption of samples were equally determined according to the ASTM C 1403 (2006) guidelines. These tests were performed after 90 days of curing.

5.5.2.2.3 Water Absorption and Volume of Permeable Voids in Concretes

After 90 days of curing, four 100 mm x 52 mm cylindrical specimens were cut from the middle of four 100 mm diameter x 200 mm long cylinders, and used for the ASTM C 642 (2006) test for the determination of percentage absorbed water and volume of permeable voids in concretes. Samples were oven dried to constant mass for 48 h at 110 °C before being immersed in water at 21 °C for 48 h. After the determination of the saturated mass of samples, they were boiled inside water for 5 h and allowed to cool for 14 h before sample apparent mass in water were determined. The percentage volume of absorbed water and voids were calculated using these mass values.

5.5.2.2.4 Potential Sulfate Expansion

The effect of copper tailings on the potential sulfate expansion of mortar prisms was investigated according to ASTM C 452 (2010) specifications. For each mixture, two 25 mm x 25 mm x 285 mm prisms were tested.

5.5.2.2.5 Acid Resistance of Mortar and Concrete

The resistance of mortar and concrete mixtures to acid attack was evaluated after 90 days of air curing by immersing four 50 x 50 x 50 mm specimens from each mixture in 5% hydrochloric acid solutions for 28 days. The acid solution was renewed every 14 days, and after 28 days of immersion, specimens were oven-dried to constant mass. Thereafter, detachable particles were removed and the percentage mass losses of specimens were used as an indicator of resistance to acid attack.

5.5.2.2.6 Rapid Chloride Permeability Test (RCPT)

RCPT evaluates the total charge transmitted through concrete specimens subjected to a 60 V voltage for 6 h. For each mixture, the test was performed using three 100 mm x 52 mm cylindrical specimens cut from the middle of three 100 mm diameter x 200 mm long cylinders and tested in accordance with the ASTM C 1202 (2010) guidelines. Figure 5.5 shows the RCPT test set up.

5.5.2.2.7 Chloride Penetration Depths in Mortar and Concrete

Actual penetration of chloride ions into mortar and concrete specimens was verified by immersing three 50 mm cubes from each mortar mixture and four 50 mm cubic specimens from each mixture, coated on all but one side in a 3% NaCl solution for 28 days. Thereafter, the specimens were split and sprayed with a 0.1N silver nitrate solution as suggested by Otsuki et al. (1992) to determine the chloride penetration depths. These depths were identified as points within the samples where free chlorides above 0.15% by mass of cement reacted with 0.1N silver nitrate ($AgNO_3$) solution to form a white precipitate of silver chloride (AgCl). The absence or limited availability of free chloride was signified by brown coloration produced from the reaction of $AgNO_3$ solution and hydroxides in the concrete samples.

Figure 5.5. Rapid Chloride Permeability Test Assemble

5.5.2.2.8 Accelerated Corrosion Test

After 90 days of air curing, concrete corrosion resistance was measured using an accelerated corrosion procedure. For each mixture, two 100 x 200 mm cylindrical concrete specimens containing a centrally embedded 14 mm diameter and 250 mm long steel reinforcing bar was used. The steel bars were embedded in such a way that the ends were 5 cm from the bottom of specimen. Prior to embedment and casting, reinforcements were pickled with a 5% HCl solution. During the test, specimens were immersed in a glass box containing 5% sodium chloride (NaCl) solution and connected to a constant 36 V DC power supply. Reinforcement bars acted as the anode while a copper plate electrode was used as the cathode. Preliminary set of samples were tested for 30 days without any crack formation. Thereafter, sample test time was rescheduled to 7 days, and attention focused on the determination of corrosion initiation time. Specimens were monitored daily and the currents transmitted through the system were recorded every 1 minute using a data logger. Figure 5.6 shows the test arrangement.

Figure 5.6. Accelerated Corrosion Test Layout

5.5.2.2.9 Half-cell Potential (HCP) Measurements

The probability of corrosion occurrence in reinforcements was investigated according to ASTM C 876 specifications immediately after accelerated corrosion tests. However, instead of the $Cu/CuSO_4$ (CSE) electrode specified in ASTM C 876, a digital Ag/AgCl electrode which converts readings to equivalent CSE potentials was used. For each specimen, readings were taken at four surface locations. HCP measurements were equally repeated 4 weeks after sample air drying.

5.5.2.2.10 Visual Inspection

After Half-cell potential measurements, samples were split, so that actual condition of reinforcements could be ascertained.

5.5.2.3 Leaching Test

Toxicity Characteristic Leaching Procedure (TCLP) developed by the United States Environmental Protection Agency (US EPA) was used in evaluating the leaching of heavy metals from crushed concrete samples. The test was performed according to the US EPA Method 1311 (1992) whereby crushed concrete samples less than 9.5 mm in size, glacial acetic acid, 20:1 liquid-solid ratio and 30 rpm agitation for 18h were used. Furthermore, the same test process was repeated using deionized water in lieu of glacial acetic acid. After the extraction and filtration of the leachates, heavy metal ions concentrations therein were determined by Inductively Coupled Plasma–Mass Spectrometry (ICP–MS). These leaching tests were performed at the Scientific and Technical Research Council of Turkey (TÜBİTAK) Laboratory in Marmara, Turkey.

Chapter 6

RESULTS AND DISCUSSIONS

6.1 Introduction

In this chapter, results obtained from fresh properties tests of mixtures such as paste consistency and setting time, mortar flow spread and yield stress, and concrete slump are given. Similarly, test results on hardened properties of mixtures such as compressive strength, flexural strength, abrasion and impact resistance, water absorption, autoclave expansion, potential sulphate expansion, acid resistance, RCPT, chloride penetration, accelerated corrosion tests, half-cell potential measurements and cost analysis are also presented.

For the pastes, the incorporation of dry copper tailings either as a cement replacement or additive increased water demand and setting time of mixtures. The use of dry copper tailings in mortars decreased mixture flow while yield stress was increased. Reductions in slumps were also observed in concrete mixtures. However, it was observed that these negative effects on fresh properties were eliminated when pre-wetted tailings were used at 5% utilization level in mixtures.

For the mixtures containing copper tailings as a partial cement substitute, highest mortar compressive strength and abrasion resistance were observed at 5% replacement level. Mortar flexural strengths slightly lower, yet comparable to those of the control samples were also observed. In concrete mixtures incorporating copper tailings, comparable compressive, flexural and tensile strengths were determined at 5% cement replacement level. Improved concrete resistances against abrasion were also obtained at 5% and 10% cement substitution levels. Furthermore, reduced sulfate resistance, higher volume of water absorption and voids, higher resistance to autoclave expansion, chemical attack, chloride penetration and corrosion compared to the control samples were observed in mixtures containing copper tailings. On the other hand, the use of copper tailings as an additive in mixtures enhanced the mechanical and durability properties of samples considerably. However, the most significant enhancements were observed in mixtures containing pre-wetted copper tailings.

6.2. Fresh Property Measurement Results

6.2.1 Paste Water Demand

Figures 6.1 and 6.2 show the water demands of pastes containing copper tailings as cement replacement and additive, respectively. These results show that the quantities of water required for the preparation of pastes of standard consistency increased as the dry copper tailings content of mixtures increased. However, C5-PW and C5A-PW mixtures which contained pre-wetted tailings showed consistencies that were superior to those of the control mixtures. These high water demands of the C5-C15, C5A and C10A mixtures contrasts with the reported improvement of workability in mixtures incorporating copper slag by Al-jabri et al. (2009a). The higher water demands witnessed in the copper tailings blended mixtures were attributed to the coarse particles of the tailings and the high water absorption capacity which adversely affected consistency by partly absorbing available mixing water. This drawback was effectively eliminated by using pre-wetted tailings, thereby ensuring that mix water remained for the designated purpose.

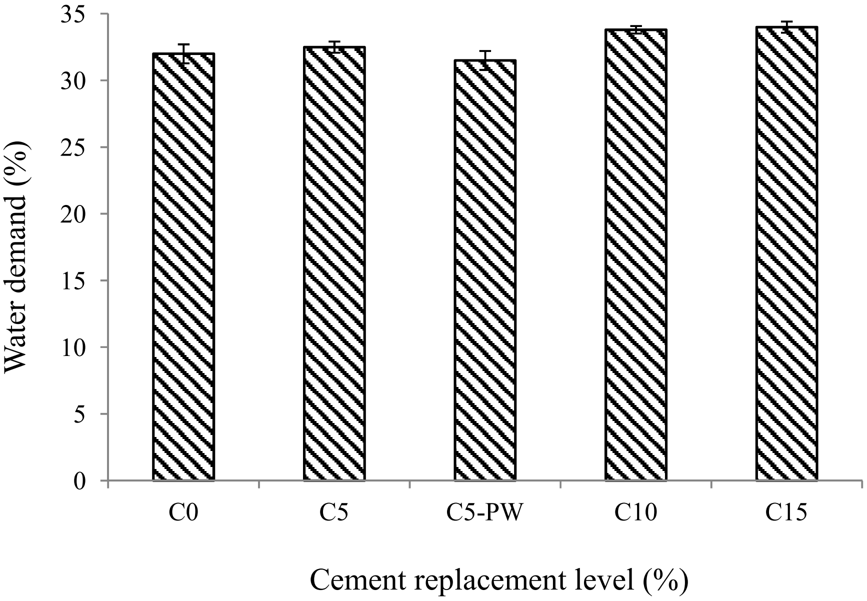


Figure 6.1. Water Demand of Pastes (cement replacement mixtures)

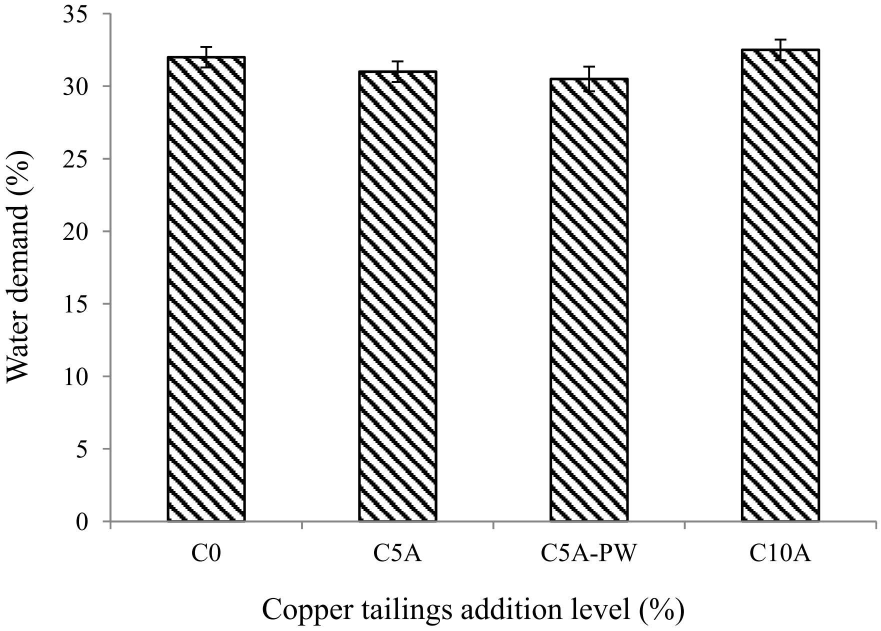


Figure 6.2. Water Demand of Pastes (mortar additive mixtures)

6.2.2 Setting Time

The setting time results shown in Figures 6.3 and 6.4 highlighted the delay in the setting time of pastes containing copper tailings. These delays in setting time became more significant as copper tailings content of mixtures increased. For the cement replacement pastes; the delays in initial setting time relative to those of the control sample were 10 min for C5, 36 min for C5-PW, 32 min for C10 and 40 min for C15 while the delays in final setting time were 44 min for C5, 86 min for C5-PW, 75 min for C10 and 95 min for C15. Similarly, for the additive pastes; the delays in initial setting time relative to those of the control sample were 11 min for C5A, 48 min for C5A-PW and 34 min for C10A while the delays in final setting time were 21 min for C5A, 100 min for C5A-PW and 50 min for C10A. The setting time behavior of C5 and C5A pastes were slightly exacerbated when pre-wetted tailings were added to these mixtures. This is understandable, given that the minor reductions in w/b ratio induced by the highly absorptive tailings were neutralized by the pre-wetted tailings. These delayed setting times of mixtures were partly caused by the presence of heavy metals in copper tailings as shown in Table 5.1. The precipitation of Cu, Pb and Zn compounds, such as the oxides and hydroxides in cement mixtures have been shown by (Diet *et al.,* 1998; Olmo *et al.*, 2001), to interfere with the cement hydration process, thereby delaying setting time. Zain *et al.* (2004) expressed similar opinion about the negative effect of compounds of Cu, Zn and Pb on the setting time of mixtures.

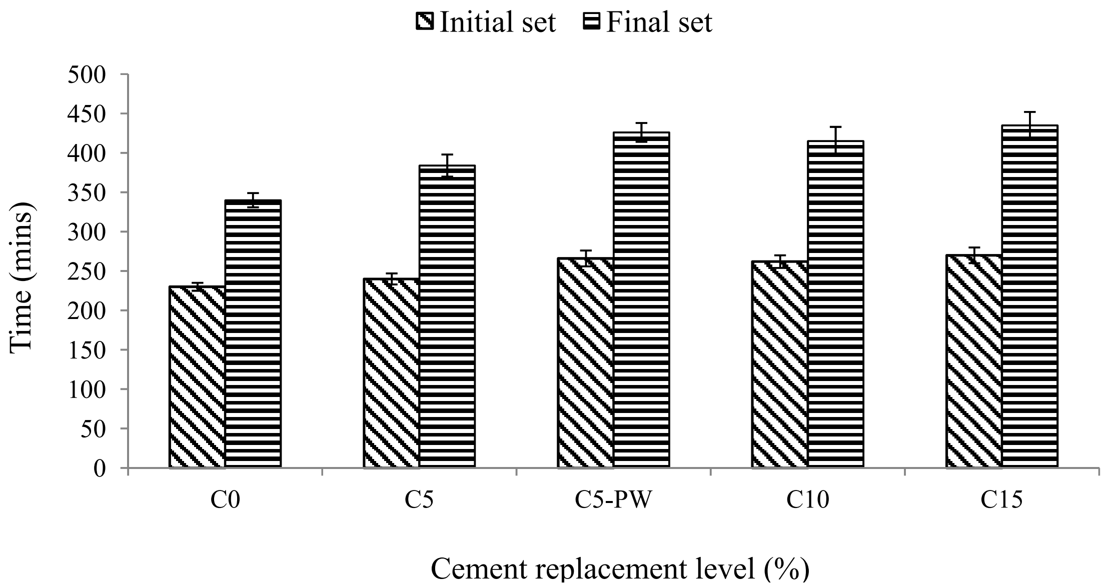


Figure 6.3. Setting Time of Pastes (cement replacement mixtures)

Furthermore, the delayed setting times observed in mixtures containing copper tailings as a cement replacement material were also attributed to the dilution of the cement matrix and the substitution of cement with the less reactive copper tailings. This postulation is supported by the observation of Ranganath et al. (1998) that large particles are less reactive in cement mixtures. However, compared to the severe copper slag induced delay in setting time reported by Ayano and Sakata (2000), these copper tailings had only a moderate impact on the cement hydration process.

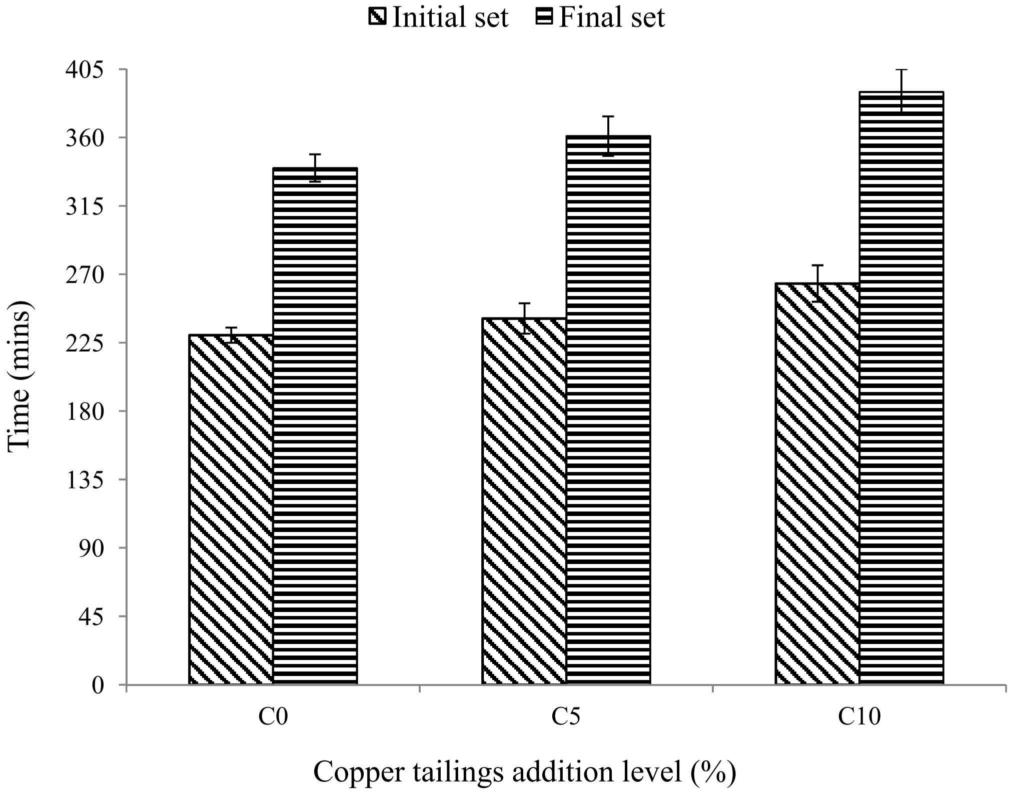


Figure 6.4. Setting Time of Pastes (paste additive mixtures)

6.2.3 Yield Stress of Mortars

A typical stress-elapsed time plot obtained from the rheology tests is shown in Figure 6.5. The curve consists of three distinct parts; elastic, peak (yield stress) and residual stress zones. The average yield stress determined from stress-elapsed time plots for all the mixtures are shown in Figure 6.6 and 6.7, respectively. Values from figure 6.6 show that at all measurement intervals, yield stress became higher as the cement replacement level became higher and test elapsed time increased. Within the 120 minutes test duration, yield stress value increased from 1.4 to 2.3 kPa for C0, 1.4 to 2.8 kPa for C5, 1.2 to 2.6 kPa for C5-PW, 1.5 to 3.6 kPa for C10 and 2.0 to 3.8 kPa for C15. Similar trend was repeated for mixtures containing copper tailings as a cement additive. The yield stress increases were 1.6 to 3.3 kPa for C5A, 1.4 to 3.2 kPa for C5A-PW and 2.3 to 4.1 kPa for C10A. The higher initial yield stress of the copper tailings mortars compared to the control mixture is traceable to the high water absorption and coarse particles of the tailings while the formation of hydration products could also have contributed to the values obtained towards the end of the test. However, the C5-PW and C5A-PW mixtures containing pre-wetted tailings recorded the yield stresses that were slightly lower and comparable to those of the control mixture immediately after mixing.

6.2.4 Mortar Flow Spread

Figures 6.8 and 6.9 show the flow spread of mixtures containing copper tailings as a cement replacement material and mortar additive, respectively. Both figures showed that flow spread decreased with increase in tailings content and test elapsed time. From Figure 6.8, the flow spreads of mixtures were 197.3 mm for C0, 188.1 mm for C5, 201.6 mm for C5-PW, 183.6 mm for C10 and 170.0 for C15 at the start of the flow test. However, by the end of the test, the flow spreads have reduced to 161.4 mm for C0, 156.8 mm for C5, 162.5 mm for C5-PW, 150.9 mm for C10 and 138.6 mm for C15. Similar flow characteristics were also shown in Figure 6.9. At the start of the flow test, the flow spreads of mixtures were 191.8 mm for C5A, 194.3 mm for C5A-PW and 178.5 mm for C10A while the values at the end of test were 159.0 mm for C5A, 160.5 mm for C5A-PW and 140.9 mm for C10A. In both figures, the flow behaviors of mixtures containing pre-wetted tailings were closest to those of the controlled sample. The flow spread of the C5-PW mixture immediately after mixing, was higher than that of the other mixtures; however, at subsequent measurement intervals, the C5-PW flow spreads were comparable to that of the control mixture. Conversely, the flow spreads of C5A-PW mixture were slightly lower than those of C0 mixtures at all intervals. The improved flow of the C5-PW and C5A-PW mixtures is attributed to the provision of moisture by the pre-wetted tailings.

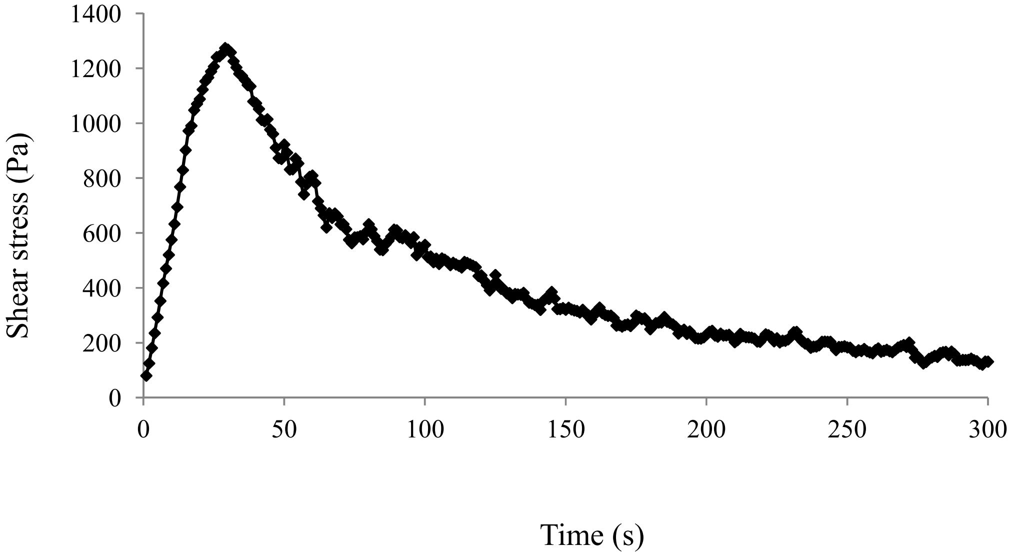


Figure 6.5. Typical Stress-time Plot Obtained with the Brookfield Rheometer

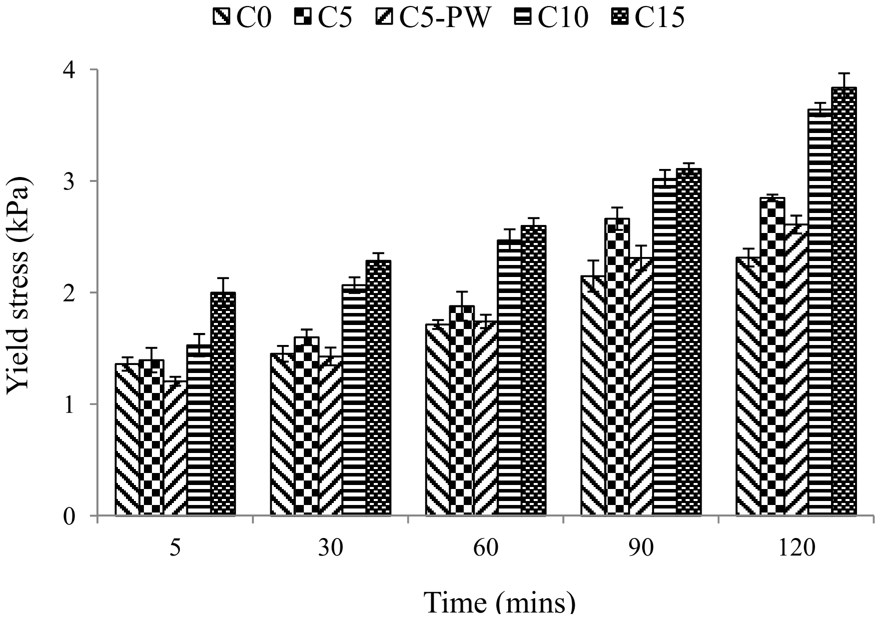


Figure 6.6. Yield Stress of Mortars (cement replacement mixtures)

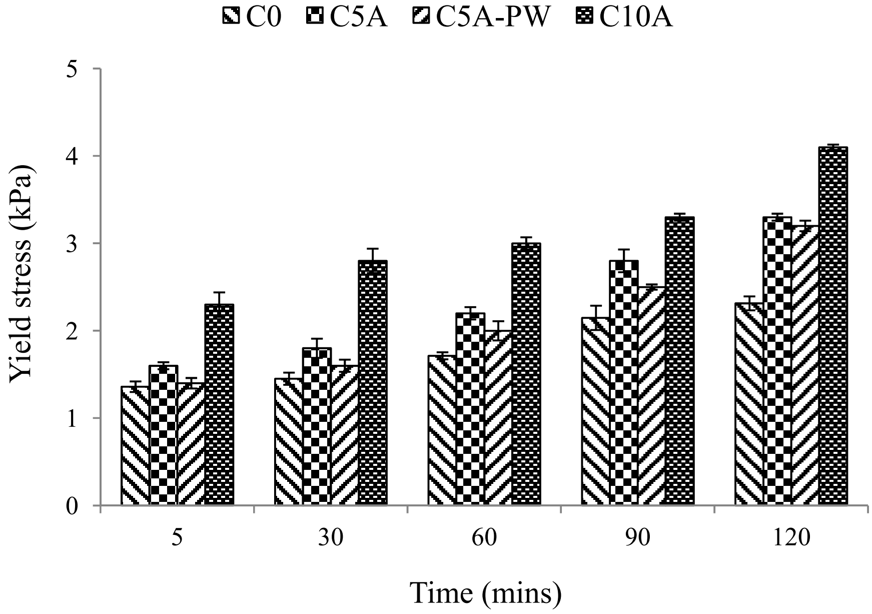


Figure 6.7. Yield Stress of Mortars (mortar additive mixtures)

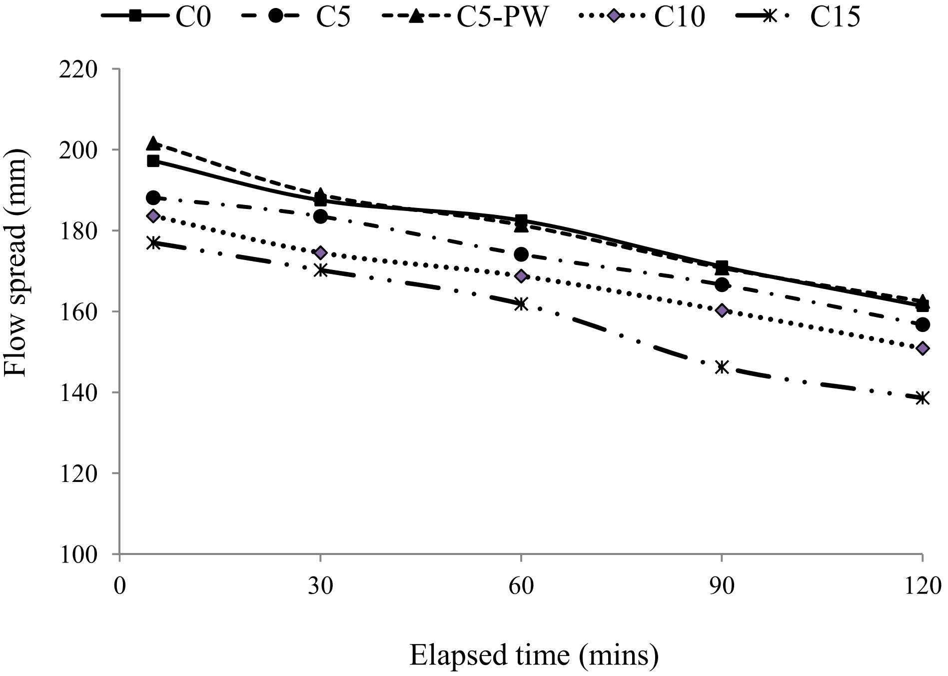


Figure 6.8. Flow Spread Curves of Mortars (cement replacement mixtures)

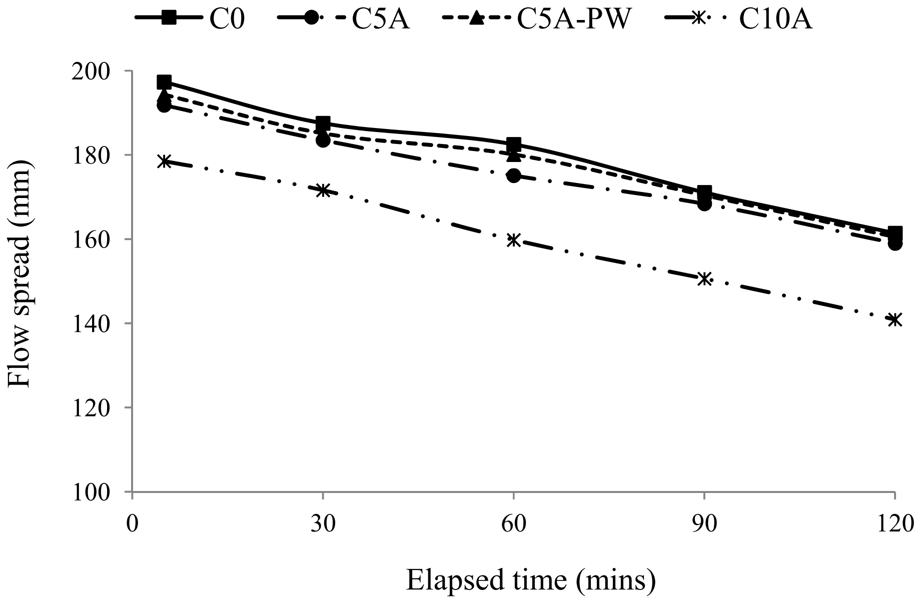


Figure 6.9. Flow Spread Curves of Mortars (mortar additive mixtures)

Figures 6.10 and 6.11 show the relationship between flow spread and yield stress in both set of mixtures. Despite the scatter in the flow spread versus yield stress chart shown in these figures, these plots suggest that flow spread, to a reasonable extent depends on yield stress. Hence, yield stresses of mortar mixtures increase as flow spreads decrease. Similar allusion was made by researchers (Senff et al., 2009) when they suggested that values from flow table test are related to yield stress. Nevertheless, comparing the two tests, yield stress measurements appeared to be a more accurate indicator of mixture fluidity since it is a direct material property which measures internal structure development. Moreover, while yield stress of mortars with varying range of w/b ratios can be measured, the measurability of the flow spreads of mortars with high w/b ratio is difficult.

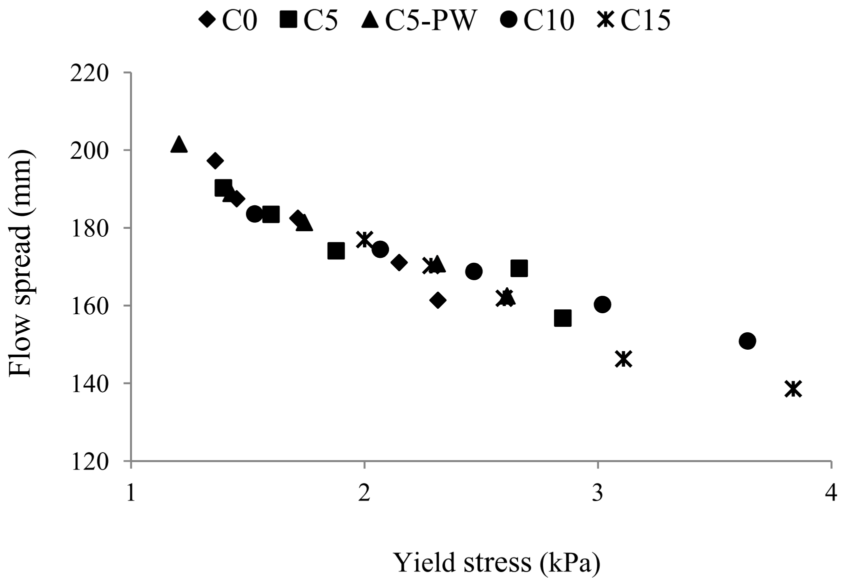


Figure 6.10. Relationship between Flow Spread and Yield Stress (cement replacement mixtures)

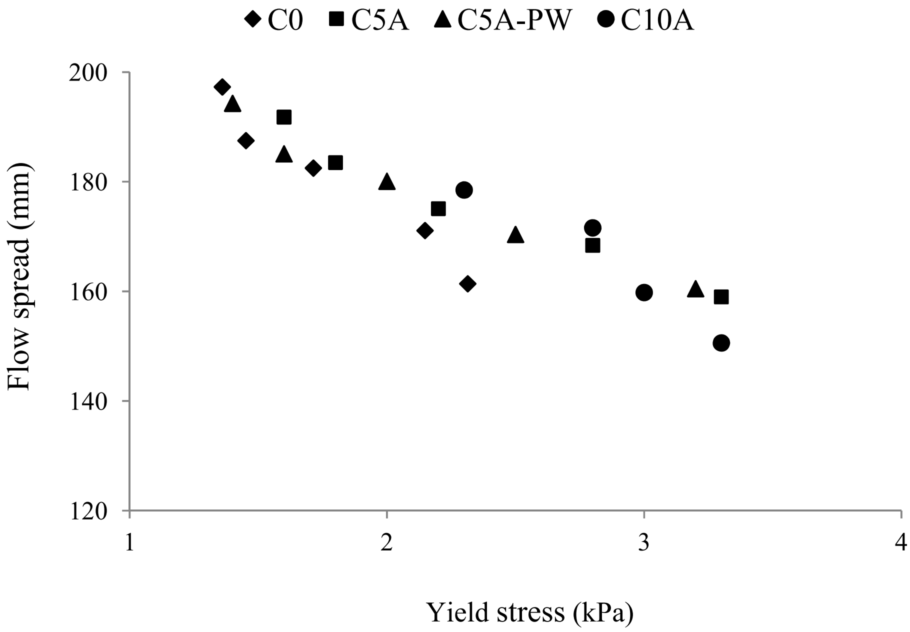


Figure 6.11. Relationship between Flow Spread and Yield Stress (mortar additive mixtures)

6.2.5 Concrete Slump

The negative effect of coarse and porous copper tailings on consistency was made more conspicuous in concrete mixtures. Figure 6.12 and 6.13 show the slump of concretes immediately after mixing. From Figure 6.12, the slumps of the 0.65 w/b ratio mixtures were 150.0 mm for C0, 140.0 mm for C5, 160.0 mm for C5-PW, 120 mm for C10 and 190.0 mm for C15. For the 0.57 w/b ratio mixtures, the slumps were 150.0 mm for C0, 100.0 mm for C5, 154.0 mm for C5-PW, 70 mm for C10 and 60.0 for C15. The slumps for the 0.50 mixtures were 140.0 mm for C0, 95.0 mm for C5, 150.0 mm for C5-PW, 60 mm for C10 and 55.0 for C15. Similarly, Figure 6.13 shows that the slumps of the 0.65 w/b ratio mixtures were 128.0 mm for C5A, 145.0 mm for C5A-PW and 86 mm for C10A. The slumps for the 0.57 mixtures were 80.0 mm for C5A, 130.0 mm for C5A-PW and 50 mm for C10A. For the 0.50 w/b ratio mixtures, the slumps were 75.0 mm for C5A, 100.0 mm for C5A-PW and 50 mm for C10A. The slumps of mixtures reduced as w/b ratio decreased. This is understandable given that more quantities of copper tailings are used as cement replacement material or concrete additive at low w/b ratio. These results further highlighted the role, pre-wetted tailings played in enhancing mixture consistency. Compared to the C5A-PW mixtures, the C5-PW mixtures seem to be more effective in improving mixture consistency. This behavior is traceable to the fact that, at each of the w/b ratio used, the C5A-PW mixtures contained higher mass of binders compared to the C5-PW mixtures.

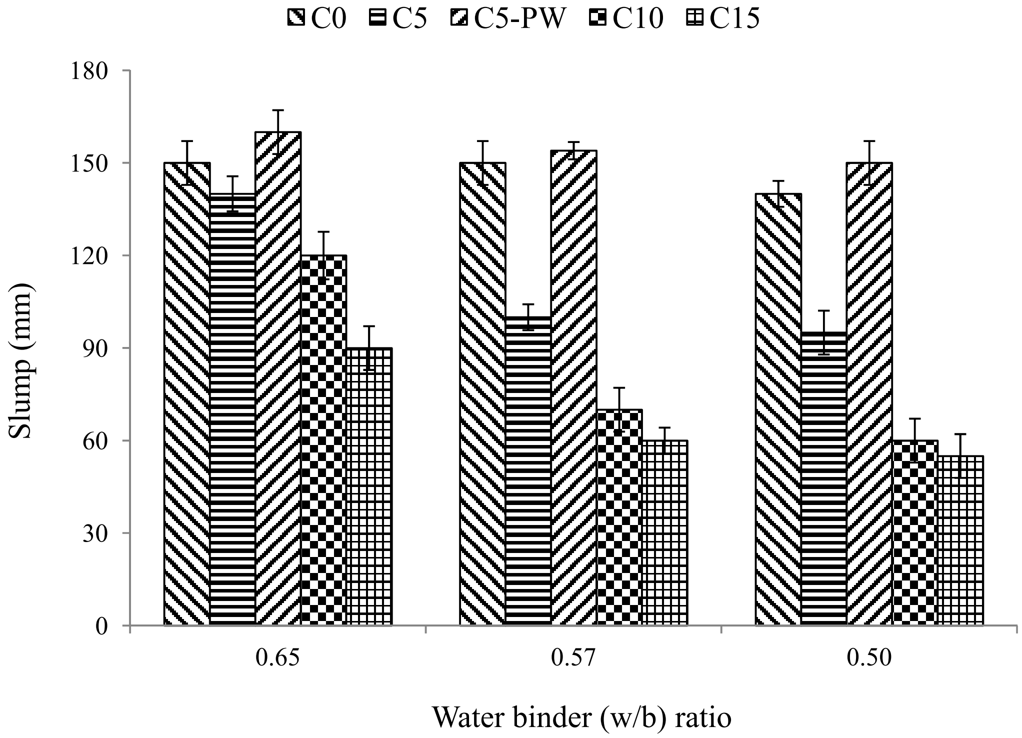


Figure 6.12. The Slumps of Concretes (cement replacement mixtures)

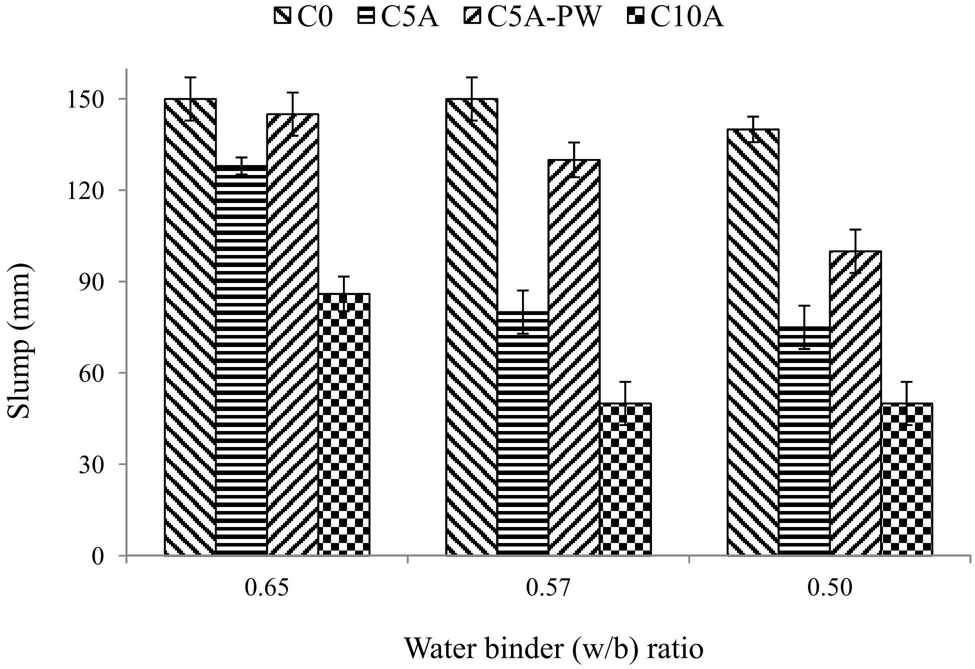


Figure 6.13. The Slumps of Concretes (concrete additive mixtures)

6.3 Hardened Properties

6.3.1 Mechanical Strength

6.3.1.1 Compressive Strength of Mortars

Compressive strength results of mortar mixtures are shown in Figures 6.14 and 6.15. For the cement replacement mixtures, the control samples recorded higher compressive strength compared to the samples containing copper tailings at the early ages of 3 days and 7 days. This occurrence is partly due to the dilution of the cement matrix. The poor fineness of the copper tailings as shown in Table 1 and the presence of heavy metals in the tailings could also have contributed in hampering early strength development. At the 90th day, the percentage compressive strengths relative to the control samples were 117% for C5, 126.2% for C5-PW, 86.4% for C10 and 86.1% for C15. The low strength of C10 and C15 is as a result of increased porosity. These C5 and C5-PW results contrast the lower compressive strength of mortar mixtures containing copper slag as a cement replacement material observed by (Al-Jabri et al., 2002; Zain et al., 2004).

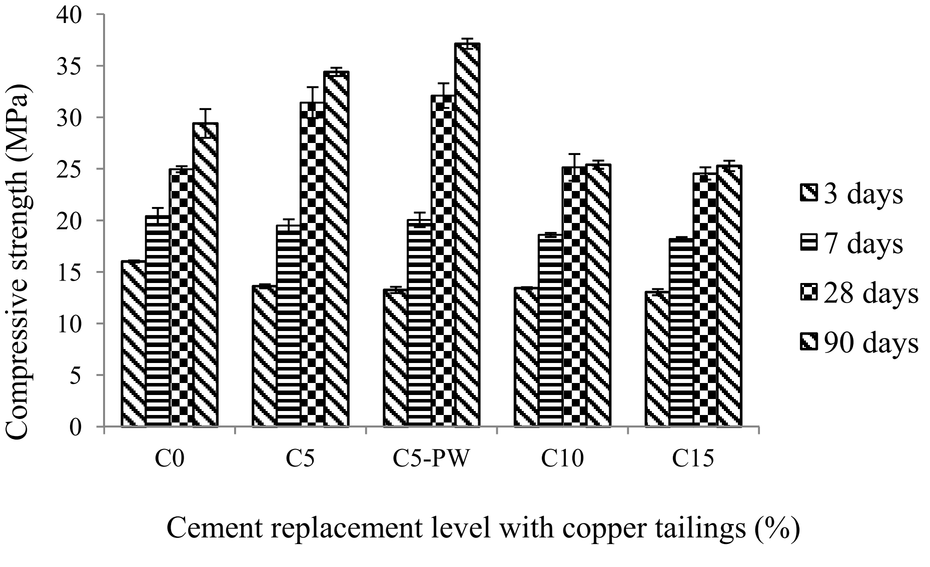


Figure 6.14. Compressive Strength of Mortars (cement replacement mixtures)

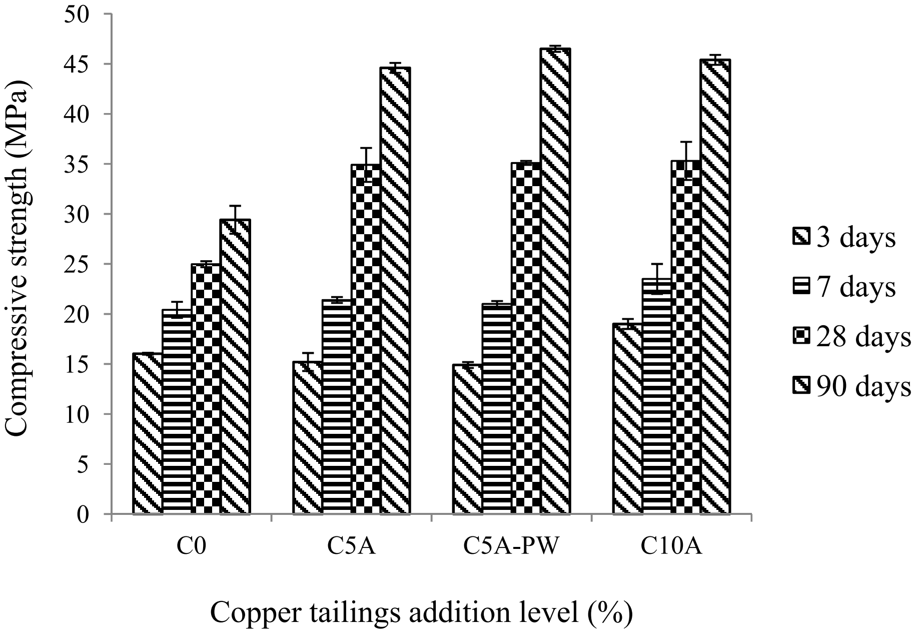


Figure 6.15. Compressive Strength of Mortars (additive mixtures)

On the other hand, higher strengths were observed in mixtures containing copper tailings as a mortar additive. At the 90th day, the percentage compressive strengths relative to the control samples were 151.7% for C5A, 158.2% for C5A-PW and 154.4% for C10A. It is suspected that the high compressive strength of the C5-PW and C5A-PW samples were as a result of slightly higher degree of hydration induced through the release of internal curing water by the pre-wetted tailings at later ages.

6.3.1.2 Compressive Strength of Concretes

Figures 6.16 to 6.21 show the compressive strength results of concrete specimens. These results indicated that irrespective of the w/b ratio used, all the mixtures containing copper tailings as a cement replacement material yielded lower compressive strengths compared to those of the control mixtures at 3, 7 and 28 days. However, by the 90th day, strengths comparable to those of the control samples were observed. The percentage compressive strengths relative to those of the control samples at the 90th day for the 0.65 w/b ratio mixtures were 87.5% for C5, 91.2% for C5-PW, 86.4% for C10 and 78.0% for C15. The percentage relative strengths for the 0.57 w/b ratio mixtures at the 90th day were 98.8% for C5, 100% for C5-PW, 95.7% for C10 and 92.3% for C15 while that of the 0.50 w/b ratio mixtures were 97% for C5, 99.5% for C5-PW, 87.4% for C10 and 86.7% for C15. In a similar study, Moura et al. (1999) also observed that at 91 days, concrete with 10% by mass of cement replaced with copper slag had a lower compressive strength compared to those of the control samples. The reduction in strength observed in the copper tailing mixtures is partly due to cement dilution, as increasing quantities of reactive cement are replaced with less reactive copper tailings. The porous concrete structure engendered by the tailings also contributed to the strength decrease.

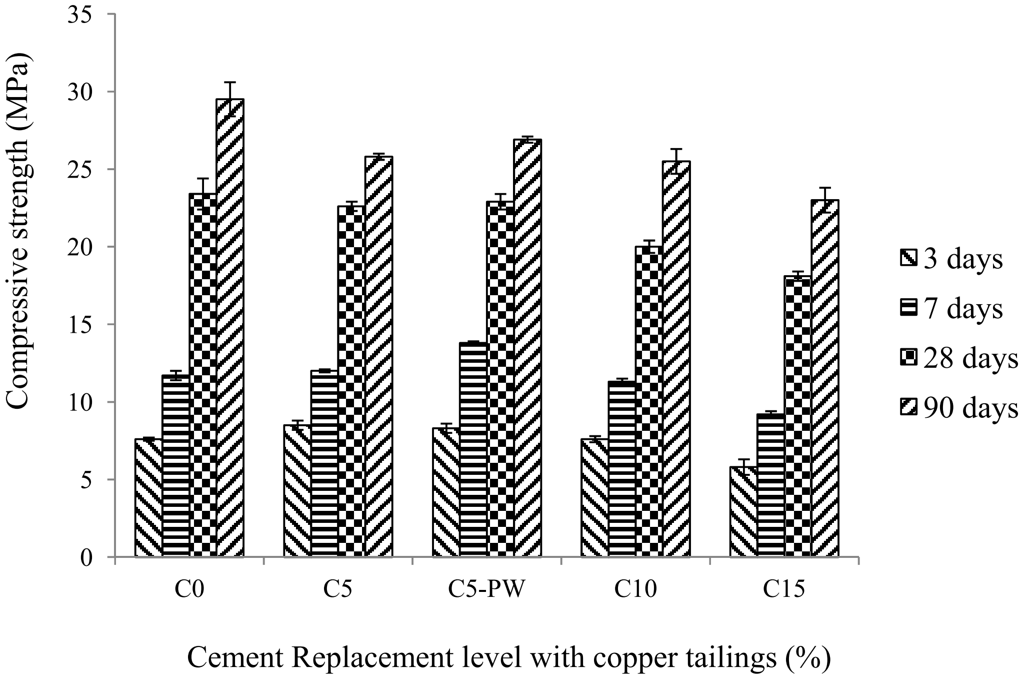


Figure 6.16. Compressive Strength of 0.65 w/b Ratio Concretes (cement replacement)

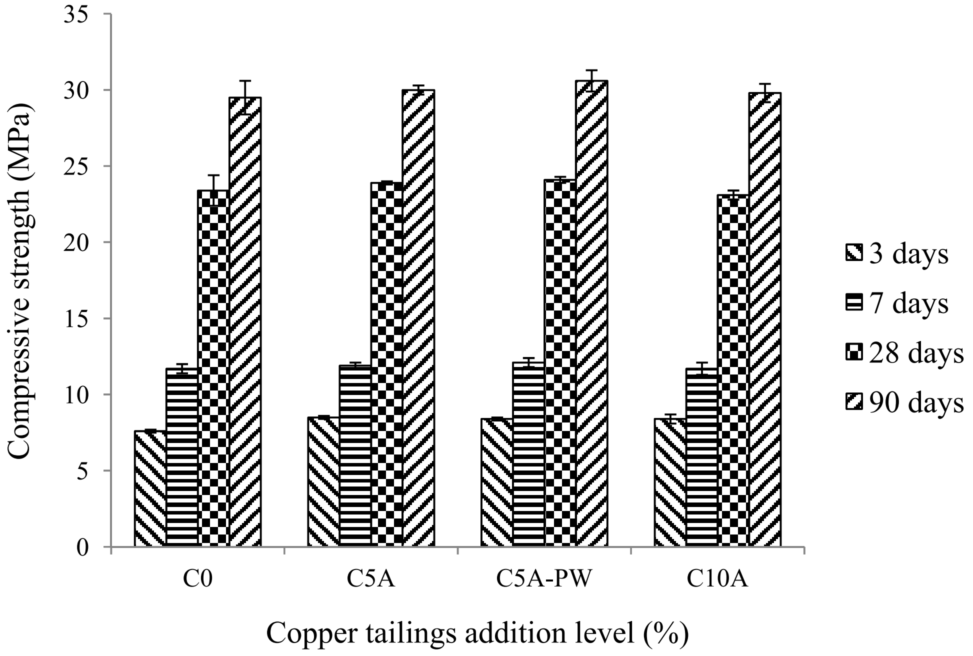


Figure 6.17. Compressive Strength of 0.65 w/b Ratio Concretes (additive mixtures)

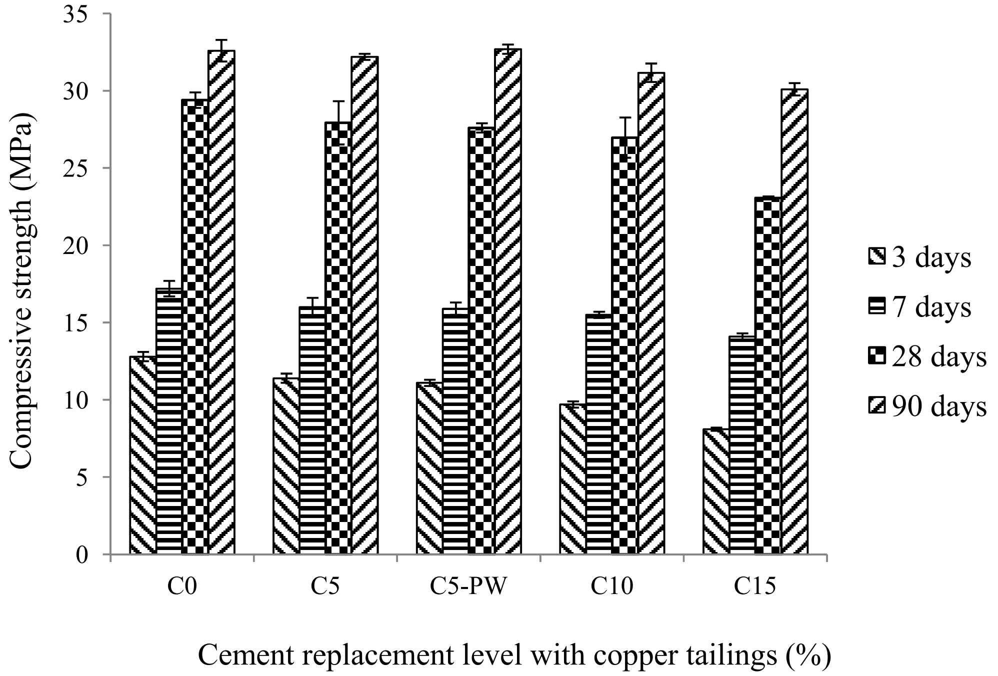


Figure 6.18. Compressive Strength of 0.57 w/b Ratio Concretes (cement replacement)

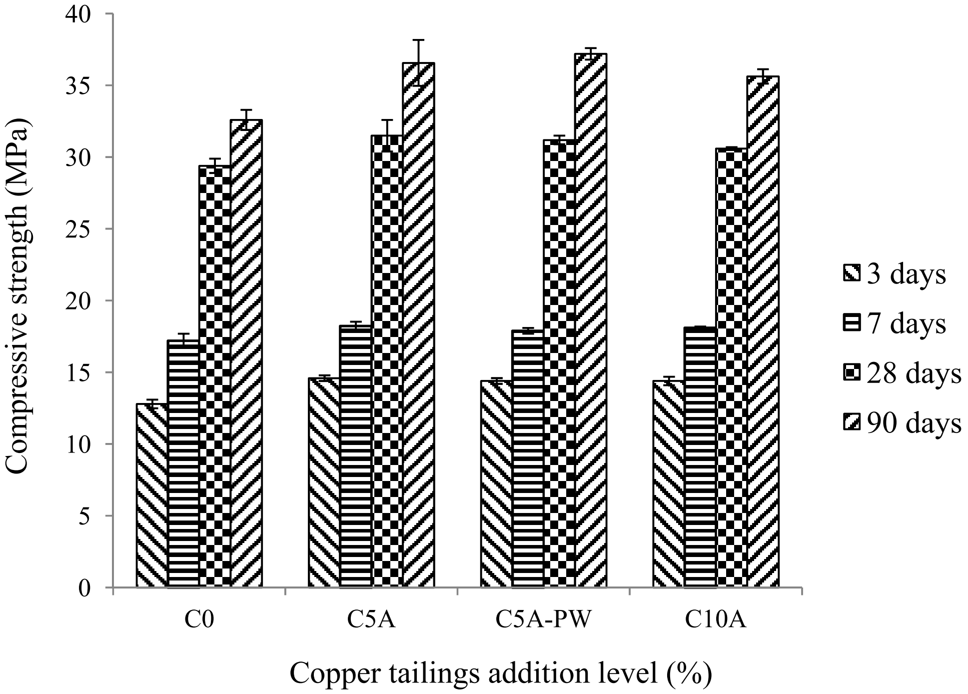


Figure 6.19. Compressive Strength of 0.57 w/b Ratio Concretes (additive mixtures)

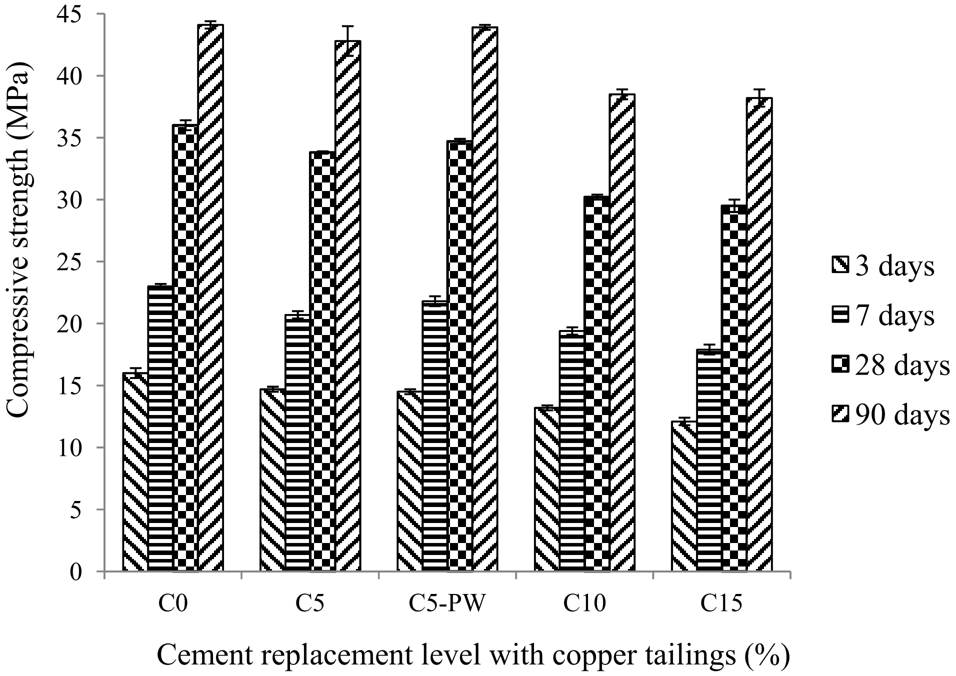


Figure 6.20. Compressive Strength of 0.50 w/b Ratio Concretes (cement replacement)

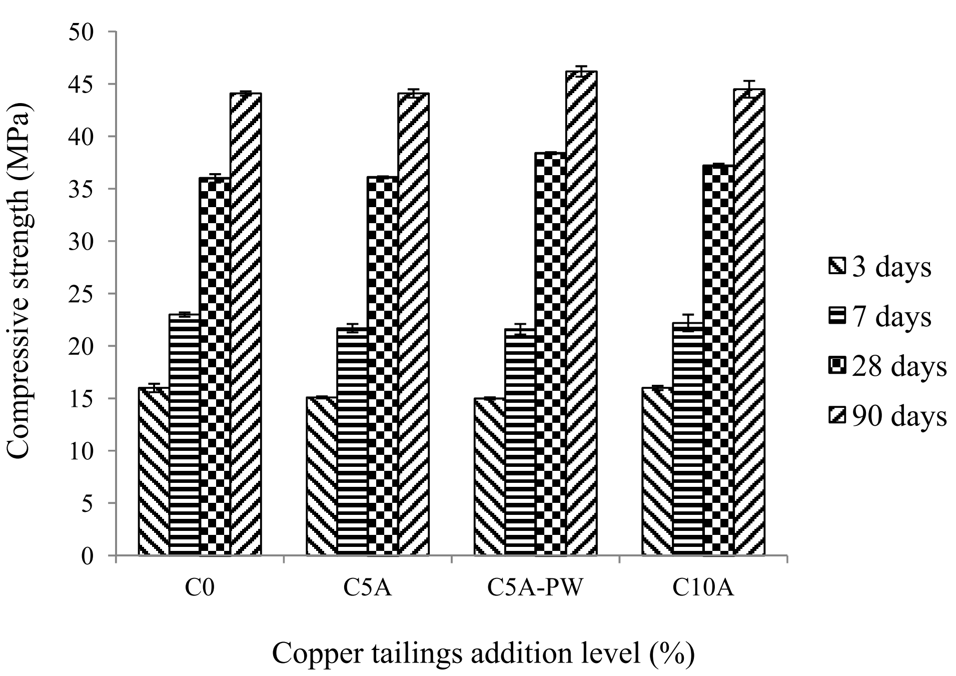


Figure 6.21. Compressive Strength of 0.50 w/b Ratio Concretes (additive mixtures)

Similarly, comparable and slightly higher strengths were recorded in mixtures containing copper tailings as a concrete additive. The percentage compressive strengths relative to those of the control samples at the 90th day for the 0.65 w/b ratio mixtures were 101.7% for C5A, 103.7% for C5A-PW and 101% for C10A. The percentage relative strengths for the 0.57 w/b ratio mixtures at the 90th day were 112.3% for C5A, 114.1% for C5A-PW and 109.2% for C10A while that of the 0.50 w/b ratio mixtures were 100% for C5A, 104.8% for C5A-PW and 100.9% for C10A.

The observed increases in strengths of the mixtures containing copper tailings could be partly traced to the slight reduction of the w/b ratio by these porous tailings particles. It is equally suspected that the filler effect of fine particles of the tailings and the gradual filling of pore spaces with additional hydration products contributed to the strength enhancement witnessed. Moura et al. (2007) also observed similar trend in the compressive strength of concrete containing copper slag as a concrete additive. The superior performance of the C5-PW and C5A-PW samples was as a result of higher degree of hydration in these samples. Dale (2007) was of the opinion that the addition of saturated lightweight aggregates as an internal curing agent in mixtures enhanced long term compressive strength.

6.3.1.3 Flexural Strength of Mortars

The average flexural strength values of mortars are presented in Figures 6.22 and 6.23. With the exception of the C5-PW samples, the rest of the mixtures containing copper tailings as a cement replacement material, recorded flexural strengths lower than that of the control samples at 3, 7 and 28 days. The reductions in strength became higher as the copper content of mixtures increased. However, by the 90th day, the percentage flexural strengths relative to the control samples were 98.1% for C5, 102.8% for C5-PW, 81.1% for C10 and 80.1% for C15. Conversely, all the mixtures containing copper tailings as an additive in mortars showed higher flexural strength at all test ages. At the 90th day, the percentage flexural strengths relative to those of the control samples were 134% for C5A, 137.7% for C5A-PW and 125.5% for C10A.

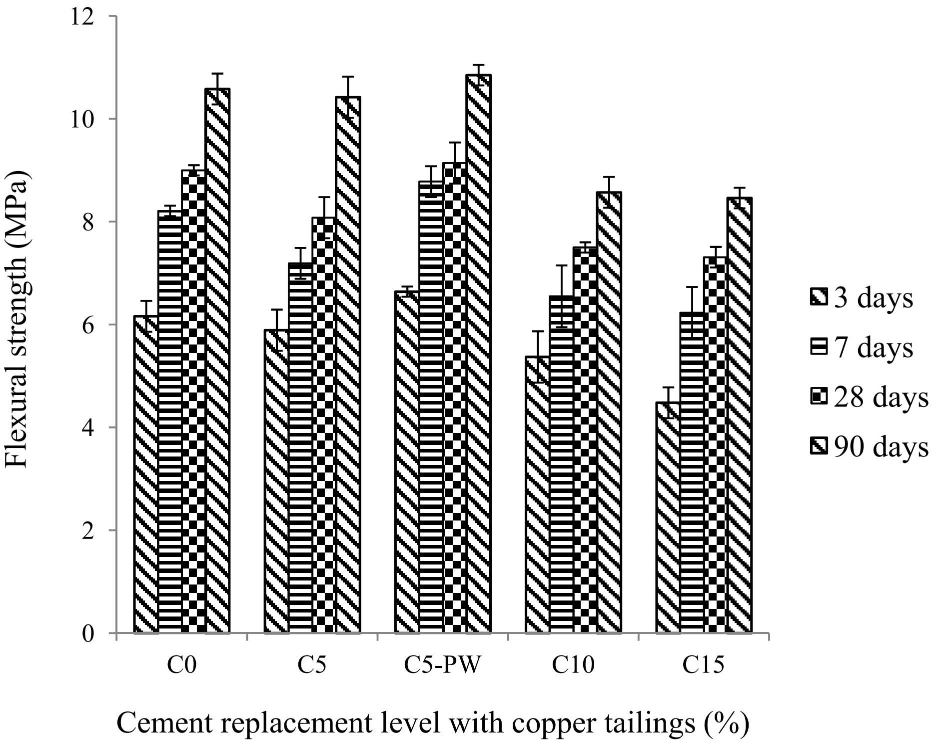


Figure 6.22. Flexural Strength of Mortars (cement replacement)

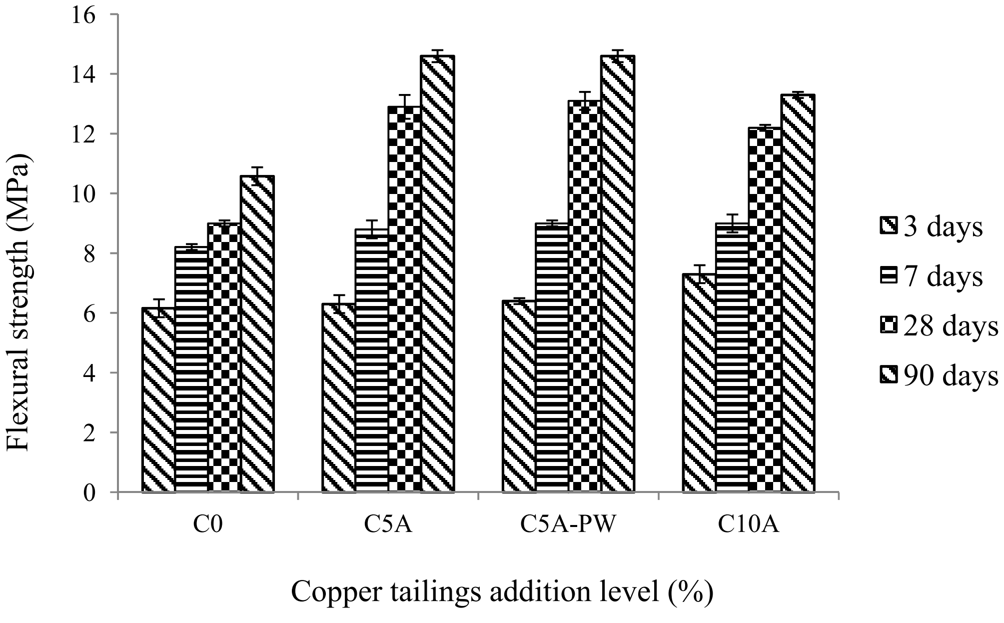


Figure 6.23. Flexural Strength of Mortars (additive mixtures)

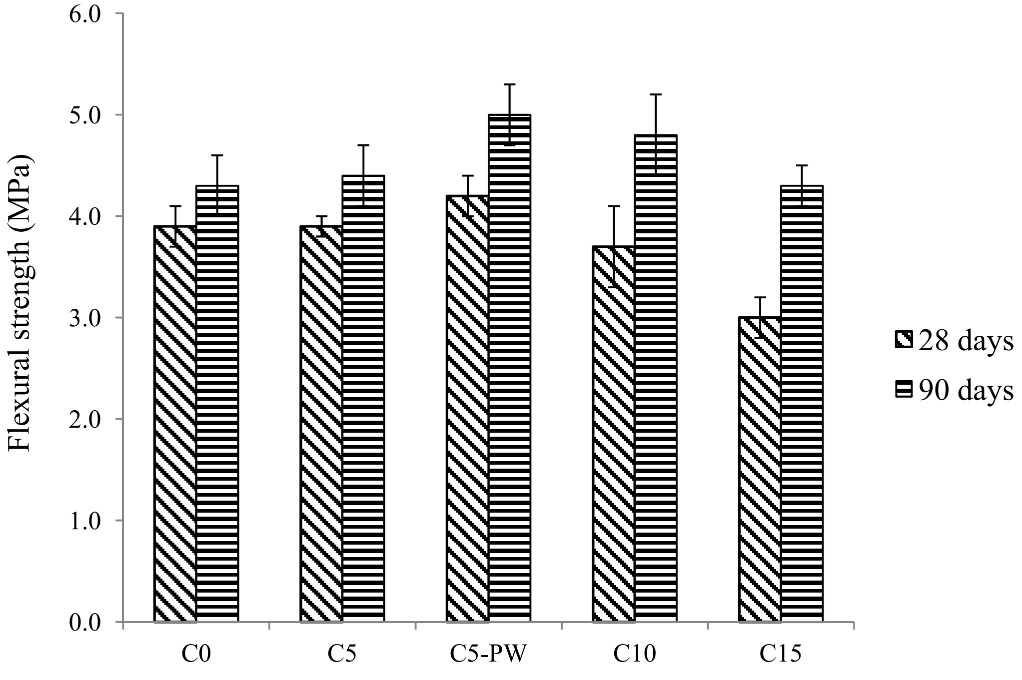
6.3.1.4 Flexural Strength of Concretes

The flexural strengths of concrete mixtures are shown in Figures 6.24 to 6.29. The percentage flexural strengths relative to those of the control samples at the 28th day for the 0.65 w/b ratio mixtures containing copper tailings as a cement replacement material were 100.0% for C5, 107.7% for C5-PW, 94.9% for C10 and 76.9% for C15. These results improved slightly at 90 days. The percentage strengths relative to those of the control samples at the 90th day were 102.3% for C5, 116.3% for C5-PW, 111.6% for C10 and 100% for C15. Similar flexural strength trend was repeated for the 0.57 w/b ratio mixtures containing copper tailings as a cement replacement material. The percentage flexural strengths relative to those of the control samples at the 28th day were 113.6% for C5, 115.9% for C5-PW, 104.5% for C10 and 100.0% for C15. At the 90th day, strength values relative to those of the control samples were 115.0% for C5, 118.3% for C5-PW, 106.7% for C10 and 103.3% for C15. For the 0.50 w/b ratio mixtures, the percentage strength values relative to those of the control samples at the 28th day were 104.5% for C5, 106.1% for C5-PW, 100.0% for C10 and 98.5% for C15. However, at the 90th day, with the exception of the C5-PW mixtures, strength losses were witnessed in samples containing copper tailings. The percentage flexural strengths relative to those of the control samples were 88.4% for C5, 102.9% for C5-PW, 81.2% for C10 and 65.2% for C15.

Similarly, with the exception of the 0.50 w/b ratio concretes, higher flexural strengths were recorded in mixtures containing copper tailings as a concrete additive. The percentage strengths relative to those of the control samples at the 28th day for the 0.65 w/b ratio mixtures were 102.6% for C5A, 105.1% for C5A-PW and 110.3% for C10A.

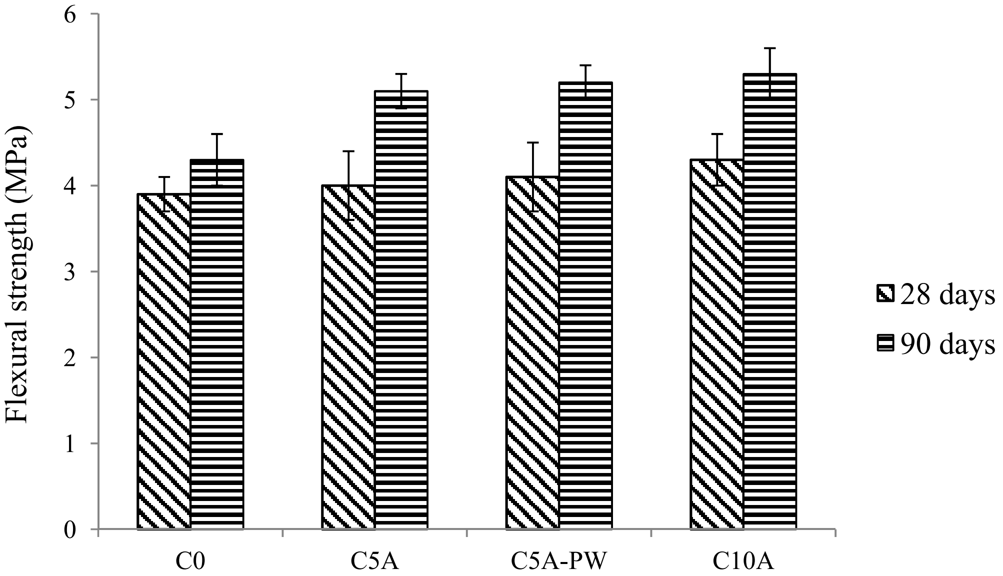
The values at the 90th day were 118.6% for C5A, 120.9% for C5A-PW and 123.3% for C10A. Likewise, the percentage flexural strengths relative to those of the control samples at the 28th day for the 0.57 w/b ratio mixtures were 122.7% for C5A, 125.0% for C5A-PW and 127.3% for C10A. These values improved to 125.0% for C5A, 126.7% for C5A-PW and 128.3% for C10A at the 90th day. For the 0.50 w/b ratio mixtures, the percentage strength values relative to those of the control samples at the 28th day were 106.1% for C5A, 107.6% for C5A-PW and 118.2% for C10A. At the 90th day, the percentage strengths relative to those of the control samples were 95.7% for C5A, 105.8% for C5A-PW and 101.4% for C10A.

Generally, the improved flexural strengths of mixtures containing copper tailings are traceable to enhanced bonding between aggregates and the cement matrix engendered by the porous particles of the tailings. Furthermore, at 90 days, drying and moisture differential induced by air curing of lower w/b ratio mixtures caused these samples to experience strength loss. However, results have shown that the use of pre-wetted tailings as internal curing agent in samples can eliminate this negative effect.



Cement replacement level with copper tailings (MPa)

Figure 6.24. Flexural Strength of 0.65 w/b Ratio Concretes (cement replacement)



Copper tailings addition level (%)

Figure 6.25. Flexural Strength of 0.65 w/b Ratio Concretes (additive mixtures)

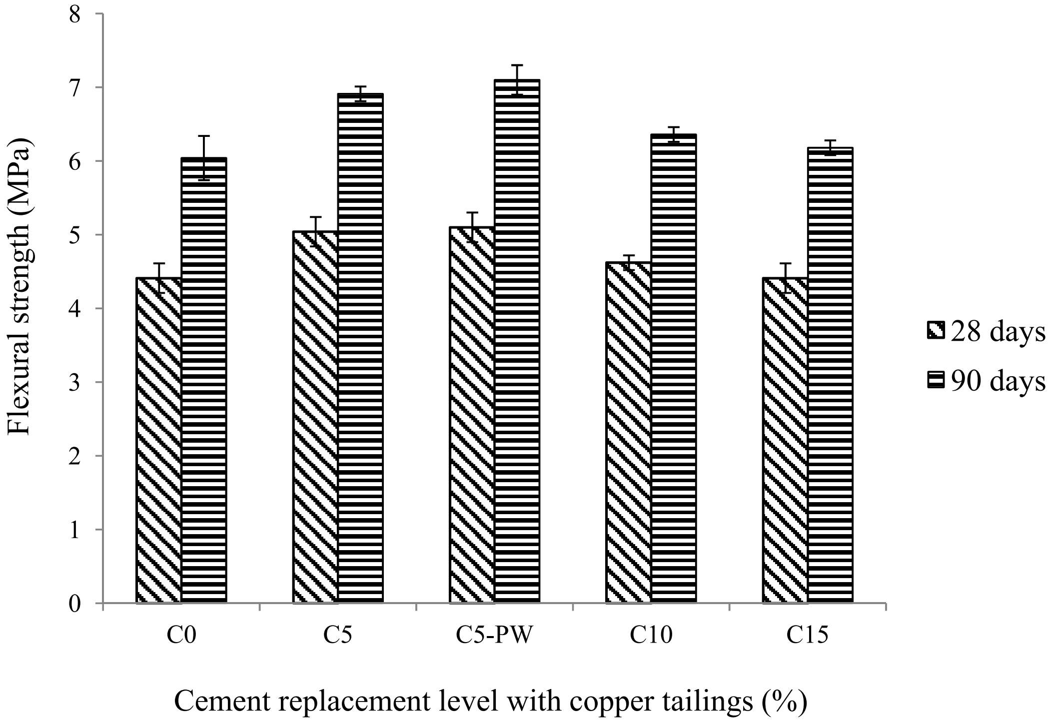


Figure 6.26. Flexural Strength of 0.57 w/b Ratio Concretes (cement replacement)

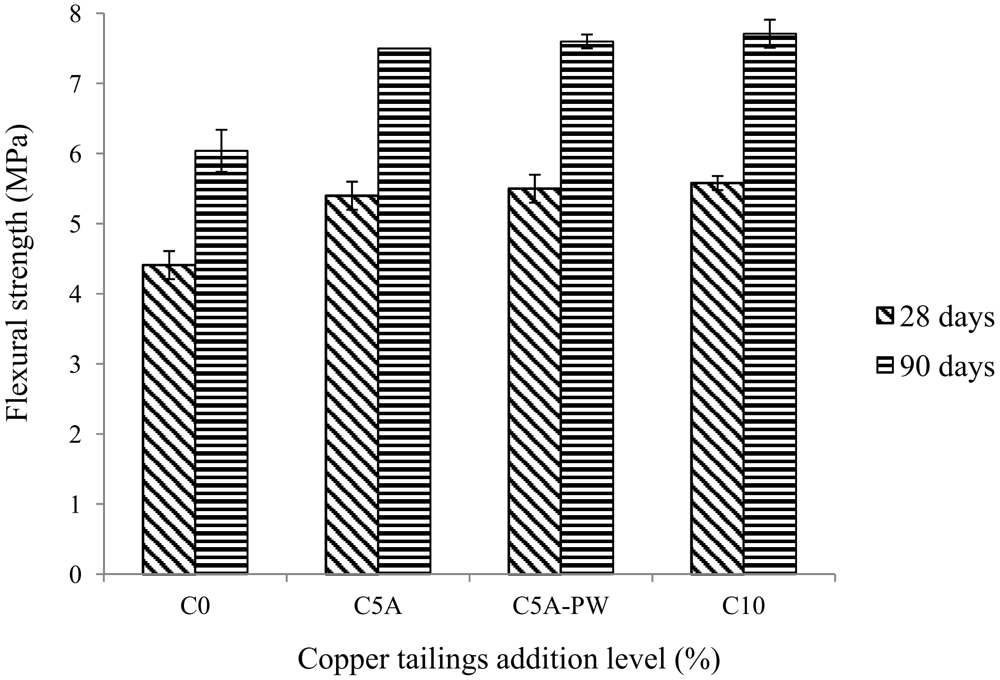


Figure 6.27. Flexural Strength of 0.57 w/b Ratio Concretes (additive mixtures)

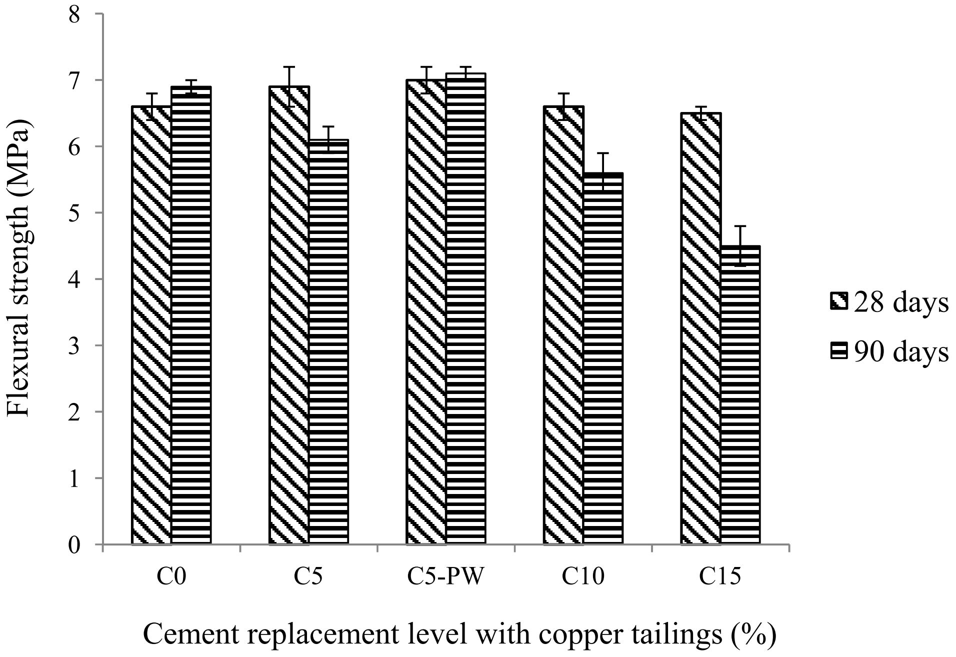


Figure 6.28. Flexural Strength of 0.50 w/b Ratio Concretes (cement replacement)

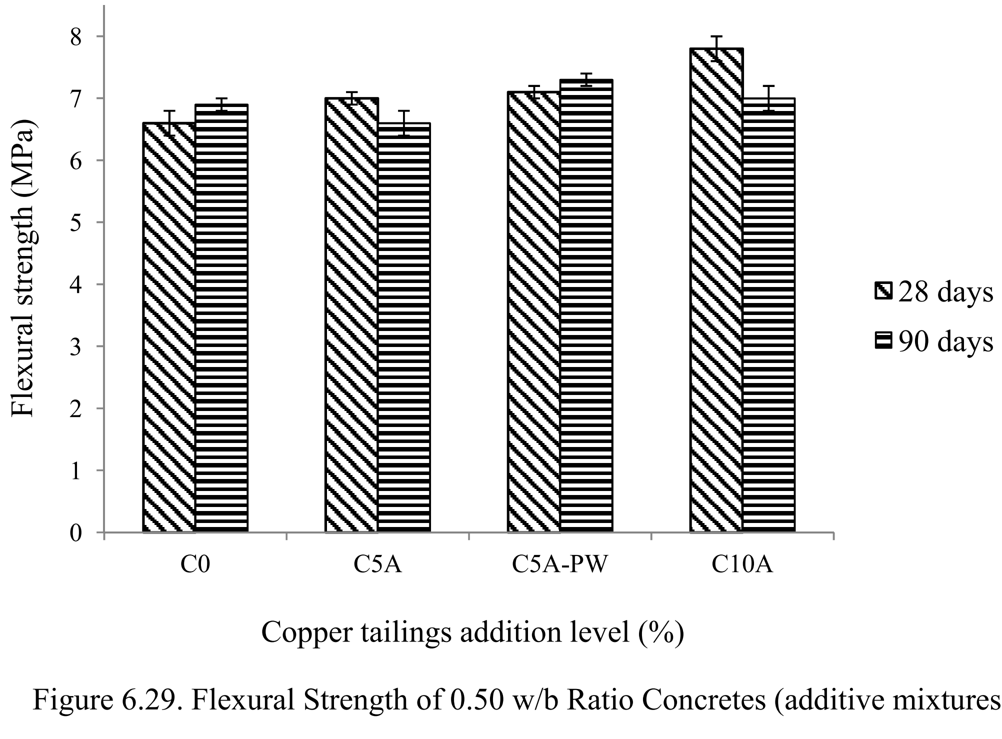


Figure 6.29. Flexural Strength of 0.50 w/b Ratio Concretes (additive mixtures)

6.3.1.5 Splitting Tensile Strength of Concrete

The splitting tensile strengths of concrete mixtures are shown in Figures 6.30 to 6.35. For the 0.65 w/b ratio concretes, containing copper tailings as a cement replacement material, the percentage strengths relative to those of the control samples at the 28th day were 100.0% for C5, 108.0% for C5-PW, 96.0% for C10 and 68% for C15. However, at the 90th day, strength values comparable to those of the control mixture were only recorded in C5-PW and C5A-PW samples. For the 0.57 w/b ratio concretes, containing copper tailings as a cement replacement material, strength values equivalent to those of the control samples were observed at the 28th day. These results improved slightly at the 90th day. The percentage strengths relative to those of the control samples at the 90th day were 100.0% for C5, 102.9% for C5-PW, 100.0% for C10 and 111.4% for C15. Similar splitting tensile strength trend was repeated for the 0.50 w/b ratio mixtures containing copper tailings as a cement replacement material. While strength values comparable to those of the control mixture at the 28th day were observed, slight improvements in strengths were seen at the 90th day. The percentage strengths relative to those of the control samples were 105.1% for C5, 107.7% for C5-PW, 97.4% for C10 and 92.3% for C15.

With the exception of the 0.65 w/b ratio concretes, which recorded mixed results, higher splitting tensile strengths were recorded in mixtures containing copper tailings as a concrete additive. The percentage strengths relative to those of the control samples at the 28th day for the 0.57 w/b ratio mixtures were 106.7% for C5A, 106.7% for C5A-PW and 110.0% for C10A. The values at the 90th day were 120.0% for C5A, 125.7% for C5A-PW and 114.3% for C10A. Similarly, the percentage strengths relative to those of the control samples at the 28th day for the 0.50 w/b ratio mixtures were 111.1% for C5A, 111.1% for C5A-PW and 105.6% for C10A. At the 90th day, the relative strength values were 107.7% for C5A, 115.3% for C5A-PW and 100.0 % for C10A.

At optimum content, the addition of copper tailings improve the tensile strength of copper tailings blended concretes, as a result of enhanced bonding of concrete ingredients. Improved tensile strength of concrete mixtures at low fly ash content and slightly reduced strength at higher volume of utilization of fly ash was reported by (Lam et al., 1998). They suggested that appropriate amount of fly ash enhances tensile strength of mixtures, through improved interfacial bond between paste and aggregates.

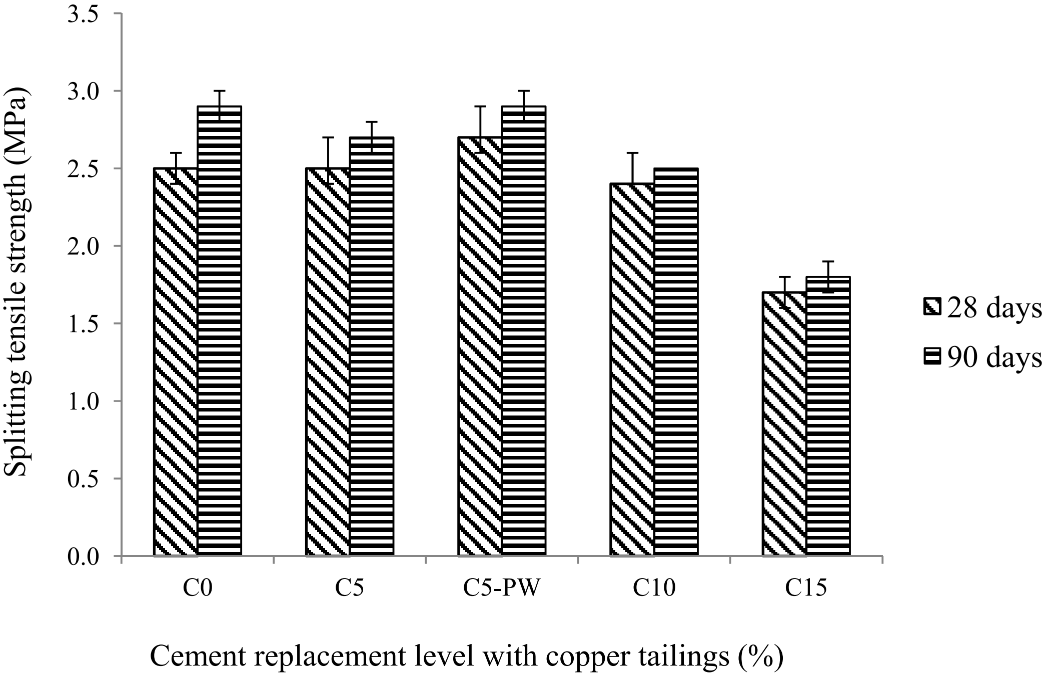


Figure 6.30. Splitting Tensile Strength of 0.65 w/b Ratio Concretes (cement replacement)

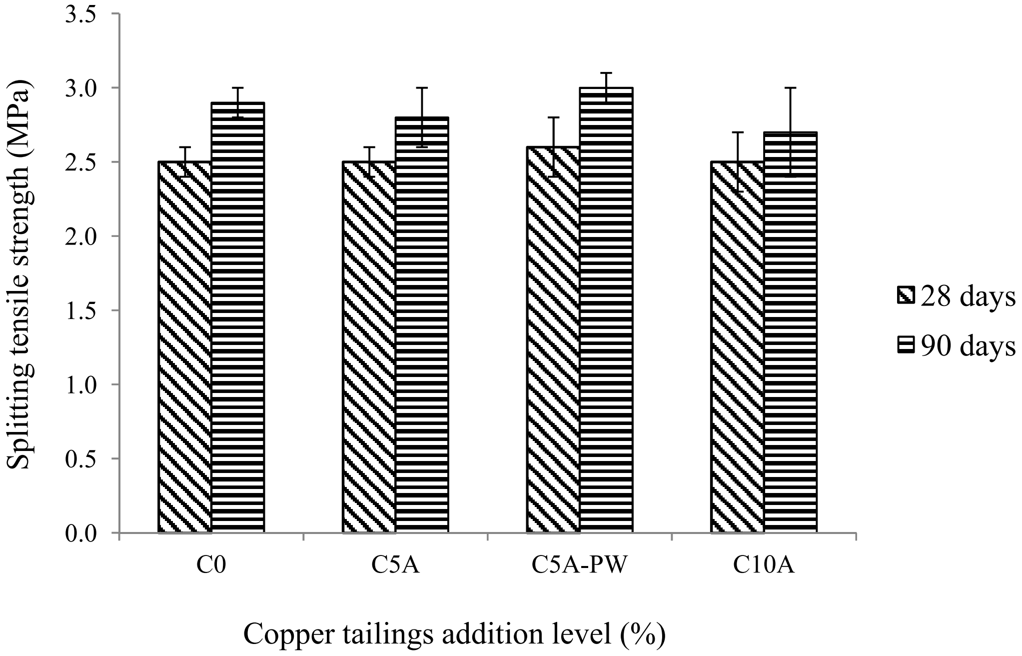


Figure 6.31. Splitting Tensile Strength of 0.65 w/b Ratio Concretes (additive mixtures)

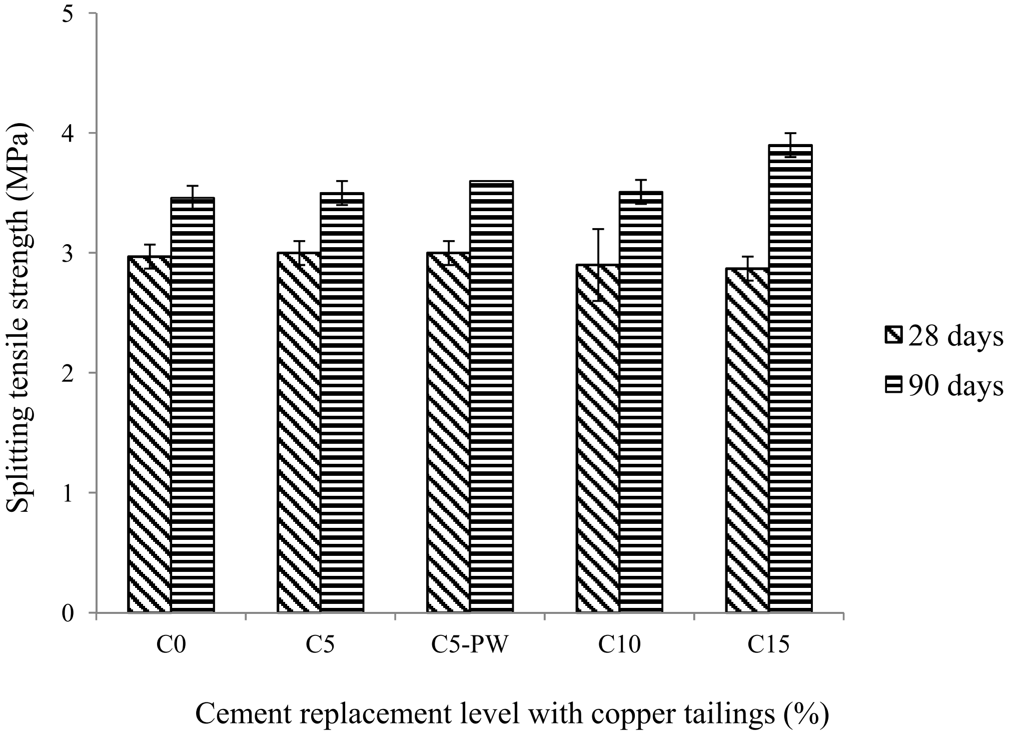


Figure 6.32. Splitting Tensile Strength of 0.57 w/b Ratio Concretes (cement replacement)

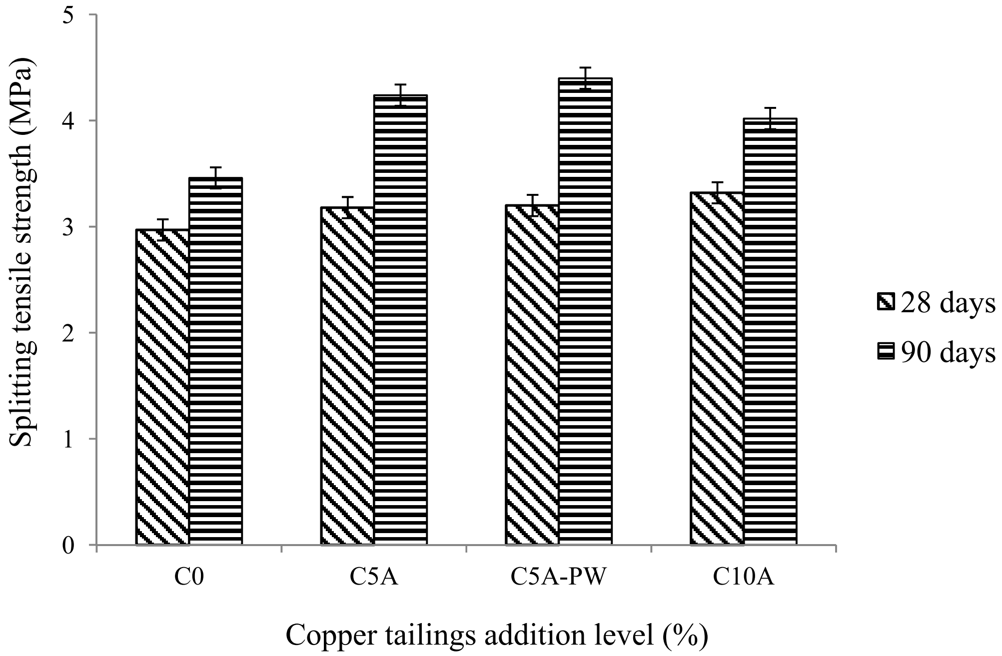


Figure 6.33. Splitting Tensile Strength of 0.57 w/b Ratio Concretes (additive mixtures)

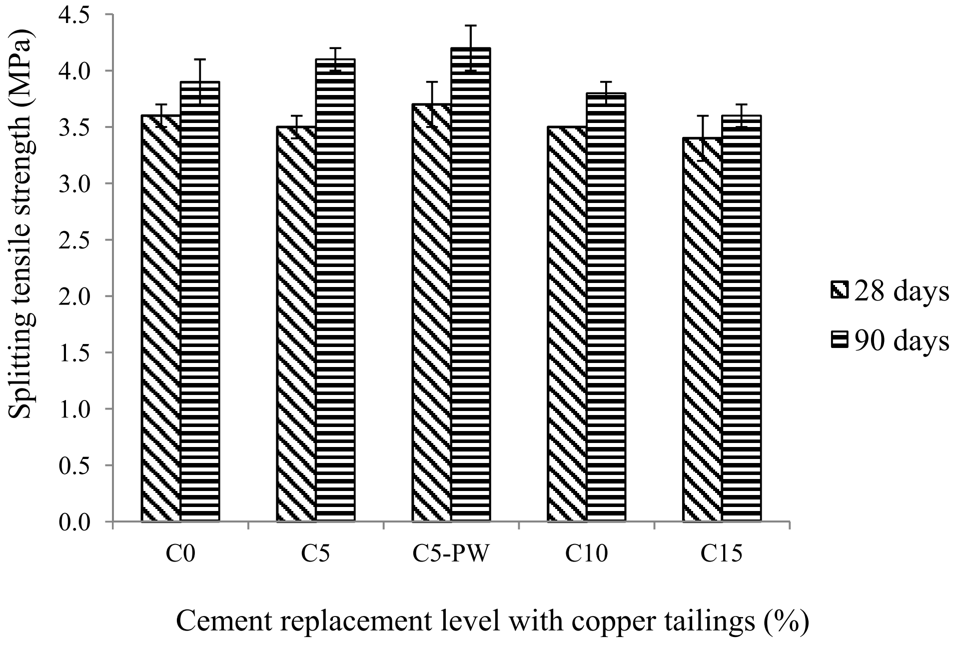


Figure 6.34. Splitting Tensile Strength of 0.50 w/b Ratio Concretes (cement replacement)

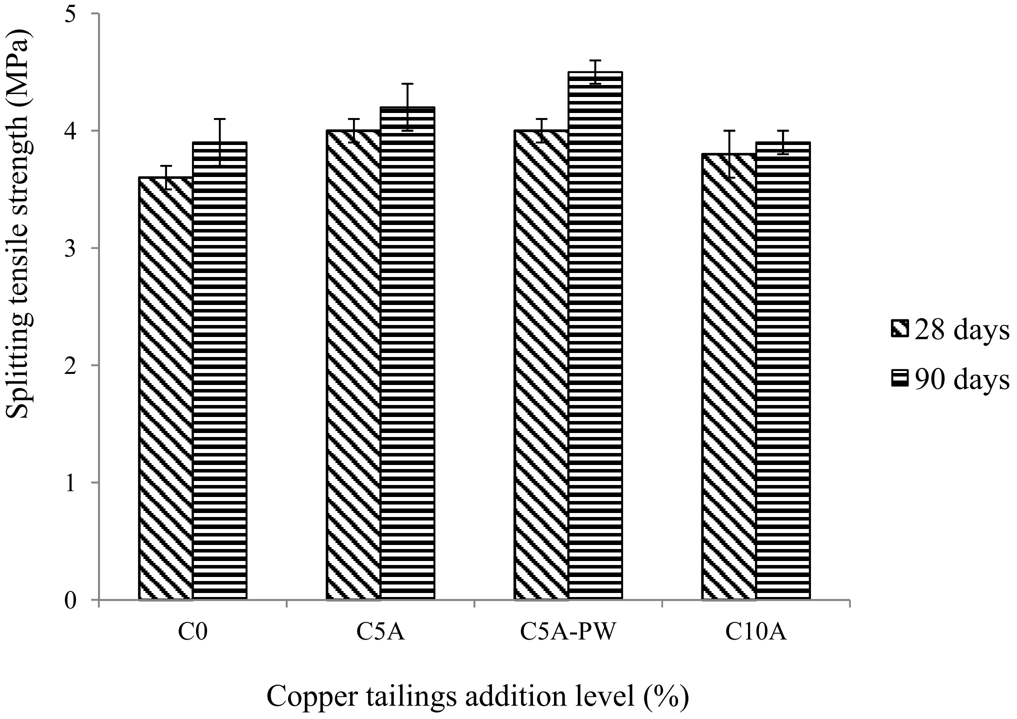


Figure 6.35. Splitting Tensile Strength of 0.50 w/b Ratio Concretes (additive mixtures)

6.3.1.6 Modified Abrasion and Impact Resistance of Mortars

The percentage mass loss of mortar samples containing copper tailings as a cement replacement material after abrasion and impact tests are shown in Figure 6.36. The values after 500 rotations were 21.9% for C0, 19.6% for C5, 19.2% for C5-PW, 20.5% for C10 and 22.8% for C15. The results for mixtures containing copper tailings as a mortar additive are shown in Figure 6.37. The mass loss values were 21.9% for C0, 18.8% for C5A, 18.5% for C5A-PW and 17.5% for C10A. Hence, with the exception of C15 samples, the rest of the mixtures containing copper tailings recorded enhanced resistance against abrasion and impact.

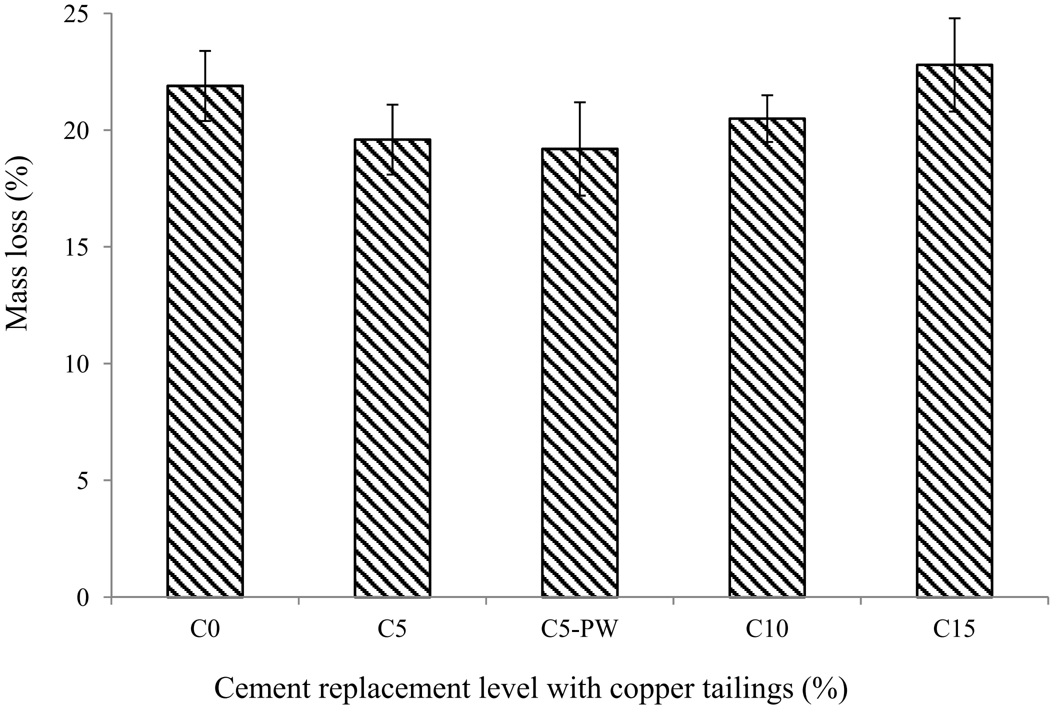


Figure 6.36. Abrasion and Impact Resistance of Mortars (cement replacement)

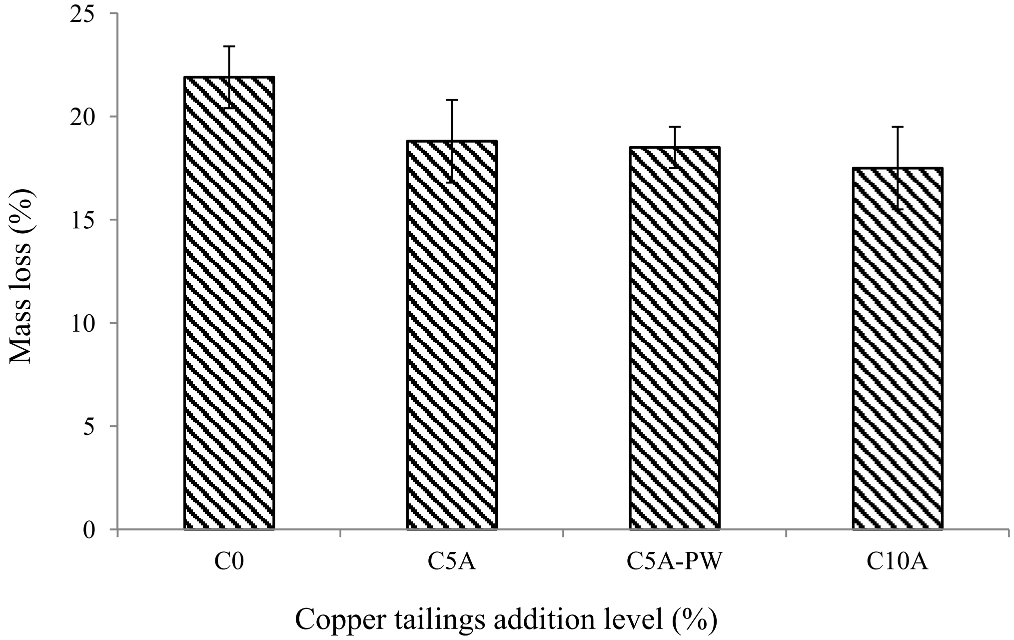


Figure 6.37. Abrasion and Impact Resistance of Mortars (additive mixtures)

6.3.1.7 Modified Abrasion and Impact Resistance of Concretes

Figure 6.38 and 6.39 shows the mass loss of 0.57 and 0.50 w/b ratio concrete samples after the abrasion and impact resistance tests. Results of 0.65 w/b ratio mixtures were not presented due to significant degradation of samples before the completion of the test, hence the reliability of test result maybe questionable. Figure 6.38 showed that the mass losses of 0.57 w/b ratio mixtures containing copper tailings as a cement replacement material were 76.6% for C0, 64.3% for C5, 63.9% for C5-PW, 70.2% for C10 and 81.5% for C15. The mass losses of the 0.57 w/b ratio mixtures containing copper tailings as a concrete additive are shown in Figure 6.39, and they are 76.6% for C0, 67.0% for C5A, 65.6% for C5A-PW and 75.8% for C10A.

For 0.5 w/b ratio samples containing copper tailings as a cement replacement material, the mass losses were 70.2% for C0, 60.7% for C5, 58.2% for C5-PW, 56.7% for C10 and 76.8% for C15. The mass loss values for samples containing copper tailings as a concrete additive were 70.2% for C0, 46.5% for C5, 44.9 for C5A-PW and 37.1% for C10A. A more enhanced resistance to degradation was obtained from the 0.50 w/b ratio mixtures containing copper tailings. The improved resistance of mixtures containing copper tailings, especially the additive mixtures could be as a result of the higher compressive strengths of these samples compared to those of the control samples. Some studies suggested that abrasion resistance is strongly influenced by concrete compressive strength (Naik et al., 1995; Li et al., 2006). Other factors such as surface characteristics of samples may have also contributed.

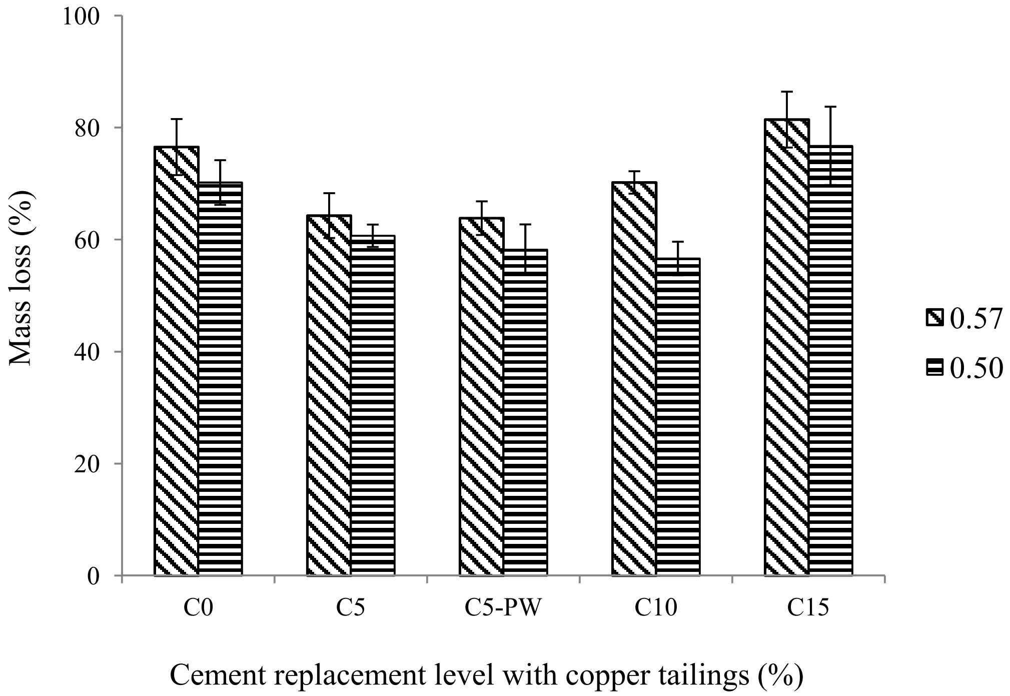


Figure 6.38. Abrasion and Impact Resistance of Concretes (cement replacement)

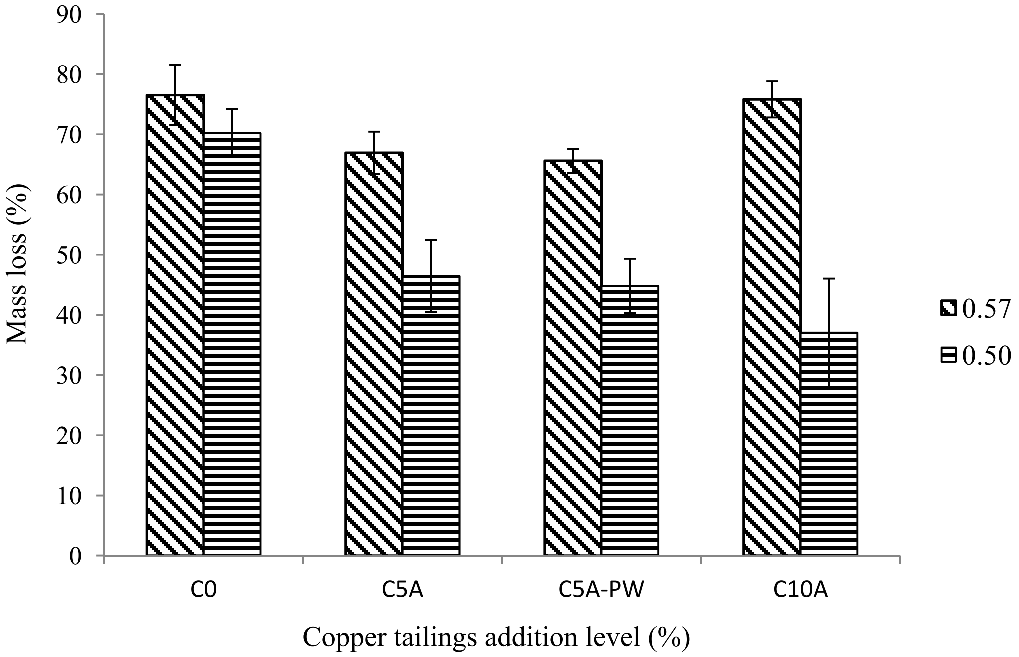


Figure 6.39. Abrasion and Impact Resistance of Concretes (additive mixtures)

6.3.2 Durability Properties

6.3.2.1 Autoclave Expansion of Pastes

Figures 6.40 and 6.41 present the results of autoclave expansion tests. The changes in length of test specimens were calculated by deducting the length comparator measurements prior to and after autoclaving, which was then presented as a percentage of the effective gage length to the nearest 0.01%. The expansion values of the paste mixtures containing copper tailings as a cement replacement material were 0.036% for C0, 0.030% for C5, 0.030% for C5-PW, 0.032% for C10 and 0.036% for C15. Similarly, the expansion values of mixtures containing copper tailings as a paste additive were 0.036% for C0, 0.023% for C5A, 0.022% for C5A-PW and 0.032% for C10A The use of high temperature in the autoclave expansion test accelerated hydration of pastes, thereby causing immediate expansion. However, the results obtained are significantly low and in agreement with the assertion by Liu et al. (1998) that fly ash and slag reduce autoclave expansion. Similar increased resistance to expansion in concrete containing porous volcanic scoria was also observed by (Hossain, 2006). It is suspected that the improved performance of the pastes containing copper tailings as a cement replacement material was partly because of the decreasing content of calcium oxide (CaO) in mixtures as the cement replacement level with copper tailings increased which consequently, reduced available free CaO. Likewise, reduced expansion of mixtures containing copper tailings as an additive is traceable to autoclave curing induced strength and microstructure enhancement in samples.

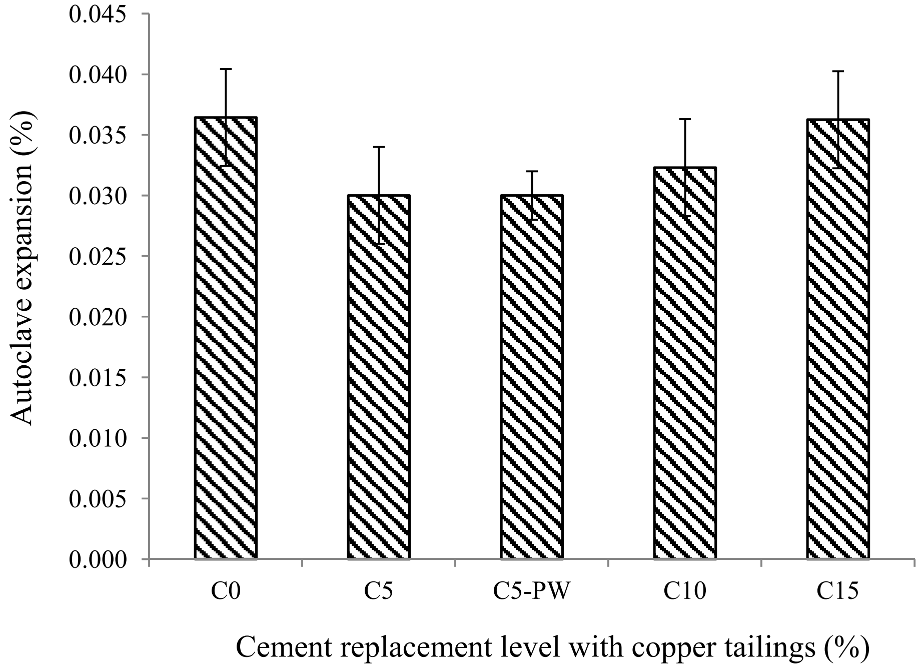


Figure 6.40. Autoclave Expansion of Pastes (cement replacement)

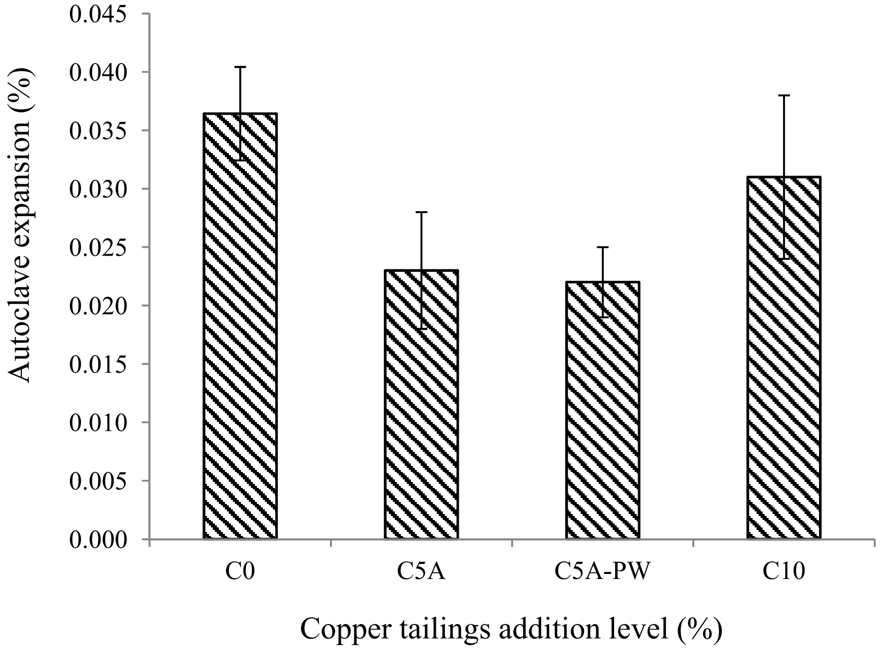


Figure 6.41. Autoclave Expansion of Pastes (additive mixture)

6.3.2.2 Water Absorption and Volume of Permeable Voids in Mortars

Figures 6.42 and 6.43 show the volumes of absorbed water and voids in mortars. For the mixtures containing copper tailings as a cement replacement material, the percentage volumes of absorbed water were 16.2% f or C0, 16.3% for C5, 16.2% for C5-PW, 16.5% for C10 and 16.8% for C15 while the volumes of permeable void were 17.6% f or C0, 17.8% for C5, 17.6% for C5-PW, 18.2% for C10 and 18.8% for C15. Similarly, while the percentage volumes of absorbed water for samples containing copper tailings as a mortar additive were 16.2% for C0, 16.0% for C5A, 15.9% for C5A-PW and 16.2% for C10A, the volumes of permeable void were 17.6% C0, 17.4% for C5A, 17.1% for C5A-PW and 18.0% for C10A. Same trend was also repeated in the results shown in Figures 6.44 and 6.45 for the rate of water absorption tests. In the first 4 h, the water absorption values were 42.4% for C0, 50.9% for C5, 48.2% for C5-PW, 53.9% for C10 and 60.1% for C15. However, at the end of 24 h, the rates of water absorption of the copper tailings samples were comparable to those of the control mixture. The water absorption values at 24 h were 81.6% for C0, 82.7% for C5, 82.1% for C5-PW, 83.3% for C10 and 83.6% for C15. The rates of water absorption after 4 h for samples containing copper tailings as an additive were 42.4% for C0, 51.6% for C5A, 49.9% for C5A-PW and 45.3% for C10A while the values after 24 h were 81.6% for C0, 81.3% for C5A, 80.4% for C5A-PW and 84.7% for C10A. These results suggest that in cement replacement mixtures, absorbed water and voids increases as the tailings content of mixtures increased. On the other hand, in mixtures containing copper tailings as an additive, results showed that the volumes of absorbed water in copper blended mixtures were comparable to those of the control mixture. However, slightly higher volume of permeable voids was recorded in C10A samples. Generally, the rate of water absorption increased slightly as copper content of mixtures increased.

Studies by Pandey and Sharma (2000) showed that the use of fly ash and slag as a cement replacement material increased mortar porosity. Water absorptions higher than that of the control mortar specimens were also noticed by Courad et al. (2003) in samples containing metakaolin as a partial substitute for cement. In a related finding, Hadj-sadok et al. (2011) also suggested that the moderately reactive ground granulated blast furnace slag they investigated appeared to increase the water porosity and pore volume of cement mortars. The increased water absorption and total permeable voids of copper tailings blended mortars in this study was attributed to the porous and coarse particles of the copper tailings and their generally low reactivity. It is expected that the increased porosity of the copper tailings blended mixtures may not necessarily be detrimental if pore interconnectivity is reduced.

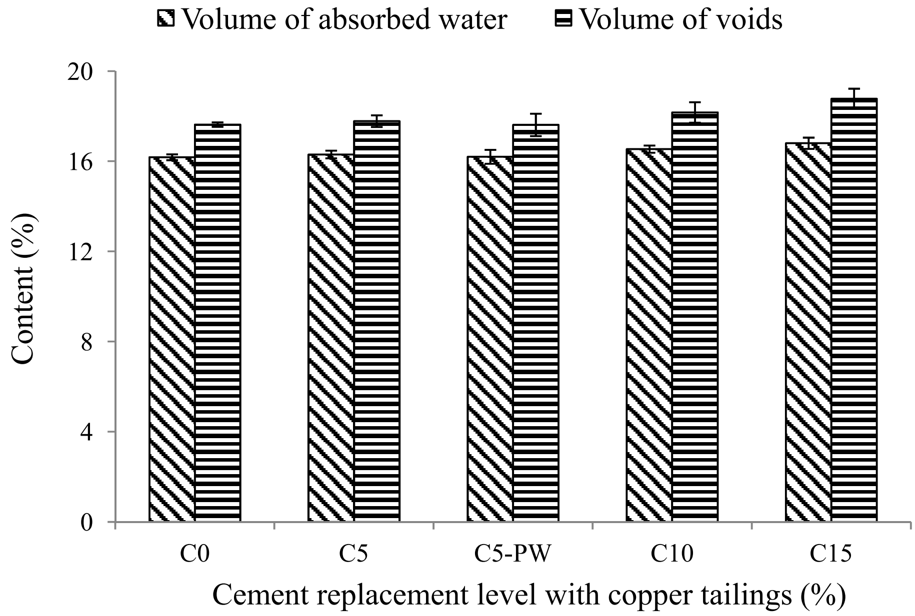


Figure 6.42. Volume of Absorbed Water and Voids in Mortars (cement replacement)

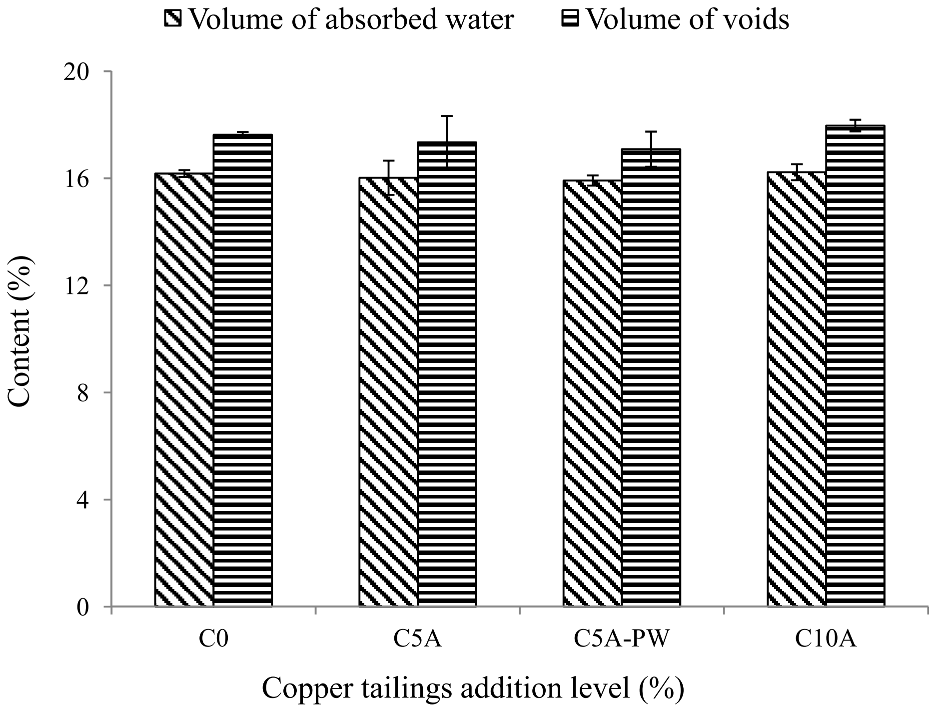


Figure 6.43. Volume of absorbed Water and Voids in Mortars (additive mixtures)

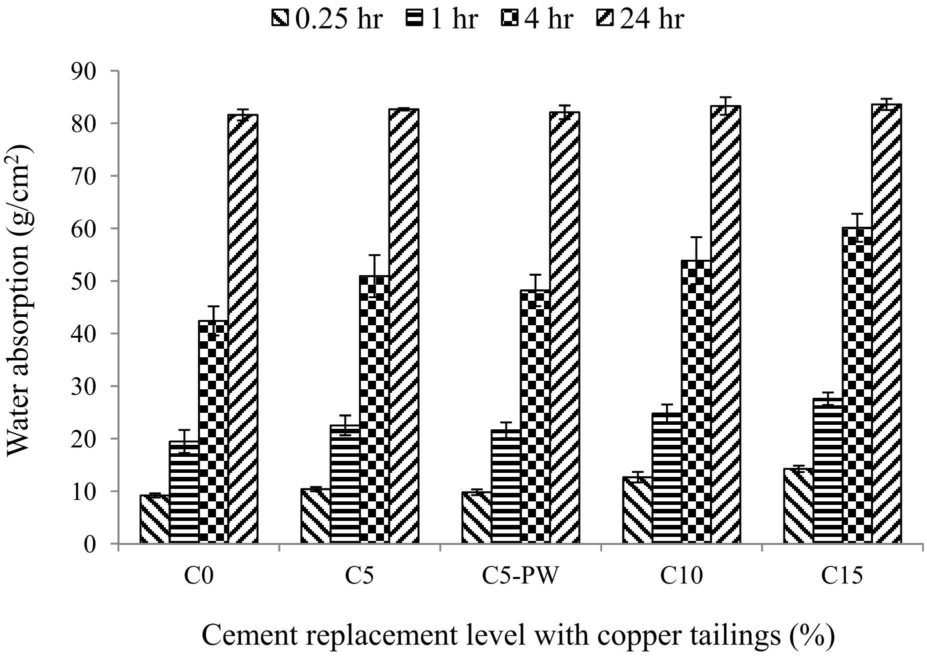


Figure 6.44. Rates of Water Absorption in Mortars (cement replacement)

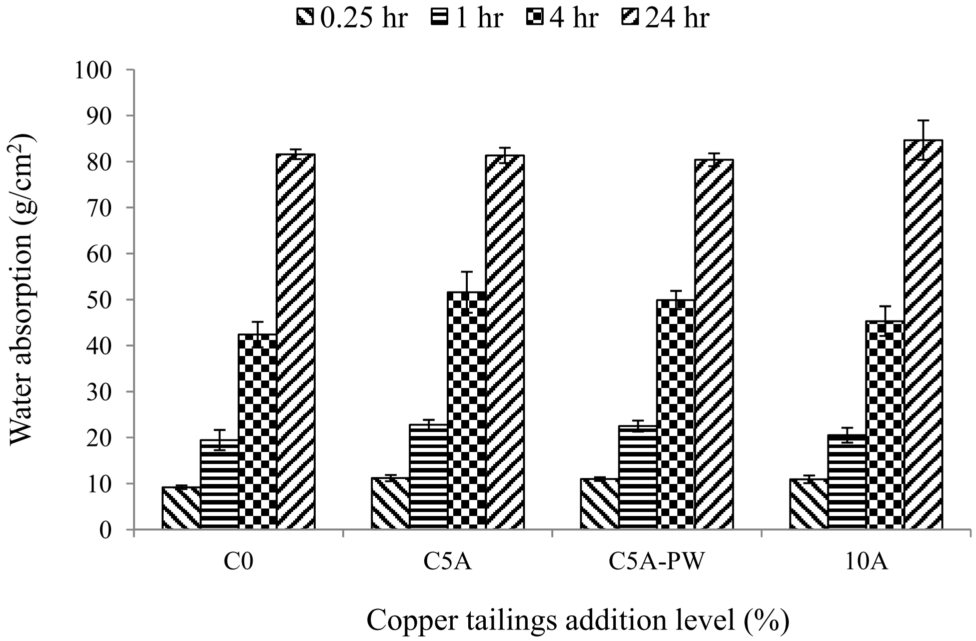


Figure 6.45. Rates of Water Absorption in Mortars (additive mixtures)

6.3.2.3 Volume of Absorbed Water and Permeable Voids in Concretes

The percentage volumes of absorbed water and volume of permeable void in concretes are shown in Figures 6.46 to 6.51. For the 0.65 w/b ratio mixtures, containing copper tailings as a cement replacement material, Figure 6.46 shows that the percentage volumes of absorbed water were 14.1% for C0, 14.7% for C5, 14.6% for C5-PW, 15.0% for C10 and 15.5% for C15 while the volumes of permeable voids were 14.9% for C0, 15.4% for C5, 15.4% for C5-PW, 15.7% for C10 and 16.2% for C15. Similar trend was recorded in the 0.57 w/b ratio mixtures, the values for the percentage volumes of absorbed water as shown in Figure 6.48 were 14.5% for C0, 14.8% for C5, 14.7% for C5-PW, 14.9% for C10 and 15.5% for C15 while the volumes of permeable voids were 15.7% for C0, 16.1% for C5, 15.9% for C5-PW, 16.2% for C10 and 16.6% for C15. For the 0.50 w/b ratio mixtures, Figure 6.50 shows that the percentage volumes of absorbed water were 14.9% for C0, 15.4% for C5, 15.2% for C5-PW, 15.8% for C10 and 16.2% for C15 while the volumes of permeable voids were 15.5% for C0, 16.2% for C5, 16.0% for C5-PW, 16.4% for C10 and 16.9% for C15.

Increasing water absorption and voids in samples as copper tailings content of mixtures increased were also observed in samples containing copper tailings as a concrete additive. For the 0.65 w/b ratio mixtures, Figure 6.47 shows that the percentage volumes of absorbed water were 14.1% for C0, 14.6% for C5A, 14.6% for C5A-PW and 14.9% for C10A while the volumes of permeable voids were 14.9% for C0, 15.3%% for C5A, 15.2% for C5A-PW and 15.5% for C10A. The percentage volumes of absorbed water as shown in Figure 6.49 for the 0.57 w/b ratio mixtures were 14.5% for C0, 15.4% for C5A, 15.3% for C5A-PW and 17.0% for C10A while the volumes of permeable voids were 15.7 for C0, 16.4% for C5A, 16.2% for C5A-PW and 18.1% for C10A. For the 0.50 w/b ratio mixtures, Figure 6.51 shows that the percentage volumes of absorbed water were 14.9% for C0, 14.5% for C5A, 14.2% for C5A-PW and 15.0% for C10A while the percentage volumes of permeable voids were 15.5% for C0, 15.3% for C5A, 15.0% for C5A-PW and 15.7% for C10A.

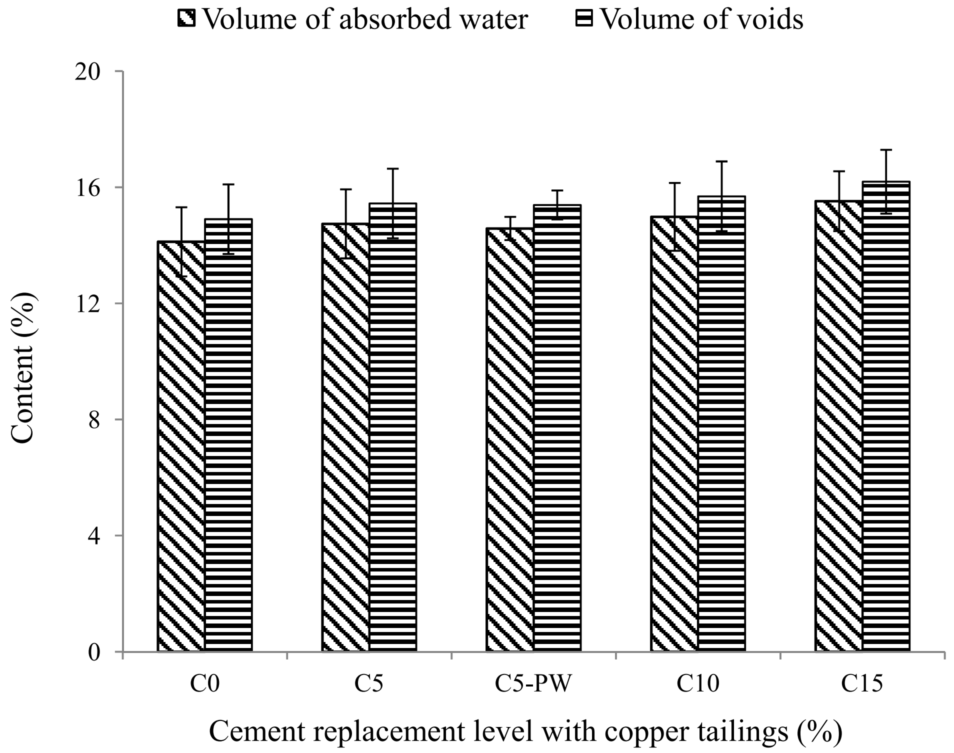


Figure 6.46. Volume of Absorbed Water and Voids in 0.65 w/b Ratio Concretes (cement replacement)

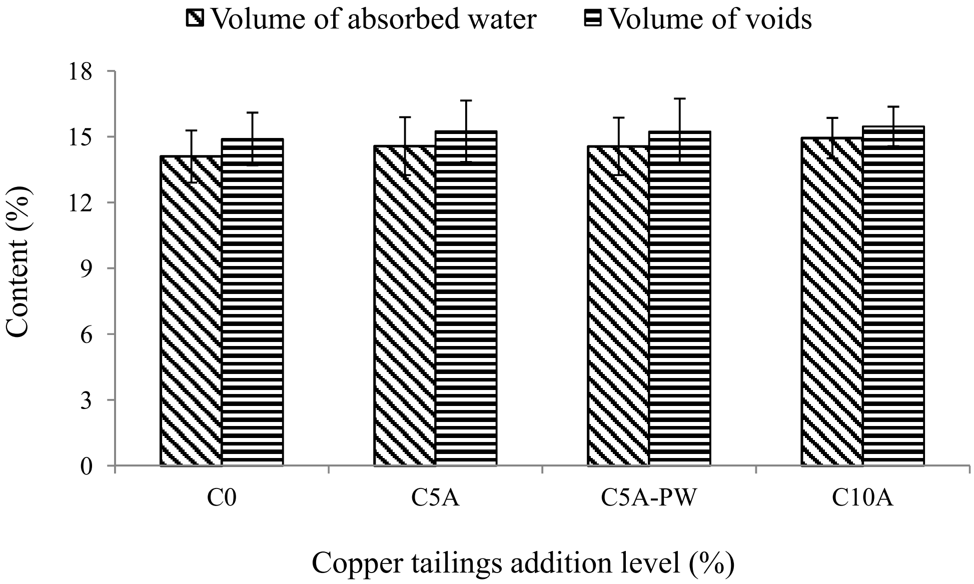


Figure 6.47. Volume of Absorbed Water and Voids in 0.65 w/b Ratio Concretes (additive mixtures)

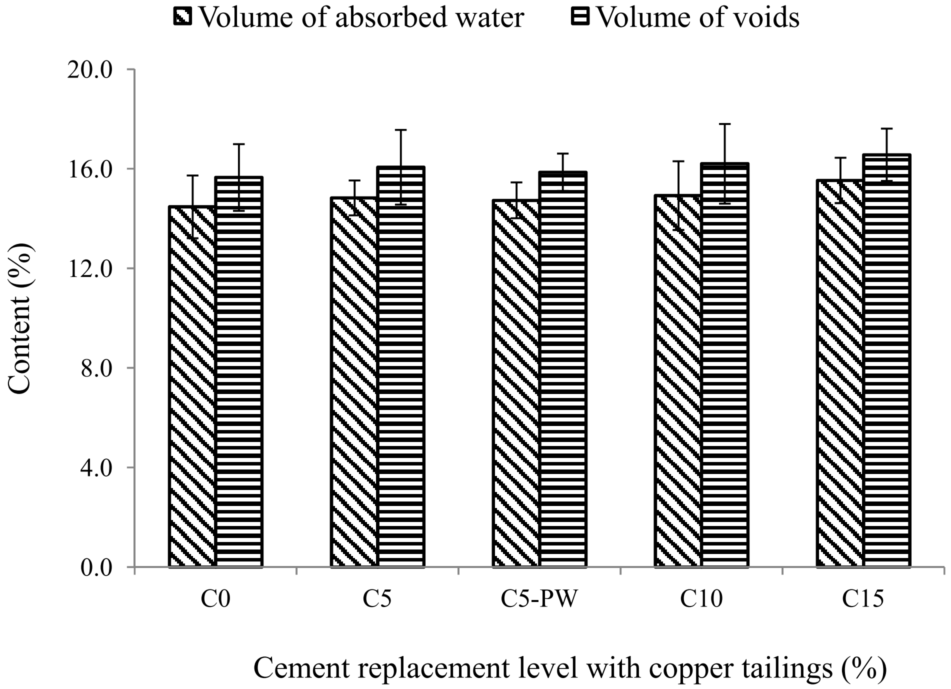


Figure 6.48. Volume of Absorbed Water and Voids in 0.57 w/b Ratio Concretes (cement replacement)

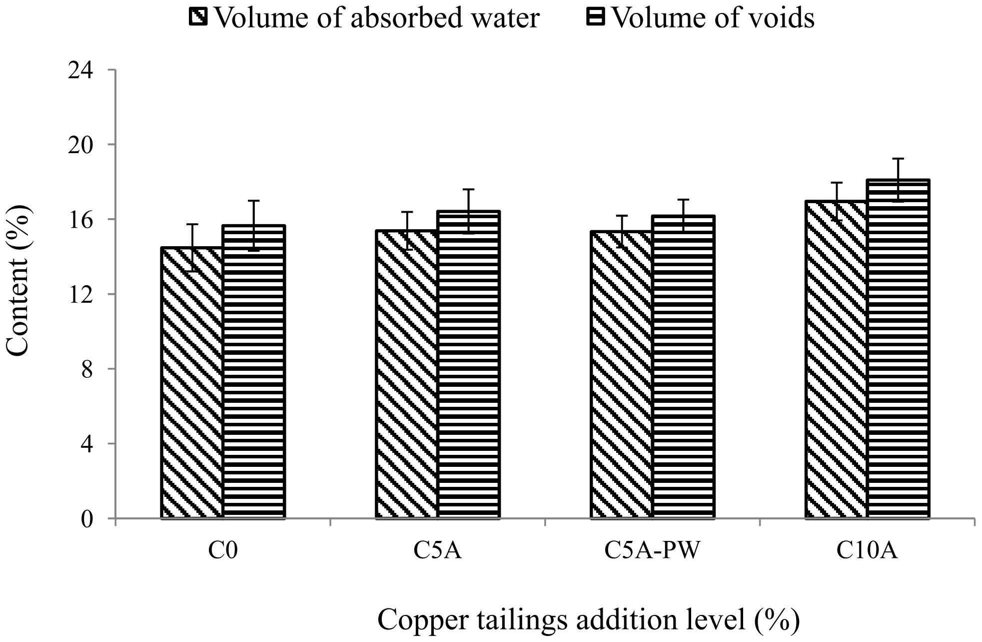


Figure 6.49. Volume of Absorbed Water and Voids in 0.57 w/b Ratio Concretes (additive mixtures)

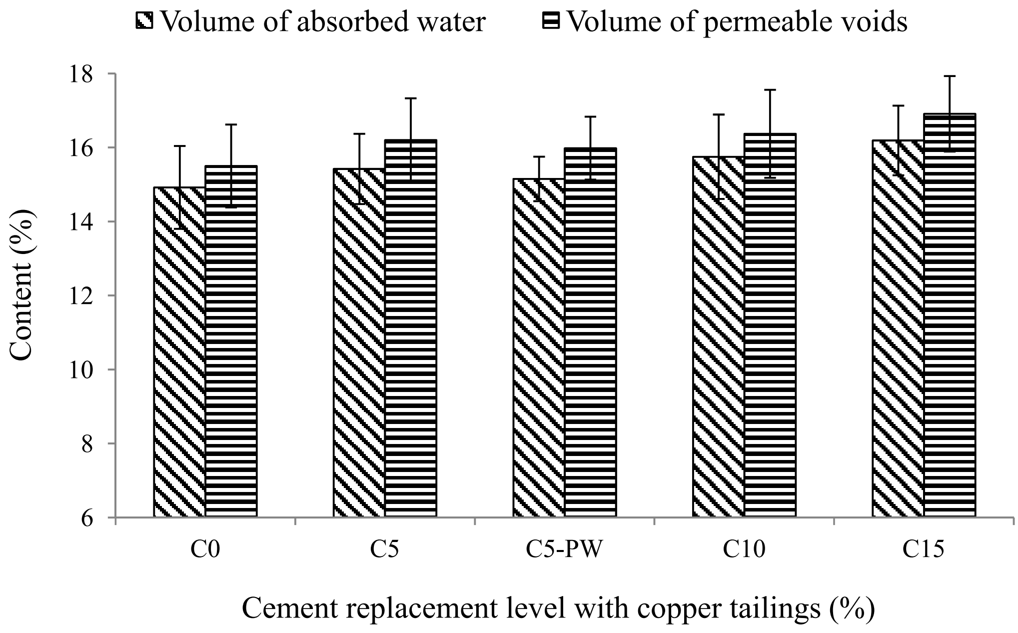


Figure 6.50. Volume of Absorbed Water and Voids in 0.50 w/b Ratio Concretes (cement replacement)

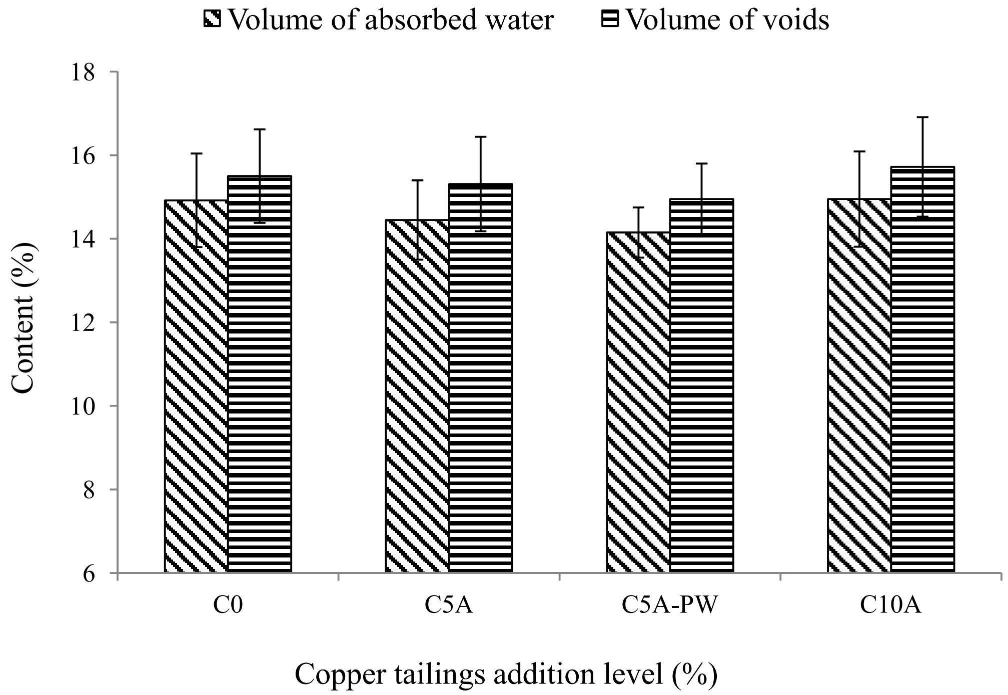


Figure 6.51. Volume of Absorbed Water and Voids in 0.50 w/b Ratio Concretes (additive mixtures)

6.3.2.4 Potential Sulfate Expansion of Mortars

Figures 6.52 and 6.53 show the expansion values of mortar specimens blended with gypsum. The values for mixtures containing copper tailings as a cement replacement material are shown in Figure 6.52 and they are 0.043 for C0, 0.047 for C5, 0.046 for C5-PW, 0.055 for C10 and 0.059 for C15. Similarly, the values shown in Figure 6.53 for mixtures containing copper tailings as a mortar additive were 0.043 for C0, 0.047 for C5A, 0.046 for C5A-PW and 0.050 for C10A. The negligible expansion of the C0 samples which are comparable to the ASTM C 150 (ASTM, 2009) limit of 0.04% for sulfate resisting cement was attributed to the low tricalcium aluminate (C3A) content of slag cement. It was also expected that in mixtures containing copper tailings as a cement replacement material, further dilution of the C3A component of the cement will lead to higher resistance against sulfate attack. However, the reverse was the case; increase in cement replacement levels with copper tailings led to a gradual increment in expansion values. Similar, trend was also observed in mixtures containing copper tailings as an additive.

The coarse and porous tailings particles with high water absorption property of 13.8% made the blended specimens more permeable. Hence, as the copper tailings content of mortars increased, the higher permeability of these specimens intensified water ingress. The readily available water may have facilitated faster migration of sulphate ions, thereby increasing sulphate attack of blended samples. Investigating the sulfate resistance of mortars containing recycled fine aggregates as a partial replacement of natural fine aggregate, Lee et al. (2005) suggested that the high water absorption characteristics of these aggregates contributed immensely to the increased expansion observed in specimens. Similarly, Hossain (2009) observed that concretes containing porous volcanic scoria as a cement supplement showed poor resistance compared to that of Type I/V control concretes after 48 months exposure to sulfate environment. Clearly, the increased expansion of the copper tailings blended samples is traceable to their higher water permeation compared to the control sample.

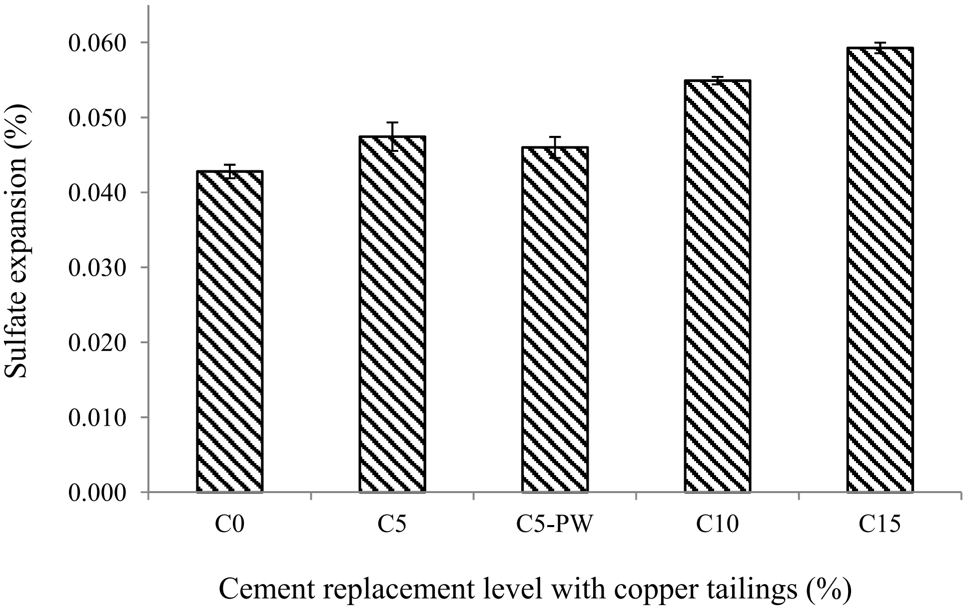


Figure 6.52. Potential Sulfate Expansion of Mortars (cement replacement)

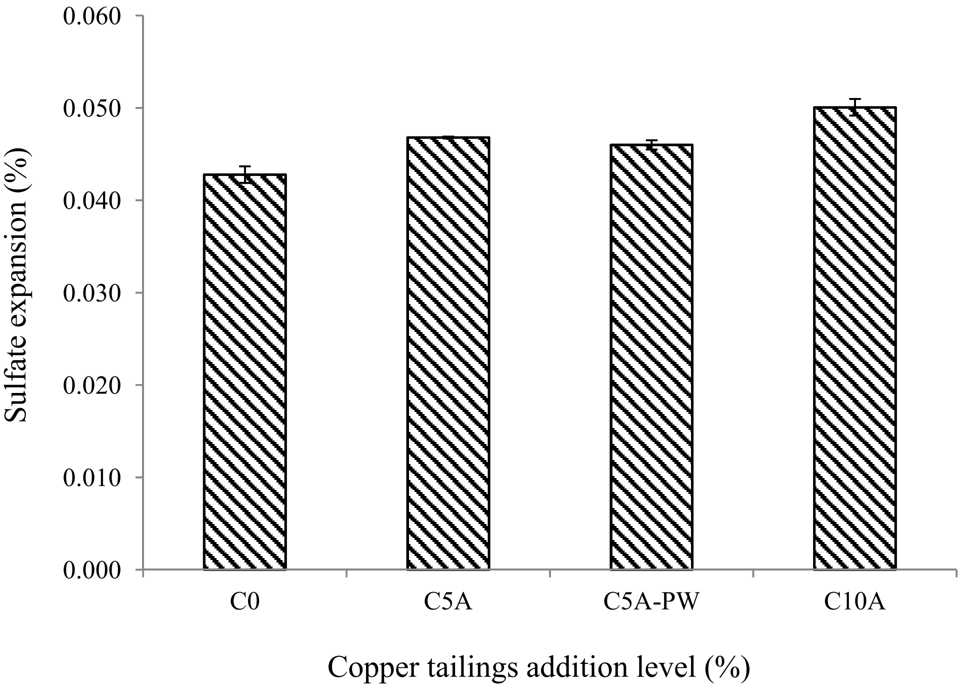


Figure 6.53. Potential Sulphate Expansion of Mortars (additive mixtures)

6.3.2.5 Acid Resistance of Mortars

Table 6.1 shows the mass loss values of mortar samples after exposure to 5% HCl aqueous solution for 28 days. The percentage losses in mass of samples containing copper tailings as a cement replacement material were 4.3% for C0, 4.1% for C5, 4.1% for C5-PW, 4.0% for C10 and 3.9% for C15. Similarly, the mass loss values of mixtures containing copper tailings as a mortar additive were 3.7% for C5A, 3.6% for C5A-PW and 3.4% for C10A. These results suggest that mixtures containing copper tailings recorded higher resistance to acid attack. It was observed that the use of copper tailings as an additive in mortars and pre-wetting of tailings before use, enhanced sample resistance to acid degradation.

Table 6.1. Acid resistance and chloride penetration depths in mortars (standard deviation in paranthesis)

Mixture name	Mass loss due to acid attack (%)	Depth of chloride penetration (mm)
C0	4.3 (0.07)	10.6 (1.0)
C5	4.1 (0.01)	6.8 (0.5)
C5-PW	4.1 (0.10)	3.7 (0.3)
C10	4.0 (0.03)	4.4 (0.7)
C15	3.9 (0.09)	3.8 (0.4)
C5A	3.7 (0.21)	3.7 (0.4)
C5A-PW	3.6 (0.23)	3.5 (0.9)
C10A	3.4 (0.22)	3.6 (0.4)

6.3.2.6 Acid Resistance of Concretes

The mass losses of concrete samples exposed to aqueous 5% HCl solution for 28 days are shown in Figures 6.54 to 6.59. Figure 6.54 shows that the percentage losses in mass of 0.65 w/b ratio concrete samples containing copper tailings as a cement replacement material were 6.0% for C0, 5.8% for C5, 5.7% for C5-PW, 5.7% for C10 and 5.5% for C15 while Figure 6.56 shows that the values for the 0.57 w/b ratio mixtures were 5.8% for C0, 5.4% for C5, 5.3% for C5-PW, 4.9% for C10 and 4.8% for C15. For the 0.50 w/b ratio mixtures, Figure 6.58 shows that the mass losses were 5.9% for C0, 5.7% for C5, 5.7% for C5-PW, 5.5% for C10 and 5.4% for C15. Similarly, Figure 6.55 shows that the percentage losses in mass of 0.65 w/b ratio mixtures containing copper tailings as a concrete additive were 6.0% for C0, 5.7% for C5A, 5.7% for C5A-PW and 5.6% for C10A while Figure 6.57 shows that the values for the 0.57 w/b ratio mixtures were 5.8% for C0, 3.1% for C5A, 3.0% for C5A-PW and 2.6% for C10A. For the 0.50 w/b ratio mixtures, Figure 6.59 shows that the mass losses were 5.9% for C0, 5.6% for C5A, 5.5% for C5A-PW and 5.4% for C10A.

Compared to the samples containing copper tailings, the C0 samples contained higher quantities of $Ca(OH)_2$ and other hydration products. Thus, it is suspected that the highest loss of mass recorded in the C0 samples was as a result of the dissolution and leaching away of the abundant hydration products present on sample surfaces by the aqueous HCl acid solution. This heightened surface decomposition predisposed the interior of C0 specimens to increased acid attack and deterioration. Conversely, the slightly lower percentage mass loss in samples containing copper tailings as a cement replacement material was partly attributed to cement dilution and secondary hydration reaction induced by copper tailings. Cement dilution caused a reduction in cement reactivity thereby limiting the volume of hydration products formed while secondary hydration reaction reduced the $Ca(OH)_2$ available for acid attack in samples. For the samples containing copper tailings as an additive, it is suspected that denser microstructure, carbonation engendered by air curing and greater bonding of particles in samples induced by the coarse and porous tailings may have also contributed to the enhanced resistance against acid attack. Depths of carbonation higher than that of the ordinary Portland cement (OPC) concrete was observed by Chatveera and Lertwattanaruk (2011) in mixtures containing black rice husk ash (BRHA). However, these BRHA samples showed higher resistance to acid attack compared to the control samples as a result of reduced alkalinity caused by their increased carbonation. Similarly, Chindaprasirt et al. (2004) in their investigation on the effect of fly ash fineness on acid resistance of mortars suggested that samples performance improved as fly ash fineness decreased.

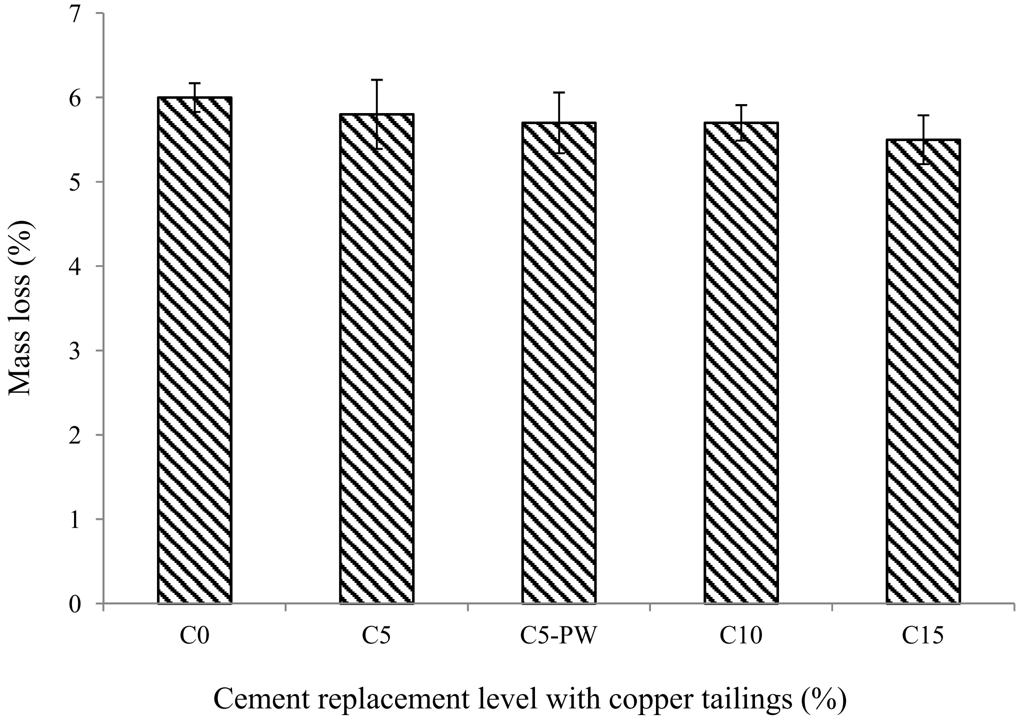


Figure 6.54. Acid Resistance of 0.65 w/b Ratio Concretes (cement replacement)

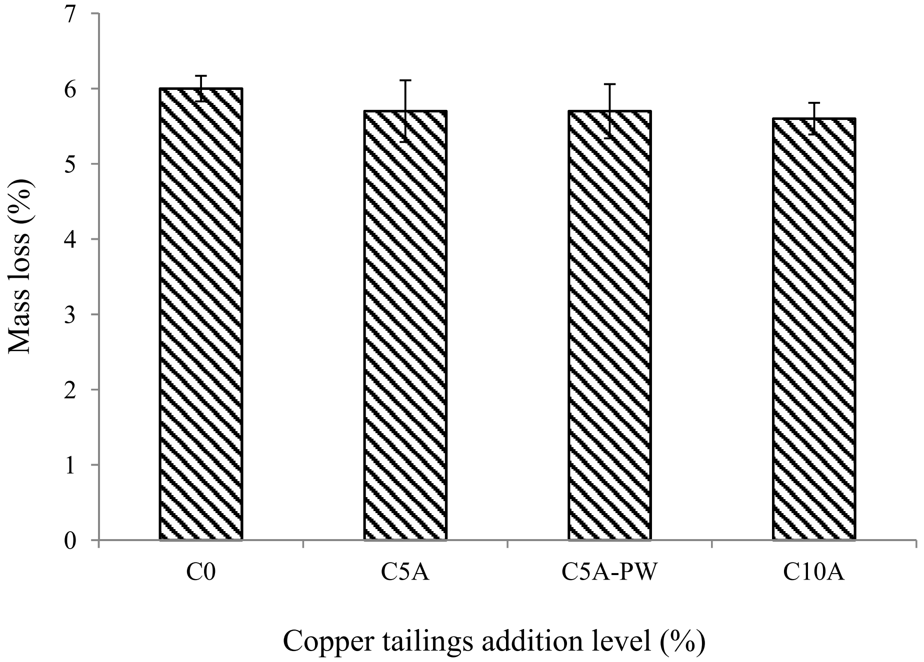


Figure 6.55. Acid Resistance of 0.65 w/b Ratio Concretes (additive mixtures)

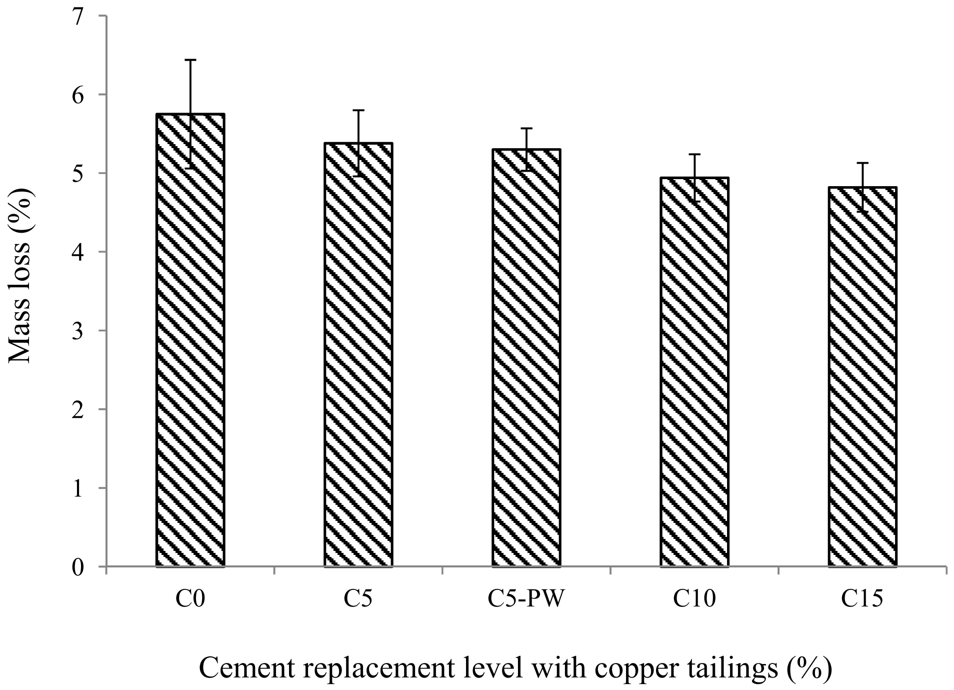


Figure 6.56. Acid Resistance of 0.57 w/b Ratio Concretes (cement replacement)

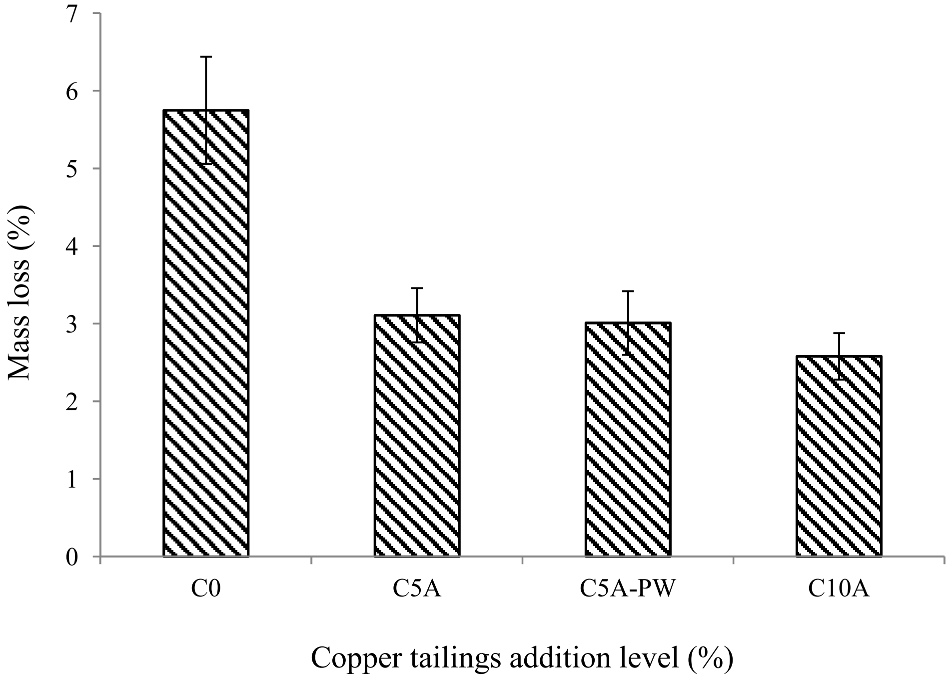


Figure 6.57. Acid Resistance of 0.57 w/b Ratio Concretes (additive mixtures)

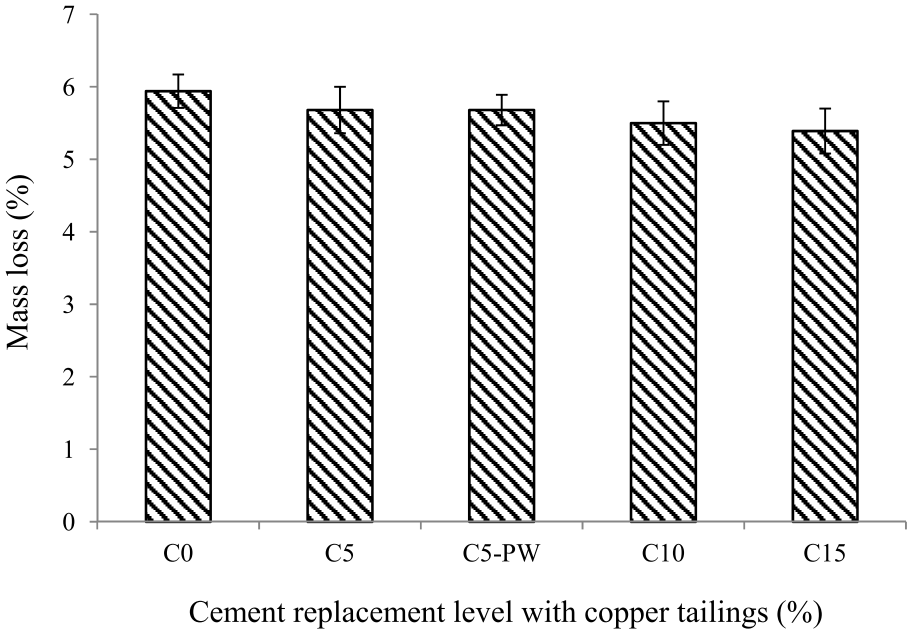


Figure 6.58. Acid Resistance of 0.50 w/b Ratio Concretes (cement replacement)

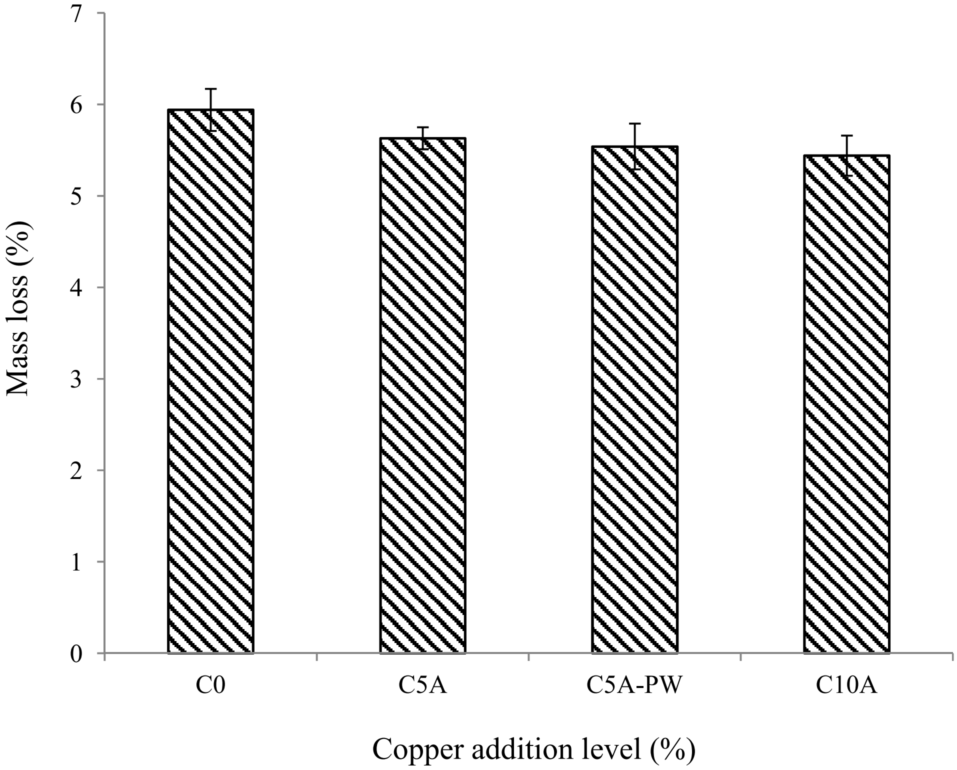


Figure 6.59. Acid Resistance of 0.50 w/b Ratio Concretes (additive mixtures)

6.3.4.7 Rapid Chloride Permeability Test (RCPT)

Several factors such as water-to-cement ratio, fineness of cementitious materials, initial curing, volume of pores, pore refinement, conductivity of pore solution, etc. have been shown to influence the chloride permeability of concrete. Table 6.2 shows the total charge in coulombs transmitted through concrete specimens during the RCPT test. The charge transmitted through the 0.65 w/b ratio concrete samples containing copper tailings as a cement replacement material were 8554.0 for C0, 9269.0 for C5, 9180.0 for C5-PW, 10579.0 for C10 and 11806.0 for C15 while the values for the 0.57 w/b ratio mixtures were 7525.0 for C0, 8256.0 for C5, 8194.0 for C5-PW, 13099 for C10 and 14678 for C15. For the 0.50 w/b ratio mixtures, the charge were 6478.0 for C0, 7076.0 for C5, 6908.0 for C5-PW, 7839.0 for C10 and 9844.0 for C15. Similar trend was observed in samples containing copper tailings as a concrete additive. Though, C10A samples recorded slightly lower charge compared to those of the C5A samples, measured values for both copper addition levels were higher than those of the control samples. The charge values for the 0.65 w/b ratio mixtures were 8554.0 for C0, 10683.0 for C5A, 10641.0 for C5A-PW and 8976.0 for C10A while the values for the 0.57 w/b ratio mixtures were 7525.0 for C0, 12975.0 for C5A, 12653.0 for C5A-PW and 11090.0 for C10A. For the 0.50 w/b ratio mixtures, the values were 6478.0 for C0, 7495.0 for C5A, 7382.0 for C5A-PW and 6841.0 for C10A.

The air curing method used in this study may have contributed to the high charge recorded. The increasing charge transmitted through samples as copper tailings content became higher was anomalous given that the filler and pore refinement effect of the fine particles of the tailings were expected to reduce chloride ingress. Several studies have shown that cementitious materials reduce the chloride permeability of concrete specimens. However, Shi et al. (1998) suggested that it is incorrect to use the total transmitted charge to determine the chloride penetration resistance of concretes containing supplementary cementing materials. The charge transmitted through concrete containing cementitious materials indicates its overall electrical conductivity rather than its resistance to chloride penetration (Wee et al., 2000). In a subsequent study, Shi (2004) asserted that the propensity of supplementary cementing materials to affect significantly the chemistry or electrical conductivity of pore solution invalidated the use of RCPT as a means of determining chloride permeability. Thus, the presence of copper ions, the high conductivity of the copper tailings, and the higher water absorption capacities of copper blended concretes may have increased the conductivity of these specimens during the tests. Hence, the test results were probably a measure of sample conductivity rather than chloride permeability. This is supported by the suggestion by Naik et al. (2006) that increase in water content of samples and concentration of ions in pore solution decrease the resistivity of cement pastes.

Table 6.2. RCPT values and chloride penetration depths in concretes

W/b ratio	Mixture name	Charge passed (coulomb)	Chloride penetration depth (mm)
0.65	C0	8554 (785)	23.8 (1.9)
	C5	9269 (798)	14.8 1.2)
	C5-PW	9180 (840)	11.9 (0.4)
	C10	10579 (943)	11.2 (1.3)
	C15	11806 (596)	6.3 (0.4)
	C5A	10683 (1130)	10.8 (1.3)
	C5A-PW	10641 (619)	10.1 (1.1)
	C10A	8976 (1256)	3.4 (0.6)
0.57	C0	7525 (875)	19.9 (1.0)
	C5	8256 (1261)	13.8 1.3)
	C5-PW	8194 (746)	11.8 (1.1)
	C10	13099 (1207)	9.1 (1.0)
	C15	14678 (1378)	4.1 (0.8)
	C5A	12975 (497)	7.6 (0.7)
	C5A-PW	12653 (710)	7.2 (0.8)
	C10A	11090 (1314)	3.4 (0.8)
0.50	C0	6478 (655)	16.1 (1.1)
	C5	7076 (648)	8.3 (1.4)
	C5-PW	6908 (874)	7.2 (0.7)
	C10	7839 (1207)	6.1 (1.1)
	C15	9844 (1068)	2.1 (0.2)
	C5A	7495 (1001)	3.2 (1.3)
	C5A-PW	7382 (943)	3.1 (1.0)
	C10A	6841 (1271)	1.6 (1.2)

6.3.2.8 Chloride Penetration Depths in Mortars

The chloride penetration depths calculated for samples after 28 days of immersion in 5% NaCl solution are also presented in Table 6.1. These results showed that mortar mixtures containing copper tailings had enhanced chloride penetration resistance compared to the control samples. It was observed that the depth of chloride penetration progressively decreased as the tailings content of samples increased. For the mixtures containing copper tailings as a cement replacement material, the depths of penetration were 10.6 mm for C0, 6.8 mm for C5, 3.7 mm for C5-PW, 4.4 mm for C10 and 3.8 mm for C15 samples. Similarly, the depth of penetrations for mixtures containing copper tailings as a mortar additive were 3.7 mm for C5A, 3.5 mm for C5A-PW and 3.6 mm for C10A.

6.3.2.9 Chloride Penetration Depths in Concretes

The average chloride penetration depths calculated for concrete specimens after 28 days of immersion in 5% NaCl solution are presented in Table 6.2. The penetration depths for the 0.65 w/b ratio concrete samples containing copper tailings as a cement replacement material were 23.8 mm for C0, 14.8 mm for C5, 11.9 mm for C5-PW, 11.2 mm for C10 and 6.3 mm for C15 while the values for the 0.57 w/b ratio mixtures were 19.9 mm for C0, 13.8 mm for C5, 11.8 mm for C5-PW, 9.1 mm for C10 mm and 4.1 mm for C15. For the 0.50 w/b ratio mixtures, the penetration depths were 16.1 mm for C0, 8.3 mm for C5, 7.2 mm for C5-PW, 6.1 mm for C10 and 2.1 mm for C15. Similar but more enhanced chloride resistance was observed in mixtures containing copper tailings as a concrete additive. The penetration depths for the 0.65 w/b ratio mixtures were 10.8 mm for C5A, 10.1 mm for C5A-PW and 3.4 mm for C10A while the values for the 0.57 w/b ratio mixtures were 7.6 mm for C5A, 7.2 mm for C5A-PW and 3.4 mm for C10A. For the 0.50 w/b ratio mixtures, the penetration depths were 3.2 mm for C5A, 3.1 mm for C5A-PW and 1.6 mm for C10A.

The reduced depths of chloride penetration witnessed in these copper blended mixtures were attributed to segmentation of pores by the filler effect of the very fine particles of the tailings and the secondary hydration products caused by it. According to Mooseberg-

Bustnes *et al.*, (2004), ultra-fine fillers improve pore structure thereby influencing long-term strength and durability properties of cement pastes positively. The interaction between chloride and metals in the tailings may have also influenced test outcomes. The presence of lead (Pb) in copper tailings (see Table 3.1), may have caused the precipitation of the almost insoluble lead (II) chloride ($PbCl_2$) from the aqueous NaCl solution, thereby decreasing the soluble chloride content and migration in samples. This is supported by the assertion by Haque et al. (1992) that fly ash may substantially decrease free chloride availability and concentration in concrete samples immersed in chloride solution.

A comparison of chloride penetration depths and RCPT values highlight an inverse relationship between these two tests, whereby chloride penetration depths decreased as charge passed increased. This is abnormal, suggesting that these two test results are independent of each other, and are affected by different factors. While RCPT results were influenced by the increased conductivity of samples induced by copper ions contained in tailings, chloride penetration depth values were mainly dependent on sample improved microstructure, reduced pore interconnectivity and the precipitation reaction between Pb and the chlorides. Lack of correlation between chloride penetrations and RCPT values obtained from concrete samples containing GGBFS and SF was also reported by (Wee et al., 2000). In a related investigation of concretes made with different types of binders, Meck and Sirivivatnanon (2003) equally observed poor correlation between RCPT test results and chloride penetration depths obtained from immersion tests. Furthermore, a comparison of results in Figures 6.46 to 6.51 and Table 6.2 suggest that depth of chloride penetration decreased as the water absorption of samples increased. This is counterintuitive and signifies that percentage water absorption is not a good indicator of the chloride resistance property of these concretes. Similar observations about the unreliability of water absorption as an indicator of chloride migration in concrete were made by (Chia & Zhang, 2002; De Schutter & Audenaert, 2004).

6.3.2.10 Accelerated Corrosion Test

During accelerated corrosion test of concrete by impressed voltage, three distinct stages can be observed. In stage 1, the current transmitted gradually increased as sample resistivity decreased and more chloride solution permeates. At chloride concentration higher than the threshold value, reinforcement depassivation whereby the thin passive protective layer on reinforcement surface is gradually removed by chloride ions occurred. The precursor to stage 2 is maximum current induced by high chloride concentration. Thereafter, formation of corrosion products, which temporarily insulates reinforcement, thereby increasing sample resistivity was initiated. Hence, decreasing current is usually associated with this stage of the test. At the 3rd stage, built-up corrosion products exert stresses on surrounding concrete, and sample cracking is expected to occur once these stresses exceed the tensile strength of concrete. The cracking of concrete is generally accompanied with a sharp increase in current since chloride ions will readily penetrate through cracks on sample. Thus, from the aforementioned discussion, the time to corrosion initiation time is the period from start of test to the time when current decrease commenced. Similarly, the time to cracking is the time interval between start of test and sudden increase in current and crack formation on sample. Figure 6.60 shows a typical current vs. time plot, and how corrosion initiation times of samples were determined.

At the end of these accelerated corrosion tests, cracks were not observed on samples. This occurrence is attributed to the slag cement, 43 mm cover to reinforcement used in the study and the storage of samples in the curing room prior to testing. It is a well known fact that slag cement has high resistance to deterioration. The positive effect of increased reinforcement cover depth is also well known. Similarly, by storing samples in the curing room, miscellaneous factors such as shrinkage cracks which may affect tests were reduced.

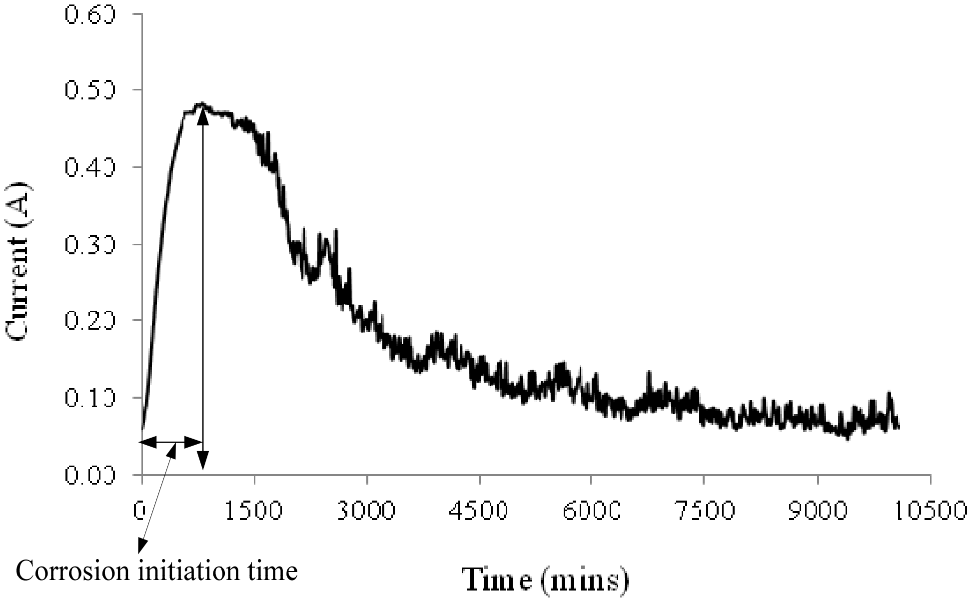


Figure 6.60. A Typical Current vs. Time Plot of Samples

Figures 6.61 to 6.66 show the time to corrosion initiation for mixtures. Figure 6.61 shows that the corrosion initiation time of 0.67 w/b ratio concrete samples containing copper tailings as a cement replacement material were 675 min for C0, 360 min for C5, 630 min for C5-PW, 645 min for C10 and 715 min for C15 while Figure 6.63 shows that the corrosion initiation time for the 0.57 w/b ratio mixtures were 975 min for C0, 673 min for C5, 935 min for C5-PW, 900 min for C10 and 985 min for C15. For the 0.50

w/b ratio mixtures, Figure 6.65 shows that the corrosion initiation time were 1065 min for C0, 895 min for C5, 1195 min for C5-PW, 1130 min for C10 and 1400 min for C15. It was anticipated that copper tailings may hasten corrosion initiation in samples. However, these results suggest that this occurred only in samples containing dry copper tailings at 5% cement replacement level. The behavior of C5 mixtures is probably as a result of increased conductivity in samples and poor void interconnectivity refinement compared to the other samples containing copper tailings. Nonetheless, the use of pre-wetted tailings ameliorated this negative effect, especially as w/b ratio decreased.

Figure 6.62 shows that the corrosion initiation time of 0.65 w/b ratio mixtures containing copper tailings as a concrete additive were 675 min for C0, 770 min for C5A, 730 min for C5A-PW and 820 min for C10A while Figure 6.64 shows that the values for the 0.57 w/b ratio mixtures were 975 min for C0, 1015 min for C5A, 1033 for C5A-PW and 1190 for C10A. For the 0.50 w/b ratio mixtures, Figure 6.66 shows that the corrosion initiation time were 1065 min for C0, 1400 min for C5A, 1480 min for C5A-PW and 1625 min for C10A. Generally, the corrosion resistance performance of mixtures became better with decreases in w/b ratio. However, compared to the mixtures containing copper tailings as a cement replacement material, these results imply that the use of copper tailings as an additive in mixtures has a more significant beneficial impact on concrete durability.

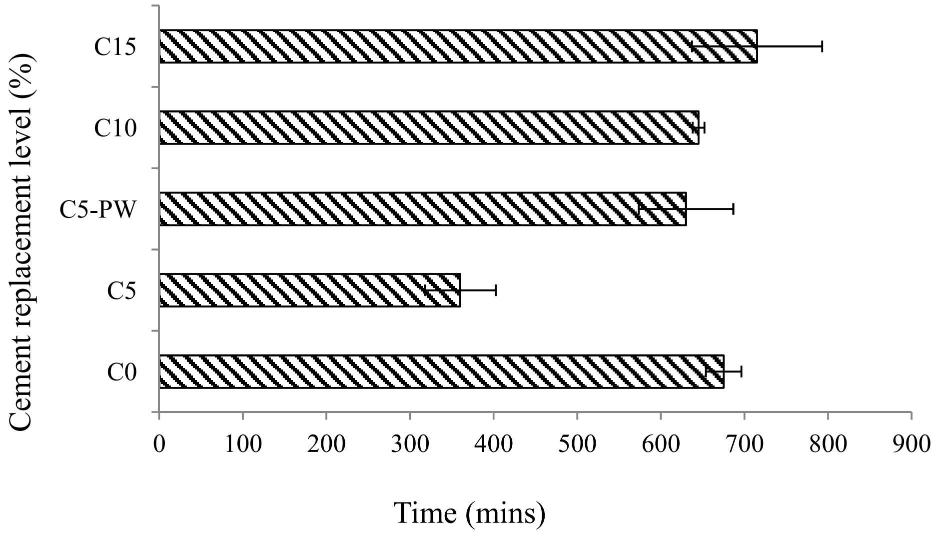


Figure 6.61. Time to Corrosion Initiation in 0.65 w/b Ratio Concretes (cement replacement)

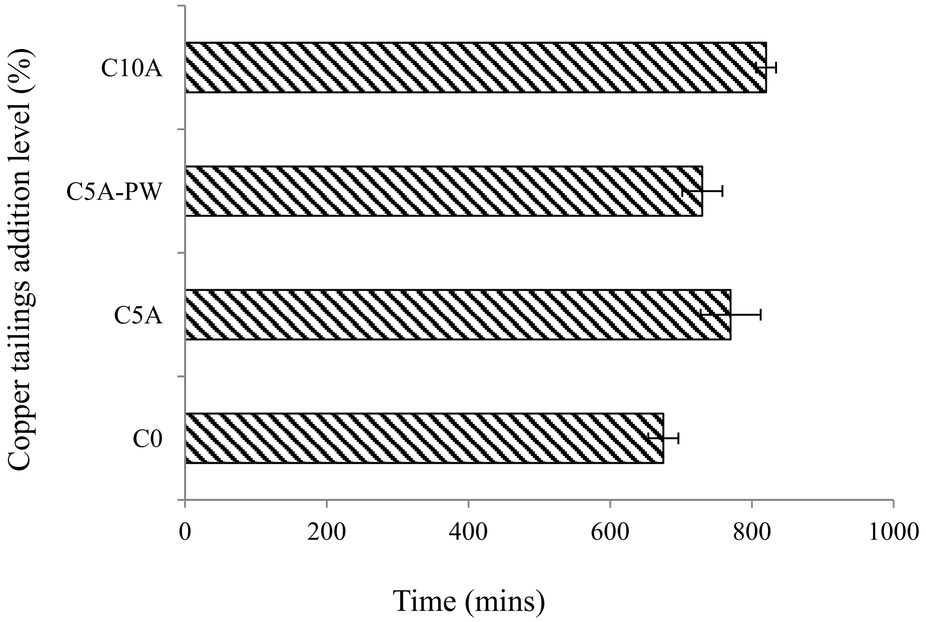


Figure 6.62. Time to Corrosion Initiation in 0.65 w/b Ratio Concretes (additive mixture)

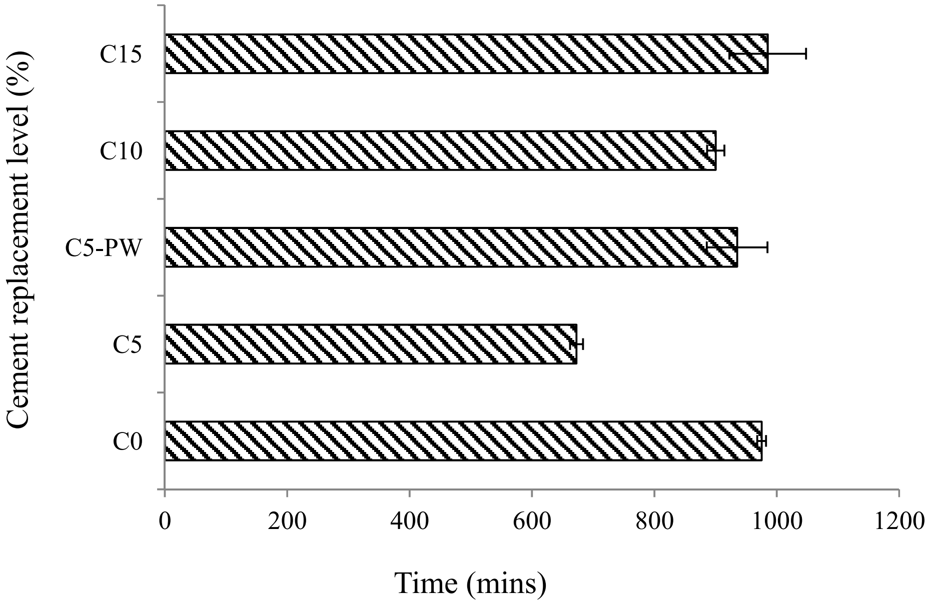


Figure 6.63. Time to Corrosion Initiation in 0.57 w/b Ratio Concretes (cement replacement)

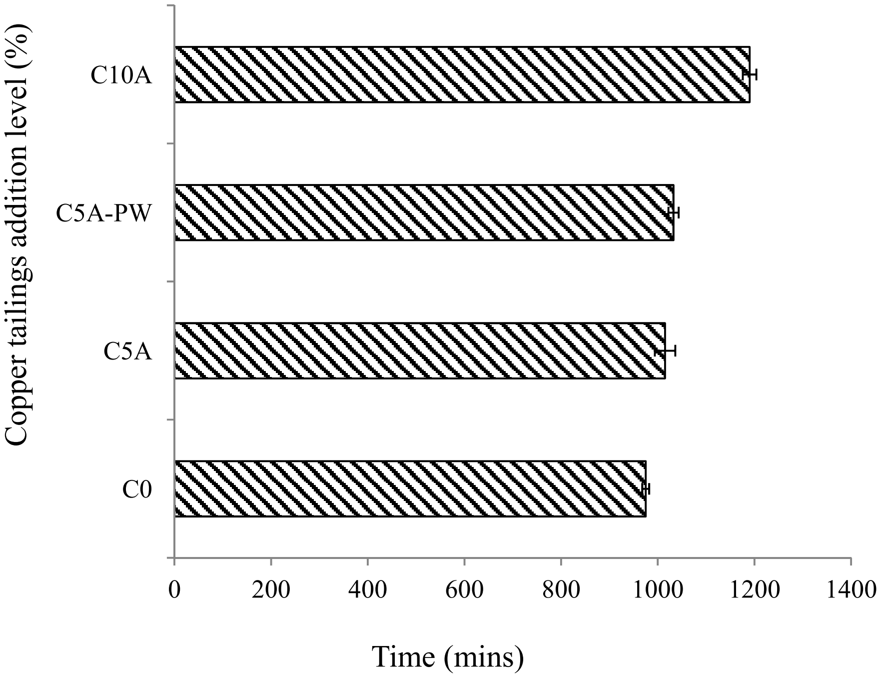


Figure 6.64. Time to Corrosion Initiation in 0.57 w/b Ratio Concretes (additive mixture)

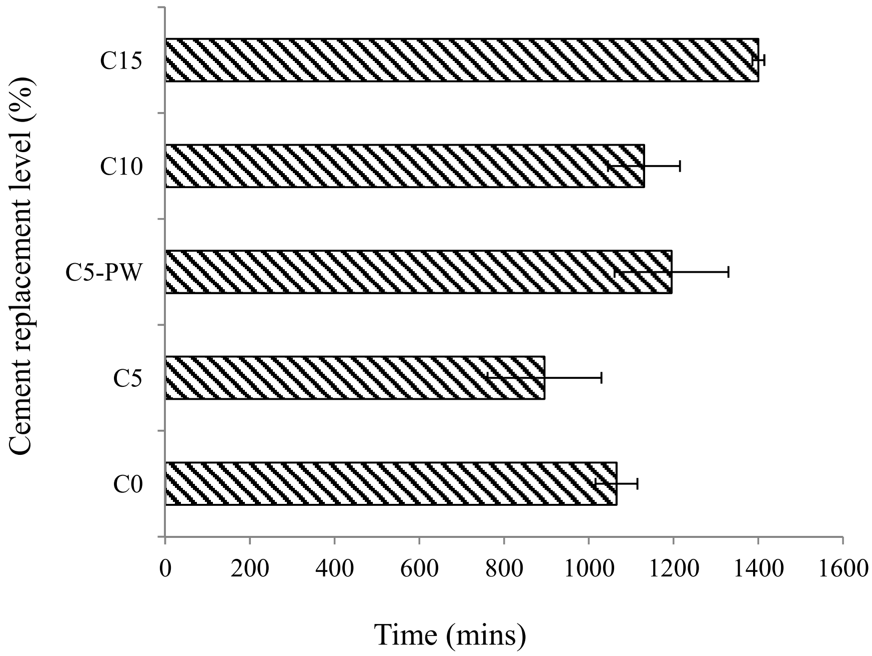


Figure 6.65. Time to Corrosion Initiation in 0.50 w/b Ratio Concretes (cement replacement)

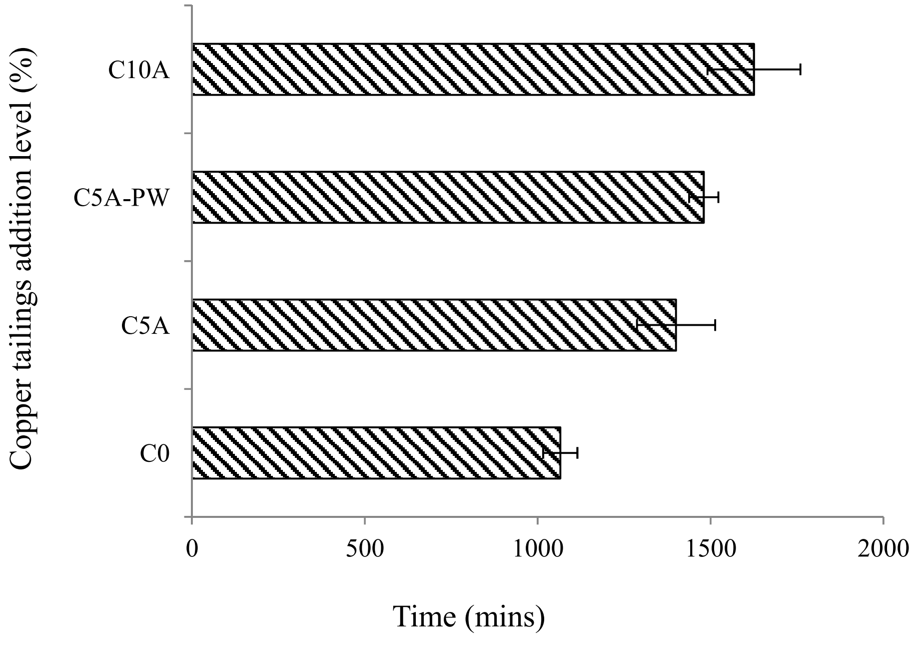


Figure 6.66. Time to Corrosion Initiation in 0.50 w/b Ratio Concretes (additive mixture)

6.3.2.11 Half-cell Potential Measurements

Table 6.3 shows the ASTM C 876 (2009) HCP guidelines while Figure 6.4 shows the corrosion potentials of samples. HCP values immediately after the accelerated corrosion test for 0.65 w/b ratio concretes containing copper tailings as a cement replacement material varied from -1205 to -1294 mV and -1205 to -1313 mV for mixtures containing tailings as a concrete additive. For the 0.57 w/b ratio mixtures containing copper tailings as a cement replacement material, the values varied from -1246 to -1308 mV and -1246 to -1328 mV for mixtures containing tailings as a concrete additive while values recorded for the 0.50 w/b ratio mixtures fluctuated between -1254 to -1312 mV and -1254 to -1292 mV for mixtures containing tailings as a cement replacement material and as an additive in concrete, respectively. These very high values seem to suggest occurrence of severe corrosion in samples. However, this is not actually the case. The high electronegative potential values were as a result of the saturation of samples at the time these readings were taken. Soleymani and Ismail (2004) were of the opinion that high moisture content can raise HCP values of samples not undergoing corrosion significantly. HCP reading taken after 1 month of air drying of samples confirmed the aforementioned submission on the effect of moisture content on HCP readings.

The second HCP values for 0.65 w/b ratio concretes containing copper tailings as a cement replacement material varied from -286 to -331 mV and -286 to -334 mV for mixtures containing tailings as a concrete additive. For 0.57 w/b ratio mixtures containing copper tailings as a cement replacement material, the variation in values were -233 to -296 mV and -233 to -265 mV for additive mixtures. Similarly, for 0.50 w/b ratio concretes, values fluctuated between -207 to -262 mV and -207 to -262 mV for mixtures containing tailings as a cement replacement material and as an additive in concrete, respectively. This final set of HCP results have some measures of validity compared to the first set of values. However, according ASTM C 876 (2009) guidelines shown in Table 6.3, the only inference which can be drawn from these HCP results is that the corrosion states of samples are uncertain.

Table 6.3. ASTM C 876 half-cell potential guidelines

HCP readings vs. Cu/$CuSO_4$ reference electrode	**Corrosion activity**
Less negative than -200 mV	90% probability of no steel corrosion
Between -200 mV and -350 mV	Steel corrosion is uncertain
More negative than -350 mV	90% probability of steel corrosion

Table 6.4. Half-cell potential measurements

Mixture type	**W/B ratio**	**Mixture name**	**Initial HCP (mV)**	**Final HCP (mV)**
Cement Replacement	0.65	C0	-1205	-286
		C5	-1274	-304
		C5-PW	-1272	-301
		C10	-1284	-318
		C15	-1294	-331
	0.57	C0	-1246	-233
		C5	-1282	-251
		C5-PW	-1269	-244
		C10	-1289	-272
		C15	-1308	-296
	0.50	C0	-1254	-207
		C5	-1274	-211
		C5-PW	-1253	-226
		C10	-1295	-233
		C15	-1312	-262
Additive	0.65	C5A	-1303	-284
		C5A-PW	-1280	-281
		C10A	-1313	--334
	0.57	C5A	-1304	-261
		C5A-PW	-1287	-259
		C10A	-1328	-265
	0.50	C5A	-1270	-248
		C5A-PW	-1250	-244
		C10A	-1292	-252

6.3.2.12 Visual Inspection

Figure 6.67 and 6.68 show embedded reinforcements after extraction from samples. Visual inspections revealed that no major deterioration and loss of section took place in all embedded reinforcements. In all samples, only thin traces of red oxide on few locations around reinforcement surfaces were observed. The absence of severe corrosion activity in samples may be attributed to the following reasons. First, the use of slag cement and concrete cover of 43 mm and sample curing time of 90 days constitute a formidable resistance measure against corrosion. Secondly, since these samples did not crack during accelerated corrosion tests, huge influx of chloride ions which would have initiated large-scale degradation of reinforcements could not take place.

Nonetheless, given the increased conductivity of copper tailings blended samples and the shorter time to initiation of corrosion compared to the control samples, especially the C5 samples, higher corrosion activity was expected. However, this was not observed. Fe has electronegative potential of -0.44 mV, and its rate of corrosion increases as it become more electronegative. However, it is suspected that the presence Cu with a standard electrode potential of +0.34V in tailings may have stalled the corrosion process by making steel less negative. Similar allusion was made by Garcés et al. (2007), when they suggested that though, the addition of conductive carbon material to concrete increases its porosity, it also reduces corrosion.

Figure 6.67. Some of the Corrosion Test Reinforcements

Figure 6.68. Close View of Some Corrosion Test Reinforcements

6.3.3 Leaching of Heavy Metals from Concretes

Some of the US Code of Federal Regulations CFR (2011) leachate quality criteria are shown in Table 6.5, while the concentrations of heavy metals in leachates are presented in Tables 6.6 and 6.7. The concentrations of the three heavy metals evaluated in leachates were very infinitesimal. However, the concentrations of Cr in leachates were much higher than those recorded for Cd and Pb. Higher leaching of Cr in mortars was also observed by (Deja, 2002; Giergiczny & Król, 2008). For all the mixtures investigated; in comparison to deionized water, the use of acetic acid as an extractant yielded higher concentrations of heavy metals in leachates. Similarly, the use of copper tailings as an additive seemed to be more effective in immobilizing heavy metals. Test results also suggest that w/b ratio has a considerable impact on the release of heavy metals from concretes containing tailings as an additive. Thus, concentrations of heavy metals in leachates generally became smaller as w/b ratio became reduced. Higher degree of immobilization was also observed as tailıngs content increased. These occurrences could be attributed to the denser microstructure of samples and improved pore refinement and the consequent reduction in concrete permeability induced by fine particles of the tailings. Overall, these leaching test results indicated clearly that the leaching of selected heavy metal ions from concretes containing copper tailings as a cement replacement material or as a concrete additive were very low and did not exceed the CFR limits shown in Table 6.4. Similar observations were made in related studies by (Zain et al, 2004; Alp et al., 2008).

Table 6.5. US CFR limits for some heavy metals

Element	TCLP (mg/L)
Cr	5
Cd	1
Pb	5

Table 6.6. Concentration of heavy metals in leachates (cement replacement mixtures)

Extractant	**W/B ratio**	**Mix name**	**Concentration in leachate (mg/l)**		
			Cr	**Cd**	**Pb**
Deionised water	0.65	C5	0.122	< 0.00004	0.0014
	0.57	C5	0.114	< 0.00004	< 0.0002
		C10	0.099	< 0.00004	< 0.0002
		C15	0.135	< 0.00004	< 0.0002
	0.50	C5	0.048	< 0.00004	< 0.0002
		C10	0.085	< 0.00004	0.0005
		C15	0.101	< 0.00004	0.0003
Acetic acid	0.65	C5	0.295	0.0002	0.0004
	0.57	C5	0.194	0.00005	0.0004
		C10	0.281	< 0.00004	0.0005
		C15	0.219	0.00009	0.0008
	0.50	C5	0.053	< 0.00004	0.0004
		C10	0.135	< 0.00004	0.0005
		C15	0.176	< 0.00004	0.0006

Table 6.7. Concentration of heavy metals in leachates (additive mixtures)

Extractant	**W/B ratio**	**Mix name**	**Concentration in leachate (mg/l)**		
			Cr	Cd	Pb
Deionised water	0.65	C5A	0.102	< 0.00004	0.00006
	0.57	C5A	0.114	< 0.00004	0.0003
		C10A	0.082	< 0.00004	0.0002
	0.50	C5A	0.120	0.00005	0.0033
		C10A	0.103	< 0.00004	< 0.0002
Acetic acid	0.65	C5A	0.323	< 0.00005	0.0007
	0.57	C5A	0.263	< 0.00004	0.0008
		C10A	0.174	< 0.00004	0.0003
	0.50	C5A	0.123	0.00005	0.0038
		C10A	0.109	< 0.00004	0.0007

6.3.4 Material Cost Analysis of Concretes

The material cost estimates for preparing 1 m^3 of concrete mixtures were determined using the local prices of construction materials in North Cyprus and are in United States dollars. The following prices were used: \$0.11 per kg of cement, \$14.50 per m^3 of fine aggregate, \$13.43 per m^3 of coarse aggregate and handling cost (HC) of \$0.02 per kg of copper tailings. Furthermore, as a basis for comparing the mixtures, the cost efficiency approach was used. The cost efficiency factor CEF (%) was calculated to show the ratio of compressive strength to cost per m^3 of each mixture. It was determined using the following formula (Agarwal and Gulati, 2006),

$$CEF = \frac{F_c}{C} \times 100 \tag{6.1}$$

Where CEF is cost efficiency factor, F_C is the average compressive strength of mixtures at 28 days and 90 days while C is the cost per m^3 of concrete.

6.3.4.1 Material Cost Analysis Results

Tables 6.8 and 6.9 present the material cost estimates of concrete mixtures. Table 6.8 showed that for mixtures containing copper tailings as a cement replacement material, the cost of producing 1 m^3 of each concrete mixture strongly depends on the cement replacement level. However, these reductions in cost as cement replacement level increased could not translate into outright cost gains since compressive strengths of concretes equally decreased with increase in copper tailings content of mixtures. The CEF indices in Table 6.7 showed that the cost efficiencies of mixtures containing copper tailings were generally lower than those of the control concretes at 28 days. This occurrence was as a result of poor strength of copper tailings mixtures at early age. However, by the 90th day, when considerable secondary hydration and strength development had occurred; improvements in CEF values were seen. However, it was also observed that the use of copper tailings as a cement replacement material in 0.65 w/b ratio mixtures did not present any cost benefit.

Table 6.9 highlights a different trend for mixtures containing copper tailings as an additive in concrete. At 28 days, comparable and slightly higher CEF values were recorded for mixtures containing copper tailings. The improvements in cost efficiencies were more noticeable in C5A-PW mixtures at the 90th day. Thus, these results suggest that there are cost benefits in using pre-wetted copper tailings as an additive in concrete, and these gains will become more significant on the long-term.

Table 6.8. Cost estimates and efficiency factors of concretes (cement replacement)

		Mix constituents			**Mix cost**					**CEF**	
W/b ratio	**Mix**	**Cement (kg)**	**Fine (m^3)**	**Coarse (m^3)**	**Cement ($)**	**Fine ($)**	**Coarse ($)**	**HC ($)**	**Cost ($)**	**28 d (%)**	**90 d (%)**
0.65	C0	346	0.34	0.35	38.1	4.9	4.7	0.0	47.7	49.1	61.9
	C5	329	0.34	0.35	36.2	4.9	4.7	0.3	46.2	49.0	55.9
	C5-P	329	0.34	0.35	36.2	4.9	4.7	0.3	46.2	49.6	58.3
	C10	311	0.34	0.35	34.2	4.9	4.7	0.7	44.5	44.9	57.3
	C15	294	0.34	0.35	32.3	4.9	4.7	1.0	43.0	42.1	53.5
0.57	C0	395	0.29	0.37	43.5	4.2	5.0	0.0	52.8	55.7	61.8
	C5	375	0.29	0.37	41.3	4.2	5.0	0.4	51.0	54.7	63.2
	C5-P	375	0.29	0.37	41.3	4.2	5.0	0.4	51.0	54.2	64.2
	C10	355	0.29	0.37	39.1	4.2	5.0	0.8	49.2	54.9	63.5
	C15	335	0.29	0.37	36.9	4.2	5.0	1.2	47.4	48.8	63.5
0.50	C0	450	0.30	0.35	49.5	4.4	4.7	0.0	58.6	61.5	75.3
	C5	428	0.30	0.35	47.1	4.4	4.7	0.4	56.6	59.7	75.7
	C5-P	428	0.30	0.35	47.1	4.4	4.7	0.4	56.6	61.3	77.6
	C10	405	0.30	0.35	44.6	4.4	4.7	0.9	54.5	55.4	70.6
	C15	383	0.30	0.35	42.1	4.4	4.7	1.3	52.5	56.2	72.7

Table 6.9. Cost estimates and efficiency factors of concretes (additive mixtures)

		Mix constituents			**Mix cost**					**CEF**	
W/b ratio	**Mix**	**Cement (kg)**	**Fine (m^3)**	**Coarse (m^3)**	**Cement ($)**	**Fine ($)**	**Coarse ($)**	**HC ($)**	**Cost ($)**	**28 d (%)**	**90 d (%)**
0.65	C0	346	0.34	0.35	38.1	4.9	4.7	0.0	47.7	49.1	61.9
	C5A	346	0.34	0.35	38.1	4.9	4.7	0.3	48.0	49.8	62.5
	C5A-P	346	0.34	0.35	38.1	4.9	4.7	0.3	48.0	50.2	63.7
	C10A	346	0.34	0.35	38.1	4.9	4.7	0.7	48.4	47.7	52.7
0.57	C0	395	0.29	0.37	43.5	4.2	5.0	0.0	52.8	55.7	61.8
	C5A	395	0.29	0.37	43.5	4.2	5.0	0.4	53.2	59.2	68.8
	C5A-P	395	0.29	0.37	43.5	4.2	5.0	0.4	53.2	58.7	70.0
	C10	395	0.29	0.37	43.5	4.2	5.0	0.8	53.6	57.1	66.5
0.50	C0	450	0.30	0.35	49.5	4.4	4.7	0.0	58.6	61.5	75.3
	C5A	450	0.30	0.35	49.5	4.4	4.7	0.4	59.0	61.2	74.8
	C5A-P	450	0.30	0.35	49.5	4.4	4.7	0.4	59.0	65.1	78.3
	C10A	450	0.30	0.35	49.5	4.4	4.7	0.9	59.5	62.6	74.9

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Copper tailings deposits constitute serious environmental menace across the world. This study explored the possibility of utilizing this waste material in cement based mixtures as a way of ameliorating the environmental devastation associated with its disposal. These copper tailings are porous, coarse and acidic with high concentrations of heavy metals. The incorporation of dry copper tailings in mortars and concretes impacted mixture consistency negatively. However, at 5% utilization level, this drawback was nullified through the use of pre-wetted tailings. The addition of copper tailings to cement pastes caused slight delays in setting time. Copper tailings improved the mechanical strengths of mortars, especially when it was used as an additive at 5% addition level. Compared to concrete mixtures containing copper tailings as a cement replacement material, mechanical strengths much better than those of the control samples were obtained from mixtures containing copper tailings as a concrete additive.

Results suggest that the ASTM C 1202 RCPT may not be appropriate for determining chloride migration in concretes containing conductive materials. Despite the increased void and water absorption properties of mixtures containing copper tailings, their resistances to acid attack and chloride ingress were superior to those of the control mixtures. Accelerated corrosion tests also showed that copper tailings generally delay corrosion initiation time in concretes; except at 5% cement replacement level, where it occurred faster than those of the control samples. These improved durability performances were more pronounced in mixtures containing copper tailings as an additive. HCP measurements performed on samples showed that the corrosion status of all samples cannot be predicted. Furthermore, visual inspections of reinforcements embedded in accelerated corrosion test samples revealed that regardless of the improved conductivity of mixtures containing copper tailings, corrosion induced deterioration did not occur in these blended samples.

TCLP tests results demonstrated that on exposure to mild and very aggressive leaching mediums, concretes containing copper tailings may not be harmful to humans and the environment. Cost efficiency analyses suggested that it is more profitable to use copper tailings as an additive in mortars, especially with pre-wetted tailings at 5% addition level. With the exception of 0.65 w/b ratio mixtures, similar trends were also highlighted for concretes. Comparing all the tests results and analyses, it seems that the use of pre-wetted copper tailings at 5% by mass of cement as an additive in mixtures is the best utilization option. Finally, the utilization of copper tailings in cement-based materials has unquantifiable environmental, financial and socio-economic benefits for local communities. Details of the conclusions drawn from this study are shown below.

7.2 Characterization of Copper Tailings

1. Copper tailings consist of porous and coarse particles. These copper tailings are moderately reactive as a result of low fineness and silica (IV) oxide content.

2. These copper tailings contain significant amount of iron (III), which increased its specific gravity.
3. While the toxic heavy metals content of these copper tailings are high, its pH is very low, and hence, they are very acidic.

7.3. Fresh Properties

7.3.1 Paste Consistency

1. The use of dry tailings in cement pastes increased water demand in mixtures. These water demands of pastes became higher as the copper tailings content of mixtures increased.
2. However, the use of pre-wetted tailings at 5% utilization level ensured that water requirement lower than those of the control mixture was obtained.

7.3.2 Setting Time

1. Copper tailings delay the setting time of pastes. This delay increased as the copper tailings content of mixtures increased.
2. This delay in setting time was slightly exacerbated when pre-wetted tailings were added to mixtures. Nonetheless, these delays in setting time were moderate.

7.3.3 Yield Stress and Flow Spread of Mortars

1. The use of copper tailings as a cement replacement material or additive in mortars increased the yield stress of mixtures. Yield stress became higher as the tailings content of mixtures became higher and test elapsed time increased.
2. The presence of copper tailings in mixtures equally affected the flow spread of mortars negatively. Trends similar to those of mortar yield stress were observed.
3. However, by using pre-wetted tailings, yield stresses and flow spreads comparable to those of the control mixture were obtained.

4. A relationship between yield stress and flow spread was determined. It showed that yield stresses of mixtures increase as flow spreads decrease.

7.3.4 Concrete Slump

1. Copper tailings reduce the consistency of mixtures. This reduction in slump increased as the copper tailings content of mixtures increased. The slump of concretes containing copper tailings equally became reduced as w/b ratio of mixtures decreased.
2. However, by adding pre-wetted tailings to mixtures, concrete slump was improved significantly.

7.4. Hardened Properties

7.4.1 Mechanical Strength

7.4.1.1 Compressive Strength of Mortars

1. Lower strengths compared to those of the control samples were obtained from mixtures containing copper tailings as a cement replacement material at early test ages. However, contrary results were obtained in mixtures containing copper tailings as a mortar additive.
2. In mixtures containing copper tailings as a cement replacement material, compressive strengths higher than those of the control samples at 28 and 90 days, were obtained at 5% substitution level.
3. Conversely, in mixtures containing copper tailings as an additive in mortar, compressive strengths higher than those of the control samples at 28 and 90 days, were obtained at 5% and 10% addition level.
4. Irrespective of the utilization method, pre-wetted tailings improved the compressive strength of mixtures at 28 and 90 days.

7.4.1.2 Compressive Strength of Concretes

1. Lower strengths compared to those of the control samples were obtained from mixtures containing copper tailings as a cement replacement material at all test ages. Strength reductions were dependent on cement substitution level and w/b ratio.
2. Strengths comparable to those of the control samples were only achieved at 90 days from 0.57 and 0.50 w/b ratio mixtures containing copper tailings at 5% cement substitution level.
3. In mixtures containing copper tailings as a concrete additive, compressive strengths comparable and higher than those of the control samples were obtained from the 3 mixture categories at all test ages.
4. The use of pre-wetted tailings at 5% substitution or addition level enhanced the compressive strengths of mixtures.

7.4.1.3 Flexural Strength of Mortars

1. Lower strengths compared to those of the control samples were obtained from mixtures containing copper tailings as a cement replacement material at early ages. However, by the 90th day, flexural strengths comparable to those of the control samples were obtained at 5% cement substitution level.
2. In contrast, strengths higher than those of the control samples were obtained from mixtures containing copper tailings as an additive in mortars at all test ages.
3. Samples containing pre-wetted tailings showed improved performance. Moreover, at 90 days, highest flexural strength was obtained in mixtures containing copper tailings as an additive at 5% addition level.

7.4.1.4 Flexural Strength of Concretes

1. At 28 days, strengths comparable and slightly higher than those of the control samples were observed at 5% and 10% cement substitution levels.
2. Similarly, strengths comparable and higher than those of the control samples were obtained at 28 days from all mixtures containing copper tailings as an additive.
3. At 90 days, substantial improvements in strengths were recorded in 0.65 and 0.57 w/b ratio mixtures containing copper tailings. However, strength retrogression was observed in 0.50 w/b ratio mixtures.
4. The only exception to the strength retrogression observed in 0.50 mixtures were samples containing pre-wetted tailings.

7.4.1.5 Splitting Tensile Strength of Concretes

1. With the exception of C15 from 0.65 w/b ratio concretes, strengths comparable to those of the control samples were obtained from all mixtures containing copper tailings at 28 days.
2. This trend was replicated at 90 days, however, with substantial improvements in the strength of mixtures containing copper tailings. Higher strengths were recorded in mixtures containing copper tailings as a concrete additive.
3. Once more, pre-wetted tailings were shown to be more effective compared to dry tailings in improving concrete strength.

7.4.1.6 Modified Abrasion and Impact Resistance of Mortars

1. In mortar mixtures containing copper tailings as a cement replacement material, resistances to abrasion and impact higher than those of the control mixture were obtained at 5% and 10% cement substitution levels.

2. Compared to the control mixture, all the samples containing copper tailings as an additive in mortar recorded higher resistance against abrasion and impact.

7.4.1.7 Modified Abrasion and Impact Resistance of Concretes

1. In 0.57 and 0.50 w/b ratio mixtures containing copper tailings as a cement replacement material, resistances to abrasion and impact higher than those of the control mixture were obtained at 5% and 10% cement substitution levels.
2. Compared to the control mixture, all the 0.57 w/b ratio samples containing copper tailings as a concrete additive recorded higher resistance against abrasion and impact.
3. Compared to the control mixture, all the 0.50 w/b ratio samples containing copper tailings as an additive in concrete recorded higher resistance against abrasion and impact.
4. With the exception of the C10A samples, the rest of the 0.57 w/b ratio samples containing copper tailings as a concrete additive recorded higher resistance against abrasion and impact.
5. It was observed that lower w/b ratio concretes and mixtures containing pre-wetted tailings showed higher abrasion and impact resistance.

7.4.2 Durability Properties

7.4.2.1 Autoclave Expansion of Pastes

1. With the exception of the C15 samples, other mixtures containing copper tailings as a cement replacement material recorded expansion values lower than those of the control sample.
2. Compared to the control mixtures, all the samples containing copper tailings as a paste additive showed higher resistance to expansion.

3. In both copper tailings utilization methods, 5% seemed the ideal usage level. Moreover, mixtures containing copper tailings as an additive at 5% addition level yielded the best performance.

7.4.2.2 Water absorption and Volume of Permeable Voids in Mortars

1. In mixtures containing copper tailings as a cement replacement material, volumes of absorbed water and voids became higher as the copper tailings content of mixtures increased.
2. Similarly, in the first 4 h, the rates of water absorption of mixtures containing copper tailings as a cement replacement material were much higher than those of the control samples.
3. For the mixtures containing copper tailings as a mortar additive; volume of absorbed water, voids and rates of water absorption similar to those of mixtures containing tailings as a cement replacement material were also observed.
4. However, the use of pre-wetted tailings in mixtures brought about a somewhat reduction in water absorption and void content.

7.4.2.3 Volume of Absorbed Water and Permeable Voids in Concretes

1. For all the w/b ratios evaluated, volumes of absorbed water and voids became higher as the cement substitution level with copper tailings became higher.
2. Similar trend was equally observed in mixtures containing copper tailings as an additive in concrete.
3. However, slight reductions in water absorption and void values were witnessed in samples containing pre-wetted tailings at 5% utilization level.

7.4.2.4 Potential Sulfate Expansion of Mortars

1. While the expansion of the control samples was negligible, increasing expansion of blended samples as the cement substitution level with copper tailings became higher was observed.
2. Similarly, samples containing copper tailings as an additive, showed expansions higher than those of the control samples at all copper addition levels.
3. Nonetheless, the addition of pre-wetted tailings to mixtures reduced expansions at 5% usage level marginally.

7.4.2.5 Acid Resistance of Mortars

1. Resistances higher than those of the control samples were obtained from mixtures containing copper tailings as a cement replacement material. The resistance of copper tailings blended samples to acid attack became more improved as cement substitution level increased.
2. Similar, but more enhanced resistances to acid attack were obtained from mixtures containing copper tailings as a mortar additive.
3. In both copper tailings utilization methods, the use of pre-wetted tailings made a minor impact on sample resistance to deterioration.

7.4.2.6 Acid Resistance of Concretes

1. Compared to the control mixtures, samples containing copper tailings as a cement replacement material showed higher resistance to acid attack.
2. The resistance of copper tailings blended samples to acid attack became more improved as cement substitution level increased.

3. Similar, but more enhanced resistances to acid attack were obtained from mixtures containing copper tailings as a concrete additive. However, best performance was obtained from 0.57 w/b ratio mixtures.
4. The effect of pre-wetted copper tailings on acid resistance of blended samples was not discernible.

7.4.2.7 Rapid Chloride Permeability Test

1. For all the w/b ratios evaluated, charge transmitted through samples was higher than those of the control samples. This charge became higher as the cement substitution level with copper tailings became higher.
2. Similar trend was equally observed in mixtures containing copper tailings as an additive in concrete.
3. This anomalous behavior was ascribed to the presence of conductive copper in blended samples.
4. Hence, it seemed that ASTM C 1202 RCPT is an inappropriate method for evaluating chloride migration in concretes containing conductive materials.

7.4.2.8 Chloride Penetration Depths in Mortars

1. Chloride penetration depths lower than those of the control samples were obtained from mixtures containing copper tailings as a cement replacement material. Resistance of copper tailings blended samples to chloride penetration became higher as cement substitution level increased.
2. Similar, but more enhanced resistances to chloride penetrations were obtained from mixtures containing copper tailings as a mortar additive.
3. Compared to the mixtures containing copper tailings as a cement replacement material, samples containing copper tailings as an additive in mortars yielded

better resistance against chloride penetration. And the use of pre-wetted tailings seemed to have equally enhanced resistance slightly.

7.4.2.9 Chloride Penetration Depths in Concretes

1. For all the w/b ratios evaluated, chloride penetration depths lower than those of the control samples were obtained from mixtures containing copper tailings as a cement replacement material. Resistance of copper tailings blended samples to chloride penetration became higher as cement substitution level increased.
2. Similar, but much better resistances to chloride ingress were obtained from mixtures containing copper tailings as an additive in concrete.
3. These results confirmed the earlier suggestions that ASTM C 1202 Test may be inappropriate for evaluating chloride migration in concretes containing conductive materials. Hence, chloride immersion test should be used.

7.4.2.10 Accelerated Corrosion Test

1. Time to initiation of corrosion, lower than those of the control samples were obtained at 5 and 10% cement substitution level for 0.65 and 0.57 w/b ratio concretes, and 5% substitution level for 0.50 w/b ratio concrete.
2. For all the concrete w/b ratios, time to corrosion initiation longer than those of the control samples were recorded in mixtures containing copper tailings as a concrete additive.
3. In these mixtures containing copper tailings as an additive, delays to corrosion initiation became extended as tailings addition level increased. Furthermore, the use of pre-wetted tailings at 5% usage level contributed in retarding corrosion initiation.

4. Compared to its use as a cement replacement material in concrete, copper tailings utilization as a concrete additive is more effective in delaying corrosion initiation in concrete.

7.4.2.11 Half-cell Potential Measurements

1. Measurements taken immediately after accelerated corrosion tests for all the mixtures were unusually high. However, subsequent measurements after moisture loss were reasonably low, which suggests that data obtained from saturated samples are inappropriate for predicting reinforcement corrosion in concrete.
2. Based on the ASTM C 876 recommendations and the last set of HCP values obtained in this study, corrosion states of reinforcements in samples were uncertain.

7.4.2.12 Visual Inspection

1. No major deterioration and loss of reinforcement section was observed in all samples.
2. The nonappearance of deteriorations was attributed to the following reasons; the use of slag cement, the use of a very thick concrete cover, curing time of 90 days prior to test and absence of cracks in samples.
3. Contrary to expectation, increased conductivity of copper blended mixtures did not increase corrosion activity in these samples.
4. It is suspected that the Cu contained in tailings, through its positive electrode potential may have stalled the corrosion process by making steel less negative.

7.4.3 Leaching of Heavy Metals from Concretes

1. In comparison to deionized water, the use of acetic acid as a leachant yielded higher concentrations of heavy metals in leachates.
2. It was also observed that compared to mixtures containing copper tailings as a cement replacement material, higher degree of heavy metal immobilization was achieved in mixtures that contained copper tailings as a concrete additive.
3. Furthermore, in mixtures containing copper tailings as an additive, higher immobilization of heavy metals occurred at lower w/b ratio and increased copper tailings addition level.
4. In both leachants, leachate concentrations obtained were infinitesimal and significantly lower than the US CFR limits. Hence, copper tailings utilization in concrete may not pose any health and environmental hazard.

7.4.4 Material Cost Analysis of Concretes

1. At 28 days, there was no efficiency in the use of copper tailings as a cement replacement material in concrete. However, by the 90th day, some improvements in CEF were observed in 0.57 and 0.50 w/b ratio concretes.
2. Improvements in CEF were more noticeable in mixtures containing copper tailings as a concrete additive. For all the concrete w/b ratios evaluated, maximum CEF values were obtained at 5% addition level, especially with pre-wetted tailings.

7.5 Economic, Environmental and Social Impact

1. Presently, successful closure of mines, mine processing facilities and the associated decontamination processes cost millions of dollars to achieve. Hence, the use of these tailings in cement-based materials instead of evacuation will

substantially reduce the overall cost of reclamation and decontamination of the Lefke-Xeros area. Globally, this can be replicated in other countries with similar copper tailings induced environmental pollution problems. The benefits will include reduced waste stabilization and clean-up costs and cheaper cost of concrete for the construction industry.

2. Locally, several important benefits will come to Lefke-Xeros inhabitants as a result of the recycling of these tailings in concrete. Further air, soil, surface water and groundwater pollution will be prevented. This is a priceless gain that forestalls continued endangering of the health of the local community who has been inhaling airborne toxic pollutants.
3. Similarly, preventing further contamination of water bodies in the study area will have profound impacts on socioeconomic activities. The restoration of the disused 4 million m^3 Xeros irrigation dam will help in revitalizing the huge agricultural potential of the study area. The reclamation of a huge surface area of land previously usurped by massive deposits of tailings will have an immense social implication for the Lefke-Xeros community and the government. Potential uses for the reclaimed land such as new business ventures, schools, real estate development and agriculture are veritable sources of economic activities, employments, infrastructure development and tax revenues for the government. Moreover, since the main foreign exchange earner in Northern Cyprus is citrus fruit export, and the bulk of the supplies come from the study area. The utilization of the reclaimed land for large scale citrus fruit cultivation will bring increased earnings to the community and the government.

4. Likewise, the expansion and rehabilitation of the existing CMC Golf Club near the study area will increase recreational opportunities and attract more golfers. Finally, a re-greened landscape comprising hazard free abandoned mine sites, processing site, equipment and loading harbor sites could be transformed into a historic tourist centre. All the aforementioned, will create more jobs, boosting the local economy and the socioeconomic life of residents and those of students of the nearby European University of Lefke. Increased revenues from the Lefke-Xeros area will also enhance the government ability to meet her obligations to the citizenry.

7.6 Recommendations

1. Because of varying ore compositions and processing methods; it is inevitable that variability in physical and chemical properties of copper tailings from different sources will exist. Hence, more studies on the use of copper tailings in cement mixtures should be carried out, so that consensus on findings will lead to the establishment of regulatory standards in the nearest future.
2. The effect of ground copper tailings on the properties of cement mixtures should be explored.
3. Most of the tests performed in this study were based on time-tested conventional techniques. In future studies, the microstructure of copper tailings blended mixtures should be investigated using advanced experimental techniques such as scanning electron microscope (SEM), X-ray diffraction (XRD), etc.
4. This study has shown that the increased porosity of copper tailings blended mixtures affect resistance to sulfate attack negatively. Hence, possible methods

of reducing the porosity of tailings, as well as long-term sulfate exposure and permeability tests should be explored.

5. The effects of binary or ternary blends of copper tailings with other industrial by-products with higher silica content, on the properties of cement-based mixtures can be investigated.
6. Further durability properties such shrinkage and freeze-thaw behavior of concretes containing copper tailings should be investigated.
7. Moreover, the high conductivity of copper tailings blended concretes can be investigated for utilization in road and walkway de-icing.
8. Finally, the actual performance of structural elements such as reinforced concrete beams and columns containing copper tailings should also be investigated.

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