**ADDIS ABABA UNIVERSITY**

**ADDIS ABABA INSTITUTE OF TECHNOLOGY**

**SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING**


# Use of Waste Paper Sludge Ash as Partial Replacement of Cement in Mortar

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**A Thesis Submitted to School of Civil and Environmental Engineering of AAiT in Partial Fulfillment of the Requirements for the Degree of Master of Science in Structural Engineering**

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## UNDERTAKING

I certify that research work titled "**Use of Waste Paper Sludge Ash as Partial Replacement of Cement**" is my own work. The work has not been presented elsewhere for assessment. Where material has been used from other sources it has been properly acknowledged / referred.

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## ABSTRACT

Various industrial wastes were employed as supplemental cementitious materials to save the environment from filling with non-biodegradable wastes and to limit the consumption of existing limestone. Waste paper sludge makes up a significant component of the numerous materials produced as byproducts in the paper industry. The overall goal of this research is to determine the suitability of waste paper sludge ash as a partial cement replacement material by conducting compressive strength and reactivity tests while substituting cement in various quantities.

The end-by-product of the paper manufacturing industry is paper sludge, which is a wet gray waste mud. This paper sludge is turned into ash and utilized as a partial cement replacement. This research is entirely based on the use of waste paper sludge ash (WPSA) as a cement replacement in mortar production. WPSA amounts of 0, 5, 10, 15, 20, 25, and 30% by volume of cement are used to make the mortar mix.

At the ages of 7, 28, and 56 days after curing under ambient conditions, the compressive strength of mortar cube specimens was measured. The results suggest that increasing the replacement level up to a certain level increases the strength of mortar cubes incorporating waste paper sludge ash (WPSA). In terms of compressive strength, 15 percent replacement yielded the optimum results.

WPSA reactivity was assessed using a variety of techniques. This was accomplished by assessing the reactivity of WPSA using a modified Chappelle test, estimating the amount of bound water, and characterization of pastes using XRD analysis was done for a sample at the optimum replacement level, i.e. 15%. The strength development was also compared to the test results.

On day 7, reference sample had a bound water content of 4.18%, whereas blended sample had a bound water level of 5.20%. WPSA has a reactivity of -1244.89 mg $Ca(OH)_2$ per gram of WPSA. These findings suggest that the increase in compressive strength is entirely due to the filler effect.



***Key words:*** Waste Paper Sludge Ash, Mortar, Compressive strength, Reactivity

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| AAiT | Addis Ababa institute of Technology |
| AAWSA | Addis Ababa Water and Sewerage Authority |
| ASTM | American Society for Testing and Materials |
| ACI | American Concrete Institute |
| AM | Aluminia Modulus |
| BA | Bagasse Ash |
| CBR | California Bearing Ratio |
| CH | Calcium Hydrate |
| CLSM | Controlled Low Strength Materials |
| CSH | Calcium Silicate Hydrate |
| CSI | Compressive Strength Index |
| DIP | De-inking paper |
| ETP | Effluent Treatment Plant |
| LSF | Lime Saturation Factor |
| LWF | Light Weight Fillers |
| OPC | Ordinary Portland Cement |
| PA | Paper Ash |
| PAWPSA | Pozzolanic Activity of Waste Paper Sludge Ash |
| PSA | Paper Sludge Ash |
| RCA | Recycled Coarse Aggregate |
| $R^3$ | Rapid, Reliable, and Relevant |
| SAI | Strength Activity index |
| SCEE | School of Civil and Environmental Engineering |
| SCM | Supplementary Cementitious Material |
| SM | Silica Modulus |
| SSD | Saturated Surface Dry |

| | |
|---|---|
| XRD | X-ray Diffraction |
| WPS | Waste Paper Sludge |
| WPSA | Waste Paper Sludge Ash |
| WSA | Waste Sludge Ash |

# CHAPTER 1 INTRODUCTION

## 1.1 General

The demand for cement is increasing from time to time. Natural resources are decreasing in the course of meeting this need. As a result, the necessity for an alternate source of environmentally safe and cost-effective raw materials in the cement manufacturing process has become unavoidable.

Cement, despite playing an important part in construction, is one of the most polluting, expensive, and environmentally unfriendly materials available. In recent years, its complete or partial replacement by other cementitious materials has become a key focus of research. This has been investigated using fly ash, bagasse ash, pulverized granulated blast furnace slag, and other materials [1]. Using supplementary cementitious materials as a partial replacement of cement is an effective way to improve the sustainability of the construction industry.

Waste paper sludge is a byproduct of paper production industry. Nearly one third of the recycled paper in recycling plants becomes residual (sludge). Disposing of this sludge is a key issue that the paper manufacturing industry is dealing with these days, owing to the growing demand for paper recycling. Simultaneously the increased recycling has led to increased sludge generated from the plants.

In Ethiopia, paper is recycled primarily in the same manner as plastic bottles: it is sorted and processed into pulp. Due to a lack of technology, funding, and experience, Ethiopia only have 15 formal and informal paper recycling plants. It is uncommon to utilize recycled paper for sanitary items or printing paper. Every year, Ethiopia imports raw materials for the paper industry worth more than $100 million USD. More than 200,000 tons of paper and carton waste are currently disposed off in landfills, burned, or just left as trash on the streets each year [2].

The waste paper sludge mainly consists of cellulose fibers, filler materials, water and other minor chemicals. The moisture content is close to 50%. When calcinated at a higher temperature, it produces a fine ash that contains reactive silica and aluminia in the form of metakaoline, as well as lime (CaO), giving it a chemical composition

comparable to cement. The kaolinite content of waste paper sludge can vary in the range of 15-17% and the calcite content from 21% to 70% [3].

Waste paper sludge ash (WPSA) is produced by calcination of waste paper sludge at higher temperature. This ash is less expensive, has a lower density, and has a lower specific gravity than cement [4]. Many studies have been conducted to study the use of waste paper sludge ash in concrete production, with the conclusion that when mixed with cement, it can improve performance of concrete. In addition to crystalline phases such as anorthite and gehlenite, WPSA may contain a pozzolanic and hydraulic component [3].

It is vital to examine the reactivity of a given material before employing it as a supplementary cementitious material. The reactivity of supplementary cementitious material (SCM) is assessed using a variety of techniques. The tests used to determine reactivity should be simple, practical, repeatable and cost effective.

The usage of WPSA as a partial cement replacement material in the manufacturing of cement mortar is evaluated in this study. The reactivity of waste paper sludge ash is assessed using compressive strength development in an experimental investigation. The optimum level of replacement is determined by the development of compressive strength. Setting time and normal consistency tests were also done on the blended cement paste. The reactivity was assessed using the modified Chappelle test and bound water determination test with oven treatment. For a better understanding of WPSA reactivity, X-Ray Diffraction (XRD) analysis was used to characterize the hydration products [5].

## 1.2 Statement of the Problem

Cement manufacturing plants are one of the most polluting industries. Cement companies are thought to be responsible for 5-8 percent of global $CO_2$ emissions, according to current estimations [6]. The raw materials, i.e. lime stone and clay, used in cement production are the main sources of $CO_2$. During the high-temperature calcination of lime stone and clay the reaction as shown in Eq. (1.1) will takes place:

$$CaCO_3 \longrightarrow CaO + CO_2 \qquad \text{(Eq. 1. 1)}$$

Waste management is a big concern for many developing countries. To address this issue, various researchers have investigated the use of industrial wastes as supplemental cementitious materials. In Ethiopia, pulp and paper manufacturing industries generate a lot of waste. The management of this garbage necessitates specific consideration. Taking this into account, evaluating WPSA's viability as a partial cement replacement material is one option.

Various studies on SCM have been conducted, but the microstructural evolution of blended cement systems is not yet fully understood. This is due to the following reasons: [7]:

- There is a lack of understanding of the mechanisms that control cement hydration. As a result, identifying changes in a more complex system is challenging.
- Most researchers have discussed the effect of a specific SCM on changes in microstructure, compressive strength, and phase assemblage evolution, but no generic knowledge has been established.
- Although SCMs have a slower rate of hydration, they contribute to the hydration process from the beginning, according to the majority of research. However, since early hydration is critical for subsequent performance, the entire hydration process must be thoroughly examined.

This research helps to increase the link between waste management and the manufacture of construction materials. Less carbon-intensive and more circular economies are urgently needed, setting the stage for a diverse future of localized sustainable binders. As a result, it is critical to identify new research, advance characterization methodologies, and gain a more comprehensive understanding of cementitious binder reaction mechanisms [6].

Previous research has revealed that substituting waste paper sludge ash for part of cement improved compressive strength, flexural strength, split tensile strength, workability, and the rate of water absorption of concrete [3, 8, 9, 10, 11]. All of these enhancements were made up to a replacement level of 10%.

However, how this improvement in concrete properties is accomplished is not clearly known. It could be as a result of the waste paper sludge ash's reactivity or the filler effect. As a filler, WPSA can either fill voids left by the cement reaction or act as hydration reaction nucleation site. Reactivity is explained by forming a hydration product. To explore the reactivity of the WPSA, characterization of the hydration product is essential. As a result, utilizing more powerful and reliable characterization approaches that allow to better understand and exploit WPSA reactivity, this study looked into the causes of mechanical property improvement via compressive strength development.

In Ethiopian construction, partial substitution of cement with WPSA is yet to be implemented. The goal of this research is to gain a better knowledge on the use of WPSA as a supplementary cementitious material in the construction sector.

## 1.3 Objective

### 1.3.1 General Objective

The principal objective of this research is to evaluate the suitability of WPSA as a partial replacing material of cement.

### 1.3.2 Specific Objectives

The specific objectives of this research work are:

- To determine of the physical properties of WPSA, cement & blended cement.
- To assess the performance of mortar and paste made with waste paper sludge ash as a partial cement replacement material by conducting laboratory experiments in the fresh and hardened states, as well as determining the amount of WPSA that can be utilized for optimum performance.
- To assess compressive strength development in cement and WPSA-cement blended mortar cubes at various ages
- To examine the reactivity of WPSA to use it as a supplementary cementitious material.

## 1.4 Scope of the Study

This study involves a laboratory examination to see how WPSA affects the mechanical performance of mortar. A set of tests are used to assess the mechanical properties of mortar. Furthermore, it attempts to evaluate WPSA reactivity utilizing several reactivity test techniques.

Physical properties of WPSA and cement alone, as well as when mixed together at a particular proportion are also determined in order to understand how the material behaves during the hydration process.

## 1.5 Organization of the Paper

This paper is divided into five sections. The first chapter covers the introduction of the study, the statement of the problem, objectives of the study, and scope of the study. The review of related literature is discussed in the second chapter. The materials and experimental program utilized in the investigation are described in Chapter three. The fourth chapter discusses the study's findings and discussion. Chapter five ends with conclusions and recommendations.

# CHAPTER 2 LITERATURE REVIEW

## 2.1 General

Various studies linked to this study are examined in this section to provide adequate background on the topics of supplementary cementitious material, waste paper sludge ash, availability of waste paper sludge ash, and its importance for application in the construction industry. The literature on test procedures for measuring mechanical performance and reactivity of SCMs is reviewed.

## 2.2 Cement

Cement is a fine grey powder that has a binding behavior when hydrated with water. It's made by incinerating lime stone, clay, or other reactive materials at about $1450^{o}$c. Partial fusion happen during this process, resulting in the formation of clinker. This clinker is mixed with calcium sulphate and ground to produce cement.

Every day, roughly 4.1 billion tons of cement are produced, releasing 0.7–1.1 tons of $CO_2$ into the atmosphere for every ton of cement produced. The cement industry is responsible for 5-8% of global $CO_2$ emissions [6].

Cement production involves eight major steps:

- The first step is raw material preparation
- The second step is crushing and milling
- The third step involves pre heating
- The fourth step is pre calcinating
- The fifth step is kiln firing
- The sixth step is clinker and additive mixing and cooling
- The seventh step is cement milling
- Finally storage/packing

The primary components for Portland cement are lime stone and clay or shale, which are combined and heated to a temperature of $1450^{o}$C. The following are the three groups of significant reactions that occur during the process: [12]

1. Reactions that occur at a temperature below 1300$^{o}$c

   a. Calcite decompositions

   $$CaCO_3 \longrightarrow CaO + CO_2 \quad \text{---------- } 800 - 900^{o}c \qquad \text{(Eq. 2. 1)}$$

   b. Clay (shale) mineral decomposition

   c. Reaction of lime from a) with quartz and minerals from clay(shale) decomposition to give belite, aluminate and ferrite.

   $$2Cao + SiO_2 \longrightarrow (CaO)_2SiO_2 \quad \text{-------} \quad 800\text{-}900^{o}c \qquad \text{(Eq. 2. 2)}$$

   $$3CaO + Al_2O_3 \longrightarrow (CaO)_3Al_2O_3 \quad \text{------} \quad 900 - 1300^{o}c \qquad \text{(Eq. 2. 3)}$$

   $$4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow (CaO)_4Al_2O_3Fe_2O_3 \quad \text{-----} 900 - 1300^{o}c \qquad \text{(Eq. 2. 4)}$$

2. Reactions that occur between 1300$^{o}$c and 1450$^{o}$c (clinkering)

   At this temperature range the aluminate and the ferrite turns in to melt. Almost all of the lime and most of the belite react in the presence of the lime to produce the alite. At the end a lump looking material is formed which is commonly known as a clinker.

   $$Ca + (CaO)_2SiO_2 \longrightarrow (CaO)_3SiO_2 \quad \text{--------} \quad (> 1300^{o}c) \qquad \text{(Eq. 2. 5)}$$

3. Reactions that occur during cooling

   At this stage the melt crystallizes giving mainly aluminate and ferrite. Alite and belite undergoes polymorphic transactions.

### 2.2.1 Phases in Clinker

The clinker contains four major phases: Alite, Belite, Aluminate, and Ferrite. Other minor phases such as calcium oxides and alkali sulphates exist in trace amount [12].

**Alite**: which constitute 50-70%of the total clinker is the most important phase. It is a tricalcium silicate ($Ca_3SiO_5$ or $(CaO)_3SiO_2$) commonly referred to as $C_3S$. $C_3S$ consists of 73.7% CaO and 26.3% $SiO_2$. It hydrates quickly when reacting with water thus making it the constituent of early stage strength development up to 28 days.

**Belite**: which constitutes 15-30% of the clinker. It is di-calcium silicate ($Ca_2SiO_4$ or $(CaO)_2SiO_2$) or commonly referred to as $C_2S$. It consists of 65.1% CaO and 34.9% $SiO_2$. It hydrates slowly when it reacts with water thus its contribution to early stage (first 28 days) strength development is less but it contributes substantially to later age strength development.

**Aluminate**: which constitutes 5-10% of the clinker is tricalcium aluminate ($Ca_3Al_2O_6$ or $(CaO)_3Al_2O_3$) commonly referred to as $C_3A$. It consistes of 62.3% CaO and 37.7%$Al_2O_3$. It reacts quickly with water and it is responsible for controlling the setting time.

**Ferrite:** which constitutes 5-15% of the clinker is tetra alumino ferrite ($Ca_4AlFeO_5$) commonly referred to as $C_4AF$. The rate of its hydration when reacting with water is variable. It consists 46.1% CaO, 21.0% $Al_2O_3$, and 32.9% $Fe_2O_3$.

The properties of the components of cement clinker are summarised in Table 2.1:

Table 2.1. Properties of the components of cement clinker [13]

| | |
|---|---|
| Alite | Main strength giving mineral |
| Belite | Produces strength more slowly than alite |
| Aluminate | Reacts rapidly, reaction rate is controlled by gypsum |
| Ferrite | Reacts fast but is immediately self-retarded |
| Alkali sulfate | Accelerates early strength growth |
| Magnesia | Can cause unsoundness if > about 5% |
| Free lime | Can cause unsoundness if > about 5% |

### 2.2.2 Chemical Targets of the Clinker

Although the quantity of each phase is one approach to measure the clinker's quality, three ratios of the primary oxides, known as the Lime Saturation Factor (LSF), Silica modulus (SM), and Alumina modulus (AM), provide another description of the chemistry of the clinker.

- **Lime saturation factor:** The ratio of the actual lime contained in the clinker to the lime required by the remaining oxides (i.e. $SiO_2$, $Al_2O_3$ & $Fe_2O_3$) in the raw mix is known as the lime saturation factor. It determines the alite-to-belite ratio and determines whether there is a free lime in the clinker. It is calculated as given in Eq. (2.6):

$$LSF = \frac{CaO}{2.8SiO_2 + 1.18Al_2O_3 + 0.65\ Fe_2O_3} \quad \text{(Eq. 2. 6)}$$

  Practically lime saturation factor is between 0.94 - 1. A value greater than 1 indicates the presence of free lime.

- **Silica modulus (SM):** The ratio of silicate to aluminate and ferrite is known as the silica modulus (SM). It has an impact on the reaction ratio and reaction kinetics. This number has an impact on the clinker's quality and burnability; as the SM value rises, the clinker becomes more difficult to burn, influencing the creation of alite. It is calculated as given in Eq. (2.7):

$$SM = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \quad \text{(Eq. 2. 7)}$$

For normal Portland cement SM is between 2 and 3

Effects of Change in SM are summarized in Table 2.2:

Table 2.2. Effects of Change in SM [13]

| Effect | Result |
|---|---|
| Increased Alite | Greater strength potential |
| Decreased liquid phases | Harder to burn |

- **Aluminia modulus**: it is the measure of proportion of the aluminate to iron oxide in the mix. It has an impact on the melt quality created at lower temperatures. The formula is as given in Eq. (2.8):

$$AM = \frac{Al_2O_3}{Fe_2O_3} \quad \text{(Eq. 2. 8)}$$

For normal Portland cement its value is 1-4

The effect of AM is summarized in Table 2.3:

Table 2.3. Table Effects of Change in AM [13]

| Effect | Result |
|---|---|
| Affects the amount of liquid formed at low temperatures | Most liquid forms at the lowest temperature with AM of 1.38 |
| High AM increases the viscosity of the liquid | Combination is more difficult |
| Proportions of alite and belite vary | High AM produces less alite at the same LSF |
| Lower AM produces more $C_4AF$ | Clinker and cement are darker |

As defined in section 2.2.2 the clinker's chemical targets, i.e. the lime saturation factor (LSF), silica modulus (SM) and aluminia modulus (AM) values can be summarized as in Table 2.4:

Table 2.4. Chemical targets of clinker [13]

| Ratio | Typical | Range |
|---|---|---|
| LSF | 96 | 93–98 |
| SM | 2.5 | 2.2–3.3 |
| AM | 1.6 | 1.4–2.2 |

### 2.2.3 Compounds in the Clinker

In 1929, Dr. Robert Herman Bougue proposed using an empirical formula to calculate the amounts of the four major compounds. The calculation is made with the following assumptions [12]:

- The compositions of the four major phases are $C_3S$, $C_2S$, $C_3A$ and $C_4AF$
- $Fe_2O_3$ occurs as $C_4AF$
- $Al_2O_3$ occurs as $C_3A$
- Subtracting the amount of $C_4AF$, $C_3A$ and free lime from the CaO and solving the resulting simultaneous equations to get the amount of $C_3S$ & $C_2S$.

According to Bougue the resulting equations are shown in Eq. 2.9 – 2.12

$$C_3S = 4.071\ C – 7.602*S – 6.719*A – 1.430*F \quad \text{(Eq. 2. 9)}$$

$$C_2S = 2.867*S – 0.7544C_3S \quad \text{(Eq. 2. 10)}$$

$$C_3A = 2.65*A – 1.692*F \quad \text{(Eq. 2. 11)}$$

$$C_4AF = 3.043*F \quad \text{(Eq. 2. 12)}$$

Where:

C is lime (CaO)

S is silicate ($SiO_2$)

A is aluminate ($Al_2O_3$)

F is ferrite ($Fe_2O_3$)

### 2.2.4 Cement Related Systems

In the characterization of cement, major components such as CaO, $SiO_2$, $Fe_2O_3$, and $Al_2O_3$ are primarily considered, although minor components such as MgO, $SO_3$, $K_2O$, $Na_2O$, $P_2O_5$, $TiO_2$, and $SrO_2$ may still have an impact on the thermodynamic

stability of the major phases. Systems containing major components are categorized in to three [13]:

- Binary system
    - The system $CaO – SiO_2$
    - The system $CaO – Al_2O_3$
- Ternary system
    - The system containing $CaO – Al_2O_3 – SiO_2$
    - The system containing $CaO – Al_2O_3 – Fe_2O_3$
- Quaternary system $CaO – Al_2O_3 – Fe_2O_3 – SiO_2$

Previous research has shown that binary system equilibrium phase interpretations are highly constrained. Due to the inclusion of metastable phases, ternary system diagrams also have limitations. However, because the additional component brings a closer approximation to the actual chemistry, they are slightly more elaborative than binary systems. The ternary ($CaO – Al_2O_3 – SiO_2$) system is more relevant from a quantitative standpoint [13].

Because of its simplicity, the $CaO– Al_2O_3 – SiO_2$ system is commonly employed in cement characterization. Figure 2.1 depicts many ternary phases. However, the CaO-rich binary phases are the most significant for cement.

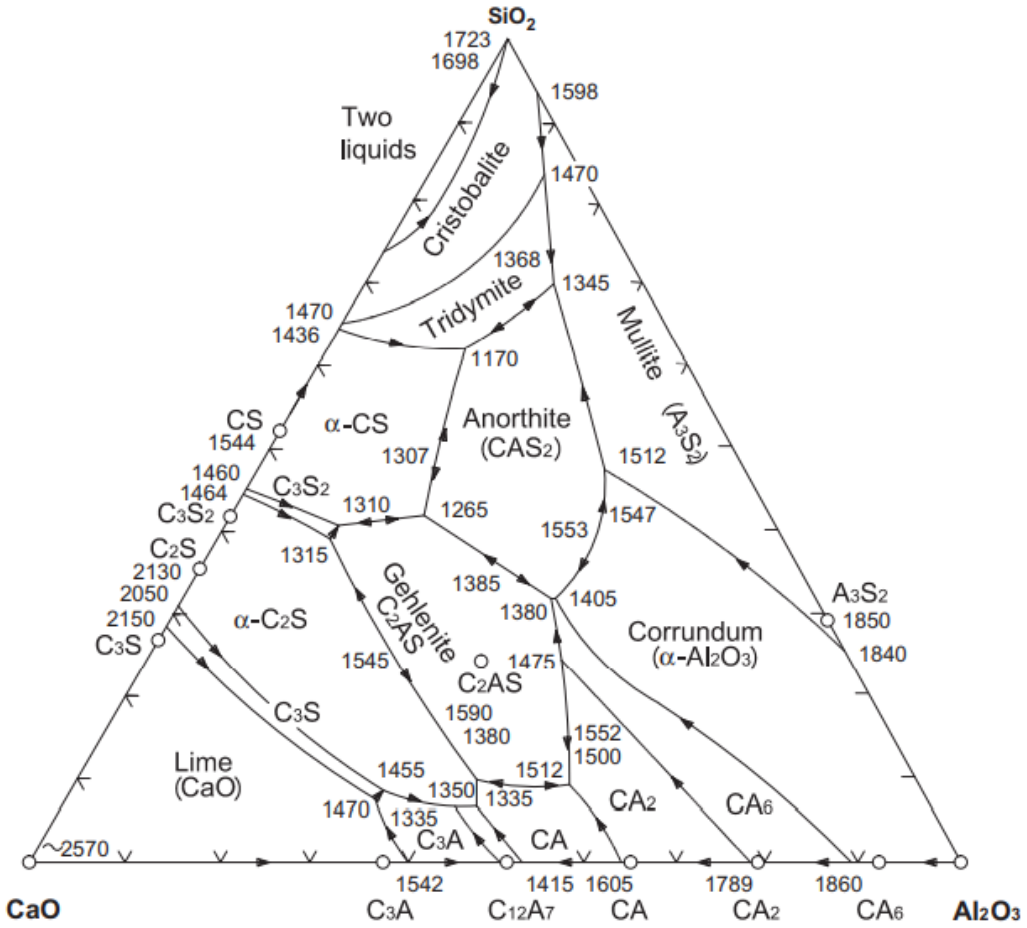


Figure 2.1. The system $CaO$-$Al_2O_3$-$SiO_2$ [13]

### 2.2.5 Hydration of Cement

The reaction of clinker components with water to produce three primary products is known as cement hydration. These products are [13]:

- Calcium silicate hydrate (C-S-H)
- Calcium hydroxide (C-H)
- $Af_m$ or ettringite (by way of $Af_t$)

The rate of the hydration process depends on [13]:

- The rate of dissolution of the involved phases
- The rate of nucleation and crystal growth of the hydrates to be formed
- The rate of diffusion of water and dissolved ions through the hydrated material already formed.

### *2.2.5.1 Calcium Silicate Hydrate (C-S-H)*

Calcium silicate hydrate is formed when alite ($C_3S$) and belite ($C_2S$) combine with water. It's a gel-like substance. The chemical make-up of C-S-H varies, although it's usually similar to $C_2S$ as shown in Eq. 2.13 and Eq. 2.14

$$Ca_2\ SiO_5 + H_2O \longrightarrow CaO.SiO_2\text{-}H_2O \quad \text{(Eq. 2. 13)}$$

$$C_2S + H \longrightarrow C\text{-}S\text{-}H \quad \text{(Eq. 2. 14)}$$

However when alite ($C_3S$) mixes with water (hydrates), the extra CaO reacts with the water to form calcium hydroxide as shown in Eq. 2.15 and Eq. 2.16

$$Ca_3SiO_5 + H_2O \longrightarrow Cao.SiO_2.H_2O + Ca(0H)_2 \quad \text{(Eq. 2. 15)}$$

$$C_3S + H \longrightarrow C_2S + CH \quad \text{(Eq. 2. 16)}$$

### *2.2.5.2 Calcium Hydroxide ($Ca(OH)_2$)*

There is always some free lime in the clinker, and when it hydrates, it produces calcium hydroxide as shown in Eq. 2.17 and Eq. 2.18. In addition to free lime, as discussed in the previous section, lime is created through the hydration of $C_3S$.

$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad \text{(Eq. 2. 17)}$$

$$C + H \longrightarrow CH \quad \text{(Eq. 2. 18)}$$

### *2.2.5.3 AFm and Aft*

When aluminates and calcium sulfate react with water, they form trisulfoaluminoferrite hydrates ($AF_t$), the most important of which is ettringite, and monosulfoaluminoferrite hydrates ($AF_m$), which are composed of calcium and aluminum platelets with positive charge in an octahedral coordination with oxygen.

In the absence of gypsum, the reaction of $C_3A$ with water is as shown in Eq. 2.19:

$$2C_3A+21H \longrightarrow C_4AH_{19} + C_2AH_8 \quad \text{(Eq. 2. 19)}$$

The paste stiffens quickly as a result of this reaction, which is known as flash set. This hexagonal calcium aluminate hydrate will progressively convert into the more stable cubic crystal $C_3AH_6$ if left in the cement mix. This can be avoided by adding sulphate to the hydration system. Sulphate is added to Portland cement in the form of gypsum ($CaSO_4.2H_2O$), $CHS_2$, or anhydrite ($CaSO_4$ or CS).

The introduction of gypsum modifies the reaction as shown in Eq. 2.20:

$$C_3A + 3CS + H_2 + 26H \longrightarrow C_6AS\,3H_{32} \quad \text{(Eq. 2. 20)}$$

The compound on the right is ettringite. It coats the surface of $C_3A$ crystals, blocking further reaction with water and the formation of $C_2AH_3$. The letters A and F stand for the presence of $Al_2O_3$ and $Fe_2O_3$, respectively, while the t stands for three calcium sulfate molecules in ettringite. $AF_t$ can dissolve and reform as $AF_m$, a phase having only one mole of calcium sulphate, unless $C_3A$, water, and sulphate are given. If the sulphate supply runs out, $AF_t$ can dissolve and reform as $AF_m$, a phase containing only one mole of calcium sulphate. A single mole of CS is represented by the letter m.

### *2.2.5.4 Mechanism of Cement Hydration*

The hydration process can be divided into four stages [13]:

1. **Pre induction period** (first few minutes): This happens as soon as the cement comes into contact with water. At this point, rapid ionic species breakdown into the liquid phase and the formation of hydrate phases start. $C_3S$ is dissolved, and C-S-H coats the cement particles.
2. **Induction (dormant) period (first few hours):** For a few hours after a brief period of fast hydration, the total hydration rate begins to slow substantially. At this stage, the hydration of clinker minerals is relatively slow.
3. **Acceleration stage (3-12 hours after mixing):** The rate of hydration rises again at this time, and is controlled by the nucleation and development of hydration products. As the rate of $C_3S$ hydration increases, the second stage C-S-H emerges. The hydration of dicalcium silicate ($C_2S$) is also noticeable.
4. **Post acceleration period:** As the amount of unreacted material diminishes, the rate of hydration slows gradually, and the hydration process becomes diffusion controlled.

The rate of hydration is influenced by the fineness of the cement. Furthermore, the method of manufacturing cement has an impact on its reactivity. Even when fineness and particle size distribution are comparable, cement ground in high pressure mills hydrates and sets faster than cement ground in ball mills. The rate of hydration is directly proportional to the mixing temperature, especially in the early stages of the process.

## 2.3 Supplementary Cementitious Materials

### 2.3.1 General

Using supplementary cementitious materials (SCMs) as a partial replacement for clinker in the production of cement is one approach that may be utilized to minimize the environmental impact, cut down the cost, increase sustainability, and improve the durability of concrete [6]. The most commonly used SCM, which includes blast furnace slag, fly ashes, and other materials, is currently in use with an annual production of approximately 800 million metric ton [6]. Crushed bricks and fired clay were the first SCM used to construct the dome of the Pantheon Coliseum in Rome. This construction, which dates from 125 B.C., demonstrates the importance of SCM in cement hydration [7].

### 2.3.2 Classification of SCM

SCM can be divided into two categories based on their physiochemical properties: pozzolanic and hydraulic materials. A hydraulic substance is a binder that hardens into a cementitious paste when it comes into contact with water. Blast furnace slag, municipal solid waste incineration ash and metakaolin show a "latent hydraulicity," i.e., their hydraulic activity is relatively low compared to Portland cement and activation by chemical or physical means is needed to initiate and accelerate the hydration reaction. Pozzolanic materials have no cementing properties on their own, but when finely powdered and chemically react with lime, they can form a cementitious compound [14]. Silica fume, coal fly ash, rice husk ash, volcanic ash, and other pozzolanic materials are examples.

SCMs, on the other hand, can be divided into two categories based on their origin: The first is natural material, whereas the second is manmade or artificial material. The first type contains naturally occurring materials that can be utilized as a SCM by simply grinding them without further processing. The second type, referred to as artificial origin, includes materials that require additional processing before being used as a SCM. Artificial SCMs can be made from high-temperature-processed industrial waste items such as fly ash blast furnace slag and others [14].

A general classification is shown in Figure 2.2

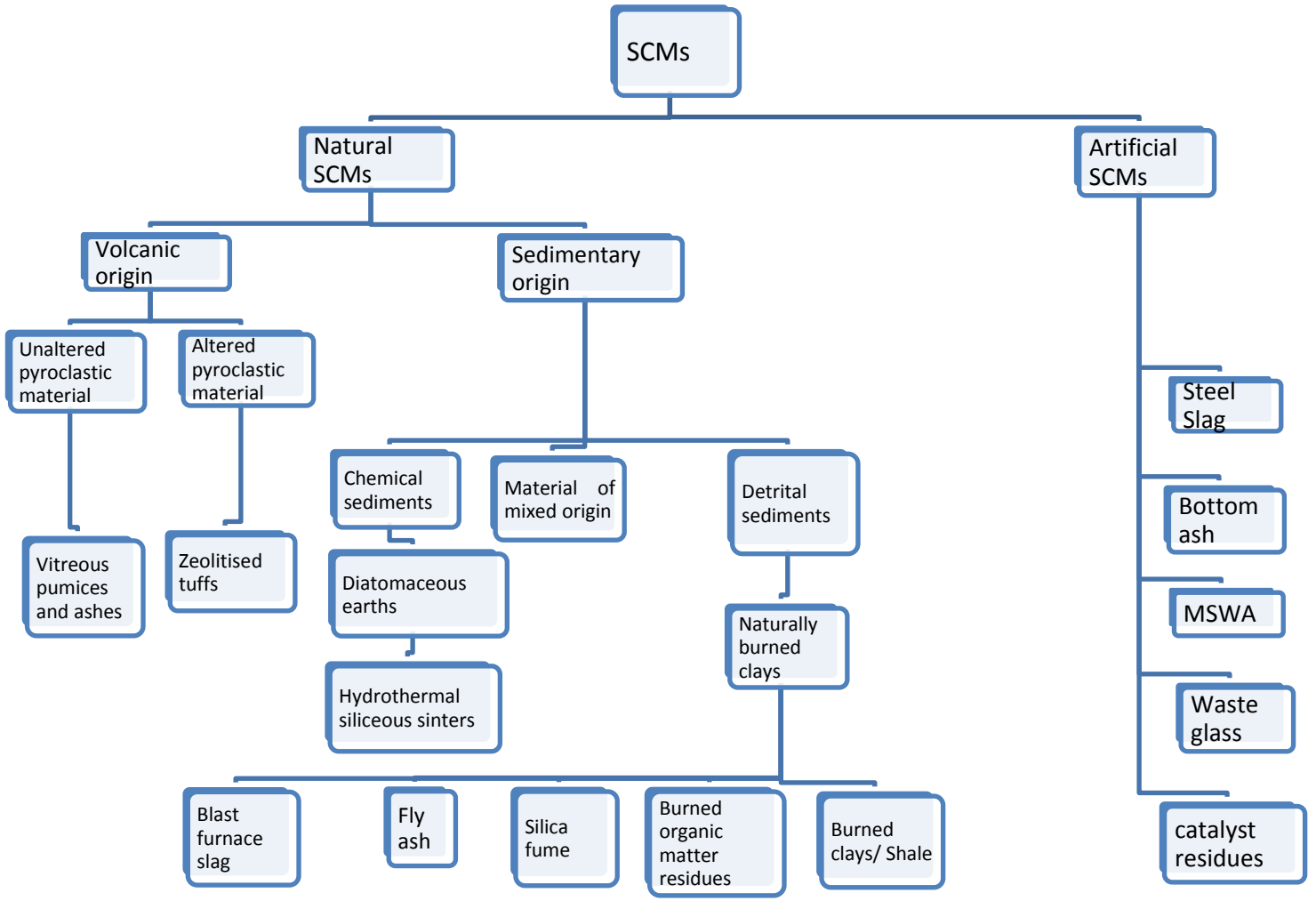


Figure 2.2. General classification scheme of SCMs [14].

Two SCMs can have different physico-chemical properties despite having the same origin. In the tertiary ($CaO$-$SiO_2$- $Al_2O_3$) variation diagram shown in Figure 2.3, the chemical composition and variability of commonly utilized groups of SCMs are shown. This diagram aids in estimating the influence of the SCM on cement and predicting reaction product assemblage, but it does not depict the material's exact behavior. The amount of three oxides, i.e. $CaO$, $SiO_2$ and $Al2O_3$ are used to locate a specific supplementary cementitious material in the ternary diagram.

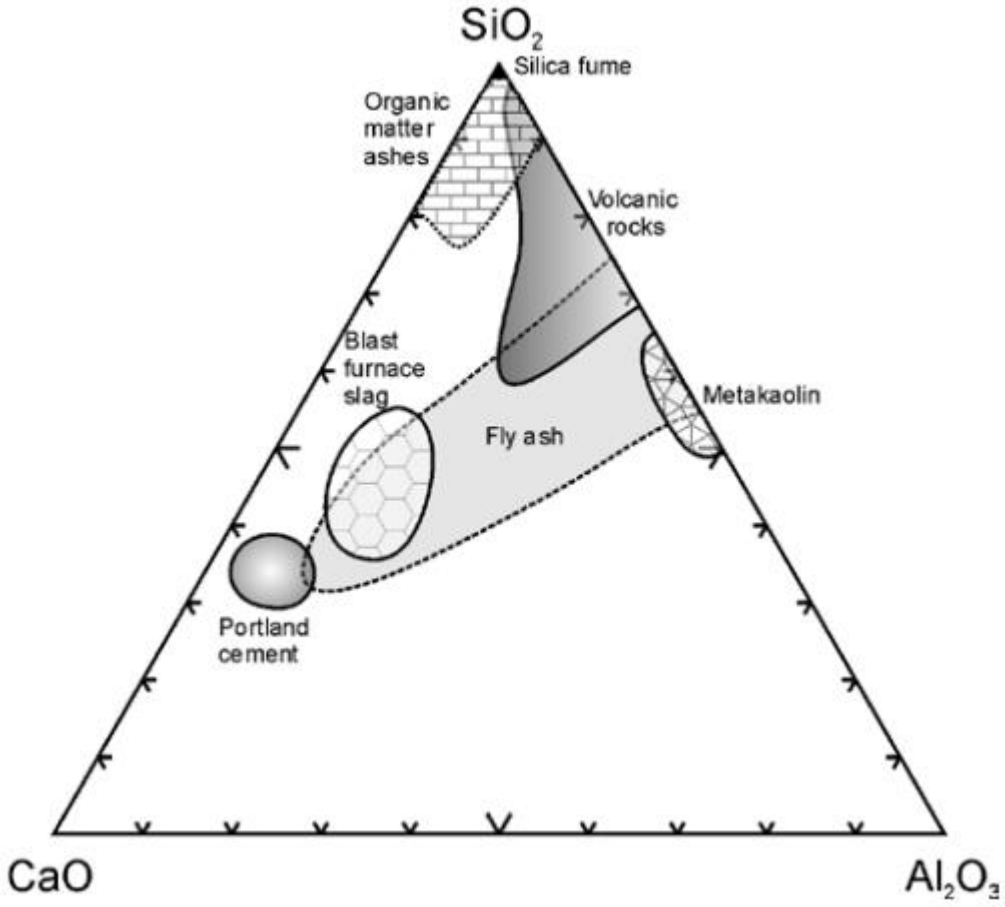


Figure 2.3. $CaO$-$SiO_2$-$Al_2O_3$ based ternary diagram (wt% based) [14]

### 2.3.3 Significance of SCM in Construction

The primary elements to consider when using a material as an SCM are material availability, cost, and consistency. They must also be quantified in terms of their effects on concrete, and the SCM should predominantly benefit concrete property development. The influence of the SCM on concrete properties is determined by chemical composition, fineness, replacement level, mixing temperature, and amorphous content. However, their

nature (i.e., whether they are latent hydraulic or pozzolanic) and reactivity are the two most crucial factors [15].

Cement hydration process is affected by the presence of SCMs in many different ways. SCMs have a filler effect due to their physical presence. This means that their surface area will serve as an additional nucleation site for un hydrated cement particles. Dilution of cement which results in higher space availability for hydration formation, changes in shearing condition resulting in higher number of nucleation sites, and dilution of cement resulting in change in the pore solution [16].

Substituting 5-20% of cement has proven to be helpful in terms of cost and mechanical properties enhancement. Replacement levels of 0-30 percent for pozzolanic materials and 0-70 percent for latent hydraulic materials are employed based on the larger categorization of SCMs as latent hydraulic and pozzolanic materials [17].

### 2.3.4 Limitation of SCM

SCMs provide a number of advantages, including lower $CO_2$ emissions, less pollution, and, in some situations, greater mechanical qualities than ordinary cement. However, they are currently limited in their use due to the following reasons [7]:

- Availability of good SCM is limited
- They have maximum replacement level
- Early age strength development is low

Table 2.5 lists the most typical physical and chemical issues that cause incompatibilities between SCM and cement, their effect on concrete property and the remedial measures that should be taken to overcome it.

Table 2.5. Challenging SCM properties for blended cements

| Physical incompatibility | Effect on concrete properties | Treatment |
|---|---|---|
| Very high fineness | Excessive water demand | Superplasticizers |
| Insufficient fineness | Lowered performance | Grinding |
| High water absorption (porous components) | Excessive water demand | Selective removal, grinding… |
| Intense color (red, black, brown…) | Undesirable color change | Selective removal of colored components, redox treatments |
| | | |
| Chemical incompatibility | Effect on concrete properties | Contingency |
| Low reactivity | Low early strength | Activators, grinding, thermal activation |
| Expansive components (CaO, MgO…) | Volume instability, cracking, pop-outs | Maturation by hydration, carbonation, oxidation… |
| Corrosive components (Cl…) | Corrosion of steel reinforcement | Cl removal (washing), alternative/no reinforcement |
| Durability impairing components (soluble alkalis, sulphate…) | Long term expansion, cracking, efflorescence | Wet chemical pre treatment |
| Environmental quality | Leaching of contaminants | Immobilization/removal by beneficiation pretreatments |

SCMs have a substantial and rising amount of research, indicating a worldwide interest in blended cements. This effort yielded successful applications for a variety of materials. Table 2.6 provides an analysis of the main examined material types and their characteristics [6].

Table 2.6. Overview of materials used or considered as SCMs [6]

| Material | Chemistry | Volume est. (Mt/y) | In use | Comments |
|---|---|---|---|---|
| Blast furnace slag | Ca-Si-Al | 300-360 | Yes | Nearly fully used, latent hydraulic |
| Coal fly ash-Si rich | Si-Al | 600-900 | yes | Subject to limitations on carbon content, reactivity |
| Coal fly ash-Ca rich | Si- Ca-Al | 100-200 | Yes | Subject to limitations on c, CaO,MgO content; latent hydraulic |
| Natural pozzolans | Si-Al | 75 | Yes | Large variety/variability, often high water demand |
| Silica fume | Si | 1-2.5 | Yes | Used in high performance concrete |
| Calcined clays | Si-Al | 2-3 | Yes | Metakaolin performs best, often high water demand |
| Lime stone | $CaCO_3$ | 300 | Yes | Cementitious contribution in combination with reactive aluminates |
| Biomass ash | Si | 100-140 | No | Competition with use as soil amendment, high water demand |
| MSWI bottom ash | Si-Al-Ca | 30-60 | No | Expansive and corrosive components, leaching issues |
| Steel slag | Ca-Si-Fe | 170-250 | No | Various types, can contain expansive components (CaO) or leachable heavy metals (Cr…), low reactivity |
| Copper slag | Fe-Si | 30-40 | No | Low reactivity, leaching of heavy metals, more research needed |
| Other non-ferro slag | Fe-Si-Ca | 5-15 | No | Low reactivity, leaching of heavy metals, more research needed |
| Bauxite residue | Fe-Al-Si | 100-150 | No | High alkali content, low reactivity, color |
| Waste glass | Si-Na-Ca | 50-100 | No | Glass recycling preferable, high alkali content |

## 2.4 Waste Paper Sludge Ash

### 2.4.1 General

Despite the advancement of digital communications, many organizations still rely on physical papers. Paper sludge (hypo sludge) is a waste product that is released into the environment by these paper mills. Paper sludge is a solid effluent that has been separated from the water at a treatment plant. Paper sludge comes in two varieties. Effluent treatment plant (ETP) waste sludge and deinking paper (DIP) sludge are the two types. DIP sludge is a waste sludge that arises from the recycling of waste paper in paper

production industry, whereas ETP sludge is a waste sludge that results from the end of a paper production process [8].

Sludge makes up one-third of recycled paper. Although paper recycling helps to reduce deforestation, it has resulted in a rise in sludge effluent. Because cellulose fibers become shorter and shorter as paper is recycled, they are unsuitable for quality paper, resulting in increased sludge production. The rules and regulations governing waste generation have made it necessary to reassess wastes in paper mills in recent years [18].

In Ethiopia, paper is recycled primarily in the same manner as plastic bottles: it is sorted and processed into pulp. Due to a lack of technology, funding, and experience, Ethiopia only have 15 formal and informal paper recycling plants. It is uncommon to utilize recycled paper for sanitary items or printing paper. Every year, Ethiopia imports raw materials for the paper industry worth more than $100 million USD. More than 200,000 tons of paper and carton waste are currently disposed off in landfills, burned, or just left as trash on the streets each year [2].

The major components of paper sludge are cellulose fibers, water, mineral fillers, inorganic salts out organic compounds [4]. The ash produced by incinerating the waste paper sludge (WPS) at a higher temperature may contain lime (CaO) and metakaoline (reactive aluminia and silica), making it appropriate for use in blended cement manufacturing [9].

In order to use WPS as a source of energy for paper and pulp facilities that run on steam engines, incinerating WPS at a very high temperature has become prevalent. The water from the effluent is removed mechanically and the wet WPS is then sundried. The dry WPS is then incinerated at a higher temperature, usually > 800$^{o}$C. Most organic chemicals are burned while incinerating at a lower temperature, such as 350-500$^{o}$C, whereas inorganic salts and mineral fillers produce their corresponding oxide at a higher temperature, such as > 800$^{o}$C [4]. The major oxides in the incinerated WPSA are CaO, $SiO_2$, $Fe_2O_3$ MgO, $Al_2O_3$ [19]. These are the same oxides present in Portland cement.

### 2.4.2 Significance of Waste Paper Sludge Ash as a Partial Cement Replacing Material

To evaluate the use of ash produced by burning paper mill sludge at a high temperature (>800$^{o}$C) as a SCM in concrete production, researchers used ash produced by burning

paper mill sludge at a high temperature (>800$^{o}$C). According to the findings, replacing up to 10% of the cement in concrete with WPSA has a good influence on mechanical performance, however WPSA has a significant water absorption due to its fineness. It is not advisable to replace more than 10% of cement by weight [4].

It was discovered that a replacement level of 5% of cement by WPSA improved the mechanical properties of concrete, such as compressive strength and split tensile strength. It has been discovered that utilizing WPSA in concrete is cost effective [10].

The use of WPSA in concrete production will help to conserve natural resources used in cement manufacture, as well as contribute to the production of environmentally friendly and sustainable concrete [20]. Another study found that WPSA requires a lot of water during hydration, therefore a superplasticizer might be applied to overcome this issue and achieve the required workability [11].

In Ethiopia construction industry the use of WPSA is not yet in practice. So detail investigation on the physical and chemical properties of WPSA is necessary.

## 2.5 Reactivity of Supplementary Cementitious Materials

### 2.5.1 General

Before utilizing a new SCM in cement, it is necessary to determine whether it is pozzolanic (materials that require calcium hydroxide and water to react), latent hydraulic (materials that can react with water once activated by mechanical grinding, high PH, or other means), or inert (filler effect). As a result, the reactivity of the SCM must be determined, which can be characterized as the degree to which it reacts with calcium hydroxide and water (pozzolanic reactivity) or the degree to which it reacts with water once activated (hydraulic reactivity) [21].

The availability of fly ash and slag has decreased as the utilization of coal-fired power stations has decreased. As a result, there is a growing demand for the development and implementation of new SCMs. However, in order to employ this alternative SCM, their reactivity must be well explored. One of the most essential considerations when choosing a material for use as an SCM is reactivity [22].

Many experiments have been designed to investigate the reactivity of SCMs, either directly or indirectly. However, all tests must meet the following criteria [23]:

- The test should be simple and practical in terms of use & cost
- It should be repeatable and reproducible
- It should applicable to all type of SCMs
- The test should be time effective
- It should enable comparison b/n test result and quality criterion (mostly compressive strength development)

### 2.5.2 Methods of Assessing Reactivity of Supplementary Cementitious Materials

Differed tests are used to assess the reactivity of SCMs. The older tests include [15]:

- Strength activity index
- Chappelle-test
- Frattini test
- SCM dissolution test
- Lime consumption test

The newly developed tests include [22]:

- Rapid, relevant and reliable ($R^3$) test
- Modified $R^3$ test
- Lime strength test
- Bulk resistivity index test
- Reactive silicate test

For a longer period of time, the strength activity index (SAI) test has been used. However, subsequent research has showed that it has a number of disadvantages, including false positives for fine fillers [24]. The rise in degree of cement hydration due to the physical presence of the material might lead the SAI test to misidentify unreactive materials that are finally ground as pozzolanic material. This is known as the filler effect. This condition must be avoided since it may compromise the concrete's durability [25].

Other tests based on the reaction between the SCM and calcium hydroxide (lime) in the system have been developed by researchers. The fratinni test, Chappele test, SCM dissolution test, and lime consumption test are among these tests [15]. Although these tests are more accurate than the SAI test in determining the reactivity of SCMs, they do have significant limitations. These tests, for example, are not recommended for latent hydraulic materials, including Ca-rich SCMs, which have a low calcium hydroxide consumption but are highly reactive [26].

Recently, reactivity tests such as the rapid, relevant & reliable ($R^3$) test [26], modified $R^3$ test test [21], lime strength test [27], and bulk resistivity test [28] have been developed.

The $R^3$ test, which can accurately distinguish between pozzolanic and inert materials, involves measuring heat release and chemically bound water in a model system comprising SCM and calcium hydroxide in a pore solution containing sulphates and carbonates at $40^oc$ [22]. The lime strength test, which is based on the compressive strength development in SCM - calcium hydroxide mortar, determines the reactivity of SCMs. This test is a variation of the strength activity index in which the curing temperature, w/c ratio, and other factors are changed.

Measurements of bulk and surface resistivity have long been employed as durability indicators, but it has only recently been discovered that they may be used to distinguish between inert and reactive materials. SCM, on the other hand, enhance bulk resistivity by modifying the continuity and composition of the capillary pore system, whereas inert materials do not. Bulk resistivity is a quick and simple test that is also non-destructive, therefore it could be employed for rapid screening [28].

### 2.5.3 Reactivity Assessment Techniques Used in This Study

In this study the reactivity of WPSA was investigated by three different methods: XRD analysis, bound water determination using oven thermal treatment and modified

Chappelle reactivity test. And Finally correlating the reactivity test results with compressive strength development.

#### *2.5.3.1 XRD Analysis*

The traditional view of using quantitative diffraction methods to determine the crystalline phases of a substance is referred to as XRD analysis. Depending on the type of machine used for analysis, this test can be done with powder or slice form of the substance.

When compared to traditional quantitative phase analysis methods such as Bogue calculations and optical microscopy, the key advantages of XRD analysis are ease of measurement, speed of measurement, and accuracy [29].

The scattering of the x-ray beam caused by the crystalline arrangement in the bulk material is the basis for the XRD technique. As a result, only the crystalline phase can be easily distinguished. The external standard technique can be used to do XRD analysis to quantify the phases of the sample [7].

A hydrating cement is a mixture of complex materials that include a variety of coexisting phases, including residual anhydrous phases and hydration products, all of which can have different compositions and crystallinities. At least ten distinct phases are expected to exist simultaneously in a standard hydrating Portland cement, while hydrating blended cement shows an extra level of complexity [30].

The most pressing issue is the considerable overlap of the contributions of the peaks from different stages. The contributions of amorphous or non-crystalline phases such as blast furnace slag or CSH, which appear as diffuse, broad peaks in XRD data, are particularly challenging to appropriately identify [31].

The presence of hydration reaction products was determined using X-ray diffraction (XRD) analysis on select pastes from blended SCM- cement matrix to evaluate if hydration reactions were truly occurring under these testing circumstances. Samples were taken from the curing pond after 28 days, and ground to the desired fineness level [31].

#### *2.5.3.2 Bound Water Determination Test*

Chemically bound (constitutive) or free (chemically unbound) water can exist in hardened cement paste. Constitutive water is tightly bonded to the crystal phase, and only calcining the material at high temperatures or chemical processes can separate it. Water vapor, physico-mechanically and physico-chemically bonded water (pellicular, sorption) are all examples of unbound chemical water . Pellicular water forms on the surface of developed pores or in the capillaries of cement paste, and with a consistent water vapor relative humidity in the pores, it stays at a constant level. As a result of material supersaturation with water vapor, physico-mechanically bound water forms [32].

Chemically bound water is defined as the water that is present in interlayer spaces or is more strongly bound, but not in pores larger than this. The water that remains after the saturated paste has occupied the bigger capillary pores is known as free water. Evaporable water, on the other hand, is the total of free water and physically adsorbed water [12]. The majority of the water in the calcium silicate hydrate is bound water, which effects strength development. The one with the most bound water will have the most strength [33].

Adding additional water results in increased hydration. As a result, the concrete will release more water throughout the heating process. The degree of hydration in the mix is determined by bound water identified by ignition. A direct proportionality was also discovered between the amount of chemically bound water and the amount of reacted cement, although the direct proportionality will be modified when the cement is blended with SCMs.

Bound water content in the cementitious paste was calculated by measuring the mass loss between 105 °C and 600 °C and normalizing to mass of the cementitious paste at 105 °C.

#### *2.5.3.3 Modified Chapelle Test*

The actual EN 196-5 standard is based on the "Fratini test". Chapelle (1958) established a pseudo-dynamic test to measure the reactivity of a SCM based on the consumption of $Ca(OH)_2$ in a saturated water medium, in contrast to Fratini's methodology. Using 1 g of pozzolan, 1 g of calcium oxide, and 250 ml of distilled water, Benoit (1967) refined the Chapelle methodology, particularly in terms of temperature ($90^oC$) and time (16 hr) of

the test, and dubbed it the "Chapelle test." Largent (1978), after criticizing the "Fratini test" for not reaching equilibrium and being performed in a static setting, modified the Chapelle test by adding continual stirring throughout the duration of the test and renaming the methodology "modified Chapelle test" [34].

The modified Chapelle test was used to determine the pozzolanic activity of metakaolins in accordance with the NF P18-513 standard. When 1 g of metakaolin is mixed with 1g of CaO and 250 ml of distilled $CO_2$ free water, the amount of $Ca(OH)_2$ fixed (consumed) can be measured.

## 2.6 Previous Studies Related to This Study

Previous research activities on bagasse ash as a partial cement replacement material and its reactivity during hydration are summarized in this section. For ease of comparison, papers and theses are reviewed and summarized in Table 2.7. The reviewed papers were done by Vicas, M., et al. [10]; Fava, G., et al. [4]; Dineshkumar, R., et al. [8], Alla, S., et al. [11]; Fauzi, M.A., et al. [21], AL-Hdabi, A., et al. [20], Shermale, Y.D.,[35], Spathi, C., et al. [36], Ridzuan, A.R.M., et al [37], Anuar, K.A., et al. [38], Malaiskiene, J., et al. [39], Ahmad, S., et al. [9], and others.

Table 2.7. Summary of related studies that have been conducted before

| No | Author(s) | % of replacement | Adopted application | Summary of findings | Limitations |
|---|---|---|---|---|---|
| 1 | Vicas, M., et al. [10] | 0 – 20% | Concrete | • WPSA was shown to be the optimum cement replacement at 10% of the binder. There was an increase in compressive strength, split tensile strength at 28 days, and water absorption was observed to be higher at this replacement level. | • There was no investigation into why concrete property improvements happened |
| 2 | Fava, G., et al. [4] | 0 – 20% | Mortars | • The paper-ash has a favorable effect on the temporal development of concrete mechanical performance, especially when it substitutes less than 10% of the cement.<br>• At 28 days, mortars containing 10% paper sludge ash had compressive strengths that were higher or equal to that of mortar prepared with ordinary cement. | • The reason for the increase in mortar property value was not investigated in the study. |

| No | Author(s) | % of replacement | Adopted application | Summary of findings | Limitations |
|---|---|---|---|---|---|
| | | | | • The dosage of PA should not be too high due to its high fineness and, as a result, high water absorption (the upper limit appears to be 10 percent by weight of cement) | |
| 3 | Dineshkumar, R., et al. [8] | 0 – 20% | concrete | • Cement can be partially replaced by ETP or dip sludge ash.<br>• A replacement level of 15% for Dip sludge ash is optimal. The concrete has a higher compressive strength, split tensile strength, and flexural strength when Dip sludge is used to replace the cement at this level.<br>• For ETP sludge ash, a replacement level of 15% is optimal.<br>• When the strength of the concrete is compared when Dip and ETP are used | • The temperature at which Dip and ETP were burned was not specified in the study.<br>• Although it compares DIP with ETP sludge ash, it does not look into the reasons for the improvements in concrete properties. |

| No | Author(s) | % of replacement | Adopted application | Summary of findings | Limitations |
|---|---|---|---|---|---|
| | | | | instead of cement, it is discovered that DIP is the better option. | • |
| 4 | Alla, S., et al. [11] | 0 – 20% | Concrete | • Considering paper sludge ash requires a lot of water in concrete, superplasticizer may be necessary to keep the workability at its optimal level.<br>• It has been determined that 5% is the optimum proportion for cement replacement in concrete, and that up to 10% paper sludge ash can replace cement in concrete because when hypo replaces cement up to 10% in concrete, these mixes produce better results than conventional concrete that contains 0% paper sludge ash. | • Because most tests are limited to concrete's mechanical performance, the results obtained only apply to a specific mixture and so cannot fully establish material pozzolanicity<br>• There is no explanation for why 800$^{o}$C was chosen as the burning temperature. |
| 5 | Fauzi, M.A., et al. [20] | 0 – 15% | concrete | • As compared to standard mix concrete set with grade C25, a 5% substitution of cement by WPSA with 50% recycled coarse aggregate (RCA) and a water content ratio of 0.45 demonstrated the best compressive strength | • The explanation for the increase or decrease in |

| No | Author(s) | % of replacement | Adopted application | Summary of findings | Limitations |
|---|---|---|---|---|---|
| | | | | improvement.<br>• The mean weight of a combination with 15% WPSA content and all percentages of RCA increases as the WPSA content decreases, making the concrete light weight. | • concrete property was not looked into. |
| 6 | AL-Hdabi, A., et al. [19] | 0 – 6% | Granular materials for sub base | • CBR increased dramatically with the addition of PSA until it reached 4% (a 173 percent increase over untreated material), after which it dropped, leading to the designation of 4% PSA as the optimum ash content.<br>• Compressive strength shows that granular materials with 4 percent PSA have a better compressive strength than those with 6 percent cement. | • The study didn't go into detail on why these gains were made. |

| No | Author(s) | % of replacement | Adopted application | Summary of findings | Limitations |
|---|---|---|---|---|---|
| 7 | Shermale, Y.D., [38] | 0 – 30% | concrete | • For M20 grade concrete, compressive strength improves as the curing period increases; compressive strength of CVC and 20% are about identical, but it increases with 10% replacement and then begins to decline in strength with 30% replacement.<br>• When 10% of the hypo sludge in M20 grade concrete replaces cement, the split tensile strength increases, and when 20% of the hypo sludge replaces cement, the split tensile strength increases slightly, or it can be said that it is equivalent, but when 30% of the hypo sludge replaces cement, the split tensile strength starts to decrease. | • Property improvements were looked into, but not how they were accomplished. |
| 8 | Spathi, C., et al. [36] | | | • PSA can be used to make high-performance LWFs with significantly better mechanical qualities when compared to conventional materials. | • It's difficult to say whether the encapsulation of developing gases within the particle body during |

| No | Author(s) | % of replacement | Adopted application | Summary of findings | Limitations |
|---|---|---|---|---|---|
| | | | | | sintering is the main cause of the LWF microstructure. There was no use of a proper approach |
| 9 | Ridzuan, A.R.M., et al [37] | 0 – 30% | CLSM | • WPSA can be used to replace Portland cement in the production of CLSM while also preserving natural aggregates through the use of waste materials and industrial recycling. | • There was no study into the role of WPSA ash in strength development. |
| 10 | Anuar, K.A., et al. [38] | 0 – 10% | Geopolymer concrete | • By increasing the molarities of sodium hydroxide, the strength of geopolymer concrete based on WPSA including recycled concrete aggregate (RCA) improves. | • The mechanism and cause of this improvement are not investigated with this method. |

| No | Author(s) | % of replacement | Adopted application | Summary of findings | Limitations |
|---|---|---|---|---|---|
| 11 | Malaiskiene, J., et al. [39] | 0 – 15% | Concrete | • PSA retards the cement's initial and final setting times, as well as the slump and density of the mix.<br>• Because PS waste delays the hydration process, a setting accelerator or a superplasticizer with such qualities should be used in the mixes. | • The role of WPSA in the development of strength has not been studied. |
| 12 | Ahmad, S., et al. [9] | 0 – 20% | Concrete | • Samples containing 5% waste paper sludge ash in place of cement exhibited a ten percent improvement in compressive strength after seven days and a fifteen percent increase after 28 days.<br>• The use of waste paper sludge ash in concrete will conserve natural resources used in cement production, making the concrete construction industry more sustainable. Waste paper sludge can be used as fuel before being used as ash in concrete for partial cement replacement, and the paper industry's disposal problem for this waste material will be completely solved. | • The study did not investigate how WPSA is utilized as a replacement material to improve strength. |

| No | Author(s) | % of replacement | Adopted application | Summary of findings | Limitations |
|---|---|---|---|---|---|
| 13 | [40, 41] | 0 – 40% | Concrete & foamed concrete | • With a weight replacement of 5–10%, mechanical performance (compressive strength, splitting tensile strength, and flexural tensile strength) improves, but beyond replacement of 30%, strength begins to decline.<br>• As fineness increases, so does water absorption, necessitating the use of more water.<br>• Unless mortar mixtures are well balanced, the usage of WSA should not exceed 10% by weight of the cement replaced. | • When bagasse ash is utilized as a replacement<br>• material, the study did not find out how strength is improved. |
| 14 | De Azevedo, A.R., et al. [42] | 0 -30% | Mortar bricks | • Because it reduces mechanical strength resistance values, which are incompatible with market criteria for brick manufacturing at 900 °C, the replacement should not exceed 10% WSA. | • The role of WPSA in the development of strength has not been studied. |

| No | Author(s) | % of replacement | Adopted application | Summary of findings | Limitations |
|---|---|---|---|---|---|
| | | | | • The waste material's hydration heat is lower, resulting in fewer reactions.<br>• The ideal firing temperature was 950$^{o}$c. As the percentage of deinking paper mill sludge increases, the thermal conductivity falls.<br>• At a fire temperature of 950°C, 15 percent deinking paper mill sludge provides the best strength. | |
| 15 | [43,44,45] | 2 – 30% | Soil stabilizing additive | • From 0 to 28 days of curing, the ideal concentration of WSA to stabilize the peat soil is around 7–20 percent of the maximal compressive strength.<br>• The application of WSA in the stabilization of sulphate soils and other clays illustrates the advantages of technology, economics, and environmental benefits over traditional stabilizers such as chalk and or Portland Cement | • The investigations did not uncover how waste paper sludge ash is utilized as a replacement material to improve strength. |

| No | Author(s) | % of replacement | Adopted application | Summary of findings | Limitations |
|---|---|---|---|---|---|
| | | | | • The California Bearing Ratio (CBR) values have been fixed for stable soil for soaked and non-invasive conditions with the addition of 10% WSA compared to control (unstable clay). | |
| 16 | Alemayehu, D and Gebreyouhannes, E. [5] | 10% | Mortar Cubes | • The blended sample had lower compressive strength than the reference sample at an early age (one day). However, the compressive strength of bagasse blended cement mortar cubes was higher than the reference sample in the later days (3, 7, 28, 56, and 90 days).<br>• The blended samples had a higher water demand than the reference sample. This is because the bagasse | • Different researchers recommended different replacement level for optimum performance but this paper did not state the reason for choosing 10% replacement level to do the other reactivity tests. |

| No | Author(s) | % of replacement | Adopted application | Summary of findings | Limitations |
|---|---|---|---|---|---|
| | | | | ash used as a cement substitute is very fine. The blended cement samples' initial and final setting times were likewise higher than the reference samples.<br>• Blending reduces the highest rate of heat flow by 10.67 J/gh on average and delays the time it takes to reach this pick by 59 seconds on average.<br>• The determined amount of pozzolanic activity of bagasse ash was found to be 346.08mg of Ca(OH)2 /g of bagasse ash. | |
| 17 | Hailu, B. and Dinku, A. [1] | 0 – 30% | Mortar and concrete | • The compressive strength of the bagasse blended cement mortar is higher than that of the control mortar up to 10% replacement level. As the bagasse ash substitution exceeds 10%, the compressive strength drops.<br>• The compressive strength of concrete with 5% cement substitution by bagasse ash had a 5% compressive strength improvement at 28 days | • The mechanism and cause of this improvement are not investigated with this method. |

| No | Author(s) | % of replacement | Adopted application | Summary of findings | Limitations |
|---|---|---|---|---|---|
| | | | | compared to the control concrete with 100% ordinary Portland cement.<br>• As the concrete's bagasse ash concentration rises, so does the depth of water penetration.<br>• This study found that bagasse ash might be used to substitute cement up to 10%. This substitution produces concrete with identical qualities to the control concrete. With a minor reduction in concrete performance, higher replacement percentages can be used. | |

## 2.7 Research gap

Previous research has revealed that substituting waste paper sludge ash for part of cement improved compressive strength, flexural strength, split tensile strength, workability, and the rate of water absorption of concrete [3, 8, 9, 10, 11]. However, how this improvement in concrete properties is accomplished is not clearly known. It could be as a result of the waste paper sludge ash's reactivity or the filler effect. As a filler, WPSA can either fill voids left by the cement reaction or act as hydration reaction nucleation site. Reactivity is explained by forming a hydration product. To explore the reactivity of the WPSA, characterization of the hydration product is essential. As a result, utilizing more powerful and reliable characterization approaches that allow to better understand and exploit WPSA reactivity, this study undertakes different reactivity assessment techniques to get a better understanding on the rationale behind compressive strength development.

In Ethiopian construction, partial substitution of cement with WPSA is yet to be implemented. The goal of this research is to gain a better knowledge on the use of WPSA as a supplementary cementitious material in the construction sector.

# CHAPTER 3 MATERIALS, METHODS AND PROCEDURES

## 3.1 Materials Used in This Research

### 3.1.1 Introduction

Various materials were employed for this project. Waste paper sludge (WPS) from Anmol paper production Ethiopia, waste paper sludge ash (WPSA) incinerated manually by muffle furnace at AAiT material testing laboratory, ordinary Portland cement from Dangote cement factory, river sand purchased from local market, and water from the Addis Ababa water and urban sewerage authority are among the materials used.

### 3.1.2 Cement

Dangote OPC which complies with the requirements of Ethiopian standards is used in this study. OPC is used to obtain a clearly seen result when cement is replaced partially based on previous results. Particle size plays an important role in the determination of reactivity. The finer the cement particles, the faster the reactivity which is the main objective to be investigated in this study.

### 3.1.3 Waste Paper Sludge Ash

The waste paper sludge was brought from Anmol paper production which is located at Ginchi, Ethiopia. The sludge is the byproduct of the recycling process of paper production. After the final processing the sludge passes through effluent treatment plant in which the dewatering takes place. After dewatering the solid waste is buried in landfills.

Figure 3.1.Waste paper sludge effluent

This sludge is bundled into bags and transported to Addis Ababa for research purposes. The extra water was then sundried out of the sludge. This dry sludge was then burned at 700$^{o}$c, 800$^{o}$c and 900$^{o}$c temperatures in a muffle furnace to determine the temperature at which the amorphous content of the sample is higher. Then after, the ashes were taken to the chemistry department at Addis Ababa University for an X-ray diffraction (XRD) test. Each sample's crystalline and amorphous phases are clearly visible in the XRD analysis. The XRD analysis result for the three sample is as shown in the Figure 3.2.

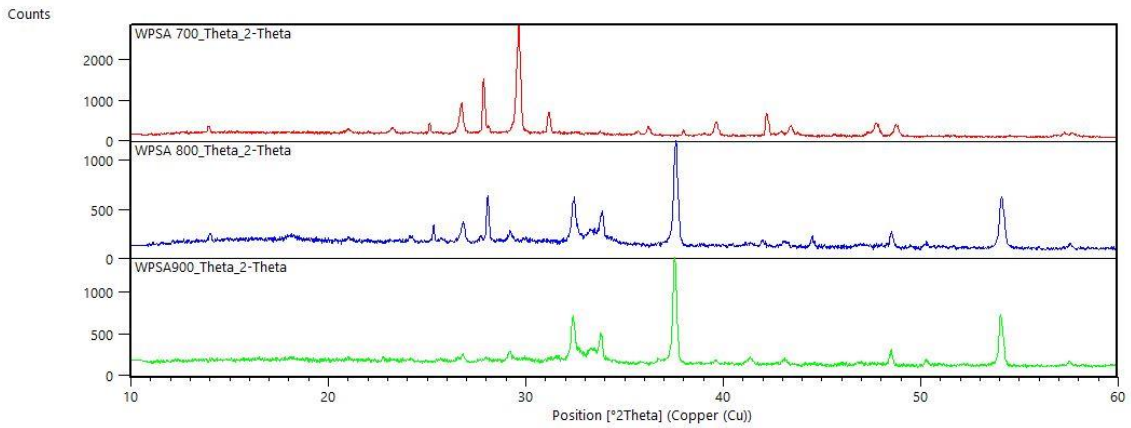


Figure 3.2. XRD patterns of WPSA incinerated at 700$^{o}$c, 800$^{o}$c and 900$^{o}$c.

Xpert high score plus 3.0.5 software was used to analyze the XRD data and Origin pro 2019b software's were used to determine the degree of crystallinity of the sample ashes. Crystallinity is calculated by deviding the area of the peaks to the total area of the curve from the XRD graph and resulting values of each sample is as shown in Table 3.1.

Table 3.1. Crystallinity of WPSA samples

| Temperature | Total area of curve | Total area of peaks | Crystallinity |
|---|---|---|---|
| 700$^{o}$ c | 5674.18 | 2702.63 | 47.63% |
| 800 $^{o}$ c | 4260.71 | 1488.35 | 34.93% |
| 900 $^{o}$ c | 3837.66 | 1660.5 | 43.27% |

It was found that the crystallinity of WPSA burned at 700$^{o}$c (47.63 % crystalline), 800$^{o}$c (34.93% crystalline) and 900$^{o}$c (43.27% crystalline). Based on this result the WPSA burned at 800$^{o}$c is used for this research because of its lower crystallinity value. The sample of WPSA is depicted in Figure 3.3.

Figure 3.3. Waste paper sludge ash incinerated at 800$^{o}$c.

To assess the chemical composition of the WPSA complete silicate analysis was done at Ethiopian geological survey geochemical laboratory. The result of the complete silicate analysis is as shown in Table 3.2:

Table 3.2. Typical chemical composition of WPSA

| WPSA | Oxide composition (%W/W) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $P_2O_5$ | $TiO_2$ | $H_2O$ | LOI |
| | 20.12 | 5.78 | 2.16 | 53.88 | 4.7 | 0.9 | 0.18 | 0.26 | 7.23 | 4.4 |

The raw WPSA sample's XRD analysis pattern was examined, chemicals were identified, and XRD patterns were drawn. Peaks and patterns of chemicals were investigated using these data. Figures 3.4 shows the results of the analysis.

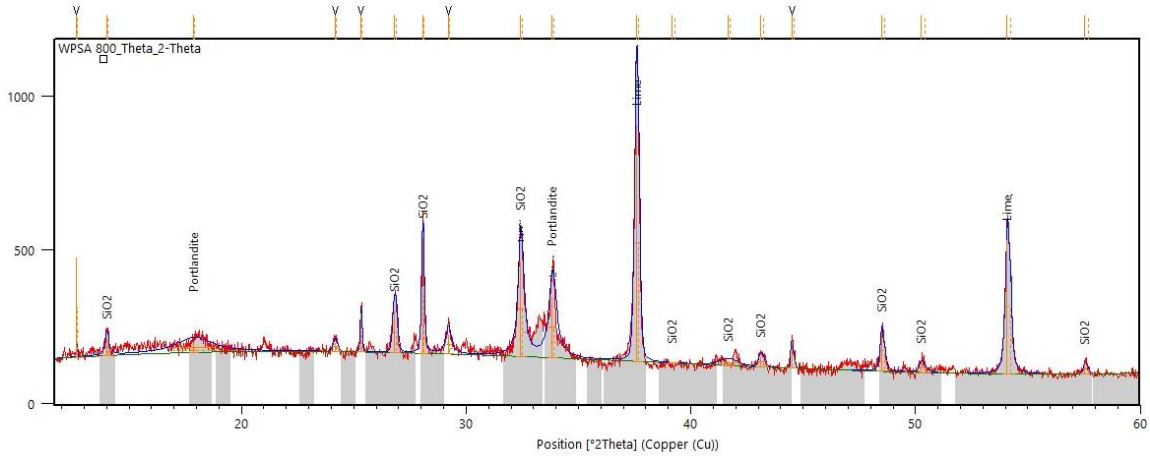


Figure 3.4. X-ray differaction of raw WPSA

Based on its chemical composition, i.e. CaO (53.88%), $SiO_2$ (20.12%) and $Al_2O_3$ (5.78%) WPSA can be located on the tertiary ($CaO$-$SiO_2$- $Al_2O_3$) variation diagram as shown in Figure 3.5. This diagram aids in estimating the influence of the SCM on cement and predicting reaction product assemblage, but it does not depict the material's exact behavior.

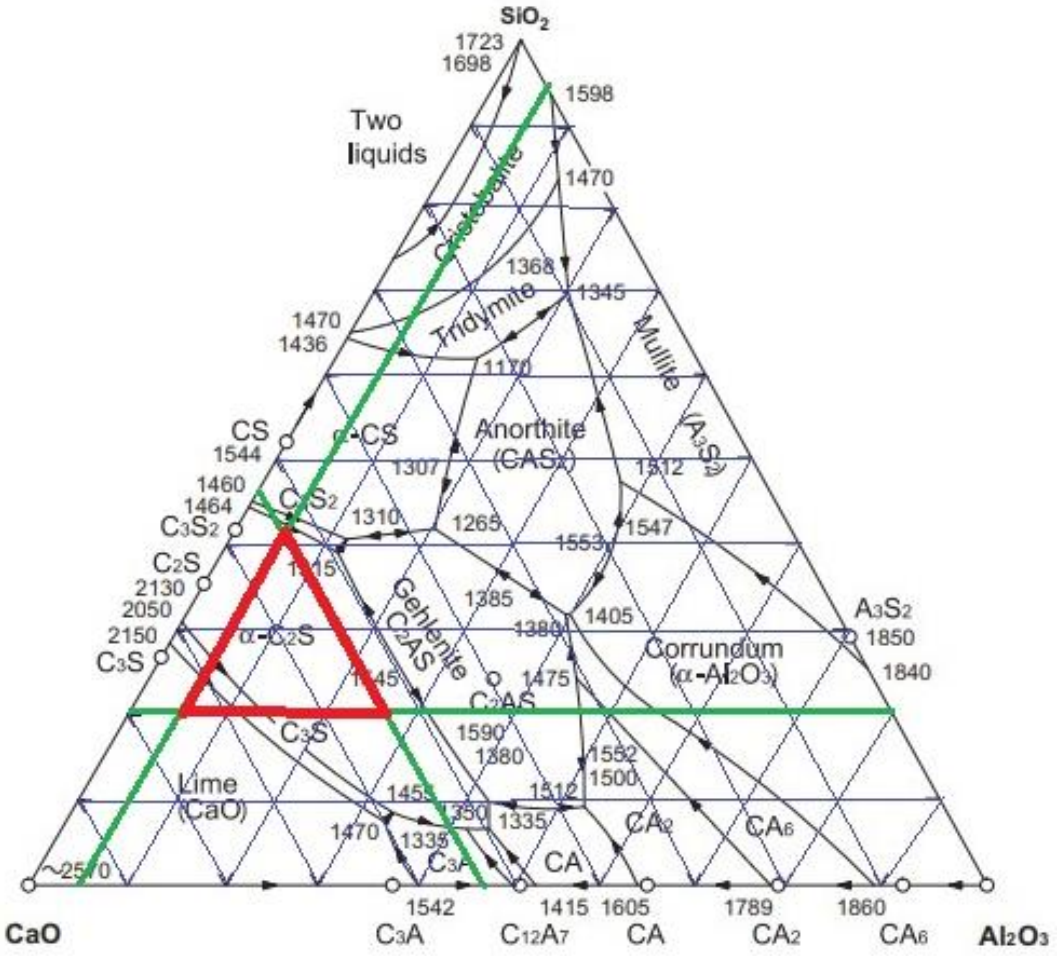


Figure 3.5. Location of WPSA on the ternary diagram

### 3.1.4 Sand

River sand from the local market is utilized to make the cement mortar. Several tests were carried out to determine the sand's suitability for this study. To lessen the amount of silt in the sand, it was washed. Physical properties were determined as well as it will be discussed in subsequent sections.

#### *3.1.4.1 Properties of sand*

Tests to determine the physical properties of the sand were performed at AAiT material testing laboratory as per the Ethiopian standard. Sieve analysis, apparent specific gravity, moisture content, absorption capacity, bulk specific gravity, silt content, unit weight, and fineness modules are among the tests that are performed.

**Sieve analysis**

This is a procedure for the determination of the particle size distribution of the aggregate. It is also used to determine the fineness modulus, an index to the fineness, coarseness and uniformity of aggregates. These properties of the aggregate greatly affect the property of the concrete. The grading requirement for fine aggregate according [46] and the grain size distribution of the fine aggregate is as shown in Table 3.3 and Figure 3.6

Table 3.3. Sieve analysis results and standard for fine aggregate

| Sieve size (mm) | Weight retained (g) | Percent of retained | Percent of cumulative retained | Percent of cumulative passing | ASTM C33 percent of passing |
|---|---|---|---|---|---|
| 9.5 | 0 | 0 | 0 | 100 | 100 |
| 4.75 | 0.6 | 0.12 | 0.12 | 99.88 | 95-100 |
| 2.36 | 21.9 | 4.38 | 4.5 | 95.5 | 80-100 |
| 1.18 | 69.8 | 13.96 | 18.46 | 81.54 | 50-85 |
| 0.6 | 177.8 | 35.56 | 54.02 | 45.98 | 25-60 |
| 0.3 | 201.9 | 40.38 | 94.4 | 5.6 | 5-30 |
| 0.15 | 25.9 | 5.18 | 99.58 | 0.42 | 0-10 |
| Pan | 2.1 | 0.42 | 100 | 0 | 0 |

The grain size distribution curve for the sieve analysis of the sand and the standard is shown in Figure 3.6

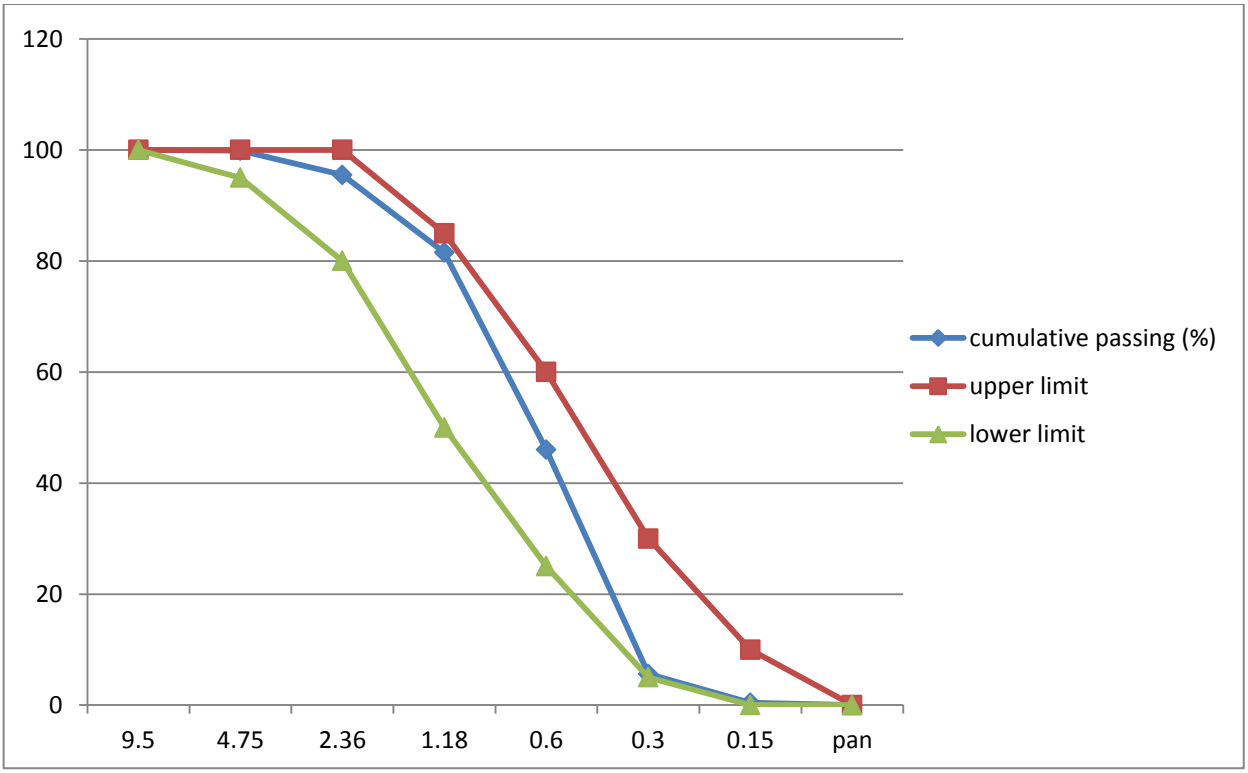


Figure 3.6. Grain size distribution of sand

$$\text{Fineness modulus} = \sum \frac{commulative\ coarser\ (\%)}{100} = \frac{271.08}{100} = 2.71 \qquad \text{(Eq. 3. 1)}$$

**Specific gravity and absorption capacity**

The specific gravity of a material is the weight of that substance divided by the weight of water of the same volume. According to ASTM D-854, a pycnometer, balance, and tamper are used to determine the specific gravity of sand. The same device is used to calculate bulk specific gravity and apparent specific gravity. Because aggregates have pores in their structure, the specific gravity is determined by whether or not the pores are included in the measurement. The apparent specific gravity of an aggregate refers to the solid materials excluding pores, whereas the bulk specific gravity relates to the aggregate's whole volume, which includes pores. Bulk specific gravity, apparent specific gravity & absorption capacity for the sand used in this study are:-

$$\text{Bulk specific gravity} = \frac{A}{B + 500 + C} \quad \text{(Eq. 3. 2)}$$

$$\text{Apparent specific gravity} = \frac{A}{B + A - C} \quad \text{(Eq. 3. 3)}$$

$$\text{Bulk specific gravity ( saturated surface dry basis )} = \frac{500}{B + 500 - C} \quad \text{(Eq. 3. 4)}$$

$$\text{Absorption capacity} == \frac{500 - A}{A} \quad \text{(Eq. 3. 5)}$$

Where:

A = weight of oven dry sample = 497.7 gm

B = weight of pycnometer filled with water = 706.6 gm

C = weight of (pycnometer + sand + water) = 1008.6 gm

Substituting this values in to Eq. 3.2 - Eq. 3.5

Bulk specific gravity= 2.51

Apparent specific gravity = 2.54

Bulk specific gravity ( saturated surface dry basis ) = 2.52

Absorption capacity = 0.462%

**Moisture content**

The workability (flow) and strength of mortar is affected by the moisture content of the sand, which absorbs or releases water into the mix [46]. As a result, determining the moisture content of the sand is required. Oven drying the sample at 105°C for 24 hours and dividing the weight difference by the oven dry weight yields the moisture content. The moisture content of the sand used in this study was found to be = 4.65%

**Silt content**

Impurities such as dust, loam, and clay can sometimes be found in sand. The presence of contaminants like these weakens the bond between sand and cement. As a result, it is vital to examine if the silt content is within the permissible range [46]. The silt content of the sand used in this study is = 1.33%

Figure 3.7**.** Silt content of fine aggregate

**Unit weight**

The weight of a specific volume of graded aggregate is known as unit weight. As a result, it is a density measurement that is also referred to as bulk density. However, because this alternate phrase is comparable to bulk specific gravity, which is a completely distinct quantity, it may not be the best option. The unit weight accurately measures the volume that the graded aggregate will occupy in concrete, taking into account both solid aggregate particles and voids between them. The unit weight is calculated by filling a known-volume container and weighing it. The quantity of void space, and hence the value of the unit weight, will obviously vary depending on the degree of compaction. Because the weight of the aggregate is determined by its moisture content, it is necessary to maintain a constant moisture content. In this test, an oven dried aggregate sample is utilized [46]. The unit weight of the sand in this study was found to be = 1490.97 kg/m$^3$

The above test results are summarized in Table 3.4:

Table 3.4. Physical properties of sand

| No | Test description | | Test result |
|---|---|---|---|
| 1 | Fineness modulus | | 2.71 |
| 2 | Specific gravity | Bulk | 2.513 |
| 3 | | Bulk (SSD) | 2.525 |
| 4 | | Apparent | 2.54 |
| 5 | Absorption capacity | | 0.462% |
| 6 | Moisture content | | 4.65% |
| 7 | Silt content | | 1.33% |
| 8 | Unit weight | | 1490.97 kg/m$^3$ |

### 3.1.5 Water

In this study tap water supplied by AAWSA that is found AAiT laboratory is used.

## 3.2 Methods and Procedures

### 3.2.1 Introduction

The major goal of this experimental study is to determine the suitability of waste paper sludge ash (WPSA) as a partial cement replacement material.

To attain this goal, several tests were carried out. The physical properties of plain and blended cement (at the optimal level of replacement) including consistency, fineness, and setting time were determined in the first experiment. The goal of the second experiment was to determine the optimal level of replacement based on compressive strength development. The third experiment focuses on assessing the reactivity of WPSA. Each experiment is discussed in detail in the following sections.

### 3.2.2 Experiment I: Physical and Chemical Property Determination

The fineness, specific gravity of cement and WPSA, normal consistency, and setting time of the reference and blended pastes were determined in the first experiment.

The replacement level of WPSA was made by volume in order to keep the volume of cementitious material per unit volume of mortar constant. The volume equivalency of WPSA is determined by using Equation (3.6): [47]

$$F_w = \frac{1}{1+\left(\frac{Gc}{Gp}\right)\left(\left(\frac{1}{Fv}-1\right)\right)} \quad \text{(Eq. 3. 6)}$$

Where:

$F_w$ = pozzolanic material percentage by weight expressed as decimal factor

$G_c$ = specific gravity of cement = 3.15

$G_p$ = specific gravity of pozzolonic material = 2.6 g/cm$^3$

$F_v$ = pozzolanic material percentages by absolute volume of the total absolute volume of cement plus pozzolanic material expressed as a decimal factor

Assuming 1% replacement by volume, i.e. $F_v$ = 1%

$$F_w = \frac{1}{1+\left(\frac{3.15}{2.6}\right)\left(\left(\frac{1}{0.01}-1\right)\right)} = 0.826\% \quad \text{(Eq. 3. 7)}$$

This implies that replacing 1% volume cement by an equal volume of WPSA is equivalent to replacing 0.826% weight cement with WPSA. In simple terms 1 kg of cement has to be replaced with 0.826 kg WPSA in order to keep the volume of cementitious material constant in the mix.

### 3.2.3 Experiment II: Compressive Strength Determination

#### *3.2.3.1 Mix Proportion of Mortar*

This experiment involves preparing different mortar mixes by replacing the cement at different levels. Replacement level is based on volume. Assuming all other parameters are kept constant, the mix is prepared by varying the cement. The mix proportion used for the preparation of mortar is as shown in Table 3.5

Table 3.5. Mix Proportions and Materials for Mortar Specimens

| Mix code | B0 | B5 | B10 | B15 | B20 | B25 | B30 |
|---|---|---|---|---|---|---|---|
| $F_v$ (%) | 0 | 5 | 10 | 15 | 20 | 25 | 30 |
| $F_w$ (%) | 0 | 4.13 | 8.27 | 12.4 | 16.54 | 20.67 | 24.8 |
| WPSA (gm) | 0 | 30.59 | 61.19 | 91.78 | 122.37 | 152.97 | 183.56 |
| Cement(gm) | 740 | 703 | 666 | 629 | 592 | 555 | 518 |
| Total binder (gm) | 740 | 733.59 | 727.19 | 720.78 | 714.37 | 707.97 | 701.56 |
| Sand (gm) | 2035 | 2035 | 2035 | 2035 | 2035 | 2035 | 2035 |
| Water (gm) | 359 | 359 | 359 | 359 | 359 | 359 | 359 |

Where:

B0 is the control mix with 100% cement

B5 is the mortar mix with 5% WPSA & 95% cement

B10 is the mortar mix with 10% WPSA & 90% cement

B15 is the mortar mix with 15 % WPSA & 85% cement

B20 is the mortar mix with 20% WPSA & 80% cement

B25 is the mortar mix with 25% WPSA & 75% cement

B30 is the mortar mix with 30% WPSA & 70% cement

### *3.2.3.2 Mix Procedure and Specimen Preparation*

The AAiT material testing laboratory's auto mix programmed mixer was utilized to mix the mortar as per ASTM C-305 [48]. The mix is prepared by mixing cement and sand in a ratio of 1:2.75 and water to cement ratio of 0.485. This method is chosen because it doesn't need any further mix design since it already gives the quantity of the materials to be mixed. The bowl was filled with cement, WPSA, and sand, which were dry mixed for about two minutes. After that, water was added to the bowl, and the mixer run for 150 seconds at various speeds. The workability of the mortar was determined using a flow table test as soon as the mixing was completed [46]. The fresh mortar was then poured into a 70 mm x 70 mm x 70 mm cube mold and compacted in two layers using a vibrating table. The top surface is smoothed using a trowel after vibration. After 24 hours, the specimens were demolded and put in a curing pond until the day of testing.

a) b)

Figure 3.8. a) Mixer and b) Flow table test

#### *3.2.3.3 Compressive Strength Determination*

Compressive strength test at 7, 28 and 56 days of age was conducted to determine the optimum level replacement. For each replacement level, 3 sets (3x3 =9) mortar cubes were prepared for destructive compressive strength test.


a) b)

Figure 3.9. Compressive strength test, a) Compressive strength testing machine, b) test setup

### 3.2.4 Experiment III: Reactivity Assessment

#### *3.2.4.1 XRD Analysis*

This experiment was undertaken to determine the existence of hydration reaction products and to characterize the hardened paste if hydraulic reactions were truly occurring under these testing circumstances. Cast samples from the same batch were cured for 28 days at 25°C. The samples were taken out of the curing pond after 28 days. The crystalline phases generated were characterized and the portlandite consumption was determined using an XRD test [32]. The hardened pastes were ground and sieved by a 0.075mm sieve to ensure adequate fineness is acquired.

### *3.2.4.2 Bound Water Determination*

The bound water content in cementitious pastes is estimated by quantifying mass loss between 105°c and 600°c and normalizing this value to the cementitious paste mass at 105°c. In various literatures, similar procedures have been described. [49, 50]. The ignition temperature of 350°C is suggested because studies demonstrated a commencement of a rate of mass loss around 400°c due to the ignition of residue of lime [28].

4mm reference and blended samples were prepared and cast in triplicate on plastic sheets, which were subsequently sealed at 25°C for 24 hours. The samples were cured for the next seven days. Following that the samples were taken in to an oven. In a 105°C oven, the samples were dried until they reached a consistent dry mass ($m_{105oc,\ stabilized}$). Samples were considered dry when the mass change within one day did not exceed 0.5 percent [51]. In this experiment, the conditions were met after two days of drying. The samples were then heated to 350°c. The temperature was kept at this level for two hours. Because higher temperatures resulted in portlandite dehydroxylation, which was not the goal of this study, the thermal treatment was limited to 350°C. The test is depicted graphically in figure 3.10.

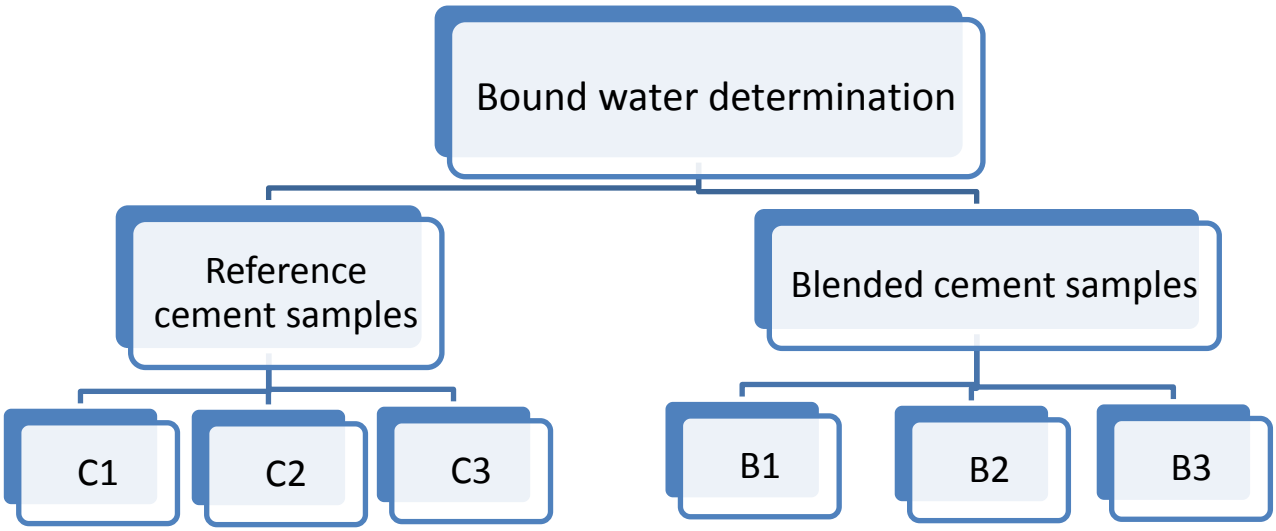


Figure 3.10. Schematic Representation of Bound Water Determination Test

After cooling the samples were taken in a desiccator to avoid moisture absorption from the atmosphere and weighed by a beam balance ($M_{350^o c,cooled}$). Finally, the bound water

was determined by computing the mass change after heating the samples, as given by equation (3.2):

$$\text{Bound water (\%)} = \frac{M_{105^o c,Stabilized} - M_{350^o c,cooled}}{M_{105^o c,Stabilized}} \quad \text{(Eq. 3. 8)}$$

The bound water measured here is not corrected for bound water in the OPC and SCMs; these changes will affect the bound water numbers but are unlikely to affect the nature of the conclusions drawn from the bound water testing.


Figure 3.11. Samples Prepared for Bound Water Determination Test

### *3.2.4.3 Modified Chappelle Test*

One way for determining the reactivity of materials is to measure the amount of calcium hydroxide consumed by 1 g of WPSA when mixed with 1 g of CaO and 250 ml of distilled $CO_2$ free water. The Modified Chappelle test iss used to determine the amount of $Ca(OH)_2$ by the reaction of CaO with WPSA. When compared to the Frattini test, this test provided a faster indication of reactivity (within a day) [52]. 1 gram of WPSA was combined with 1 gram of calcium oxide and 250 milliliters of deionized water for this experiment.

The WPSA-lime samples were prepared parallel with the reference samples made entirely of lime. The mixture was heated at 90°C for 16 hours, stirring continuously. The plastic bottles were sealed to minimize water loss.

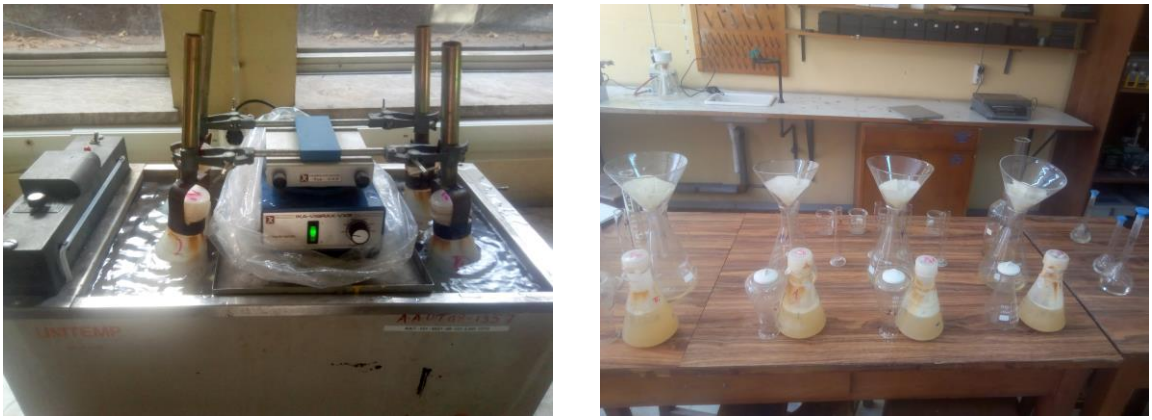

Figure 3.12. Modified Chapelle Test Experiment Under Investigation

After cooling down to 20°C (room temperature), a solution of 60g sucrose in 250ml of deionized water was added to complex the calcium ions in the solution and to dissolve the unreacted portlandite. The liquid was titrated with a 0.1M solution of HCl using phenolphthalein as a PH indicator after being filtered through a filter paper.

The amount of portlandite consumed, meaning that the reactivity of WPSA (RWPSA) is determined using Equation 3.11 [31, 52].

The result is determined by titrimetry with HCl and the titration reactions are given by:

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O \quad \text{(Eq. 3. 9)}$$

$$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O. \quad \text{(Eq. 3. 10)}$$

The RWPSA is calculated using Eq. (3.11)

$$\text{RWPSA(in mg } Ca(OH)_2 \text{ consumed / g WPSA )} = 2 * \frac{V_1 - V_2}{V_1} * \frac{74}{56} * 1000 \quad \text{(Eq. 3. 11)}$$

Where:

PAWPSA - Pozzolanic Activity of WPSA, expressed in mg Ca(OH)2 fixed / g WPSA;

$V_1$ - Volume of HCl added to the solution obtained from without WPSA (blank test);

$V_2$ - Volume of HCl added to the solution obtained with WPSA.

The blank test (without WPSA) must verify $V1 * \frac{56}{2} < 1000$ and the repeatability of the modified Chapelle test is 10% [35].

# CHAPTER 4 TEST RESULTS AND DISCUSSION

## 4.1 Introduction

This section presents and discusses the results of laboratory tests on waste paper sludge ash for its applicability as a partial cement-replacing material. Results on OPC and WPSA physical and chemical characteristics, microstructure characterization of pastes using XRD analysis, and WPSA reactivity assessment using modified Chappelle test, bound water determination using oven treatment, and mortar cube compressive strength determination are all covered.

Experiments were carried out at the material testing laboratory of the Addis Ababa Institute of Technology, the Chemical Engineering laboratories of Addis Ababa University, and the Ethiopian geological survey laboratory. The test results and an explanation of each experiment are presented in the sections that follow.

## 4.2 Test Results and Discussion on Experiment I:

### 4.2.1 Physical Property Test Results and Discussion

Physical properties such as fineness and specific gravity of cement and WPSA were measured. Normal Consistency and setting time of the reference and blended paste were also tested and discussed in this part.

#### *4.2.1.1 Fineness Test Result and Discussion*

The fineness has a direct relationship with the hydration rate and strength development. Bleeding can be reduced by increasing fineness. Fineness is measured by specific surface value. One method to determine fineness is by blain air permeability method [53]

The specific surface value is calculated according to Eq. (4.1):

$$S = \frac{Ss\sqrt{T}}{\sqrt{Ts}} = \frac{3774*\sqrt{97}}{\sqrt{37.8}} = 6045.6 cm^2/gm \quad \text{(Eq. 4. 1)}$$

Where:

S = specific surface of the test sample, $cm^2/gm$

$S_s$ = specific surface of the standard sample used in the calibration of the apparatus, $cm^2/gm$ = 3774 $cm^2$ /gm

T= measured time interval of monometer drop for test sample, sec= 97sec

$T_s$ = measured time interval of monometer drop for standard sample used in the calibration of the apparatus, sec = 37.8 sec

Figure 4.1. Blaine Value Apparatus (left) and Measured Samples (right)

As can be observed from the results above, WPSA had a blaine surface area of 6045.6 $cm^2/gm$. OPC cement, on the other hand, has a blaine surface area of 3,601 $cm^2/gm$ [5]. These demonstrate that compared to cement, WPSA has greater surface area.

The surface area of cement is a helpful predictive parameter since it is closely related to many important characteristics, such as strength and permeability. A higher specific surface area leads to a higher calcium-silicate-hydrate reaction product

### *4.2.1.2 Specific gravity Test Result and Discussion*

As per ASTM C-188, the test is performed with Le Chatelier's flask and kerosene.

The specific gravity of WPSA = 2.6 $g/cm^3$

Specific gravity which is also known as density is used in the calculation of the weight of replacing material. Since the densities of cement and WPSA differ, the estimation of specific gravity is critical in calculating the mass equivalent of the replacement material.

#### *4.2.1.3 Normal Consistency and Setting Time Test Result and Discussion*

The normal consistency and setting time for reference and blended pastes were determined, and the findings are presented in Table 4.1 The optimal level of replacement, as mentioned in section 4.3.2, is 15%. As a result, this ratio is used to prepare blended samples for physical property determination tests.

Table 4.1. Normal Consistency and stiing time Test Results

| Cement hype | Normal consistency (%) | Setting time (min) | |
|---|---|---|---|
| | | Initial setting time | Final setting time |
| OPC | 29.5 | 129 | 345 |
| Blend (WPSA15) | 32 | 69 | 330 |

Table 4.1 shows the normal consistency of reference and blended (containing WPSA) pastes. The consistency of the control paste, i.e. the paste without WPSA, was 29.5%. while that of the blended sample was found to be 32%. WPSA-containing pastes had a higher consistency than the control paste.

The consistency of the blended pastes was found to be consistent with prior studies [9]. For a normal consistency, the water to cement ratio should be between 26 and 33% [46]. The pastes that had a 15% replacement exhibited consistency in this range.The increased water demand is most likely due to WPSA's higher fineness (6045.6 $cm^2$ /g) and porosity when compared to cement.

The initial setting time of cement must not be shorter than 45 minutes, and the final setting time must not exceed 10 hours, according to Ethiopian standards. The results for the setting time in Table 4.1 showed that adding WPSA results in shorter setting time. The setting time has been decreasing as the WPSA material has increased.

For the paste containing 15% WPSA, a faster setting time was noted. This is due to the presence of around 53% CaO in the WPSA, which causes quick initial hydration and setting. This problem is expected to be solved in the future with the use of appropriate plasticizer/retarder admixtures.

Some researchers concurred that the setting time of OPC-SCMs blended pastes decreases. The adsorption of water on the WPSA surface could be the cause of the shorter setting time. As the fineness of cementitious particles increases, so does the rate

of hydration, which could explain why the setting time has accelerated [54]. The higher the WPSA proportion, the greater the water adsorption, which increased the normal consistency and enhanced the setting time.

## 4.3 Test Results and Discussion on Experiment II:

This section presents and examines various test results on blended mortars. Workability (flow) and compressive strength of the OPC-WPSA blended mortars are among them.

### 4.3.1 Workability (Flow) of Mortar

The flow table test is used to determine the workability of the mortar before it is cast into the mold. The workability values for the control and blended mortars are listed in the Table 4.2 below.

Table 4.2. Flow table values of OPC-WPSA blended mortar

| **MIXCODE** | B0 | B5 | B10 | B15 | B20 | B25 | B30 |
|---|---|---|---|---|---|---|---|
| **FLOW** | 126.1 | 115.33 | 110.91 | 97.84 | 89.77 | 85.26 | 84.04 |

As it can be seen in Figure 4.2, the flow value falls slightly as the WPSA content rises. This is because the WPSA has a larger specific surface area than the OPC in the control specimen, requiring more water to wet the surface.

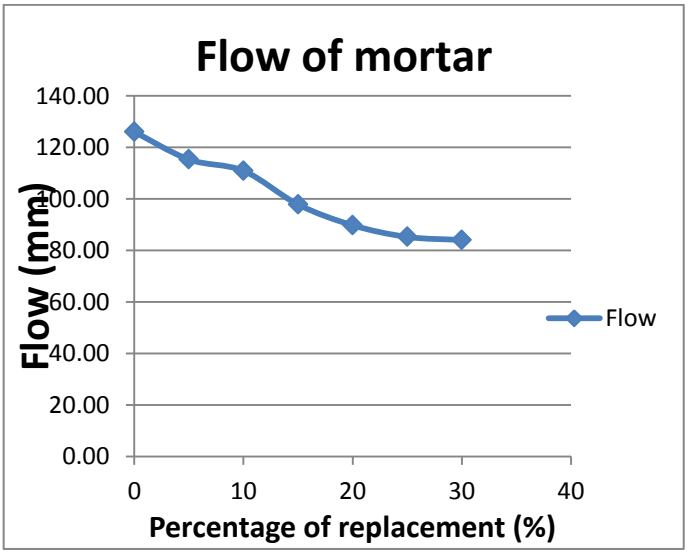


Figure 4.2. Variation of flow (Workability)

### 4.3.2 Compressive Strength of Mortar

The variation of compressive strength as measured by the Compressive Strength test is shown in Figure 4.3. At the ages of 7, 28, and 56 days, compressive strength tests were performed on both blended and reference mortars. Figure 4.3 shows the average strength values, whereas Annex A.A has the detailed results.

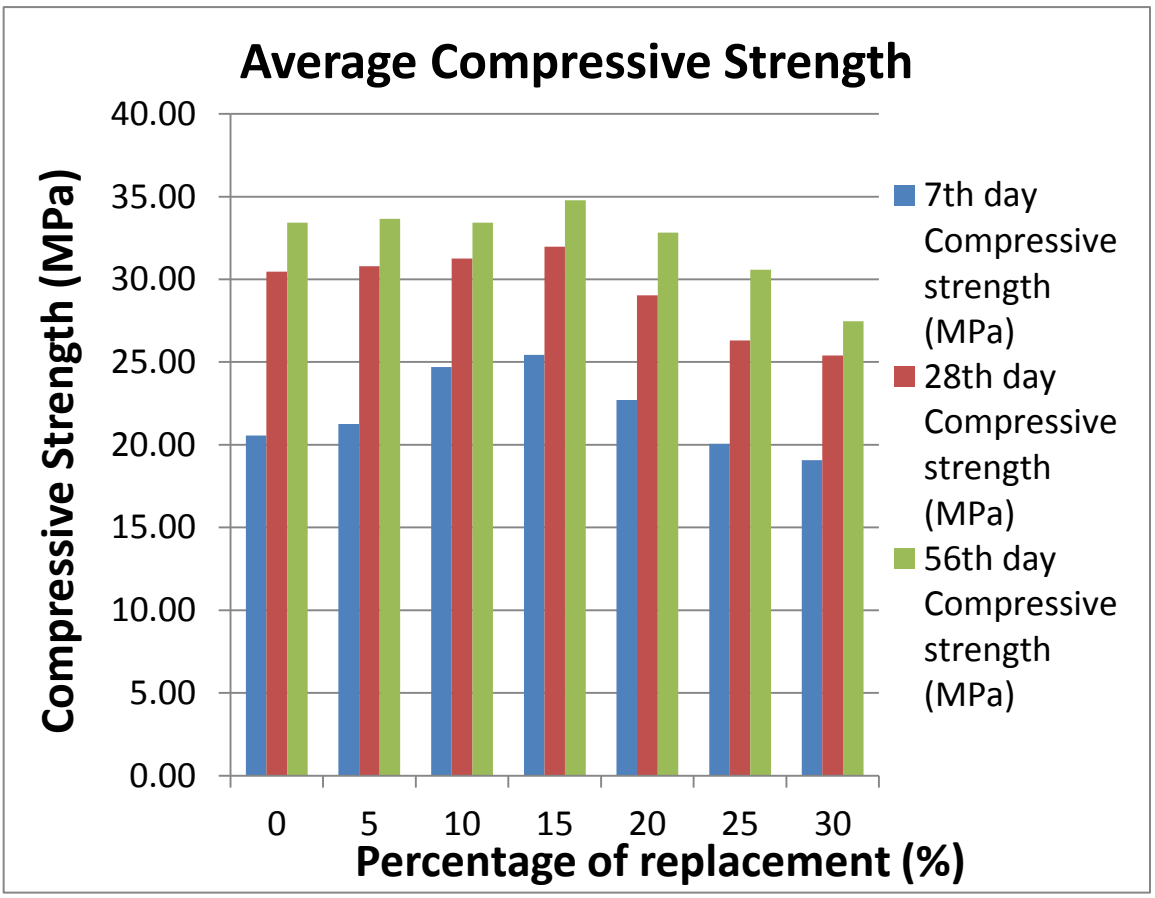


Figure 4.3. Evolution of compressive strength values of the mortar cubes

The compressive strength values shown in figure 4.3 are the averages of three specimens made from each mix. Individual specimens' compressive strength variations should be within acceptable limits (with standard deviation within 3 MPa) [55]. All test results fall within this range.

The compressive strength of the control group is 20.55 MPa, 30.46 MPa, and 33.42 MPa after 7, 28, and 56 days of curing, respectively. Compressive strength increased up to 15% replacement of cement by WPSA, but it began to decline after that, as shown in Figure 4.3. Despite the fact that mixes containing 5% or even 10% sludge ash have

slightly higher compressive strength than the control group, the maximum compressive strength was achieved at B15, i.e. 15% cement replacement with WPSA. The maximum compressive strength tested at the 7th, 28th, and 56th days was slightly greater than that of the reference mix by 23.76 percent, 4.99 percent, and 4.04 percent, respectively, at this optimum level of replacement. Since the results are more or less the same after partially replacing cement by WPSA, it can be seen that using WPSA as a partial cement replacing material is possible.

According to other authors, the strength enhancement could be related to a modest pozzolanic effect [56]. Or to the fact that waste paper sludge ash particles could act as extra sites for the nucleation and development of hydration products, improving the overall hydration process [57]. The test results demonstrate that compressive strength increased until it reached 15% replacement, after which it began to decline.

As can be observed on figure 4.3, beyond 15% replacement level all the blended mortars assessed present a value lower than that obtained for the control mortar. These findings are particularly intriguing because the blended mortars showed a large reduction in Portland cement use (up to 30% by mass) and, as a result, a decrease in greenhouse gas emissions associated with this new blended cement. The results obtained are likewise highly noteworthy in terms of mechanical strength, and they can be expressed by their compressive strength activity index (CSI) [58]. CSI is calculated using equation (4.2):

$$CSI = \frac{R_b}{R_C} \qquad \text{(Eq. 4. 2)}$$

where:

CSI is the compressive strength index;

$R_b$ is the compressive strength for the blended mortar;

$R_c$ is the compressive strength for the control mortar.

For all the assessed mortars, the obtained CSI is presented in Table 4.3

Table 4.3. Strength activity index of OPC-WPSA mortar

| MIX CODE | CSI | | |
|---|---|---|---|
| | $7^{th}$ day | $28^{th}$ day | $56^{th}$ day |
| B 0 | 1 | 1 | 1 |
| B 5 | 1.03 | 1.01 | 1.01 |
| B 10 | 1.20 | 1.03 | 1 |
| B 15 | 1.24 | 1.05 | 1.04 |
| B 20 | 1.11 | 0.95 | 0.98 |
| B 25 | 0.98 | 0.86 | 0.92 |
| B 30 | 0.93 | 0.83 | 0.82 |

Although the variation is small, it can be stated that using 15 percent WPSA as cement may result in a greater compressive strength value than the control sample.

Figure 4.4 illustrates that when the percentage of WPSA increases, mortar density falls. In mortar mix ratios, the maximum density is 2.129 g/cm$^3$ at 0 percent WPSA, while the minimum density is 2.09 g/cm$^3$ at 30 percent WPSA. Although the difference in density is negligible the presence of WPSA has resulted in the decrease of density. This drop in density could be explained by the fact that WPSA has a lower bulk density than other mortar constituents, and WPSA blended mortar entrapped more air than control mix mortar. These are two possible explanations for the decrease in density of the mortar.

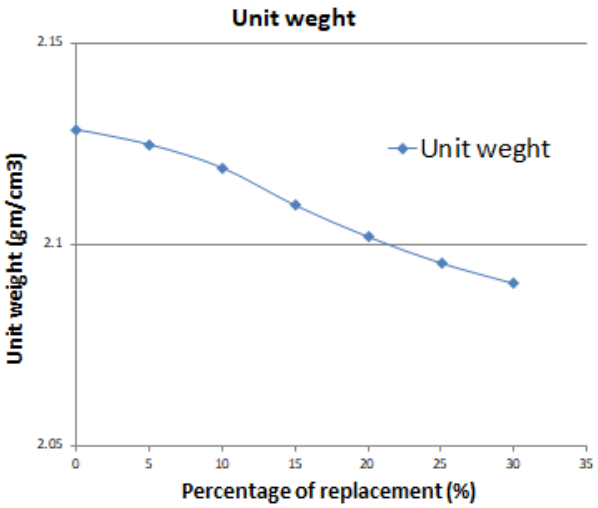


Figure 4.4. Variation of unit weight

## 4.4 Test Results and Discussion on Experiment III:

### 4.4.1 XRD Analysis

The purpose of this experiment is to examine the microstructure of pastes after the hydration process. Two samples were prepared to accomplish this through the use of XRD analysis to characterize the hardened paste. The first sample was a pure cement paste, while the second sample was created by replacing 15% of the cement by WPSA. 15% replacement level is chosen because with respect to compressive strength the optimal level of replacement, as mentioned in section 4.3.2, is 15%. CuK radiation diffractometer which is located at Addis Ababa University's Chemistry department was used to conduct the test. XRD patterns were created after samples were evaluated and chemicals identified. Peaks and patterns of chemicals were investigated using these as a starting point. Figures 4.5 and 4.6 show the results of the analysis.

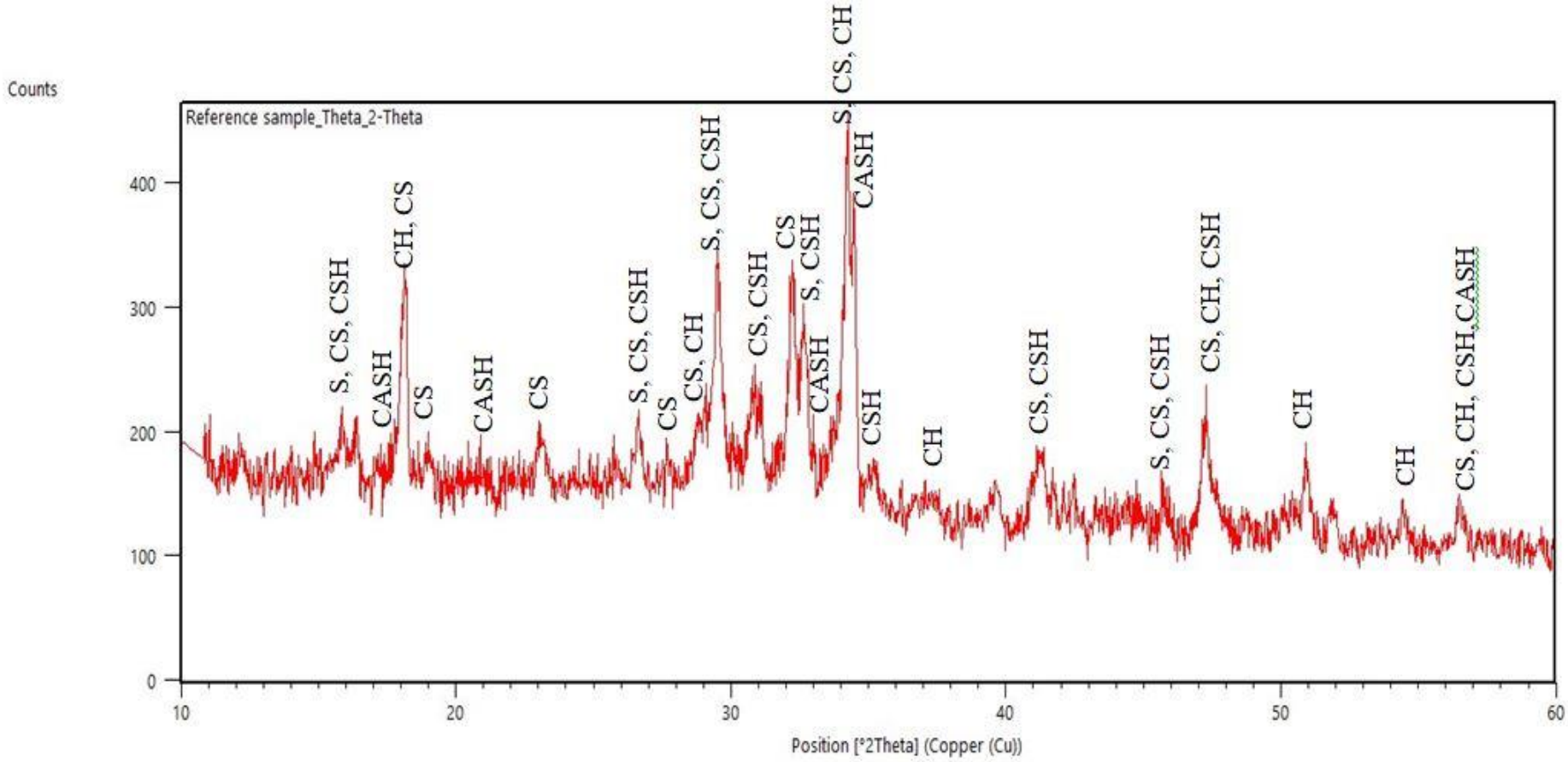


Figure 4.5. Chemical Compounds Detected in Reference Sample at Day 28

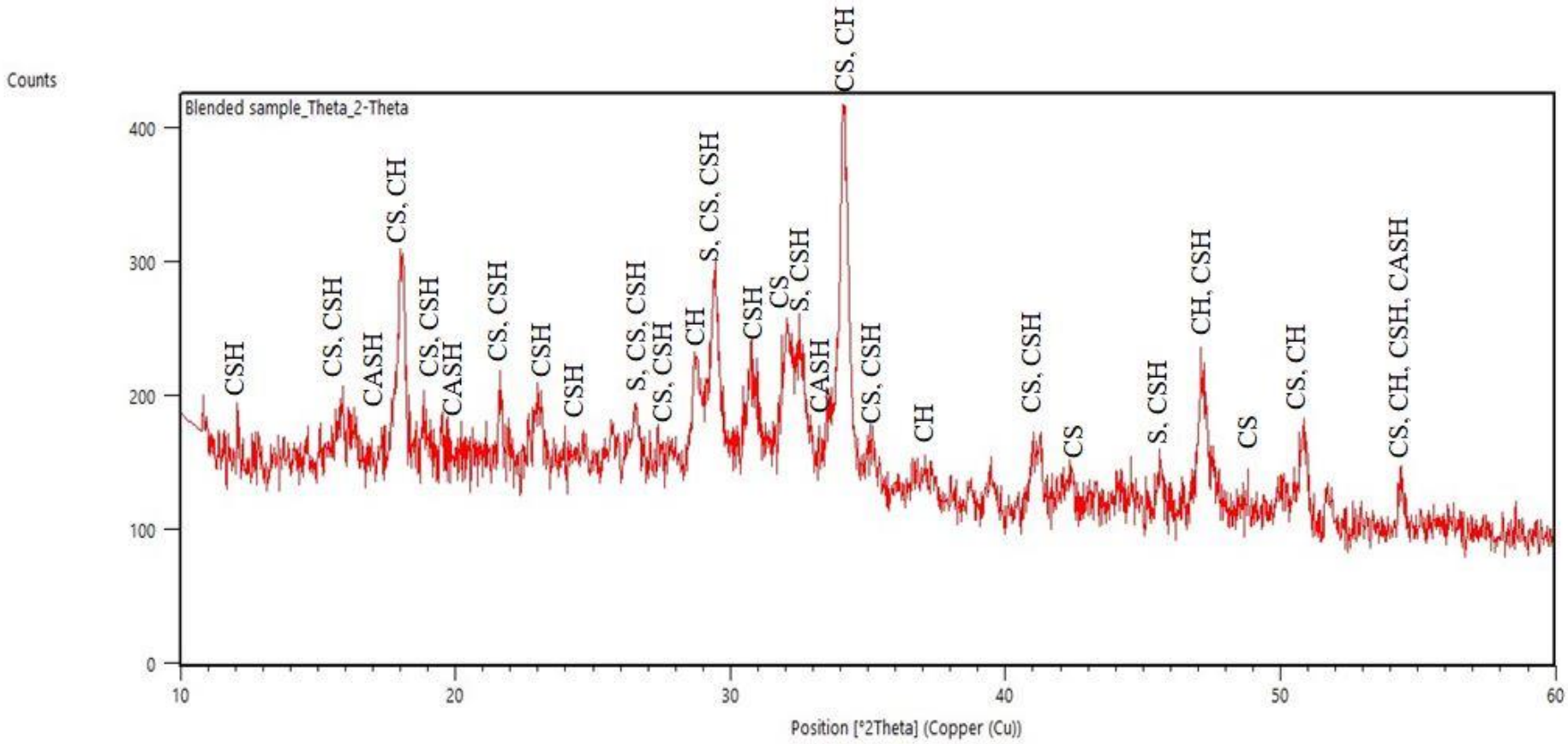


Figure 4.6. Chemical Compounds Detected in Blended Sample at Day 28

Table 4.4. Abbreviations of Compound used in the XRD diagram

| Abbreviation | Compound Name | Chemical formula |
|---|---|---|
| S | Silicon di oxide | $SiO_2$ |
| CS | Calcium silicate | $Ca_3SiO_5$ or $Ca_2SiO_3$ |
| CH | Calcium hydroxide | $Ca(OH)_2$ |
| CSH | Calcium silicate hydrate | $Ca_3Si_3O_9.H_2O$ |
| CASH | Calcium aluminate silicate hydrate | $CaAl_2Si_3O_{10}.H_2O$ |

S, CS, CH, CSH, and CASH are the peaks observed in both the reference and blended samples, according to the XRD data. In the blended sample, however, there were more CSH peaks. This indicates that the blended sample has had more hydration reaction products than the reference sample. A higher hydration is a clear indication of a higher compressive strength. This is in line with the results of the compressive strength test.

### 4.4.2 Bound Water Determination Test

Measurement of mass loss between 105°C and 350°C was used to measure the bound water content of cementitious pastes, which was then normalized to the mass of the cementitious paste at 105 °C [28].

Three samples from each of the control and blended batches were prepared, cast, and cured at 25°C for 7 days. The blended samples were prepared for the optimal level of replacement as mentioned in section 4.3.2 i.e. 15% of cement replaced by WPSA. As a result, this ratio is used to prepare blended samples for physical property determination tests.

The samples were heated in a 105°C oven until they reached a consistent dry mass. After that, the samples were placed in the furnace at 350°C for 2 hours before the temperature was lowered to 105°C. To eliminate moisture absorption from the atmosphere, samples were placed in a desiccator and weighed using a beam balance.

The reference samples had 4.18% bound water on average, while the blended samples had 5.21% bound water on average, according to the results of the studies. The amount of bound water in the blended samples was higher. Table 4.5 shows the results of the cast sample measurements as well as the bound water amount determined.

Table 4.5. Bound water determination test results

| Sample | Oven dry mass (gm) @$m_{105^{o}c,stabilized}$ | Incinerated mass (gm) @$m_{350^{o}c,cooled}$ | Bound Water (%) | Average |
|---|---|---|---|---|
| C1 | 52.2881 | 50.322 | 3.7601 | 4.1788 |
| C2 | 47.0166 | 45.0073 | 4.2735 | |
| C3 | 50.7154 | 48.4317 | 4.5029 | |
| B1 | 48.7106 | 46.2654 | 5.0198 | 5.2094 |
| B2 | 48.0597 | 45.5289 | 5.2659 | |
| B3 | 48.5206 | 45.9283 | 5.3426 | |

Where:

C1, C2 & C3 are paste mixes with 100% cement and 0% WPSA

B1, B2 & B3 are paste mixes with 85% cement and 15% WPSA

At various stages of hydration, the bound water content of cementitious pastes can be determined. For mixes with lower w/c ratios and higher bound water content, a higher rate of hydration was observed [59].

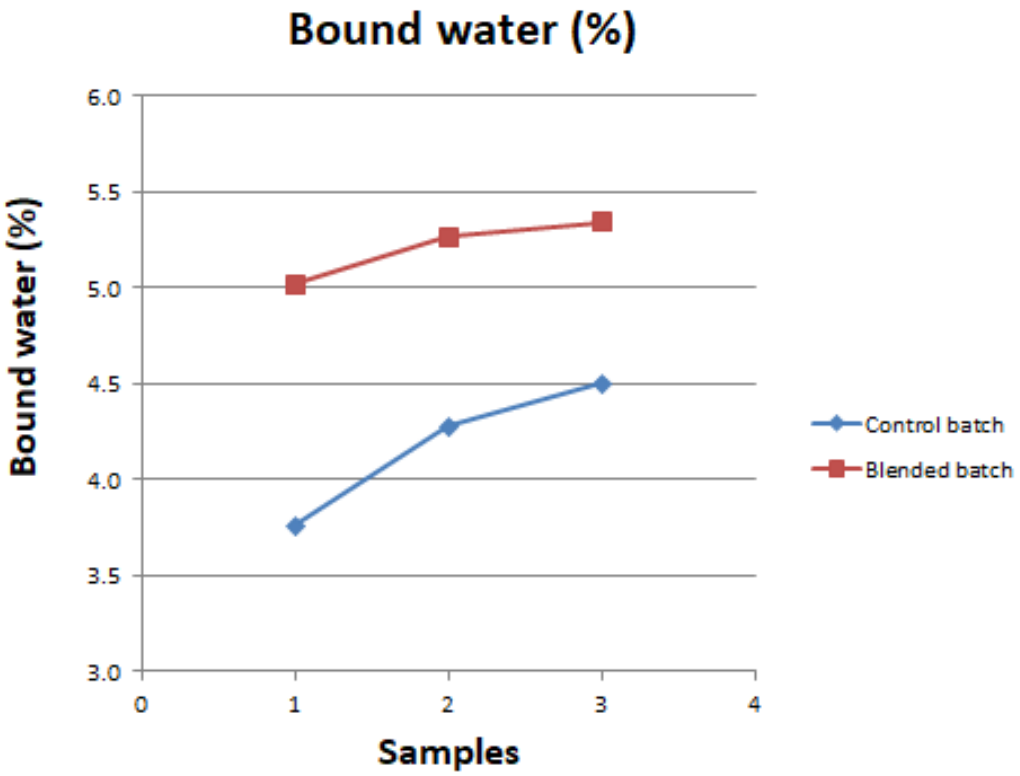


Figure 4.7. Experiment Results for Bound Water Determination Graphically Represented

The degree of hydration in the cement mix is determined by the amount of chemically bonded water detected by ignition. The above result revealed that blended samples had a higher percentage of bound water. During the hydration period (28 days), there is more hydration reaction (CSH formation) in blended samples, implying higher strength. From this it can be concluded that the inclusion of WPSA enhanced the hydration reaction that led to higher compressive strength.

### 4.4.3 Modified Chappelle Test

In the AAiT water treatment laboratory, the reactivity of WPSA was determined using the Modified Chappelle test. By quantifying the fixed lime, the test utilizes a direct laboratory method to determine the reactivity of WPSA. Figure 4.8 depicts the test setup and titration of the filtered solution.

Figure 4.8. Test setup for titration of the filtered solution.

HCl titration is used to determine how much calcium oxide (lime) was consumed. The test was replicated, and similar results were observed. The outcome is measured in milligrams of fixed $Ca(OH)_2$ per gram of WPSA. Table 4.6 shows the results of these testing.

Table 4.6. Reactivity of WPSA

| Measurements | Volume of HCl Samples (ml) | | | |
|---|---|---|---|---|
| | Blank | Blend 1 | Blend 2 | Blend 3 |
| 1 | 9.1 | 13 | 12.8 | 13.5 |
| 2 | 9.2 | 12.9 | 13.7 | 12.7 |
| 3 | 7.6 | 12.6 | 12.6 | 10.5 |
| Average | 8.63 | 12.83 | 13.03 | 12.23 |
| RWPSA (mg $Ca(OH)_2$/ g WPSA) | | -1285.71 | -1346.93 | -1102.04 |
| Grand average | | -1244.89 | | |

This test requires the reference sample to verify V1 ∗ 56/2 < 1,000, and all of the reference sample values meet this requirement. On the basis of this, an average pozzolanic activity value of -1244.89 mg $Ca(OH)_2$ / g WPSA was calculated. This demonstrates the absence of a pozzolanic response. The negative number denotes that the WPSA-lime solution contains more lime than the blank solution. From this result it can be concluded that there is a lack of reactive silica in the WPSA, and the compressive strength enhancement is attributed to filler effect of SCMs rather than the development of extra calcium silicate hydrate (C-S-H).

The presence of SCM alone increases the hydration of the clinker phases. This effect is usually referred as the filler effect. The SCM's replacement level and fineness have been proven to be key determinants of hydration kinetics [60, 61]. Several theories have been proposed to explain the filler effect based on these findings [62]. The first theory is linked to cement dilution. Because ground clinker has been replaced by other materials, there is now greater space available for the creation of hydrates from clinker hydration [63]. As a result, when compared to plain clinker cement paste, the cement is diluted, which is thought to alter the kinetics and microstructure development. The second theory suggested is the heterogeneous nucleation of C-S-H on the filler surface, as there is a significant reliance on the SCM particles' surface [64, 65]. The increase in C-S-H nucleation sites is thought to be responsible for the increased hydration rate and in turn higher strength [65].

Since WPSA lacks reactive silica, the improved compressive strength can be attributed to the filler effect of WPSA, according to the modified Chappelle reactivity test results.

# CHAPTER 5 ECONOMIC ANALYSIS

The WPSA can be used in civil engineering construction applications to get advantages. The benefits include lowering disposal costs and opening up land for other purposes. Additionally, it is regarded as cost-effective because the sale of by-products can at least pay the costs of processing and disposal.

Due to the lack of the requisite data, a detailed cost breakdown and economic analysis of the cost benefits of employing waste paper sludge ash was not conducted. Further studies are needed on this matter.

# CHAPTER 6 CONCLUSIONS AND RECCOMENDATIONS

## 6.1 Conclusions

The overall goal of this research is to assess WPSA's viability as a partial cement replacement material. Physical property determination tests, characterization of the hardened paste by XRD analysis, estimation of the amount of bound water, analyzing the reactivity of WPSA, and determination of the compressive strength of mortar cubes were all carried out to achieve this goal. The following conclusions can be derived from the test results:

- The compressive strength development of mortar mixes containing 5%, 10%, and 15% WPSA shows a slight improvement. However, once this level of replacement is exceeded, the compressive strength gradually decreases.

- WPSA can play a role in the hardening of cement paste. The dosage of WPSA, on the other hand, should not be too high due to its high fineness and, as a result, high water absorption. The blended samples had a higher water demand (Normal consistency) than the reference sample. The blended cement samples' initial and final setting times were likewise shorter than the reference samples.

- According to the results of the XRD examination, both the reference and blended samples contain CS, CH, CSH, and CASH. However, the blended sample had more CSH peaks than the reference sample. The presence of WPSA improved the hydration process, which in turn slightly improved the compressive strength of mortars made by partially substituting the cement with WPSA.

- Based on the reactivity test results it can be concluded that the enhancement of compressive strength can be solely attributed to the filler effect of WPSA.

- The use of waste paper sludge ash in the construction industry will solve the waste paper sludge ash disposal problem, minimize harmful pollutants released into the environment by cement production industries, and thus prove to be environmentally friendly, opening the way for greener cement.

## 6.2 Recommendations

The following recommendations are made based on the findings of this study.

- As per the conclusion, the study recommends cement factories to use WPSA as a partial cement replacing material up to 15%
- Paper factories are recommended to supply the waste paper sludge to cement factories instead of land filling while at the same time contributing to an effective waste management system
- Further studies are needed on the long term performance, shrinkage, heat of hydration and durability.
- Detail economic analysis should be undertaken to evaluate the feasibility of using waste paper sludge ash as apartial cement replacing material.

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# APPENDIX A

Annex A.A Results of Compressive Strength of Mortar Cubes

Table A.A.1 Detail Results of Compressive Strength of Mortar Cubes

| NO. | Test age (days) | Flow (mm) | Dimensions (cm) | | | Weight (gm) | Fracture load (KN) | Compressive strength (Mpa) | Unit weight ($gm/cm^3$) |
|---|---|---|---|---|---|---|---|---|---|
| | | | L | W | H | | | | |
| **At 0% WPSA-Cement Replacement** | | | | | | | | | |
| 1 | 7 days | 129.06 | 7 | 7 | 7 | 738.9 | 102.4 | 20.89 | 2.154 |
| 2 | | 123.94 | 7 | 7 | 7 | 728 | 106.4 | 21.71 | 2.122 |
| 3 | | 126.3 | 7 | 7 | 7 | 732.6 | 93.4 | 19.06 | 2.136 |
| Mean | | 126.43 | | | | 733.2 | 100.73 | 20.55 | 2.138 |
| 1 | 28 days | 125.73 | 7 | 7 | 7 | 727.5 | 155.67 | 31.27 | 2.121 |
| 2 | | 125.63 | 7 | 7 | 7 | 733.3 | 157.09 | 31.56 | 2.138 |
| 3 | | 122.88 | 7 | 7 | 7 | 725.4 | 142.34 | 28.55 | 2.115 |
| Mean | | 124.75 | | | | 728.7 | 151.70 | 30.46 | 2.125 |
| 1 | 56 days | 127.39 | 7 | 7 | 7 | 723.7 | 168.6 | 34.41 | 2.110 |
| 2 | | 127.8 | 7 | 7 | 7 | 730.9 | 155.5 | 31.73 | 2.131 |
| 3 | | 126.2 | 7 | 7 | 7 | 730.8 | 167.3 | 34.13 | 2.131 |
| Mean | | 127.13 | | | | 728.5 | 163.8 | 33.42 | 2.124 |
| **At 5% WPSA-Cement Replacement** | | | | | | | | | |
| 1 | 7 days | 114.7 | 7 | 7 | 7 | 724.5 | 101.3 | 20.67 | 2.112 |
| 2 | | 115.1 | 7 | 7 | 7 | 722.1 | 101.6 | 20.74 | 2.105 |
| 3 | | 116.7 | 7 | 7 | 7 | 728 | 109.5 | 22.36 | 2.122 |
| Mean | | 115.50 | | | | 724.9 | 104.13 | 21.26 | 2.113 |
| 1 | 28 days | 118.42 | 7 | 7 | 7 | 730.7 | 144.2 | 29.43 | 2.130 |
| 2 | | 115.43 | 7 | 7 | 7 | 725.4 | 144.6 | 29.52 | 2.115 |
| 3 | | 118.33 | 7 | 7 | 7 | 730 | 164 | 33.46 | 2.128 |
| Mean | | 117.39 | | | | 728.7 | 150.93 | 30.80 | 2.124 |
| 1 | 56 days | 110.83 | 7 | 7 | 7 | 734.3 | 165.8 | 33.85 | 2.141 |
| 2 | | 115.75 | 7 | 7 | 7 | 729 | 160.96 | 32.85 | 2.125 |
| 3 | | 112.71 | 7 | 7 | 7 | 735.5 | 168 | 34.3 | 2.144 |
| Mean | | | | | | | | | 2.137 |
| **At 10% WPSA-Cement Replacement** | | | | | | | | | |
| 1 | 7 days | 112.32 | 7 | 7 | 7 | 727.2 | 121.9 | 24.87 | 2.120 |
| 2 | | 110.4 | 7 | 7 | 7 | 720 | 110.3 | 22.51 | 2.099 |
| 3 | | 109.2 | 7 | 7 | 7 | 726.7 | 131 | 26.73 | 2.119 |
| Mean | | 110.64 | | | | 724.6 | 121.07 | 24.70 | 2.113 |

| NO. | Test age (days) | Flow (mm) | Dimensions (cm) | | | Weight (gm) | Fracture load (KN) | Compressive strength (Mpa) | Unit weight ($gm/cm^3$) |
|---|---|---|---|---|---|---|---|---|---|
| | | | L | W | H | | | | |
| 1 | 28 days | 118.8 | 7 | 7 | 7 | 727.6 | 154.9 | 31.61 | 2.121 |
| 2 | | 111.5 | 7 | 7 | 7 | 725.8 | 146.1 | 29.82 | 2.116 |
| 3 | | 112.3 | 7 | 7 | 7 | 730.8 | 158.61 | 32.37 | 2.131 |
| Mean | | 114.20 | | | | 728.1 | 153.20 | 31.27 | 2.123 |
| 1 | 56 days | 110.37 | 7 | 7 | 7 | 727 | 163.7 | 34.41 | 2.120 |
| 2 | | 107.26 | 7 | 7 | 7 | 730 | 155.5 | 31.73 | 2.128 |
| 3 | | 106.05 | 7 | 7 | 7 | 726.6 | 167.2 | 34.13 | 2.118 |
| Mean | | 107.89 | | | | 727.9 | 162.13 | 33.42 | 2.122 |
| **At 15% WPSA-Cement Replacement** | | | | | | | | | |
| 1 | 7 days | 93.46 | 7 | 7 | 7 | 727.1 | 126.8 | 25.88 | 2.120 |
| 2 | | 97.02 | 7 | 7 | 7 | 715.2 | 123.4 | 25.18 | 2.085 |
| 3 | | 92.64 | 7 | 7 | 7 | 724.5 | 123.7 | 25.25 | 2.112 |
| Mean | | 94.37 | | | | 722.3 | 124.63 | 25.44 | 2.106 |
| 1 | 28 days | 101.08 | 7 | 7 | 7 | 726.3 | 163.12 | 33.29 | 2.117 |
| 2 | | 94.7 | 7 | 7 | 7 | 729.5 | 147.78 | 30.16 | 2.127 |
| 3 | | 96.7 | 7 | 7 | 7 | 724.7 | 159.2 | 32.49 | 2.113 |
| Mean | | 97.49 | | | | 726.8 | 156.70 | 31.98 | 2.119 |
| 1 | 56 days | 102 | 7 | 7 | 7 | 723.5 | 168.1 | 34.3 | 2.109 |
| 2 | | 101.9 | 7 | 7 | 7 | 719.2 | 169.6 | 34.61 | 2.097 |
| 3 | | 101.1 | 7 | 7 | 7 | 722.9 | 173.5 | 35.41 | 2.108 |
| Mean | | 101.67 | | | | 721.9 | 170.40 | 34.77 | 2.105 |
| **At 20% WPSA-Cement Replacement** | | | | | | | | | |
| 1 | 7 days | 90.77 | 7 | 7 | 7 | 718.6 | 114.7 | 23.4 | 2.095 |
| 2 | | 91.4 | 7 | 7 | 7 | 716.2 | 107.5 | 21.93 | 2.088 |
| 3 | | 90.04 | 7 | 7 | 7 | 722.4 | 111.8 | 22.82 | 2.106 |
| Mean | | 90.74 | | | | 719.1 | 111.33 | 22.72 | 2.096 |
| 1 | 28 days | 89.18 | 7 | 7 | 7 | 724.8 | 142.73 | 29.13 | 2.113 |
| 2 | | 90.85 | 7 | 7 | 7 | 715.2 | 139 | 28.38 | 2.085 |
| 3 | | 86.69 | 7 | 7 | 7 | 724.2 | 145.04 | 29.6 | 2.111 |
| Mean | | 88.91 | | | | 721.4 | 142.26 | 29.04 | 2.103 |
| | 56 days | 90 | 7 | 7 | 7 | 722.2 | - | - | 2.106 |
| | | 90 | 7 | 7 | 7 | 727.5 | 156.5 | 31.95 | 2.121 |
| | | 89 | 7 | 7 | 7 | 717.7 | 165 | 33.69 | 2.092 |
| Mean | | 89.67 | | | | 722.5 | 160.75 | 32.82 | 2.106 |

| NO. | Test age (days) | Flow (mm) | Dimensions (cm) | | | Weight (gm) | Fracture load (KN) | Compressive strength (Mpa) | Unit weight ($gm/cm^3$) |
|---|---|---|---|---|---|---|---|---|---|
| | | | L | W | H | | | | |
| **At 25% WPSA-Cement Replacement** | | | | | | | | | |
| 1 | 7 days | 87.09 | 7 | 7 | 7 | 715.7 | 109.1 | 22.27 | 2.087 |
| 2 | | 89.94 | 7 | 7 | 7 | 709.2 | 89.4 | 18.24 | 2.068 |
| 3 | | 86.3 | 7 | 7 | 7 | 720.3 | 96.3 | 19.66 | 2.100 |
| Mean | | 87.78 | | | | 715.1 | 98.27 | 20.06 | 2.085 |
| 1 | 28 days | 82.42 | 7 | 7 | 7 | 717.2 | 133.9 | 27.32 | 2.091 |
| 2 | | 84 | 7 | 7 | 7 | 721.3 | 123.7 | 25.25 | 2.103 |
| 3 | | 81.49 | 7 | 7 | 7 | 730.3 | 129.2 | 26.37 | 2.129 |
| Mean | | 82.64 | | | | 722.9 | 128.93 | 26.31 | 2.108 |
| 1 | 56 days | 84.7 | 7 | 7 | 7 | 719.2 | 140.2 | 28.62 | 2.097 |
| 2 | | 83.86 | 7 | 7 | 7 | 710.7 | 160 | 32.67 | 2.072 |
| 3 | | 87.5 | 7 | 7 | 7 | 724.7 | 149 | 30.48 | 2.113 |
| Mean | | 85.35 | | | | 718.2 | 149.73 | 30.59 | 2.094 |
| **At 30% WPSA-Cement Replacement** | | | | | | | | | |
| 1 | 7 days | 87.29 | 7 | 7 | 7 | 712.4 | 93.3 | 19.04 | 2.077 |
| 2 | | 80.5 | 7 | 7 | 7 | 713 | 90.7 | 18.82 | 2.079 |
| 3 | | 80.3 | 7 | 7 | 7 | 714.6 | 94.8 | 19.34 | 2.083 |
| Mean | | 82.70 | | | | 713.3 | 92.93 | 19.07 | |
| 1 | 28 days | 87.31 | 7 | 7 | 7 | 721 | 122.6 | 25.03 | 2.102 |
| 2 | | 81.62 | 7 | 7 | 7 | 719.2 | 132.3 | 27 | 2.097 |
| 3 | | 79.7 | 7 | 7 | 7 | 718.7 | 118.3 | 24.14 | 2.095 |
| Mean | | 82.88 | | | | 719.6 | 124.40 | 25.39 | |
| 1 | 56 days | 84.38 | 7 | 7 | 7 | 712.3 | 129 | 26.33 | 2.077 |
| 2 | | 86.74 | 7 | 7 | 7 | 720 | 133.1 | 27.17 | 2.099 |
| 3 | | 88.5 | 7 | 7 | 7 | 721.7 | 131.8 | 28.89 | 2.104 |
| Mean | | 86.54 | | | | 718.0 | 131.30 | 27.46 | |

Annex A.B Chemical Composition Test Result

| | GEOLOGICAL SURVEY OF ETHIOPIA | Doc.Number: GLD/F5.10.2 | Version No: 1 |
|---|---|---|---|
| | GEOCHEMICAL LABORATORY DIRECTORATE | | Page 1 of 1 |
| Document Title: | Complete Silicate Analysis Report | Effective date: | May, 2017 |

Issue Date: -14/09/2021

Customer Name:- Bonsa Teshome.

Request No:- GLD/RQ/170/21

Report No:- GLD/RN/829/21

Sample type :WPSA 800

Sample Preparation: - 200 Mesh

Date Submitted:-08/09/2021

Number of Sample:-One (01)

Analytical Result: In percent (%) Element to be determined Major Oxides & Minor Oxides.

Analytical Method: $LiBO_2$ FUSION, HF attack, GRAVIMETERIC, COLORIMETRIC and AAS.

| Collector's code | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | MnO | $P_2O_5$ | $TiO_2$ | $H_2O$ | LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B-T-01 | 20.12 | 5.78 | 2.16 | 53.88 | 4.70 | 0.90 | <0.01 | 0.02 | 0.18 | 0.26 | 7.23 | 4.40 |

**Note:** - This result represent only for the sample submitted to the laboratory.

| Analysts | Checked By | Approved By | Quality Control |
|---|---|---|---|
| Lidet Endeshaw<br>Nigist Fikadu<br>Yirgalem Abraham | Tizita Zemene | Yohannes Getachew | Gosa Haile |

Annex A.E Pictures During Research

Insert pictures during the research!!!!!!!!!!!!!!!!