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Potential Value-added Utilization of Wood Ash in Construction Materials

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POTENTIAL VALUE-ADDED UTILIZATION OF WOOD ASH IN CONSTRUCTION MATERIALS

By

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B. Tech., Jawaharlal Nehru Institute of Technology, 2016

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the degree of

Master of Science

(in Civil Engineering)

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May 2019

Advisory Committee:

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POTENTIAL VALUE-ADDED UTILIZATION OF WOOD ASH IN CONSTRUCTION MATERIALS

By Naveen Saladi

Thesis Advisor: Dr. Warda Ashraf

An Abstract of the Thesis Presented
in Partial Fulfillment of the Requirements for the
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Wood ash is a byproduct from biomass power plants. Most of the wood ash is currently being disposed as landfilling material that causes severe economic and environmental concerns. This project focuses on the feasibility of using this wood ash in construction materials. Wood ash was found to contain varieties of mineral phases including calcium carbonate, calcium aluminate and quartz. Based on the chemical composition, the efficacy of wood ash (i) as supplementary cementitious materials (SCM), (ii) in the controlled low strength materials (CLSM) production and (iii) Portland cement production was evaluated.

Wood ash with adequate pozzolanic properties can be used as supplementary cementitious materials (SCM) in concrete production. In practice, coal fly ash, slag and silica fume are commonly used SCMs in concrete and these materials positively contribute to the concrete strength and durability at later ages via pozzolanic reaction. Controlled low strength materials (CLSM) are typically produced with high coal fly ash content, low cement content, water and aggregates and the strength is attained via pozzolanic reaction. Because of the probable pozzolanic properties, wood ash can partially or fully replace fly ash in the production of controlled low strength materials

(CLSM). Production of Ordinary Portland Cement (OPC) requires 60 to 70% of CaO phases and generally, it is supplied by using limestone ($CaCO_3$) phases. The significant amount of calcium carbonate phase present in wood ash makes it a potential material to be used as a raw material for cement production.

For SCM, the test results illustrated that the workability of wood ash blended samples is found to reduce as the replacement level is increased, this is because of the presence of metallic alumina. The replacement of wood ash in both ground and sieved form is studied because of the presence of less fine particles. The ground samples are noted to give better strength than that of the sieved ones. The samples with ground wood ash is found to have hydraulic properties. The ground wood ash can replace cement up to 30% and sieved wood ash can replace cement up to 20% in mortar samples without any significant effect on compressive strength. In the CLSM production, the wood ash can replace fly ash by 100 percent without any decrease in the target strength. The cement clinker produced using wood ash as a raw material is found to have a higher reaction rate than that of Ordinary Portland Cement (OPC). The wood ash cement clinker is found to have very similar chemical composition as that of an ordinary Portland cement clinker.

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CHAPTER 1

INTRODUCTION

Concrete as a construction material is used all over the world because of its availability and strength. Cement is a major component used to produce concrete. Cement production in the world has been constantly increasing over the years. And there are a lot of environmental impacts like CO_2 emissions, heavy metals emissions etc. associated with the cement production. Cement industry is a high energy consumption sector and utilizes limestone and shale which are naturally occurring materials in the production process which might result in scarcity of those materials in the future. So, it is necessary to find an alternative to cement in construction materials to overcome the issues listed above. Research has been done on using supplementary cementitious materials like coal fly ash, silica fume and blast furnace slag in the concrete production without having any impact on the strength. Wood ash is a by-product of thermal power plants where it is mainly used for soil stabilization as it rich in silica content based on the preliminary analysis done using the XRD and XRF techniques as described in Chapter 3. Since coal fly ash is also a by-product of power plants and was being used as a supplementary cementitious material in concrete production and in the controlled low strength material production, wood ash can also be a potential material which can be used as a cement replacement and in the production of controlled low strength materials. Minimum research has been done so far to evaluate the performance of wood ash in the construction materials. Because of the high calcium content of the wood ash it can potentially be used as a raw material for cement clinker production.

1.1. OBJECTIVES

The work described in this thesis is focused on the evaluation of wood ash in

- Supplementary Cementitious Materials (SCM) to understand the
    - Compressive strength and effect on hydration rate
    - pozzolanic activity and the rheology of the cement mortar systems
- Controlled low Strength Materials (CLSM) to understand the
    - Compressive strength and rheology
- Cement clinker production and to study the
    - Phase formation
    - Heat of hydration

1.2. SIGNIFICANCE

With the increase in scarcity of coal fly ash sources, it is necessary to find an alternative material which has similar properties as coal fly ash. And coal fly ash is used extensively in construction materials. So, if the use of wood ash in the construction materials shows promising results, new standards can be developed for the use of wood ash in the construction sector in the applications like the production of low strength materials and in the use of wood ash as a supplementary cementitious material and in production of cement. The applications listed above are the major applications of coal fly ash in the construction sector. In this way wood ash can successfully replace coal fly ash. And that would also reduce the economic costs and environmental impacts associated with its landfill.

1.3. ORGANIZATION

The second chapter of the thesis is a review of literature including a general summary of the various applications of coal fly ash and wood ash and the experimental techniques used in evaluating the concrete properties. Experience and the results of various researchers in this field is summarized.

The third chapter describes the physical and chemical characteristics of raw wood ash and the experimental techniques used to evaluate them.

The fourth chapter describes the use of wood ash as a supplementary cementitious material and the resulting change in the characteristics of the cement system.

The fifth chapter describes the use of wood ash in the production of controlled low strength materials and its effects on strength and rheology

The sixth chapter describes the use of wood ash as a raw material for cement production and the chemical composition of the cement formed and the hydration rate of it.

The overall summary and the future recommendations are described in the chapter seven.

CHAPTER 2

LITERATURE REVIEW

2.1. BACKGROUND

Coal fly ash is produced by the combustion of coal in thermal power plants. Most of the coal fly ash produced is disposed as a landfill and the rest is used in various applications like concrete production, agricultural uses, soil stabilization etc. With the increase in the environmental impacts associated with the use of coal, fly ash production has been greatly reduced which impacted the availability of it for the applications consisting of coal fly ash. So, the demand for an alternative source which has similar characteristics had increased over time. Wood ash is also a by-product of thermal power plants. Wood ash produced from wood chips and coal fly ash produced from polish coal contains similar phases but with varying elemental compositions which is dependent on the raw material used etc. [1]. The usage of wood ash or coal fly ash in a certain application is completely dependent on the elemental composition. The elemental composition of the industrial wood ash is a function of production temperature [2]. Different applications of coal fly ash in construction sector include cement substitute in concrete production, aggregate replacement in concrete mixture, flowable fill production and cement clinker production [3]. Based on the material characterization of wood ash particles as described in chapter 3, potential use of wood ash instead of coal fly ash in applications like supplementary cementitious materials, flowable fill production and cement clinker production is considered. As aggregate replacement is affected by the variable particle size distribution, high water absorption and the strength of the wood ash raw particles, use of wood ash as an aggregate replacement is not considered.

2.2. SUPPLEMENTARY CEMENTITIOUS MATERIALS

2.2.1. INTRODUCTION

Supplementary cementitious materials (SCM) are primarily pozzolanic, some of them might have slight hydraulic properties. However, we use SCM for their pozzolanic properties. In the United states SCMs are utilized in more than 60% of the ready-mix concrete production facilities[4]. SCMs have become highly desirable materials to improve the durability and the sustainability of concrete. Hydration of cement systems results in the formation of C-S-H, portlandite, Ettringite(AFt) and calcium aluminate monosulfate (AFm) phases. The silica present in the SCMs reacts with portlandite ($Ca(OH)_2$) and forms additional calcium-silicate-hydrate (C-S-H) via pozzolanic reaction. The additional C-S-H increases the strength of cementitious matrix and creates a denser microstructure[5]–[7]. Utilization of SCM also improves the resistance of cementitious matrix to alkali-silica reaction (ASR)[8] and deicers. The chemical composition and the material characteristics of a SCM can affect the kinetics of its reaction. *Figure 1* represents the chemical compositions of supplementary cementitious materials[9].

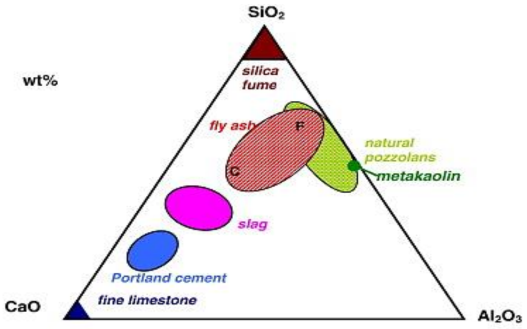

Figure 1: CaO-Al_2O_3-SiO_2 ternary diagram of cementitious materials[9]

The most commonly used supplementary cementitious materials are blast-furnace slag, silica fume, calcined clays and coal fly ash or similar products. SiO_2 is a major component in coal fly ash. Coal fly ash is also found to contain significant amounts of Al_2O_3 due to which formation of aluminum rich phases occur. The physical characteristics and chemical composition of wood ash is very similar to that of coal fly ash[10]. As seen in Figure 1 SCMs generally contain low calcium content than an ordinary Portland cement due to which there will be difference in the reaction products. This affects the strength and durability of cement systems. The amount of ettringite and AFm formation in a cementitious system is also dependent on the chemical composition of the SCMs. Effects of SCM on properties like workability, hydration, pozzolanic activity and compressive strength have been discussed below.

2.2.2. EFFECTS OF SCMs ON CEMENTING PROPERTIES

2.2.2.1. WORKABILITY

Use of SCMs in cement systems alters their rheological properties. It depends on the type of material, their chemical and mineralogical compositions, physical characteristics reactivity etc. Workability seems to reduce with the increase in the wood ash replacement due to the presence of high combustible organic content, high water absorption of particles and due to large surface area of the particles[11]. In case of coal fly ash induced mixes, the workability improved but in presence of materials larger than 45 microns and the presence of unburnt carbon can reduce the workability[12].

Workability can be improved by modifying the physical properties of the material.

2.2.2.2. HYDRATION

The SCMs are found to have an impact on the cement hydration kinetics, phases in a hydrated system and the C-S-H composition via filler effects. SCMs with very small particle sizes can improve the hydration properties of via nucleation effect. Addition of SCMs is found to result in an increase in the hydration period which helps in providing additional time for the formation of C-S-H. The variation in the alkali and the chlorine content of the wood ash used can probably lead to an decrease in the hydration rate and cause a shift in the hydration temperatures[13].

2.2.2.3. POZZOLANIC ACTIVITY

According to ASTM C618[14] defines pozzolanic material as a siliceous and aluminous material which possess little or no cementitious properties but in finely divided form react with portlandite from cement hydration to form a product with cementitious properties. Pozzolanic activity of a SCM is dependent on the silica and alumina content, amount of portlandite ($Ca(OH)_2$) and the loss of ignition (LOI). The presence of high silica content results in a higher pozzolanic activity. The concentration of OH- ions and the concentration of CaO in wood ash can impact pozzolanic activity[11].

2.2.2.4. SHRINKAGE BEHAVIOR

Strain due to shrinkage leads to cracking in concrete. This problem can be solved by using filler material like coal fly ash[15]. Mixtures containing SCMs are found to exhibit high drying shrinkage because of the presence of a refined pore structure than that of OPC. Because of this reason, more smaller capillary voids are present in the blended system which results in a higher drying shrinkage[16]. Using coal fly ash as a SCM is found to reduce the damage due to autogenous shrinkage[17]. And Class F and Class C coal fly ash are found to reduce the drying shrinkage by densifying the mix to prevent the internal moisture evaporation[17][18].

2.2.2.5. COMPRESSIVE STRENGTH

Use of wood waste ash as cement replacement resulted in the reduction of compressive strength due to the wood ash particles acting like filler material. The increase in ash content contributed to an increase in the filler material's surface area to react with the decreasing cement content led to an decline in the strength of the system[19]. In certain cases, use of wood ash or coal fly ash as a partial cement replacement is found to increase the long-term compressive strength with an increase in the replacement level. The increase in strength is due to the pozzolanic activity of the wood ash or coal fly ash materials. The presence of amorphous silica in wood ash reacted with the portlandite to form the C-S-H gel resulting in an increased strength[11].

2.3. CONTROLLED LOW STRENGTH MATERIALS

2.3.1. INTRODUCTION

Controlled low strength material is defined as a self-compacted and flowable cementitious material used primarily as a structural fill instead of compacted fill [20]. CLSM can be used for various other applications like erosion control, pavement bases, void filling etc. The compressive strength for CLSM mixtures varies from 2.0 – 8.3 MPa based on the type of application. There are many advantages of using CLSM in construction, as it is time and cost effective and can be produced using industrial by-products like coal fly ash, wood ash etc. Wood ash is a major by-product of biomass power plants. U.S. pulp and paper mills produce about one million tons of wood ash every year out of which only one-third of ash is utilized, and the rest is discarded as landfill causing environmental and economic impacts. CLSM is generally produced with high coal fly ash content and less cement content. As the sources of coal fly ash are reduced, there is a need for an alternative material in the CLSM production. And due to possible pozzolanic properties of wood ash, it can be used to fully replace coal fly ash in CLSM production without having an impact on the performance of the mixture[21]. According to ACI 229R, the materials used for CLSM production does not require to be in accordance with the ASTM standards.

2.3.2. RHEOLOGY

Workability is a critical factor for CLSM mixtures. The flowability of fresh CLSM mix should be good enough for it to act as a self-compacting material and to meet the requirements. One problem associated with the high flowability is segregation. When targeting a fixed flowability, the water content is varied in accordance with the constituents of the mix. For example, use of fine sands requires a higher water content than the common sands in order to achieve the desired flowability characteristics. The flowability of CLSM mix is found to increase with an increase in the water content[22]. The use of different percent levels of replacement of coal fly ash did not show any significant changes in the flowability of the CLSM mix[23].

2.3.3. COMPRESSIVE STRENGTH

The compressive strength is completely dependent on the water-cement ratio, types of aggregate and coal fly ash used. Different mix proportions containing both coal fly ash and wood ash are tested for different target strengths ranging from 0.7 MPa to 8.3 MPa. The compressive strength results revealed that the target strength can be achieved even after replacing the cement by 100 percent with the coal fly ash[22]. The compressive strength of batches with wood ash is found to achieve the 28 days target strength but no evaluation of 100 percent replacement of cement with wood ash is done. But in general the increase of wood ash in the CLSM mix resulted in a increase in the compressive strength[24].

2.4. CEMENT PRODUCTION FROM WOOD ASH

2.4.1. INTRODUCTION

As discussed earlier, coal fly ash is a major by-product of the power plants and is mostly used as a landfill which is associated with the environmental and economic concerns. High amounts of chlorides and dioxins found in certain types of coal fly ash products will affect the rheology and the strength properties of the cement concrete when the coal fly ash is used as a partial replacement to cement[25]. Dioxins are hard to get rid of when subjected to chemical techniques. But when subjected to high temperatures, heavy metals volatilize and the dioxins disappear[26][27][28]. Based on the findings listed above, the coal fly ash can be used in the cement clinker production as it is a high combustion process and it results in the elimination of organic compounds present in coal fly ash. The presence of compounds like Calcium oxide (CaO), Silicon Dioxide (SiO_2), Aluminum oxide (Al_2O_3) and Iron oxide (Fe_2O_3) in the coal fly ash makes it a potential material to be used in the cement production as it has similar phases as that of raw materials used for cement production. Research has been done in using the municipal solid waste incineration (MSWI) coal fly ash in order to evaluate the effect of coal fly ash properties on the phase formation and hydration products[29][30].

2.4.2. PHASES IN CEMENT CLINKER

The phases in a cement clinker is completely dependent on the chemical composition of the raw material used. A regular cement system consists of phases like tricalcium silicate (C_3S) and calcium aluminate (C_3A). Presence of sulphate in the raw mix affects the formation of the C_3S and C_3A and instead form calcium sulfoaluminate (C_4A_3S) which tends to replace the alumina with other impurities like titanium, iron, manganese etc. present in the raw mix[31]. Presence of zinc oxide (ZnO) in excess amounts in the system helps in improving the burning of raw mix. The production temperature also plays a key role in the formation of phases. Production of cement clinker at 1400 C shows more significant phases than the clinker produced at 1300 C. Unreacted lime content is also dependent on temperature[29]. The XRD patterns can be used to identify the presence of phases like CH, C_3S, C_2S, C_3A and C_4AF.

2.4.3. HYDRATION PRODUCTS

The MSWI ash is found to have high alkali content which increases the rate of hydration by increasing the heat of hydration. If there are significant amounts of Zn, Pb and Cd in the cement clinkers then the rate of hydration decreases. The hydrated MSWI ash clinker showed the formation of C-S-H gel, C_3AH_8 and $Ca(OH)_2$.

CHAPTER 3

WOOD ASH CHARACTERISTICS

3.1. WOOD ASH PRODUCTION

The wood ash used in this project was supplied from the Stored Solar LLC. company which is in West Enfield, Maine. Plant debris and woodchips were used as fuel in the furnace for generating power. The boiler uses Circulating fluidized bed technology for complete combustion of the fuel. The temperature in the bed area at which the ash was produced was 1000 degrees Celsius. The total ash content obtained is typically less than 2 percent of the wood burned. The ash generated is collected by an electrostatic precipitator. There are 3 fields and each field has two hoppers. The ash goes through a rotatory seal from each hopper onto a drag chain. Each field has a drag chain that drops onto the main drag chain. Ash is collected in a silo and batch processed 2 to 3 times a day. The ash is fed through a plug mill and water is mixed in to condition the ash. This helps in keeping the ash from turning into hard chunks if it gets wet. Stored solar alone produces 4000 metric tons of ash every year which is later disposed as a landfill.

Figure 2: Aerial view of Stored Solar industry in West Enfield

3.2. METHODS OF INVESTIGATION

3.2.1. PARTICLE SIZE DISTRIBUTION

Since wood ash obtained from the industry contained a lot of coarse particles, sieve analysis was performed to determine the particle size distribution of the wood ash particles. The test was done in accordance with ASTM C136.

3.2.2. PARTICLE SIZE ANALYSIS BY LASER DIFFRACTION

Since wood ash is being used as a supplementary cementitious material, it is necessary to understand the particle size distribution of material passing through #200 sieve. The material passing through #200 sieve was taken and are suspended in a solution. The laser diffraction analysis has been performed using Malvern Instruments Mastersizer. The instrument measures the angular variation in the intensity of light scattered as a laser beam passes through the dispersed particles. Large particles scatter light at small angles while the smaller particles scatter light at larger angles. Laser diffraction uses Mie’s theory of light scattering.

3.2.3. X-RAY DIFFRACTION

X-Ray diffraction is primarily used to identify and characterize different phases of crystalline materials based on their diffraction patterns. X’Pert3 MRD XL was the equipment used to perform X-Ray Diffraction. X-Ray diffraction is based on Bragg’s law. The raw wood ash sample is finely ground and was placed on a glass plate with scotch tape attached to it. The glass plate was attached to a mounting disc and was placed inside the equipment to determine different phases present in wood ash.

3.2.4. X-RAY FLUORESCENCE

X-Ray fluorescence is a technique used to describe the composition of elements in a material. The sample is subjected to high energy X-rays, when the sample is struck with the X-ray, an electron from one of the atom's inner orbital gets dislodged. The atom regains stability by filling the vacancy with another electron from a higher orbital. During this process the electron releases a fluorescent X-ray. The energy of this X-ray is equal to the difference between two quantum states of the electron. This energy measurement is used for XRF analysis. During this process the peaks with different intensities are recorded. The peak location describes the element while the intensity describes the composition of that element.

3.2.5. THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analyzer measures the weight change of a sample over time with an increase in the temperature. Around 35 – 50 mg of sample is taken in a pan and was loaded into a furnace. The sample was subjected to constant increase in temperature and the software collects the weight change data. Based on the weight change data obtained by thermogravimetric analysis carbon dioxide content, free water etc. can be determined.

3.3. RESULTS

3.3.1. PARTICLE SIZE DISTRIBUTION

Figure 3 represents the particle size distribution of wood ash. Wood ash obtained from the industry contains 7.25 percent of coarse material and only 1.5 percent of fine material passing #200 sieve.

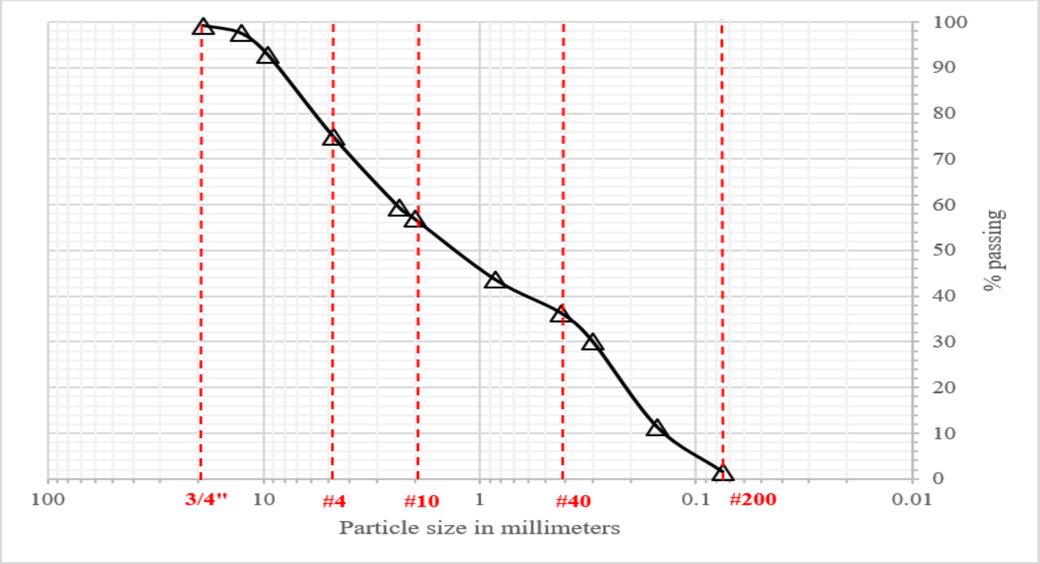

Figure 3: Particle size distribution of wood ash

3.3.2. PARTICLE SIZE DISTRIBUTION BY LASER DIFFRACTION

Figure 4 represents the particle size distribution of material passing #200 sieve. This test is performed to understand the distribution of fine material which can contribute to the strength of the cement system.

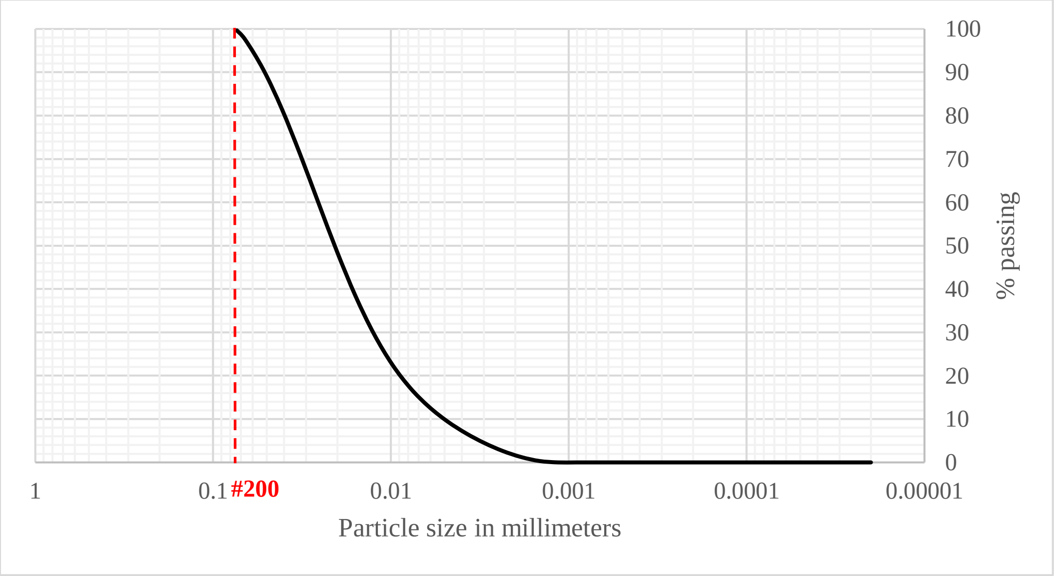

Figure 4: Particle size distribution of material passing #200

3.3.3. X-RAY DIFFRACTION

Figure 5 represents the various phases of raw wood ash sample obtained from the biomass industry.

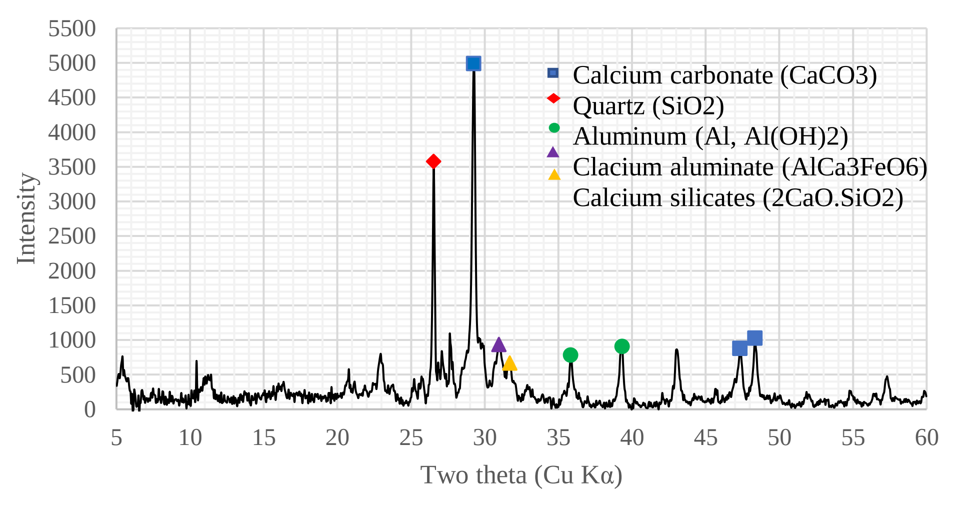

Figure 5: XRD pattern of raw wood ash

3.3.4. X-RAY FLUORESCENCE

Figure 6 represents the change in elemental composition of wood ash over time.

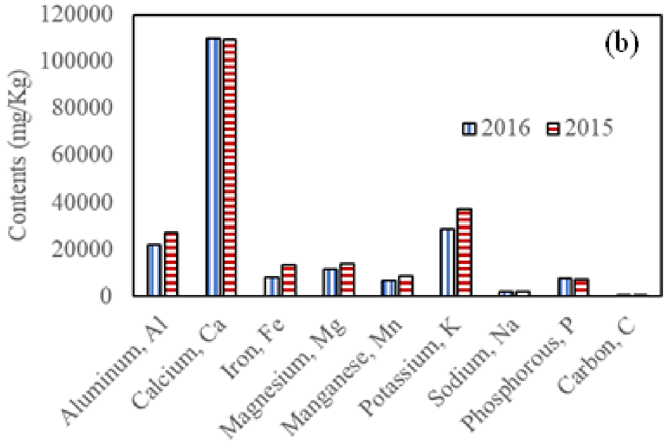

Figure 6: Elemental composition of wood ash over time

3.3.5. THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis reveals the presence of carbon dioxide in wood ash in its inorganic form. Figure 7 represents the thermogravimetric analysis plot of wood ash.

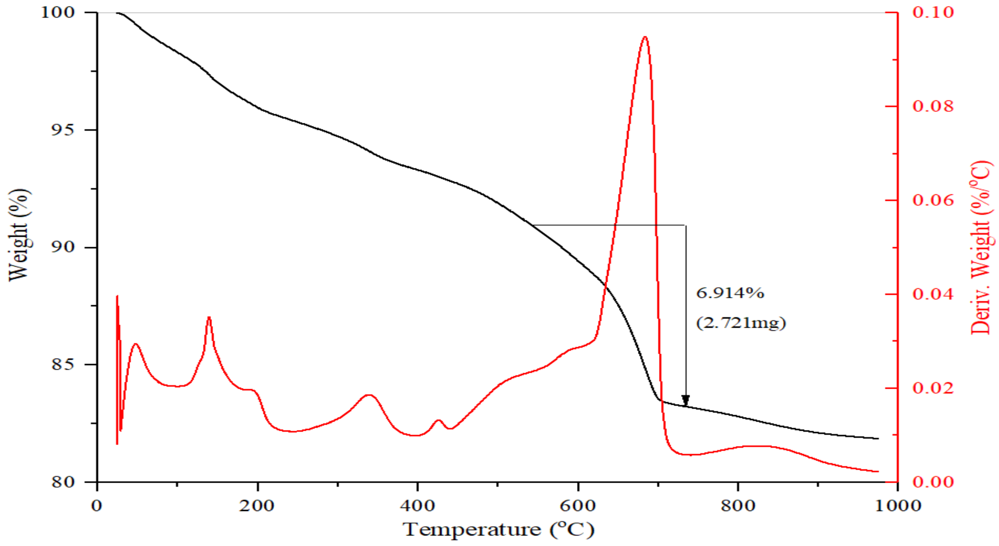

Figure 7: Thermogravimetric analysis of Raw Wood Ash

3.4. CONCLUSION

From the particle size distribution, it is evident that the wood ash obtained from the industry contains 1.5 percent material passing through #200 sieve. In order to use wood ash as a supplementary cementitious material, it needs to be modified. The presence of large particles also reduces the workability of the cement systems. Because of the presence of 98.5 percent of material retained above #200 sieve, any modification to raw wood ash increases the cost of the project. From the X-Ray diffraction pattern, wood ash contains calcium-silica-alumina phases. The calcium carbonate phase is most prominent is wood ash. From the X-Ray Fluorescence, it can be observed that wood ash contains significant amounts of silica, calcium and alumina. And there is a presence of carbon dioxide in wood ash which is mostly in its inorganic form i.e. in the form of Calcium Carbonate [$CaCO_3$] which is observed from the thermogravimetric analysis.

CHAPTER 4

SUPPLEMENTARY CEMENTITIOUS MATERIALS

4.1. OBJECTIVES

The main goal of this application is to understand the use wood ash as a SCM in order to evaluate the pozzolanic and hydraulic reactivity of bioash produced from biomass power plants with wood as the primary feedstock. To evaluate this issue, the main objectives of this study were to investigate how the additional processing of bioash can affect the pozzolanic properties, investigate the pozzolanic activity of wood ash when compared to coal fly ash and the suitable replacement level with bioash.

4.2. MATERIALS AND METHODS

4.2.1. RAW MATERIALS

Woody bioash was supplied by the Stored Solar biomass power plant located in West Enfield, Maine, USA. Ordinary Portland cement (OPC) type I/II was used for mortar sample preparation. Bioash was used to replace 10 to 50% of cement by weight in mortar and paste samples. The chemical composition of bioash is similar to Class-C coal fly ash. However, because of the unavailability of class-C coal fly ash, class-F coal fly ash was used to compare the performance level of bioash. The chemical compositions of OPC and Class-F coal fly ash (as obtained from the supplier) are given in Table 1[10].

Table 1 : Oxide contents of OPC and Class-F Coal Fly ash[10]

Oxides	OPC	Class-F Coal Fly ash
Silicon dioxide (SiO_2)	20.1	
Aluminum oxide (Al_2O_3)	4.7	82.8
Ferric oxide (Fe_2O_3)	3.5	
Calcium oxide (CaO)	63.7	6.4
Magnesium oxide (MgO)	0.7	
Sulfur trioxide (SO_3)	3.1	0.2
Loss on ignition (LOI)	2.6	2.5

4.2.2. EXPERIMENTAL TECHNIQUES

A total sixteen batches of 50 mm mortar cube samples (water to binder ratio=0.4 and sand to binder ratio= 2.75) were prepared as per the ASTM C 305-14 [32] for compressive strength tests. Control batch denotes 100% OPC was used as the binding material. Ground and sieved bioash were used to replace 10%, 20%, 30%, 40%, and 50% of cement by weight in the mixture. The sample containing ground and sieved bioash as partial replacement of cement are addressed as BAG and BAS, respectively. All mortar samples were cured in lime-saturated water. The compressive strengths of mortar samples were determined as per ASTM C109 [33] using a loading rate of 200~400 lb./sec after 7, 14, 28, 56, and 90 days of curing. Flow table test was used (as per ASTM C230/C230M – 14 [34] and ASTM C1437-15 [35]) to monitor the effects of cement replacement levels on the workability of mortar samples. Paste samples were prepared by mixing cement and bioash/ coal fly ash with water (water to binder ratio = 0.484) using a spatula. After mixing for two minutes, about 15g paste sample was placed into a glass vial which was then used for heat release measurements. The heat releases of the paste samples were monitored using an isothermal calorimeter (TAM Air, TA instruments). The heat of hydration was monitored for 100 hours and the temperature during the measurement was 25°C. Paste samples with water to binder ratio of 0.484 were prepared for microscopic phase evaluation using thermogravimetric analysis (TGA) and X-ray diffraction (XRD) techniques. Acetone was used to stop the hydration after specific curing durations (7 days and 28 days) and the paste samples were then dried in a vacuum oven at 50°C for 24 hours. Finally, the dried paste samples were ground using mortar-pestle and the powder was used for TGA and XRD measurements. Commercially available instrument (TA instrument, TGA 55) was used for TGA measurements. Approximately 30-45 mg powder sample was tested for each batch. The powdered sample was loaded into the pan and kept under the isothermal condition for 5 min. The temperature of the chamber was then raised continuously up to 980°C with an increment of 10°C per minute. X-ray diffraction patterns of the powdered samples were obtained using a Cu Kα source. The diffraction patterns were obtained for the 2θ range of 5º to 60 º using a step size of 0.02 (2θ) per second.

4.3. RAW MATERIAL CHARACTERIZATION AND PROCESSING

4.3.1. PARTICLE SIZE DISTRIBUTION

Figure 3 shows the particle size distribution of as received bioash as determined from sieve analysis. As it can be observed from this figure, the particle size of bioash was in the range of millimeter with around 1% passing below #200 sieve.

Reactivity of cementitious materials largely depends on its total surface area. It was expected that replacing cement large particles of bioash will not result in desirable binding characteristics. As such, two approaches were followed to improve the reactivity of bioash, these are: (i) grinding with a high energy planetary ball mill for two hours and (ii) sieving with #30 sieve (corresponds to 50% passing of raw bioash size distribution). Figure 8 shows the particle size distribution of bioash after these processes as obtained from laser particle size analyzer. Grinding of bioash produced smaller particle sizes as compared to those of sieving. However, the grinding process would presumably consume more energy than that of sieving. Further, the sieving process would discard around 50% of weight bioash from utilization in the production of cementitious matrixes.

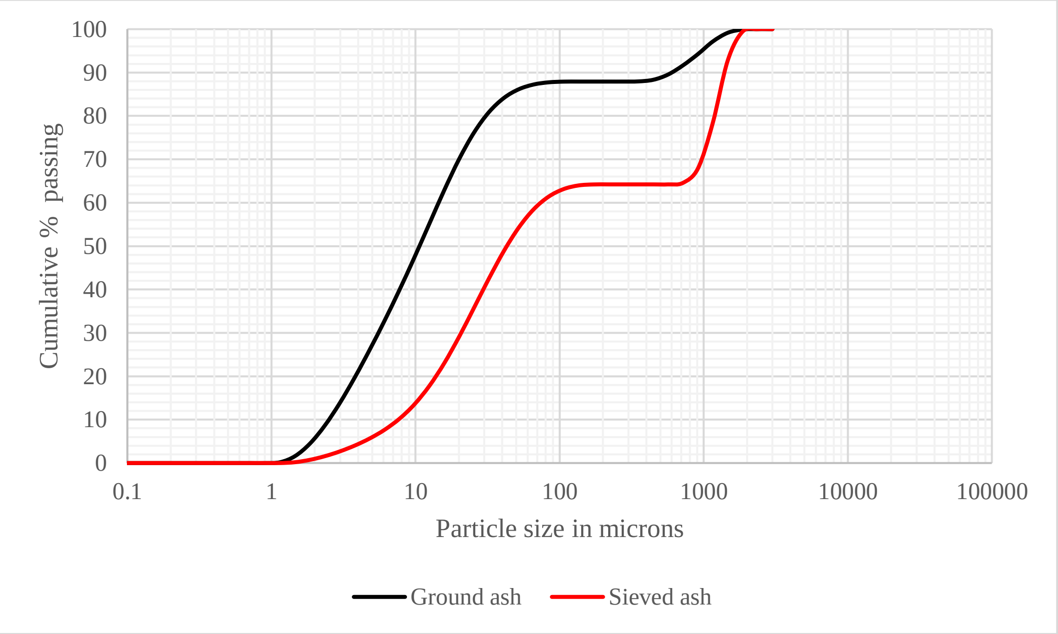

Figure 8: Particle size distribution of processed bioash

4.3.2. MINERALOGY and CHEMICAL COMPOSITION (XRF and XRD)

The oxide contents of bioash samples are given in Figure 9(a). The oxide contents were similar in these batches, except ground bioash had higher amounts of SiO_2 and slightly lower CaO content compared to those of sieved bioash. The total SiO_2 + Al_2O_3 + Fe_2O_3 content of bioash is around 50%, indicating this ash satisfies the requirement of class-C coal fly ash as per ASTM C 618. However, the loss on ignition (LOI) of the bioash samples were around 10% which is higher than the maximum limit (6%) as specified in ASTM C-618. This standard specified the maximum LOI value to limit the presence of organic carbon content in pozzolanic materials. The organic carbon content of ash adsorbs air entraining admixtures (i.e., surfactants) used in concrete and thus, can result in adequate air void parameters [36]. To provide a better understanding of the phase contributions to the total LOI, TGA test was performed on raw bioash (Figure 9(b)). The minerals decomposed with increasing temperature were identified based on literature (details can be found in [37]). The TGA result indicates that a major portion of LOI is due to the decomposition of ettringite, monosulphate and calcium carbonate ($CaCO_3$). The inorganic carbon ($CaCO_3$) does not absorb air entraining admixture and thus, should not be a limiting factor for pozzolanic materials. Considering the decomposition of the inorganic phases, the total weight loss due to the organic carbon content was around 5%.

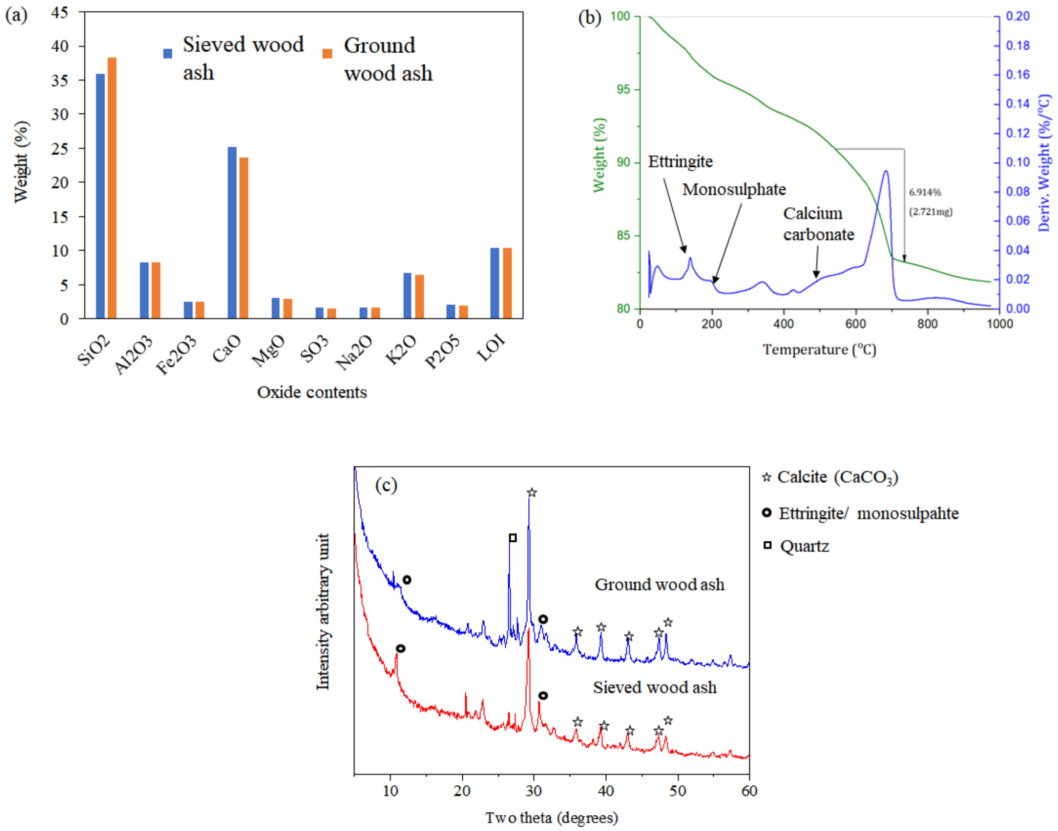

Figure 9: (a) oxide contents (b) thermogravimetric analysis (TGA) (c) X-ray diffraction patterns of raw and ground bioash

4.4. WORKABILITY

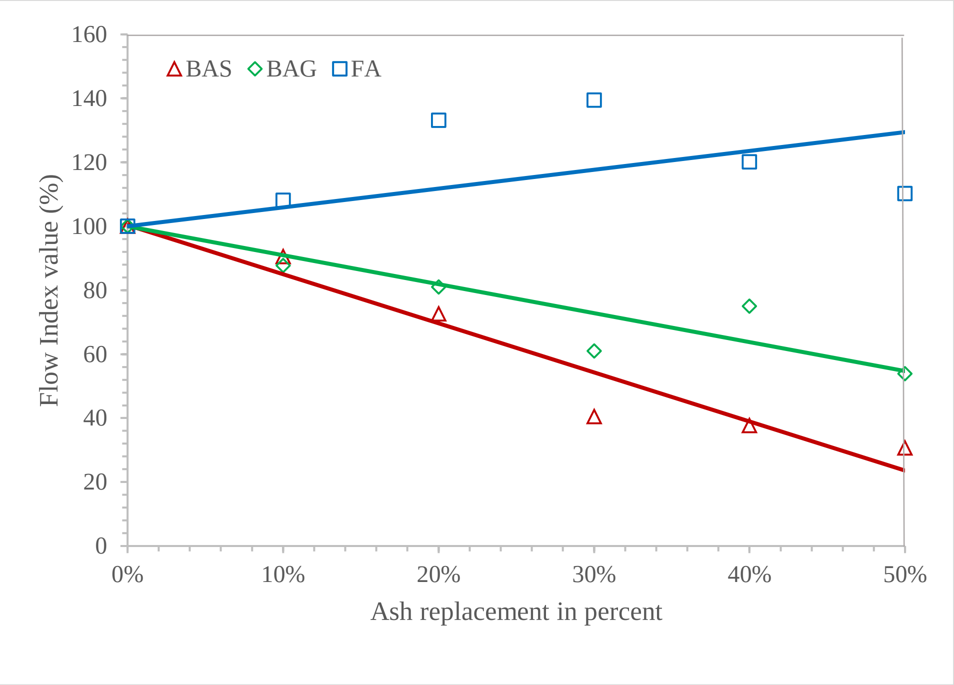

Figure 10: Workability of mortar samples prepared with bioash (BAS is sieved and BAG is ground) and coal fly ash (FA)

The workability (flow index) of mortar samples containing wood ash and coal fly ash with respect to that of control batch is presented in Figure 10. Spherical particles of coal fly ash have a gliding effect and improve the workability of mortar mixes. Both, ground and sieved wood ash were found to decrease workability of mortar with increasing cement replacement levels. This could be because of several reasons, (i) the angular shapes of wood ash increased the friction level of paste mixture, (ii) the porous large particles of wood ash absorb water, and (iii) the free metal contents of wood ash oxidize in the presence of water and alkali ions following the chemical reaction in equation 1. The oxidation of metallic ions will consume free water and the decrease in free water content can decrease the workability.

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 \uparrow \qquad eq. (1)$$

In case of the oxidation of metallic ions, the release of Hydrogen gas will create bubbles in the mixtures. Such bubbles were identifiable during mixing indicating the water loss due to the oxidation process. Excessive formation of such hydrogen bubbles can also decrease the strength of hardened cementitious matrixes. To avoid such a strength reduction effect, throughout the study we have first mixed wood ash with water for 2 minutes and then added cement to the mixture. As can be observed from Figure 10, the decrease in workability due to the ground bioash was lower than those of sieved wood ash. The possible reason could be some of the free metals might have oxidized during the grinding stage. Also, grinding decreases the size of wood ash particles and thus, the total moisture adsorption.

4.5. EFFECTS ON CEMENT HYDRATION

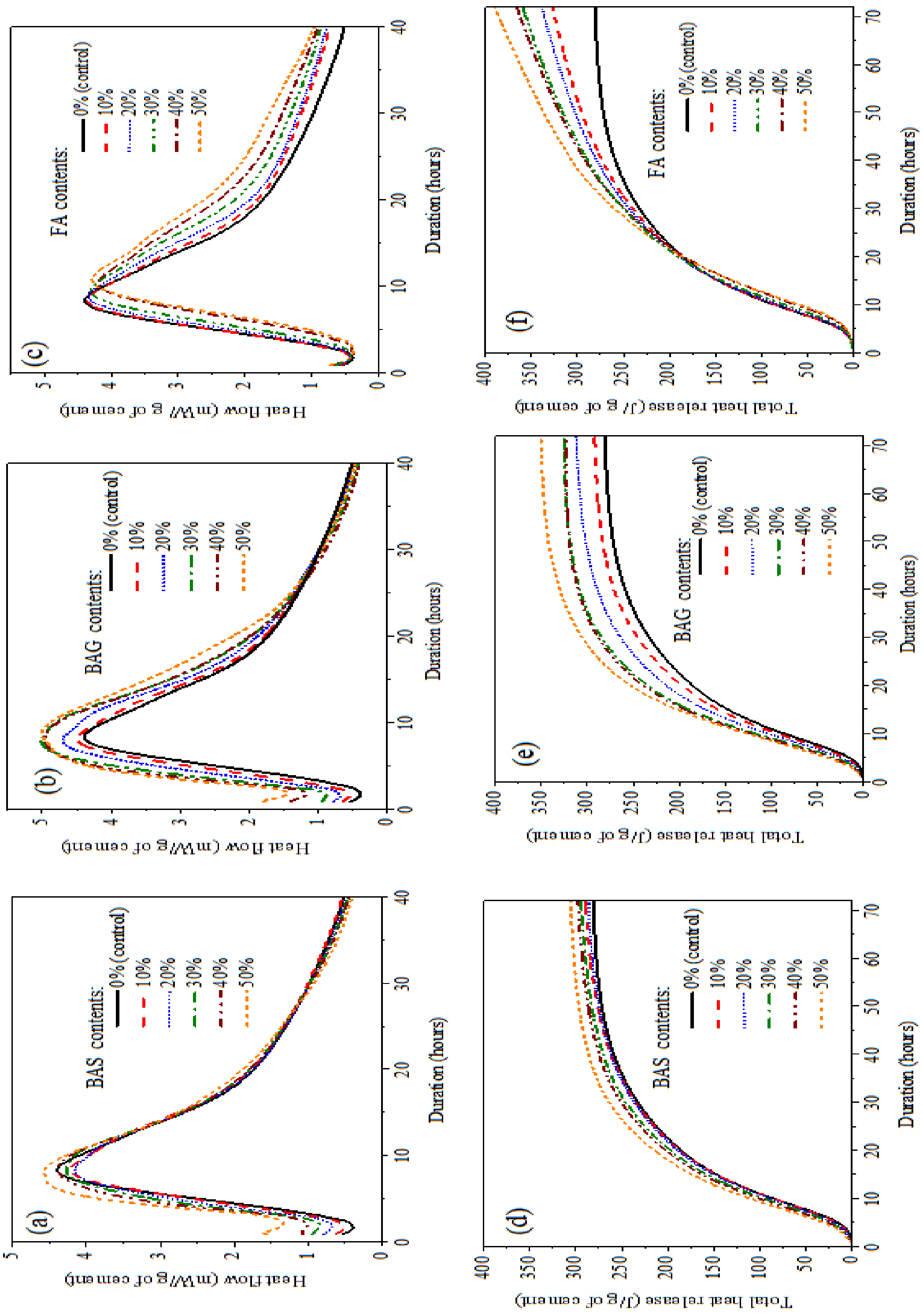

Figure 11: Heat flow and total heat evaluation of cement paste containing bio ash and coal fly ash

Figure 11 (a) to (c) shows the heat flow of cement paste containing BAS, BAG and FA, respectively. The peak heat flow shifted to the right due to the addition of coal fly ash indicating the hydration delaying effect of this ash. The delay in cement hydration at the early stage was increased with the increasing content of coal fly ash. Such a retarding effect of coal fly ash is well-known [38]. In the case of bioash batches, there is an increase in heat flow within the first 1~2 hours of hydration compared to that of control batch. This heat release at the early stage of hydration could be attributed to the oxidation of metallic ions and/or hydration of some highly reactive phases. Overall, the addition of bioash shifted the primary heat flow peak to the left side indicating the acceleration of cement hydration. The peak heat flow of the cement per gram also increased with the bioash addition. The increase of this peak heat flow indicates that the bioash also has hydraulic reactivity. This hydraulic reactivity was more intensive for batches containing ground bioash compared to that of sieved batches. Such hydraulic reactivity of bioash was attributed to the presence of reactive calcium aluminate, calcium silicate and aluminosulphate phases. Furthermore, in case of coal fly ash batches, the heat flow was higher compared to the control batch after around 10 hours of cement hydration. The increase of heat flow at this stage was attributed to the pozzolanic reaction of coal fly ash[9]. However, at this stage (after 20 hours), heat flow of bioash containing batches were equal or lower than that of control batch, indicating the pozzolanic properties of bioash is lower compared to that of Class -F coal fly ash. The total heat releases after 75 hours of hydration for cement batches containing BAS, BAG and FA are given in Figure 11(d), (e), and (f), respectively. Both sieved and ground bioash increased the total heat compared to the control batch after 75 hours, indicating a higher degree of reaction. However, the higher effectiveness of ground bioash compared to that of sieved bioash is apparent due to the higher heat release of the former batch. Coal fly ash containing paste batches showed the highest heat flow among these three types of ashes Figure 11(f). Also, the total heat release showed a steep increasing trend in case of FA containing batches. This was attributed to the continuing pozzolanic reaction of the coal fly ash. On the other hand, bioash batches showed higher heat release up to around 50 hours after which the slope of heat release increased for coal fly ash batch. Thus, all these ashes enhance the cement hydration up to 75 hours. However, FA is the most effective followed by BAG and then BAS.

4.6. POZZOLANIC ACTIVITY

The pozzolanic activities were measured by quantifying the amounts of $Ca(OH)_2$ consumed by ash samples. The consumption level of $Ca(OH)_2$ was determined by thermogravimetric analysis (TGA), Differential thermogravimetry (DTG) and the Chapelle test (titration based procedure).

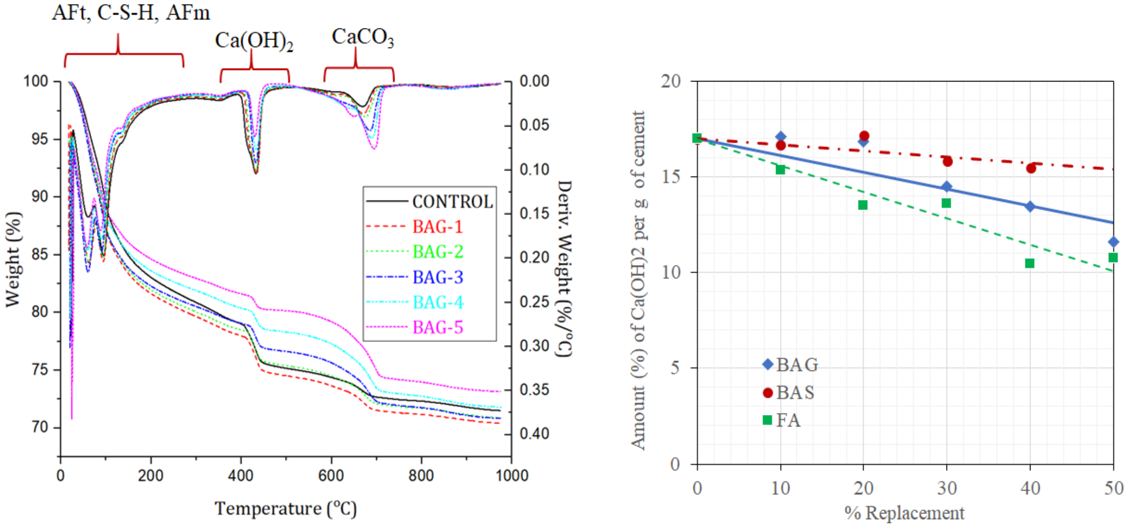

Figure 12: Typical TGA and DTG plot of cement paste

Figure 12(a) shows the typical TGA and DTG plot for cement pastes containing ground bioash. The mass loss observed in the temperature range of 40 to 160 °C was attributed to the decomposition of ettringite (Aft), monosulfate (AFm), and gel water from C-S-H. The mass loss due to the decomposition of $Ca(OH)_2$ can be observed in the temperature range of 400 to 500 °C and those due to $CaCO_3$ decomposition was in the range of 600 to 800 °C. The amount of $Ca(OH)_2$ was determined by integrating the DTG peak within the temperature range of 400 to 500 °C. Details of this procedure for determining the weight fraction of a phase in the hydrated cement system can be found in [37]. This procedure was used to determine the total $Ca(OH)_2$ content (g) per gram of hydrated cement paste, which was then converted to '$Ca(OH)_2$ content (g) per gram of cement' using the w/c ratio. Considering same cement was used for all the paste batches, the amount of $Ca(OH)_2$ should remain constant for inert inclusion, should increase for 'hydration acceleration or hydraulic materials addition' and should decrease due to the pozzolanic material addition. Incorporating relatively inert material can also increase the $Ca(OH)_2$ content due to the dilution and nucleation effect [9]. However, such an effect was considered to be similar for all of the ash samples. As it can be observed from Figure 12(b), the amount of Ca $(OH)_2$ per gram of cement decreases with the ash content after 28 days of curing, indicating pozzolanic activity of the ash products. Specifically, the cement pastes with coal fly ash were found to have the lowest amount of $Ca(OH)_2$ and thus, confirming the pozzolanic activity of coal fly ash. Pozzolanic activity of coal fly ash was followed by ground bioash and finally sieved bioash. The enhanced pozzolanic activity of ground bioash compared to those of sieved batches was due to the finer particle size distribution of the former one. According to the Chapelle test [39], the pozzolanic material is allowed to react with lime (CaO) solution at 85±5°C for 16 hours. The amount of unreacted $Ca(OH)_2$ after this period was determined using titration method containing hydrochloric acid (HCl), which was then used to calculate the amounts of reacted $Ca(OH)_2$. The reacted $Ca(OH)_2$ is a direct indication of the pozzolanic activity of ash. Based on this experiment, one gram of coal fly ash, ground bioash, and sieved bioash were found to consume 713.7, 131.54 and 104.74 mg of $Ca(OH)_2$, respectively. Based on these results, it can be concluded that grinding improved the pozzolanic activity of bioash by 25%. Also, the pozzolanic activity of class-F coal fly ash was about 5 times higher than that of ground bioash.

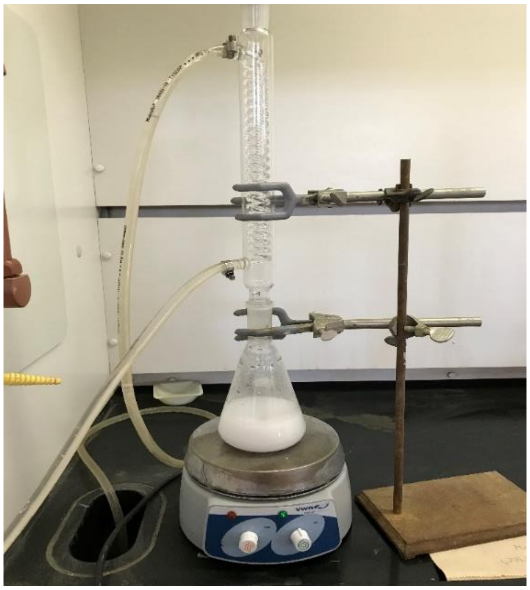

Figure 13: Chapelle test setup for testing the pozzolanic activity of ash products

4.7. COMPRESSIVE STRENGTH

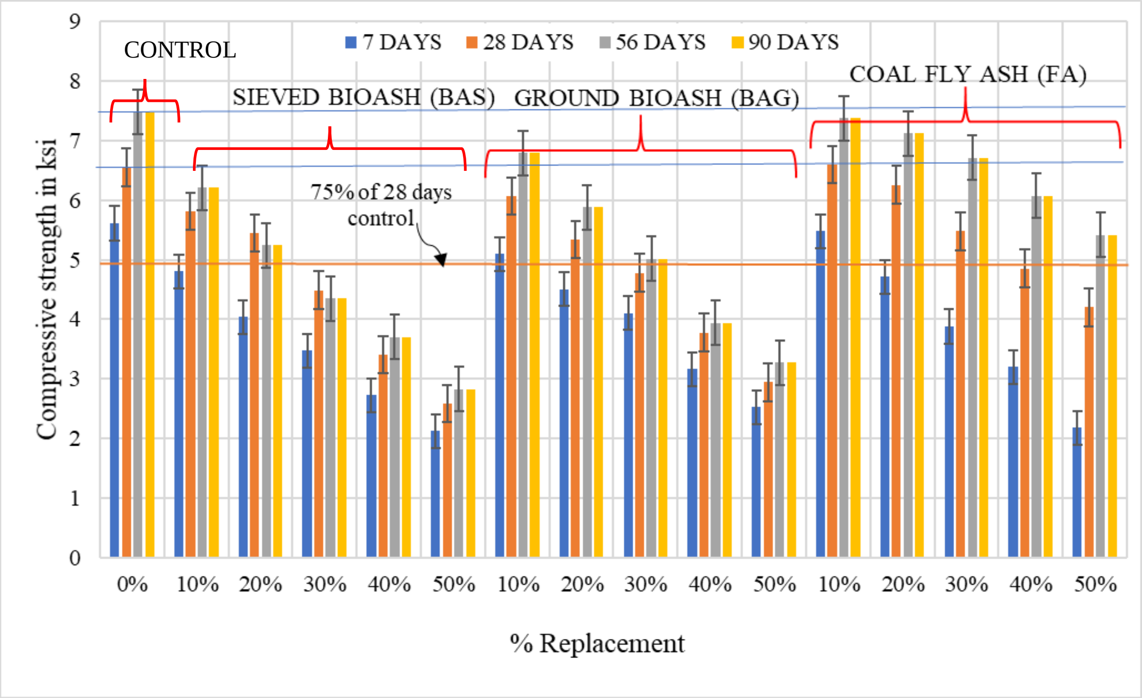

Figure 14: Compressive strengths of mortar samples

The compressive strengths of the mortar samples containing ash as cement replacement were determined after 7, 28 and 56 days of curing (Figure 14). The strength of the control batch was highest among all the batches for all of the above-state curing durations. That is strength decreases with an increase of the ash content as cement replacement for both bioash and coal fly ash. This was expected because the pozzolanic reaction is a slow reaction and the strength benefits often observable after long-term curing (i.e., 365 days). In general, the mortar batches containing class-F coal fly ash were found to have the second highest strength range followed by ground bioash and finally, sieved bioash. 75% strength of the control batch after 28 days of curing is often used as a minimum strength requirement for pozzolanic materials (similar to ASTM C618). Considering this as a guideline, ground bioash can be used to replace approximately 30% (by wt.) of cement in mortar preparation without producing any negative effects on strength. For class-F coal fly ash and sieved bioash, the possible replacement levels are 40% and 20% by wt., respectively. However, it should be considered as a recommendation and the exact replacement levels should be determined based on the project needs. It is also noticeable that at the later age the rate of strength increase was prominent in coal fly ash containing mortar batches. Whereas, mortar batches containing ground bioash and sieved bioash showed only a slight increase of strength due to the limited pozzolanic activity.

4.8. MINERALOGY

The X-ray diffraction patterns of the paste samples are given in Figure 15. The ICDD PDF cards used for phase identification are as follows: C_2S, C_3S #00-029-0369, $Ca(OH)_2$ #04-006-9150, $CaCO_3$ #00-005-0586, C-S-H #00-033-0306, AFt #00-013-0350, Al_2O_3 #04-015-8642, SiO_2 # 01-078-4813, $MgCO_3$ #04-012-1189, and Calcium aluminoferrite ($Ca_2(Al, Fe)_2O_5$) #00-030-0226. The XRD patterns were collected only for control batch and paste batches containing 30% (by wt.) cement replaced by bio or coal ash. Only a qualitative comparison was made based on the XRD patterns. The paste sample containing bioash (both sieved and ground) was found to have a higher amount of ettringite formation compared to that present in control batch and cement paste containing coal fly ash. This was expected due to the presence of ettringite and monosulphate in the raw bioash samples. Based on the XRD pattern, all of the paste sample batches were found to contain nearly equal amount of portlandite after 7 days of curing (Figure 15(a)), indicating the Pozzolanic effect of ashes were negligible at this stage. After 28 days of curing, the intensities of the portlandite peaks were found to be lower in BAG and FA batches.

Whereas, BAS and control batch had almost the same intensity of portlandite peak. Thus, the pozzolanic activity of sieved bioash was negligible even after 28days of curing. Furthermore, ettringite content was highest in BAS batch after 28 days of curing. Formation of an excessive amount of ettringite is concerning because this phase can produce expansive cracks in cement matrixes. The cement paste samples containing bioash also were also found to have monocarboaluminate. Formation of this phase could be due to the reaction between the calcium carbonate present in bioash with aluminate phases of cement [40]. Paste samples with the ground or sieved bioash found to contain aluminum oxide (Al_2O_3) which appeared to form during the oxidation of free alumina (Al) present in bioash. Presence of quartz (SiO_2) was also apparent in cement pastes containing ground or sieved bioash after 7-days of curing (Figure 15(a)). However, this quartz peak was disappeared after 28 days of curing, indicating it was consumed by the pozzolanic reaction. The pozzolanic activity of crystalline quartz is known to be extremely slow. However, the quartz present in bioash could be in disordered form due to the high production temperature of bioash which can enhance the reactivity of this phase. Calcium aluminoferrite (brownmillerite) and magnesium carbonate were also found to be present in cement paste samples prepared with the ground or sieved bioash. Presence of these phases was also attributed to the raw bioash.

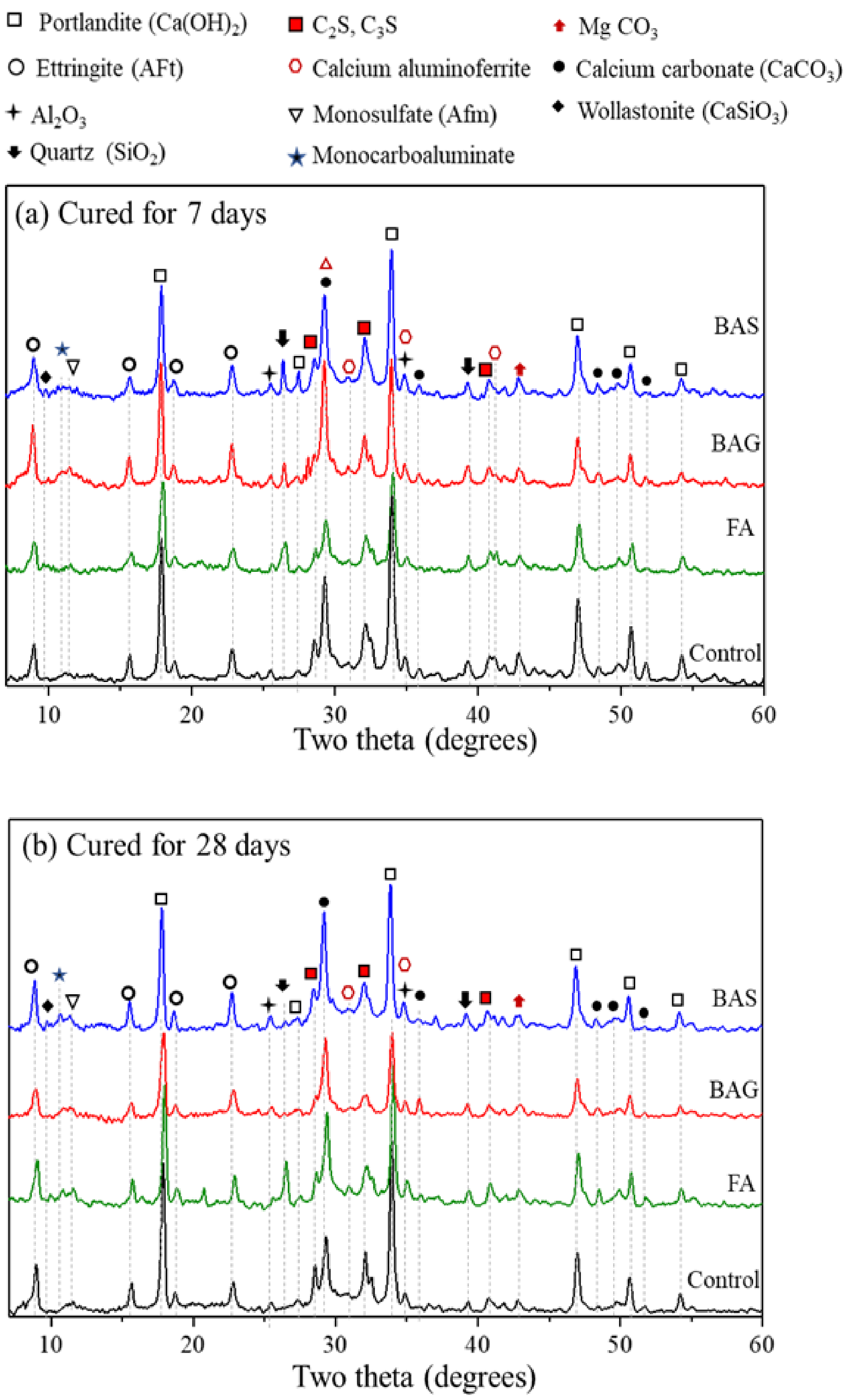

Figure 15: X-ray diffraction patterns of cement paste containing bio and coal fly ash (a) 7 days cured and (b) 28 days cured

4.9. VOLUMETRIC STABILITY

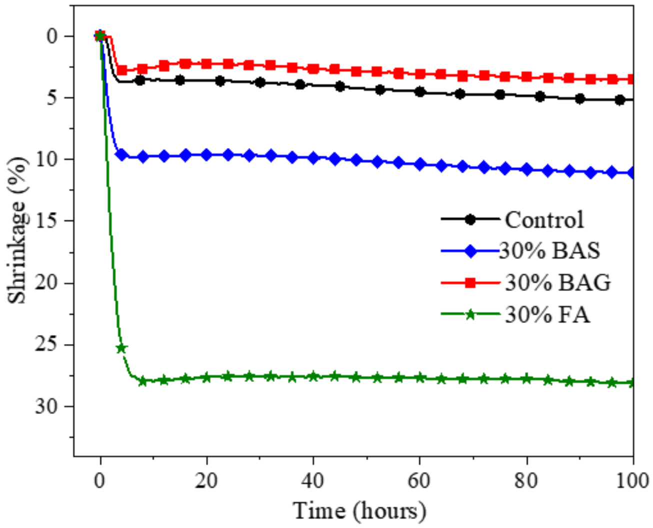

Figure 16: Total shrinkage of cement paste containing ash samples with 0.36 water to binder ratio

From X-ray diffraction patterns it was apparent that using bioash to replace portland cement will result in the formation of higher fraction ettringite and monosulphate. An excessive amount of ettringite can be concerning as this phase can imbibe water and expand which will eventually crack the specimen [41]. To examine such volume change associated with ettringite formation due to the presence of bioash was monitored by measuring the length change in a corrugated tube setup. Such a setup is primarily used for autogenous shrinkage measurements [42] and requires to analyze the shrinkage after the final setting time. However, the goal of this project was to compare any possible expansion due to the ettringite formation and thus, the total length change was monitored here without differentiating between chemical and autogenous shrinkage. The total shrinkages of cement paste samples (control batch and pastes with 30% cement replaced by ash) with 0.36 water to binder ratio are shown in Figure 16. The change in length was monitored up to 100 hours. Several factors are expected to contribute to the total length change of the paste samples, including (i) extent of chemical reaction, in general, higher degree of hydration will increase the shrinkage, (ii) formation of ettringite will reduce the shrinkage due to the volume expansion of this phase, (iii) free water imbibed by the ash particles with increase the shrinkage due to the self-desiccation. Based on Figure 16, the higher shrinkage was observed as follows: FA> BAS>OPC> BAG. While this trend is unusual compared to those observed for strength and pozzolanic reactivity, it confirms that the expansion due to the addition of bioash sample is not significant. The high shrinkage of FA batch was attributed to both chemical reactivity and small particle size distribution of this ash. The small particles of class-F coal fly ash refine the pore size distribution in cement paste which generates higher capillary pressure when water is consumed by hydration [43]. The particle sizes of ground and sieved bioash are larger than those of class-F coal fly ash and thus, resulting in lower shrinkage of BAS and BAG batch. The shrinkage of BAS batch was found to be higher than BAG, even though from other test methods former ash sample was found to be less reactive. Further, the average particle size of BAS was higher than that of BAG and thus, the capillary pressure due to self-desiccation should be lower. Presumably, the high shrinkage of BAS batch is due to the free water imbibed by the large and porous ash particles in this batch. A similar mechanism was proposed to be the reason for low workability of mortar containing BAS as partial replacement of cement. Because of the shrinkage resulting from water absorption by sieved bioash, the expansion due to the ettringite formation appeared to be negligible. Finally, BAG batch was found to have lower shrinkage than that of the control batch. This low shrinkage of BAG batch was attributed to (i) the low reactivity of BAG batch compared to the control batch and (ii) ettringite formation in BAG batch.

4.10. CONCLUSIONS

This work investigated the possibility of using bioash as SCM instead of coal ash. While it is a promising option, such an action will require additional processing as well as standardization of bioash. Followings are the specific findings of this study:

The bioash obtained from the biomass power plant was found to have both bottom and coal fly ash. Due to wide particle size variation of this ash, the bioash should not be directly used as cement replacement. There are two options to use bioash as partial replacement of cement: (i) sieve the ash with #30 sieve, that ensures at least 50% of the ash will be used and (ii) to grind the ash in a high energy ball mill, this procedure ensures a higher amount of ash use, however, at the expense of energy-intensive grinding procedure. The free metal ions present in bioash oxidizes in the presence of moisture and releases hydrogen gas bubbles. This process consumes free water and thus, reduces the workability of cementitious mixtures. Bioash was found to have hydraulic properties due to the presence of reactive aluminate phases. Ground bioash can be used to replace up to 30% of cement in concrete without any significant effect on the compressive strength. The allowable replacement level of sieved bioash is up to 20%. Grinding enhances the pozzolanic reactivity of bioash. Nonetheless, the pozzolanic activity of Class-F coal fly ash is five times higher than that of bioash. Use of bioash as partial replacement of cement can increase the ettringite formation in concrete. However, such ettringite formation did not appear to result in an excessive expansion of cement paste samples.

CHAPTER 5

CONTROLLED LOW STRENGTH MATERIALS (CLSM)

5.1. OBJECTIVES

Construction using CLSM is a sustainable practice. Typically, CLSM is used as a structural backfill where future excavation is uncertain. The CLSM mix is a very flowable. Use of CLSM as an excavatable fill application is very rare. So, the main objective of this part of project is to produce a controlled low strength material by replacing the coal fly ash content with wood ash to achieve a target strength of 1.5 MPa or less and with a normal flowability, such that it can be used as an excavatable backfill. The freshly prepared CLSM mix is used to study the workability and flowability characteristics.

5.2. MATERIALS AND PROPERTIES

The materials used in the CLSM production are the Ordinary Portland Cement (OPC) Type I/II conforming to ASTM C150, coal fly ash or similar products, fine aggregate or coarse aggregate or both and water. The contents of each of the constituents vary based on the application type. All the materials used in the CLSM mix met the ASTM standards requirements. The chemical composition of wood ash and coal fly ash is done based on the X-Ray Fluorescence test data. Based on the chemical compositions and ASTM C618, Wood ash is classified as Class C ash and coal fly ash is classified as Class F ash. Wood ash particles are angular in shape which reduces the workability of concrete. The coal fly ash particles are spherical in shape which helps to increase the workability. Particle size analysis revealed the presence of 25 percent wood ash particles retained on #4 sieve and only 2 percent passing #200 sieve. As any modifications like grinding etc. of the wood ash particles would increase the cost, the wood ash obtained from the bio-mass industry is used as it is in the CLSM production. The larger diameter of the wood ash particles is due to the conglomeration of finer particles as a result of the storage condition. But the large wood ash particles are not as strong and can be easily broken using a mortar and pestle which means most of the large particles might have broken down to smaller particles during mixing. From the XRF results, the wood ash is found to contain lesser silica content than the coal fly ash which might result in a lower pozzolanic reaction.

5.3. PROPORTIONING & MIXING

5.3.1. MIXTURE PROPORTIONING

Different trials have been done to come up with a mix proportion to produce CLSM mixture to have normal flowability which according to ACI 229R is a mix with a slump value of 15 to 20 centimeters and to achieve a target strength as low as 1.5 MPa to make it feasible for future excavation. Six different mix proportions (WA1, WA2, WA3, WA4, WA5, FA) have been considered based on the mix proportion examples for different compressive strengths and the typical contents of individual materials used to produce CLSM given in ACI 229R. The typical CLSM mix contents are provided in Table 2. All the mix proportions are given in the Table 3. In the mix proportions the contents of cement, water, aggregates are kept constant while the wood ash and coal fly ash contents varied. FA batch consists of cement, coal fly ash, fine and coarse aggregates and water. WA5 batch contains cement, wood ash, fine and coarse aggregates and water. The batches WA1, WA2, WA3 and WA4 contains both wood ash and coal fly ash where the wood ash content is being increased by 20 percent while coal fly ash content is being decreased by the same amount.

Table 2: Proportions of each material in a CLSM mixture

Material	Proportions (kg/m^3)
Aggregate	1483 - 2076
Water	237-297
Portland Cement	15-119
Coal Fly Ash	0-415

Table 3: Mix proportions of different CLSM mixtures

Batch ID	OPC (kg/m3)	Wood Ash (kg/m3)	Coal Fly Ash (kg/m3)	Fine aggregate (kg/m3)	Coarse aggregate (kg/m3)	Water (kg/m3)
WA 1	60	29.6	118.4	863	1127	165
WA 2	60	59.2	88.8	863	1127	165
WA 3	60	88.8	59.2	863	1127	165
WA 4	60	118.4	29.6	863	1127	165
WA 5	60	148	0	863	1127	165
FA	60	0	148	863	1127	165

5.3.2. MIXING AND BATCHING

All materials are individually batched and mixed in a concrete mixer according to ACI 229R [20]. The freshly prepared CLSM mix is taken into a bin and is placed into cylindrical molds for compressive strength testing. The fresh mix is tested for workability and flow consistency before casting the cylindrical specimens, in accordance with the ASTM standards.

5.4. EXPERIMENTAL METHODS

The freshly prepared CLSM mix is tested for workability using Slump cone test which is performed in accordance with ASTM C143. Flowability of the freshly prepared CLSM mix was determined in accordance with ASTM D6103. CLSM cylinders were prepared to determine the compressive strength in accordance with the ASTM D4832. The CLSM mix is poured into 150 * 300 mm cylindrical molds to be tested at an age of 7, 28, 56 days.

Figure 17: CLSM cylinders

5.5. RESULTS

5.5.1. FLOW CONSISTENCY

Figure 18 represents the variation in the flowability of different freshly prepared CLSM mixtures. From the figure below it is clear that there is an increase in flowability of the CLSM mixture with an increase in the wood ash content in the mixture. Considering the shape of the wood ash which is angular and the coal fly ash, which is spherical in shape, the flowability of batches containing high coal fly ash content is supposed to have more flowability than the batches containing high wood ash.

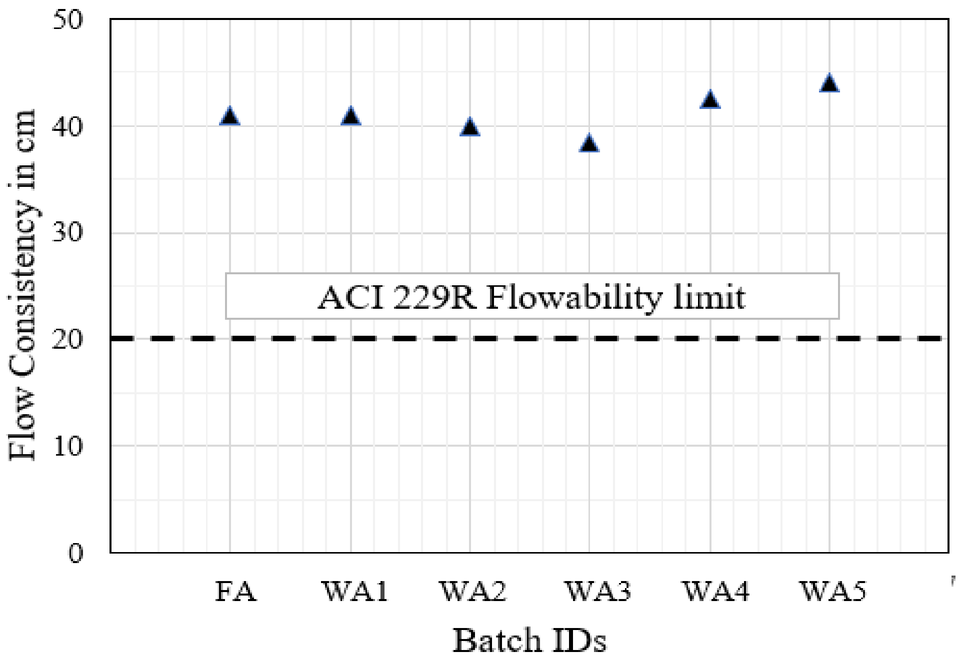

Figure 18: Flowability of CLSM mixtures

The increase in flowability is mainly associated with the particle size distribution of the wood ash and the water absorption capacity of wood ash. The wood ash used consisted of all ranges of particle sizes. The CLSM batches showing higher flowability might be due to the presence of large particles more than that of small particles. As the large wood ash chunks have a lower surface area and thus a lesser friction than that of finely distributed particles, the flowability increases with the presence of large wood ash particles.

5.5.2. SLUMP CONE TEST

Figure 19 represents the variation in the workability of different freshly prepared CLSM mixtures.

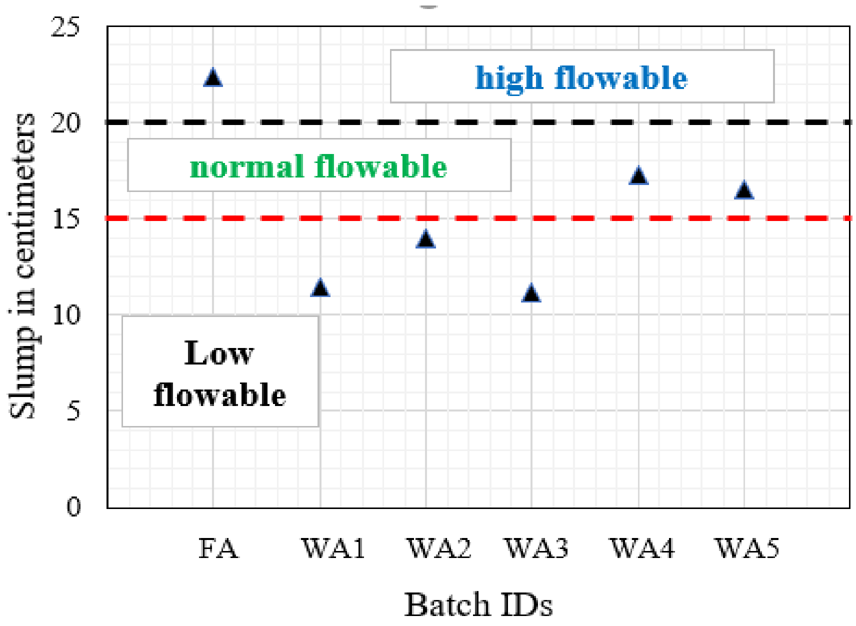

Figure 19: Workability of CLSM mixture

With an increase in the wood ash content in the CLSM mixture, there is a decrease in the workability. The result is relevant as the workability of batches with coal fly ash should be higher than that of wood ash batches. And the slump cone test is done the same way as the conventional concrete mixture. Generally, mixtures containing more larger particles has more voids due to less friction between the particles. One of the reasons might be when the CLSM mixtures are compacted, the void ratio is reduced thereby reducing the workability. And the shape of wood ash particles and the absorption capacity of wood ash can also play a major role in the reduction of workability.

Figure 20: Slump cone test of CLSM mix produced using wood ash

5.5.3. COMPRESSIVE STRENGTH

Figure 21 represents the compressive strengths of CLSM batches at the ages of 7, 28 and 56 days.

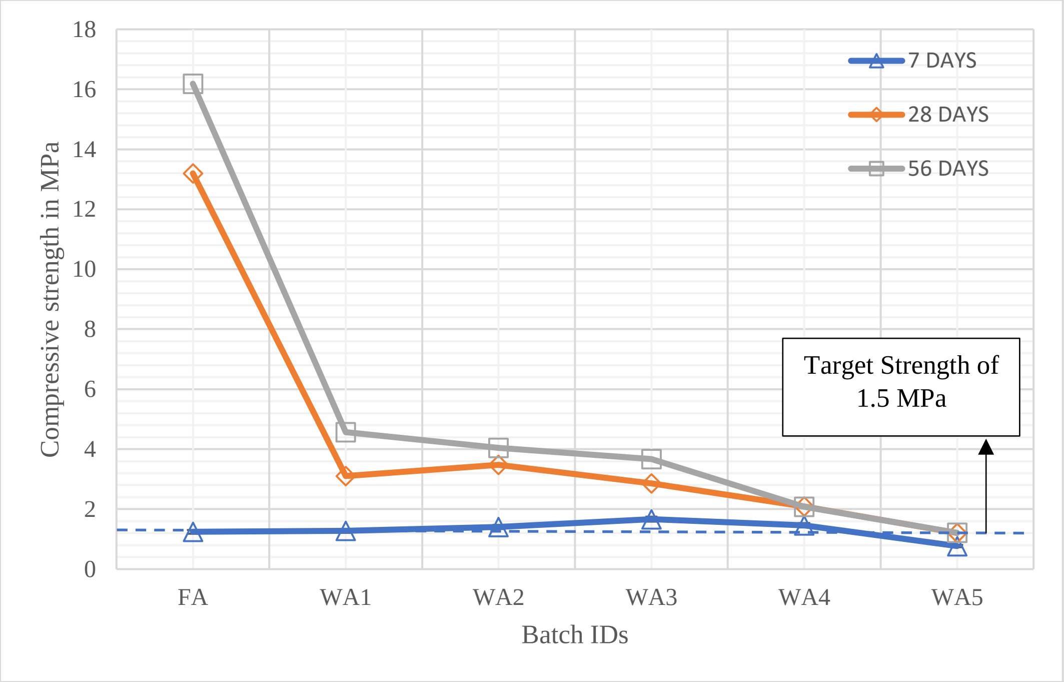

Figure 21: Compressive strength of CLSM mixes

A typical compressive strength of a CLSM mix should be less than or equal to 8.3 MPa[20]. The coal fly ash batch is giving a compressive strength about two times the target compressive strength of a CLSM mix. This is mainly because of the utilization of class F coal fly ash in the production of CLSM. Since class F coal fly ash is highly pozzolanic, the increase in strength is very significant with age of the CLSM. But all the batches containing both the wood ash and coal fly ash have a compressive strength more than that of the target compressive strength of 1.5 MPa at 28 days.

5.6. CONCLUSION

A CLSM mix is defined as a good flowable mix if it has a spread of more than 20 cm[20]. FA batch has a slump value greater than 20 cm which makes it a highly flowable mix. WA1, WA2 and WA3 batches have a slump less than 15 cm which makes it a low flowable mix. WA4 and WA5 can be classified as normal flowable mixes as it has a slump value between 15 to 20 cm. Having a good workability means that the CLSM mix can attain self-compacting and self-consolidating properties. The variation in the workability and the flowability is because of the random distribution of coarse to fine particles. By considering a fixed ratio of coarse to fine particle distribution the desired workability and flowability can be achieved. All the batches containing coal fly ash achieved a compressive strength greater than that of the target compressive strength because as the pozzolanic activity of coal fly ash is almost seven times greater than that of wood ash. The batch with only wood ash achieved the target strength. It can be concluded that wood ash can completely replace coal fly ash in the production of CLSM mixes without affecting the flowability, workability and compressive strength.

CHAPTER 6

CEMENT PRODUCTION USING WOOD ASH

6.1. INTRODUCTION

Since a lot of research has not been done on cement production using waste products from the biomass powerplants, very little literature was found regarding the use of by-products like MSWI fly ash to produce cement clinkers[29]. Based on the chemical characterization of wood ash, it has similar properties as coal fly ash but in high temperature applications like cement production it is uncertain that cement produced from wood ash acts like coal fly ash blended cement. And there is no standard which states that wood ash can be used in cement systems, but literature shows that wood ash acts like coal fly ash and is potential material for production of supplementary cementitious systems and controlled low strength materials. Since wood ash gave positive results when used as a SCM and in CLSM production[9], [20], [21], [44], and also due to the high calcium content present in it, use of wood ash as a raw material for cement clinker production is evaluated.

6.2. MATERIALS AND METHODS

The typical raw materials used for cement production are limestone which is a primary source of calcium and clay which is a source for silica, alumina and iron. For cement clinker production the raw materials used are wood ash, aluminum oxide (Al_2O_3) and calcium oxide (CaO) are the raw materials used for the cement production. From the Chapter 3 (wood ash characteristics), wood ash is found to contain SiO_2 of 35.85%, Al_2O_3 of 8.28%, Fe_2O_3 of 2.5% and CaO of 25.18% by weight. The three important factors which control the quality of cement are Lime saturation factor (LSF), Silica ratio (SR) and

Alumina Ratio (AR). The allowable values for LSF are 0.92-0.98, for SR 2-3 and for AR 1-4[45]. The formulas for computing LSF, SR and AR are as follows[45]

$$LSF = \frac{\%CaO}{2.8 * \%SiO2 + 1.2 * \%Al2O3 + 0.65 * \%Fe2O3} \qquad eq(2)$$

$$SR = \frac{\%SiO2}{\%Al2O3 + \%Fe2O3} \qquad eq(3)$$

$$AR = \frac{\%Al2O3}{\%Fe2O3} \qquad eq(4)$$

For the raw wood ash, the values of LSF, SR and AR are found out to be 0.23, 3.33 and 3.31. The LSF and SR values does not satisfy the allowable limits. In order to satisfy the allowable values, for 100 g of wood ash, 83 g of CaO and 1.8 g of Al_2O_3 are added which resulted in a 0.95 LSF value, 2.85 SR value and 4.03 AR value. All the materials are mixed by adding a tiny bit of water in order to achieve uniform mixing and is then placed in a conventional oven at 100 ˚C for the excessive water to evaporate. The dried mix is ground to fine powder passing through #200 sieve.

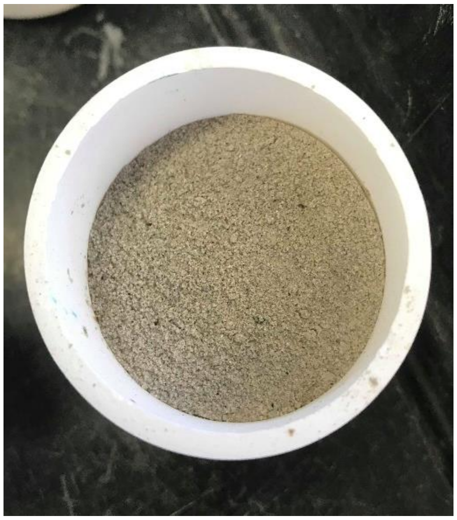

Figure 22 : Raw wood ash mix in a zirconium crucible

Zirconium crucibles are used for clinker production. As shown in Figure 22 the raw mix is taken into the crucible and is placed in the furnace at 1420 ˚C for a dwell time of 10 minutes. The produced wood ash cement (WAC) clinker as shown in Figure 23, is ground to a fine powder and is subjected to XRD where the presence of free lime in the wood ash cement is found.

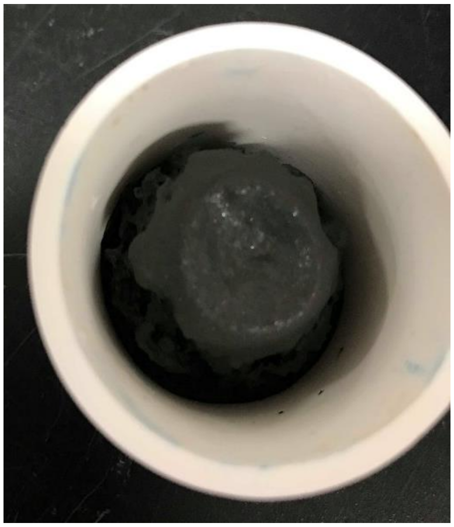

Figure 23 : Lab produced wood ash cement clinker before incinerating

Figure 24 : Wood ash cement clinker

The WAC cement powder is incinerated for 3 more times at the same temperature and dwell time and XRD analysis is done each time to check the presence of free lime. At the end of third incineration the free lime content is found out to be negligible. The final product as shown in Figure 24 is ground along with 3% gypsum and is stored in an air tight container to be used for further tests.

6.3. XRD ANALYSIS

Figure 25 shows the XRD patterns of raw wood ash cement at each trial and OPC. The change in the phases of wood ash cement with each trial can be observed. WAC-1 , 2 and 3 represents the wood ash cement at trial 1, 2 and 3. The presence of amorphous hump in WAC-2 is mainly due to the material preparation for the test.

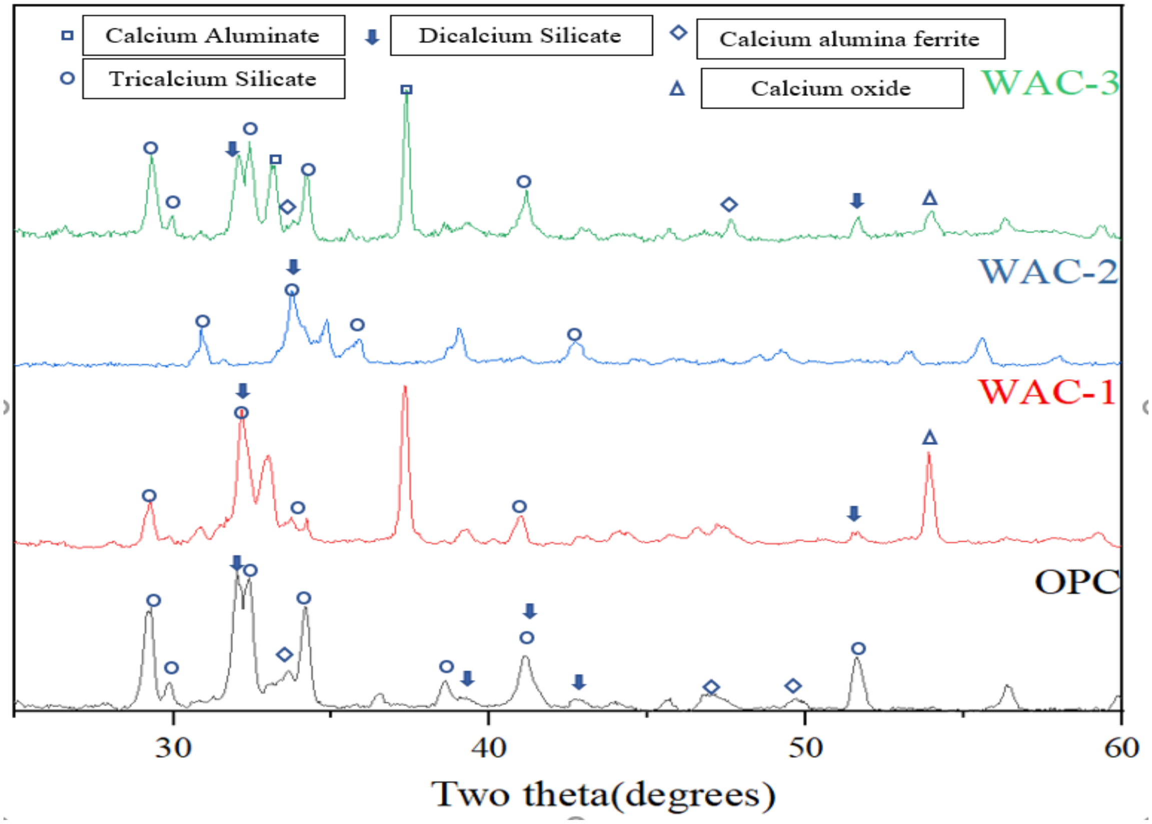

Figure 25: XRD patterns of trial 1, 2 and 3 of wood ash cement and OPC

The XRD analysis of raw wood ash cement reveals the formation of phases represented in the figure which are very much similar to OPC but contains calcium aluminate peaks in excess. XRD analysis of the hydrated wood ash system revealed the formation of Calcium hydroxide ($Ca(OH)_2$), Monosulfate (Afm), Monocarboaluminate (Mc), Calcium carbonate ($CaCO_3$), Ettringite (Aft), C_2S, C_3S and C_3AF phases[37]. OPC XRD patterns does not show the presence monosulfate and monocarboaluminate phases. The XRD data of wood ash cement and OPC at 14 days hydration is represented in Figure 26.

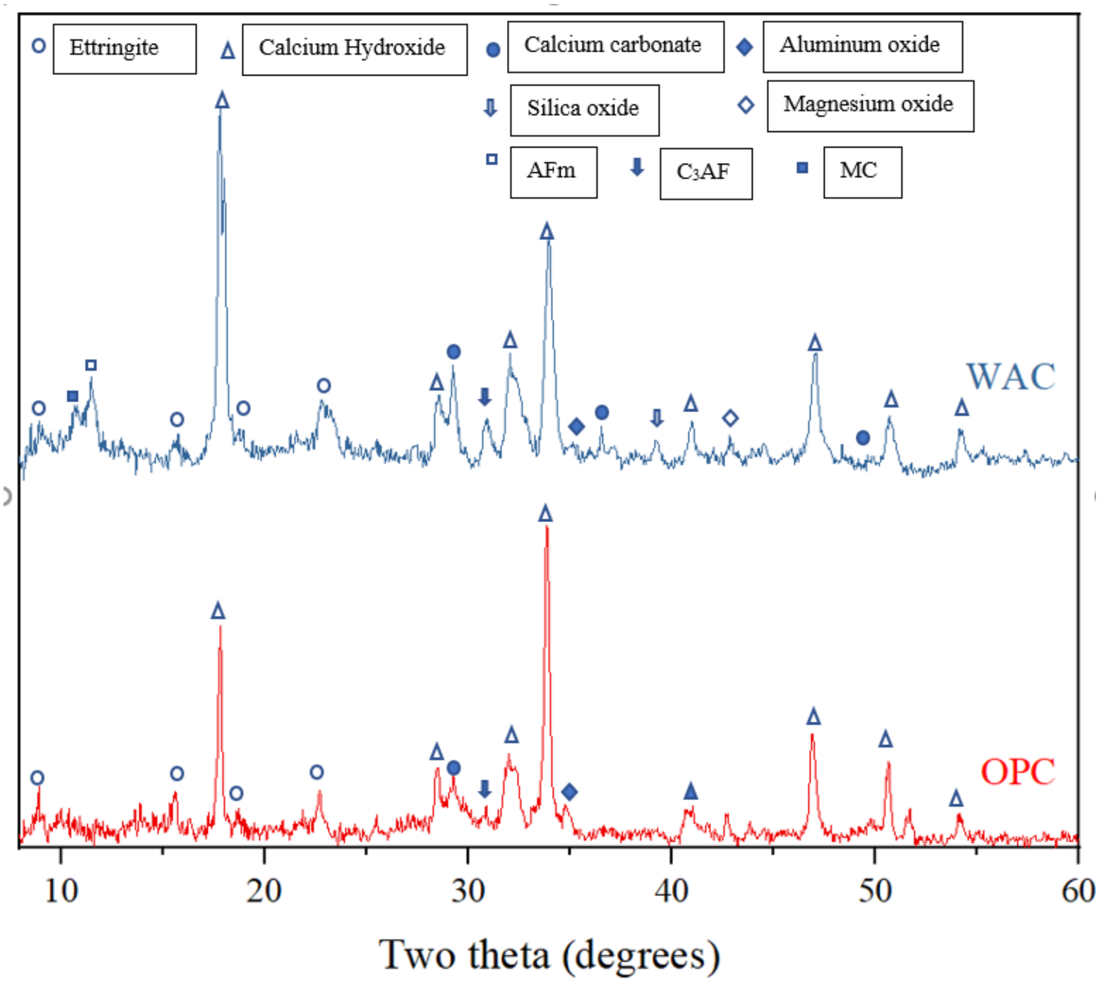

Figure 26 : XRD analysis of hydrated WAC and OPC

6.4. HYDRATION PRODUCTS

Hydration of wood ash cement is studied using the thermogravimetric analysis and isothermal calorimetry at 24 hours, 7 and 14 days respectively and is compared with the hydration of ordinary Portland cement. Wood ash cement with and without gypsum is used to understand the rate of hydration. WAC_G is wood ash cement blended with 3 percent gypsum and WAC is the wood as cement without gypsum.

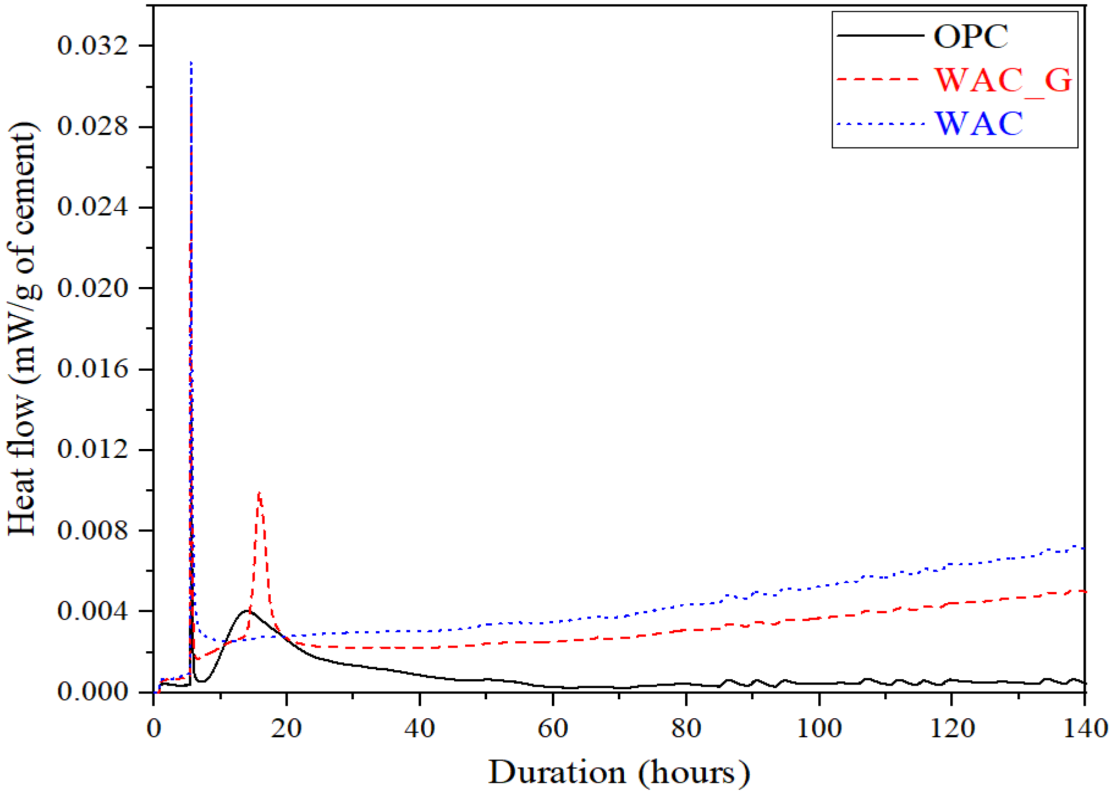

Figure 27 : Heat flow per gram of wood ash cement

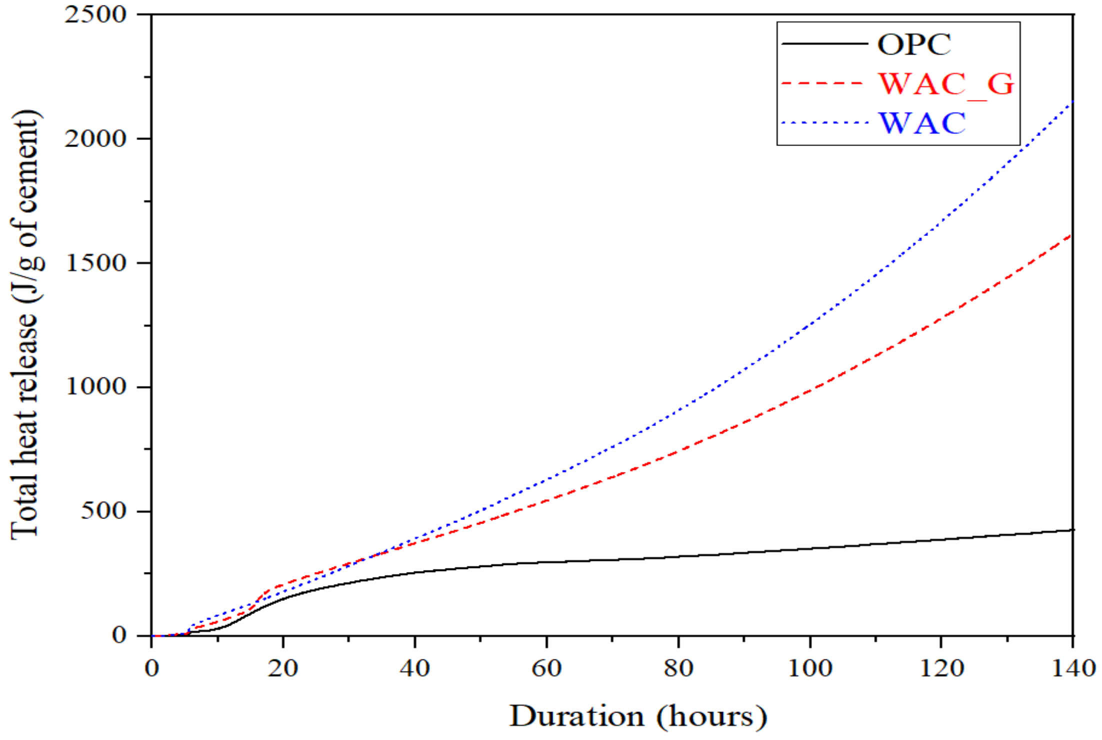

Figure 28: Total heat released by the wood ash cement

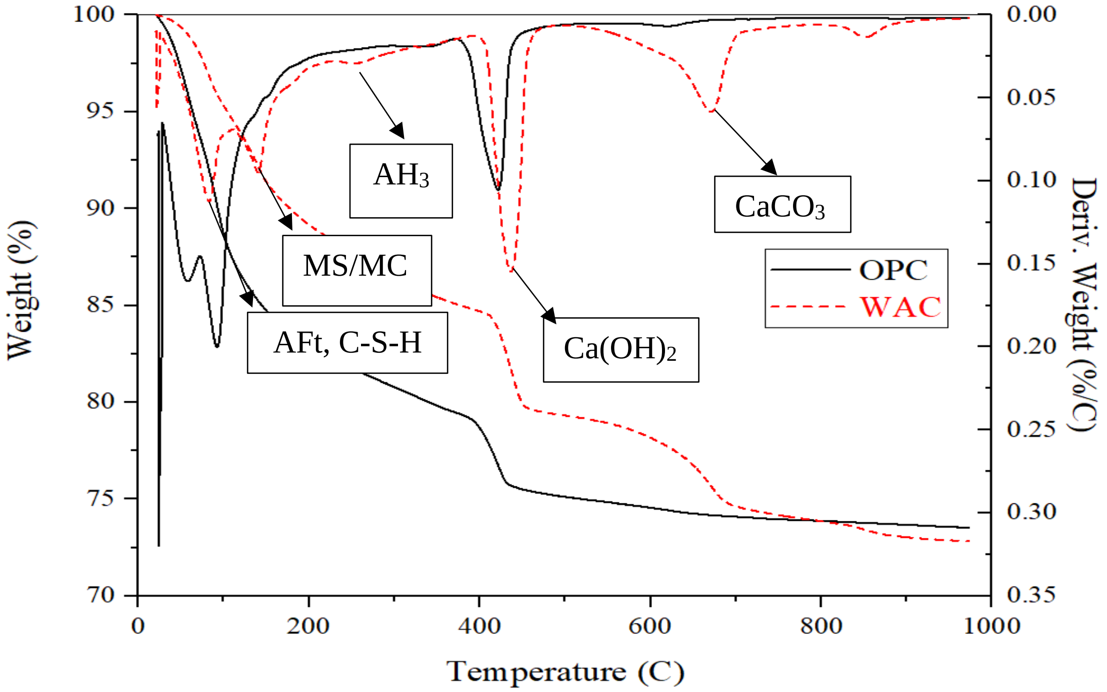

Figure 29 : TGA curve for OPC and WAC for 14 days hydration

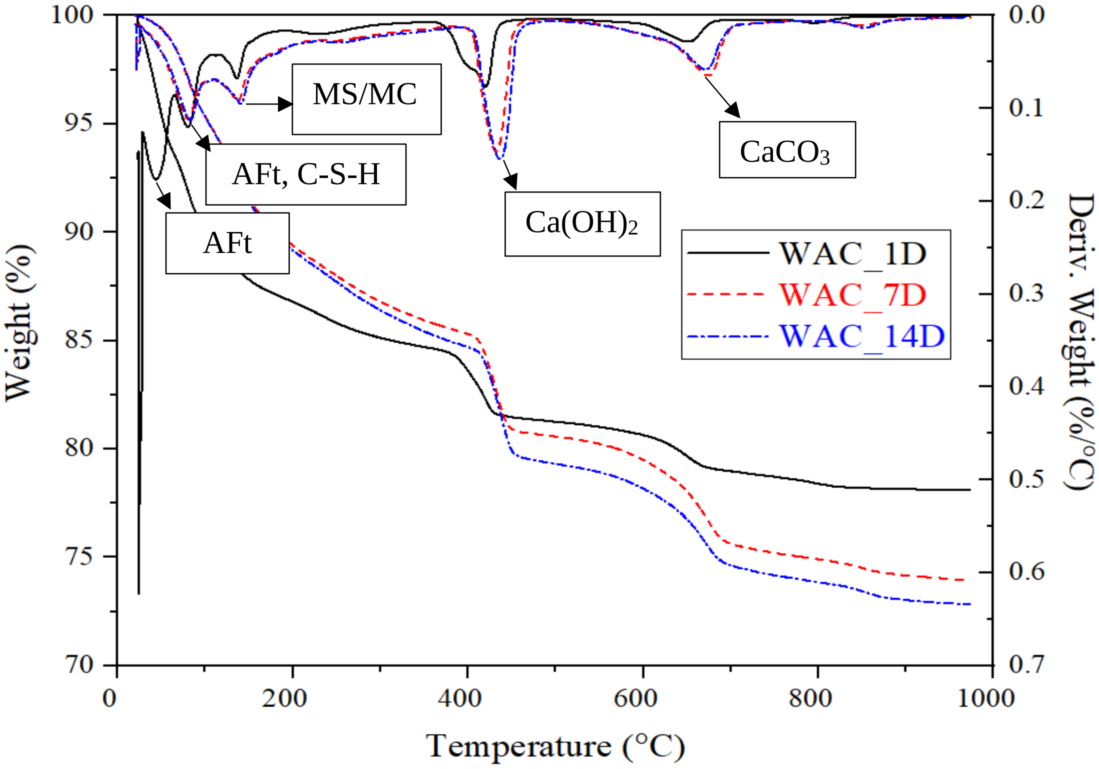

Figure 30: TGA of WAC at 1, 7 and 14 days

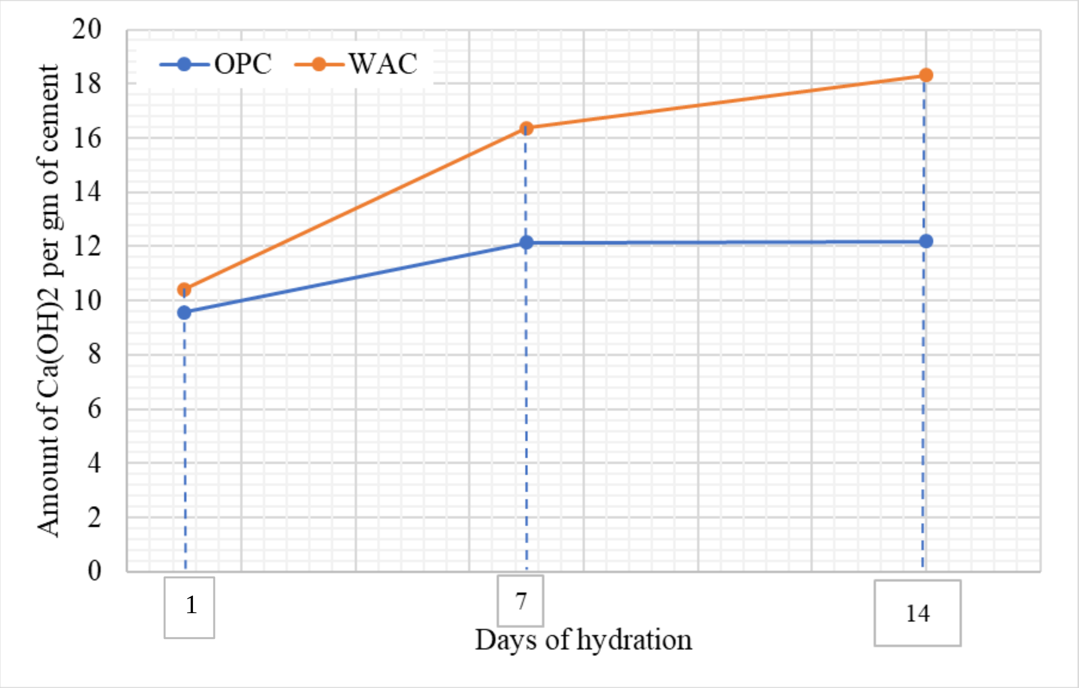

Figure 31: Amount of calcium hydroxide formed in 1, 7 and 14 days of hydration of wood ash cement

Figure 27 and Figure 28 shows the heat release due to wood ash cement is very high when compared to OPC. Wood ash cement without any gypsum content shows the highest hydration rate. Addition of gypsum retarded the hydration rate of wood ash cement. The wood ash cement is a highly reactive material. Thermogravimetric analysis confirms the formation of Calcium hydroxide ($Ca(OH)_2$) as seen in Figure 29. Figure 29 also shows the phases being formed in the hydrated wood ash cement system[37]. From the thermogravimetric analysis the formation of ettringite and monosulphate is observed. The formation of monosulphate is due to the imbalance in the reactivity of tricalcium aluminate and the dissolution of calcium sulphate which causes an inadequate supply of sulphate ions. This results in an initial rapid reaction and then a decrease in the hydration rate. From the isothermal calorimetry data (Figure 27) the wood ash cement with gypsum has a steeper peak while the wood ash cement without gypsum doesn't have any peak at all. The gypsum present in the wood ash cement with gypsum batch acts as a source of sulphate ions and the calcium aluminate present in the wood ash cement reacts it to form ettringite and then the ettringite reacts with the additional calcium aluminate to form monosulphate. This explains the presence of two peaks in OPC and wood ash cement while the wood ash cement batch without gypsum has no second peak as the hydration reaction is carried out as soon as the water is added[45]. Figure 31 shows the amount of calcium hydroxide being formed over time. And it is clear that $Ca(OH)_2$ formed in the hydrated WAC system is much higher than that of in a hydrated OPC system.

6.5. CONCLUSION

The above results show that cement can be produced using wood ash as a raw material. From the isothermal calorimetry analysis, the wood ash cement is found to be very reactive. XRD analysis reveal the formation of phases in WAC which is very similar to the phases in OPC. Wood ash cement is rich in alumina which makes it a rapid setting cement without the presence of gypsum. The hydration rate is more significant in WAC than in OPC. The wood ash cement showed the presence of $CaCO_3$ which is formed due to the reactivity of WAC with atmospheric CO_2. The ettringite, monosulfate phases are not so significant in the hydrated WAC system. XRD results doesn’t show any presence of gypsum, which means there is no possibility for more ettringite to form.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1. CONCLUSION

This study ensures that the wood ash can be used in the construction materials. In order to use wood ash in the cement systems, the number of fine particles needs to be higher, so modification is necessary if the wood ash contains higher coarse particles. Presence of high alumina content reduced the workability of the wood ash blended cement system. Grinding the wood ash is a reliable technique as it not only increased the workability and pozzolanic activity but also gave a better strength when compared to the sieved batch. The ground batch can be used up to 30 percent as a cement replacement and the sieved batch can be replaced up to 20 percent and still the blended cement system gives more than 75 percent of the strength achieved at 28 days by the ordinary Portland cement. The ettringite formed in the cement system did not result in an excessive expansion of the cement paste. Even though wood ash is used in the production of CLSM without any modification, the target strength is achieved without any impact on the rheology. Wood ash can completely replace coal fly ash in the production of CLSM. First of all, the target strength is very low and secondly CLSM can be produced using any class of coal fly ash or similar products irrespective of their chemical compositions. So, wood ash can be used as a potential material in the production of CLSM and as a supplementary cementitious material. For the cement production using wood ash, the chemical composition of wood ash plays a huge role in the cement composition. So, the Lime saturation factor, silica and alumina ratio needs to be adjusted according to the allowable limits in order to achieve the desired characteristics. Evaluation of hydration characteristics revealed that wood ash cement is very reactive than the Ordinary Portland cement.

7.2. FUTURE RECOMMENDATIONS

When wood ash is used as a supplementary cementitious material, soundness needs to be evaluated in accordance with ASTM C618. Since the hydraulic properties in wood ash are found to be not significant, wood ash can be used as a filler material in cement systems and the properties can be studied. Effects of wood ash on long term durability which includes initial surface absorption, water absorption, porosity, Alkali-silica reaction and sulfate attack can be studied. Since wood ash properties are variable based on their production process, wood ash having high pozzolanic activity can be used in the production of ultra-high-performance concrete. Controlled low strength materials can be used in various applications apart from structural backfills like conduit bedding, pavement bases, insulating and isolation fills etc. where typically coal fly ash is used, so wood ash can be used to evaluate the effect of wood ash when used in the applications listed above. Compressive strength of wood ash cement paste samples needs to be studied. The effect of wood ash cement on the workability, long-term durability needs to be studied.

CHAPTER 8

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