DEVELOPMENT OF SUSTAINABLE CEMENT MORTAR INCORPORATING RICE HUSK ASH

BY

Muhammad Harunur Rashid

Department of Civil Engineering
Khulna University of Engineering & Technology
Khulna

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Muhammad Harunur Rashid

A dissertation submitted in partial fulfilment of the requirement for the degree of Ph.D. in Engineering

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Khulna University of Engineering & Technology
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DECLARATION

This is to certify that the thesis work entitled as "Development of Sustainable Cement Mortar Incorporating Rice Husk Ash" has been carried out in partial fulfillment of the requirement for Ph.D. degree in the Department of Civil Engineering, Khulna University of Engineering & Technology, Khulna-9203, Bangladesh. The above research work or any part of the work has not been submitted to anywhere for the award of any degree or diploma except publication. No other person's work has been used without due acknowledgement.

Supervisor

27.9.11

(Prof. Dr. Md. Keramat Ali Molla)

Candidate

26.9.11

(Muhammad Harunur Rashid)

Co-supervisor

28/09/11

(Prof. Dr. Tarif Uddin Ahmed)

DEDICATION

TO MY PARENTS AND MY FAMILY

KHULNA UNIVERSITY OF ENGINEERING & TECHNOLOGY
DEPARTMENT OF CIVIL ENGINEERING

Certificate of Thesis Work

A THESIS ON
DEVELOPMENT OF SUSTAINABLE CEMENT MORTAR
INCORPORATING RICK HUSK ASH

By

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has been accepted as satisfactory in partial fulfillment for the degree of Doctor of Philosophy in Civil Engineering and it is certified that the student demonstrated a satisfactory knowledge in the field covered by his thesis in an oral examination held on December 14, 2011.

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ABSTRACT

The study for the development of sustainable cement mortar incorporating rice husk ash was conducted by several approaches. Several researchers have been conducting research to replace the ordinary Portland cement by new materials with pozzolanic and cementitious properties. The aim of this study was to investigate the performance of cement mortar with rice husk ash for its sustainable development. A detail investigation was conducted to produce the rice husk ash with appropriate properties by effective incineration process. The fineness of rice husk ash based on different incineration systems, retention time and grinding time was determined. Characterization of rice husk ash was performed with XRD, SEM and chemical composition analysis. The effect of rice husk ash on heat of hydration was examined. Eventually, the performance of cement mortar with different proportions of rice husk ash was evaluated based on strength, permeability, sorptivity, salt crystallization, resistance to sulphate attack and effect of elevated temperature ranging from 200 to 700°C. The result shows that the highest fineness of 6894 cm^2/gm was obtained for rice husk ash produced in laboratory burning system with 60 hours retention and 180 minutes grinding. The result of XRD confirmed the amorphous state of rice husk ash produced in laboratory burning system at 663.6°C. The maximum compressive strength of 33.09 MPa at 28 days was found for control sample. The highest compressive strengths at later age of 90, 350, 600 and 900 days were found to be 38.08, 38.80, 39.09 and 39.23 MPa respectively for 20% replacement with rice husk ash. The highest permeability of 4905 columbs was found in case of control sample at 28 days age. The result indicates that the permeability is inversely proportional to rice husk ash and curing age of sample. The trend of sorptivity was found similar to permeability and the highest value of control sample was found to be 0.214 kg/m^2-$min^{0.5}$. It was found that the mortar samples with 15% and 20% rice husk ash sustained up to standard 20 cycles in salt crystallization. No crack or spalling was observed due to sulphate attack on the mortar samples with 15 and 20% replacement of OPC with rice husk ash. The control sample exhibits the highest strength of 44.47 and 23.85 MPa at 200 and 700°C respectively. The sample having 15% rice husk ash shows maximum strength of 48.26 and 43.52 MPa at 300°C and 400°C respectively while the highest strength was obtained at 500°C for sample with 20% rice husk ash. The findings of the present study would contribute to the sustainable development of cement mortar incorporating rice husk ash.

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ASTM	American Society for Testing and Materials
BC	Before Christ
C/C	Cement to Carbon ratio
C-H	Calcium Hydroxide
C-S-H	Calcium Silicate Hydrates
DC	Direct Current
FAO	Food and Agriculture Organization
FM	Fineness Modulus
FT	Fourier Transform
FT-IR	Fourier Transform Infra-Red
ICSD	Inorganic Crystal Structure Database
ISO	International Organization for Standardization
keV	kiloelectron volt
LOI	Loss on Ignition
MJ/kg	Mega-joule per kilogram
MPa	Mega Pascal
MtC	Million Tonnes of Carbon
NRDC	National Research and Development Centre
OECD	Organization for Economic Cooperation and Development
OPC	Ordinary Portland Cement
PCA	Portland Cement Association
PDF	Powder Diffraction Files
ppm	Parts per million
PVC	Polyvinyl Chloride
RCPT	Rapid Chloride Permeability Test
RHA	Rice Husk Ash
RILEM	Reunion Internationale des Laboratoires et Experts des Materiaux
S	Sorptivity
SCM	Supplementary Cementing Materials
SE	Secondary Electrons
SEM	Scanning Electron Microscope
SSA	Specific Surface Area

SSD	Saturated Surface Dry
UNIDO	United Nations Industrial Development Organization
W/C	Water Cement ratio
XRD	X-ray Diffraction
θ'	Slopes of trend-lines
μ	Plastic viscosity
d	Distance of inter lattice planes
eV	Electron volt
i	Water absorbed per unit cross-sectional area
n	An integer representing the order of the diffraction peak
S_y	Yield stress
t	Time
V	Volt
W_d	Weight of sample before contact with water
W_t	Weight of sample at time interval "t"
θ	The scattering angle
λ	Wavelength of the X-ray
μm	Micro meter

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Researchers are always trying to introduce new materials in cement to make it economical and improve the quality. New materials with pozzolanic and cementitious properties have been investigated to mix with cement during the past years (Neville, 1995; Mehta, 1983) for technical and economic reasons. Among these materials some are industrial and agricultural waste by-products and some are naturally active materials. Different materials with pozzolanic properties such as blast furnace slag, silica fume, fly ash, and rice husk ash have played an important role in the production of cement mortar/concrete. According to Graciela et al. (2009) among the different existing residues and by-products, the possibility of using Rice Husk Ash (RHA) has attracted more attention to researchers than other crop residues.

Rice is grown in all over of the world except Antarctica. It is a key source of food for billions of people. In addition, it ranks second to wheat in terms of area and production (FAO, 2002). Globally, the production of paddy rice was close to 683 million tons in the year of 2008, where Asian countries comprised nearly 91%. In fact, Bangladesh is holding the forth position in all over the world (FAO, 2009) in terms of rice production. Production of rice is dominated by Asia, where rice is the only food crop that can be grown during the rainy season in the tropical areas. During growth, rice plants absorb silica from the soil and accumulate it into their structures. In order to make the ash valuable, this silica needs to be concentrated by burning at suitable temperature.

Rice husks are the natural sheaths that form on rice grains during their growth. At the time of refining rice, the husks which come out from this process usually have no commercial interest. However, it can be useful through a variety of thermo-chemical conversion process. The major compounds from rice husks are silica and cellulose which yields carbon when thermally decomposed (Adylov, et al., 2003).

Most of the husk from the rice milling industry is either burnt or dumped as waste in open fields and a small amount is used as fuel for boilers, electricity generation, etc. (RHA market study, 2003). Paddy on an average consists of 72% of rice, 5% - 8% of bran, and 20% - 22% of husk, on weight basis (Ou, et al., 2007; Basha, et al., 2005; Bouzoubaa and Fournier, 2001; Prasad, et al., 2000). This husk contains about 75% - 80% organic volatile matter and the balance 20% - 25% of the weight of this husk is converted into ash during the firing process, which is known as rice husk ash (RHA). This husk is used as fuel in the rice mills to generate steam for the parboiling process. This RHA usually contains around 85% - 97% amorphous silica with small amount of alkalis and other trace elements (Ou, et al., 2007; Basha, et al., 2005; Bui, et al., 2005; Asavapisit and Ruengrit, 2005; Adylov, et al., 2003; Bouzoubaa and Fournier, 2001; Saha, et al., 2001; Prasad, et al., 2000; Natio, 1999). This silica is highly porous and light weight, with exceedingly external surface area. Rice husk ash (RHA) is a term describing all types of ash produced from burning rice husks which vary considerably according to burning techniques. The silica in the ash undergoes structural transformations depending on conditions (time and temperature) of combustion.

According to Sugita (1993) and Joseph et al. (1989), amorphous ash is formed at incineration temperature of 550°C to 800°C and the change occurs from amorphous to crystalline form at approximately 800°C to 900°C. Some other researchers reported that RHA produced below 700°C would be in amorphous form and above 800°C would result in crystalline form (Nair, et al., 2008; Nair, et al., 2006; Khurama and Khurama, 2003; Maeda, et al., 2001; Bouzoubaa and Fournier, 2001; Mehta, 1979). Tendency of formation of crystalline material was observed by Spence and Cook (1983) at or above 600°C - 700°C firing temperature for RHA. In another study (Cook, 1980), it was found that the optimum firing temperature for rice husk ash varies from 500°C to 750°C. The RHA should have favourable structure and desirable properties such as amorphous structure, high specific surface area (SSA), and high reactivity to be used as a cementitious material. These structures and properties in general can vary by the burning process. In other words, to some extent, the structure and properties of RHA depend on the burning temperature. James and Rao (1986) indicated that isothermal heating at a minimum of 402°C is required for complete destruction of organic matter within rice husk and to liberate silica.

The incinerating conditions essentially control the quality of ash (Nair, et al., 2006; Bui, et al., 2005; Shomglin, et al., 2001; Maeda, et al., 2001; Mehta, 1979; Yoeh, et al.,1979), which may either be in crystalline or amorphous form. Geographic location can also affect the ash properties such as fineness and colour (Prasad, et al., 2000; Bouzoubaa and Fournier, 2001; Bui, et al., 2005). The RHA in amorphous state can exhibit active pozzolanicity under normal conditions (Nair, et al., 2006; Shomglin, et al., 2001; Maeda, et al., 2001; Moayad and Hana, 1984; Mehta, 1979). Nair et al. (2008) stated that not only the temperature ranges, but also the duration of incineration controls the ash quality. In principle, higher temperature-short duration or lower temperature-long duration will result in amorphous ash. The reactivity of silica in rice husk ash (RHA) depends on the complex and interlinked factors of temperature and duration of incineration (Nair, et al., 2008; Moayad and Hana, 1984). Burning temperature and duration dictate the quality of RHA production.

Water demand is one of the major problems for RHA addition in cement mortar/concrete. RHA being highly porous and its fineness is a crucial issue to control its water demand in cement mortar/concrete. Some researchers showed that addition of RHA up to 3% by mass of cement does not adversely affect the water demand (Nehdi, et al., 2003; Moayad and Hana, 1984). Currently, researches reported that the partial replacement of OPC with RHA will improve the concrete performance, either in strength or durability (Sensale, 2006).

Mehta (1992) and RILEM committee (1988) reported that the RHA is a mineral admixture for concrete. Robert (1990) disclosed in a report that RHA is a pozzolanic material if the firing temperature is acceptable. Pozzolans are a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value, but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (Mielenz, 1983). In this study the pozzolanicity of RHA was determined by following ASTM C593.

To find out the use of RHA as cement replacing material in mortar, samples were prepared with different replacement level of Ordinary Portland Cement (OPC) by Rice Husk Ash (RHA). Different studies showed that some percentage of cement replaced by RHA indicate excellent performance when compared to control concrete (Sensale, 2006; Zhang, et al., 1996; Zhang and malhotra, 1996; Mehta, 1994; James, et al., 1986; Mehta and Pitt, 1977). The durability of cementitious material has an indirect effect on economy, serviceability and maintenance.

Available literature showed that most of the researches have been conducted by producing RHA through controlled combustion process. A little research was conducted by considering uncontrolled burning processes though the researchers failed to achieve desired performance of mortar/concrete with RHA (Mehta, 1983). However, the RHA that is produced in Bangladesh through uncontrolled burning in rice husking mills. Therefore, the present study was undertaken to conduct research on RHA obtained from the uncontrolled combustion process. The RHA is used to replace the Ordinary Portland Cement (OPC) for the preparation of mortar. Thousands of tone of RHA produced every year, therefore, the study on the performance and durability of cement mortar using RHA will bring benefits in technical, economical and environmental terms.

1.2 SIGNIFICANCE OF THE STUDY

A considerable research and development efforts need to be executed to find the uses of RHA as a partial replacement of cement or to consider as an alternative material of cement. Rice husk is an agricultural by-product material from rice milling industry and used as a fuel in the boiler for parboiling of paddy. After burning, the ash is generally dumped in low land which creates environmental pollution. Unfortunately, rice milling industries in all over Bangladesh have no controlled incineration system. For this reason, uses of RHA as a cement replacing material can save cost and environmental pollution. In order to achieve the economy of cementing materials as well as to minimize the environmental impact, investigations on the cement mortar incorporating different percentage of RHA addition are being considered.

1.3 OBJECTIVE OF THE STUDY

The aim of this study is to investigate the sustainability of RHA available in Bangladesh as cement replacing material and improve the local combustion techniques for quality ash production. The specific objectives are outlined below:

a) To observe the influence of uncontrolled incineration techniques on the quality of Rice Husk Ash.
b) To explore the optimum conditions for the production of amorphous silica from rice husk in uncontrolled incineration process.
c) To investigate the mechanical properties of cement mortar incorporating RHA.
d) To determine the durability of mortar with RHA.
e) To find the long time performance (900 days) of mortar with RHA.
f) To justify the performance of RHA mortar under elevated temperature.
g) To examine the adverse environmental effect and permeability of mortar incorporating RHA.

1.4 SCOPE OF THE STUDY

The major aim of this study is to investigate the sustainability of mortar incorporating RHA produced from an uncontrolled burning technique. In this study rice husk from Khulna and Rajshahi district of Bangladesh was used as a raw material. The collected Rice Husk was dried properly in sunlight before burning. The dried rice husk was burned in open heap burning system and also in laboratory burning system. The Rice Husk Ash also directly collected from husking mill of three different locations (Khulna, Rajshahi and Dinajpur district) of Bangladesh. The Blaine fineness, XRD and SEM techniques were applied for the characterization of rice husk ash which fulfils the first two objectives.

Following tests were performed to satisfy the remaining objectives of this study.

- Setting time
- Workability
- Mechanical strength
- Water sorption

- Salt crystallization
- Permeability
- Resistance to sulphate attack
- Fire performance

1.5 STRUCTURE OF THE DISSERTATION

This dissertation describes the research work to find out the effect of uncontrolled burning of rice husk and the acceptability of use of the rice husk ash as a cement replacing materials for mortar. The dissertation has been presented in five chapters comprising different aspects of this study shown in below:

Chapter 1 provides a general account of rice husk ash and its utilization in cement mortar. And also present the background of this study including significance of the study, objectives and scope of the research work.

Chapter 2 provides the history of research on combustion of rice husk and performance of cement mortar incorporating rice husk ash. It also reviews the previous findings on the combustion process of rice husk, including the effect of Rice Husk Ash on cement mortar.

Chapter 3 presents the methodology to carry out the study, which includes the necessary information of materials and details of the experimental techniques.

Chapter 4 discuss about the characterization of the rice husk ash produce from uncontrolled combustion technique. The results of the investigation of combustion process of rice husk to produce amorphous, carbon free siliceous ash. The effect of combustion techniques on the quality of rice husk ash were discussed here. Also, the time-temperature relation for production of amorphous form of rice husk ash was determined.

The water demand, setting time, mechanical strength of mortar incorporating rice husk ash are discussed. The strengths of mortar were investigated at different ages by using different types of sand, OPC, Rice Husk Ash and water. The effects of rice husk ash in mortar were investigated in this chapter and identified the suitable RHA for mortar.

The durability of mortar incorporating rice husk ash was discussed in this chapter. Porosity, salt crystallization, water sorption, permeability and resistance to sulphate attack were performed and determined the acceptable replacement levels of Ordinary Porland Cement (OPC) by Rice Husk Ash (RHA).

The performances of mortar with rice husk ash under elevated temperature were discussed. SEM and FT-IR tests results were discussed to ascertain the possible changes in compounds due to addition of rice husk ash and/or elevated temperature.

Chapter 5 provides the conclusions of the study based on the experimental evidence for potential use of RHA as a cement replacing material to develop a sustainable mortar. It also provides the recommendations for future study.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

Sustainable development is an emerging social and political issue of global significance. The increasing need of the concrete industry demands the sustainable development and to reduce its impact on the environment. To achieve this goal, researchers and scientists are trying to improve the properties of concrete materials. At the same time, the challenging issue is to find out the effective and economical use of various wastes in cement based products. To support this research work, the available literatures have been reviewed in detail in this chapter.

2.2 CEMENT

Cement is one of the major compounds and key building material worldwide used for development. Cement consists of inorganic and non-metallic material with hydraulic binding properties. Mixed with water it forms a paste, which hardens owing to formation of hydrates. After hardening, the cement retains its strength. It is used mostly for the production of concrete. Concrete is a mixture of inert mineral aggregates, e.g., sand, gravel, crushed stones, and cement. Cement consumption and production is closely related to construction activity and, therefore, to the general economic activity.

Muga and Betz (2005) point out that the cement production is only 2 million tons (Mt) in the year of 1880. The global cement production grew from 594 Mt in 1970 to 1453 Mt in 1995 at an average annual rate of 3.6% (Cembureau, 1998). Cement consumption and production is cyclical, synchronized with business cycles. After 1995 the production rate is higher and nearly 2.1 billion tons/year, and exponentially increases to approximately 3.5 billion tons/year by 2015 (Coutinho, 2003).

Cement is widely used throughout the building industry. Cement manufacturing is an energy consuming process; the cost of energy constitutes approximately 25 % of the price of finished cement. Three major processes are involved for manufacturing of cement as follows:

i) Raw material preparation,
ii) Clinker making in the kiln, and
iii) Cement making.

Raw material preparation and cement making are the main electricity concentrated processes, while the clinker kiln uses almost all the fuel in a typical cement plant. Clinker production is the most energy-intensive production step, responsible for about 70%–80% of the total energy consumed for cement production (World Energy Council, 1995). The theoretical energy consumption for producing cement can be calculated based on the enthalpy of formation of 1 kg of Portland cement clinker, which is about 1.76 MJ (Taylor, 1992). Energy consumption by the cement industry is estimated at 2% of the global primary energy consumption (World Energy Council, 1995), or 5% of the total global industrial energy consumption.

Due to the dominant use of carbon intensive fuels, e.g. coal, in clinker making, the cement industry is also a major emitter of CO_2. Besides energy consumption, the clinker making process also emits CO_2 due to the calcining process. The cement industry contributes 5% of total global carbon dioxide emissions. It is the third largest CO_2 producer.

The threat of climate change is considered to be one of the major environmental challenges for our society. Carbon dioxide (CO_2) is one of the key greenhouse gases. Anthropogenic sources of CO_2 are the combustion of fossil fuels, deforestation, unsustainable combustion of biomass, and the emission of mineral. The production of cement contributes to the emission of CO_2 through the ignition of fossil fuels, as well as through the decarbonization of limestone. An indirect and significantly smaller source of CO_2 is from consumption of electricity, considering that the electricity is generated from fossil fuels.

Process CO_2 is formed by calcining, which can be expressed by the following equation:

$$\begin{array}{lcl} CaCO_3 & \rightarrow & CaO + CO_2 \\ 1\ kg & & 0.56\ kg + 0.44\ kg \end{array}$$

The specific process CO_2 emission per ton of cement depends on the ratio of clinker to cement. This ratio varies normally from 0.5 to 0.95. Estimated carbon emissions from cement production in 1994 were 307 MtC; 160 MtC from process carbon emissions and 147 MtC from energy use. These emissions account for 5.0% of 1994 world carbon emissions based on a total of 6199 MtC reported by the Carbon Dioxide Information and Analysis Center (Marland, et al., 1998).

2.2.1 Cement Hydration

The hydration development is important because it directly influences the workability, setting behavior, strength gain rates, and pore structure development of the cement mortar. Therefore, proper information on the hydration development of cementing materials is necessary to expect the performance.

The hydration of cementitious materials results in a number of exothermic chemical reactions which liberate heat. The hydration progress can be observed by determining the total released heat (via temperature changes) over time. Research has established that the rate and amount of heat released from hydration intensely depends on the chemical compositions, physical properties of the cement, supplementary cementitious materials and chemical admixtures. The mix proportions and curing temperature of mortar play an important role in this case. As an outcome of these sensitivities difference in the amounts or characteristics of the mortar or concrete elements, particularly the type and amount of cementitious materials used, can be eagerly detected by monitoring the heat of hydration (PCA, 1997).

Cement is the most active binding materials in concrete. The hydration process initiates when the cement mixed with water. During this process, the cement particles react with water to produce primarily calcium silicate hydrate (C-S-H), which is nearly an amorphous material having the properties of a rigid gel. Hydration proceeds by a gradual reduction in the size of the anhydrous cement particles and formed a layer or shell, of C-S-H around the cement grains. The concrete is said to be 'set' once the shells from adjacent cement grains begin to coalesce filling in the initially water-filled space. The continued hydration of the cement will gradually fill in the capillary pores, which are the remnants of the initially water filled space. Therefore, it is vital that moisture is available to the concrete past setting to allow the cement to continue to hydrate. The chemical reactions (not exact stoichiometric equations) take place during the hydration process (Taylor, 1997) is shown below in equation 2.1 and 2.2:

$$C_3S + 5.3H \rightarrow C_{1.7}SH_4 + 1.3CH \qquad (2.1)$$

$$C_2S + 4.3H \rightarrow C_{1.7}SH_4 + 0.3CH \qquad (2.2)$$

Out of the two main products of hydration, calcium silicate hydrates (C-S-H) and calcium hydroxide (CH), the C-S-H provides the strength and durability properties of concrete. The calcium hydroxide, which occupies about 20% by mass of the cement matrix, forms large, weak crystals spread throughout the hardened cement paste and are commonly concentrated at aggregate interfaces due to the porosity left the film of water on the aggregates. Therefore, in order to produce strong and durable concrete, it is desirable to minimize the amount of CH in the cement paste, while increasing the volume of C-S-H in the cement matrix (Hoa, 2005).

The water exists in the cement paste matrix is categorized into three different forms: chemically bound, physically adsorbed and free water (Powers and Brownyard, 1947). The chemically bound water is the primary component of the cement gel after the reaction between the water and the cement paste (i.e. interlayer water). The physically adsorbed water is absorbed at the external surfaces of the layers of C-S-H, occupying the so-called gel pores. Any remaining water, including those that occupy the capillary pores is indicated as free water. The physically adsorbed water and the free water are usually identified together as evaporable water. Evaporable water can easily be removed from the cement paste by means of heating at 105°C. Non-evaporable water is chemically bound to the gel, which can be removed at different phases of temperature up to 1050°C. Both the evaporable and non-evaporable water content depends on several key factors such as w/cm (Water to Cementitious materials ratio), age, SCM (Supplementary Cementing Materials) and cement types. Powers and Brownyard (1947) suggested that the degree of hydration of the cement can be calculated by measuring the non-evaporable water content of the cement paste.

It is well-known that the hydration of fly ash-cement binders includes two complex phenomena: the hydration of cement clinker and the pozzolanic reaction between fly ash and free lime. Researchers have pointed out in the past that both processes accelerate each other (Pane and Hansen, 2005; Wang, et al., 2004). The active effect of fly ash in a fly ash-cement binder can be divided into two aspects: the pozzolanic activity of fly ash and its ability to promote the hydration of cement (Wang, et al., 2004). The most difficult part is separating the kinetics of both processes in order to determine the individual hydration degree of the cement clinker and the pozzolanic reaction degree of fly ash (Pane and Hansen, 2005; Wang, et al., 2004).

The hydration of cement is a much faster process than the pozzolanic reaction of fly ash, which can be still active, even after one year. Several researchers tried to distinguish the contributions of cement and fly ash in the overall hydration reaction, all with their own measuring techniques (Pane and Hansen, 2005; Wang, et al., 2004).

2.2.2 Determination of Heat of Hydration

Different methods can be used to determine the heat of hydration. Conventionally, it has been found out by measuring the heat of the solution (ASTM C 186). In recent times, the calorimetric test is increasingly used because the heat of hydration can be easily monitored in this system with time. This process has also been treated as a heat signature or thermal fingerprint experiment since it determines a temperature connected property that is unique to a given mortar mix. There are four major categories of calorimeters used in cement science and technology which are adiabatic calorimeters, semi-adiabatic calorimeters, isothermal calorimeters, and solution calorimeters.

A "perfect" isothermal or adiabatic calorimetric experiment is almost impossible to perform without delicate equipment (and thus expensive); a hybrid named, semi-adiabatic calorimetric testing is more commonly in used (FHA, 2006).

2.2.2.1 Adiabatic and semi-adiabatic calorimeters

Since it is impossible to achieve an adiabatic environment, the calorimeter is considered to be adiabatic as long as the temperature loss of the sample is not greater than 0.02 K/h. The heat loss is prevented by controlling the temperature of the surrounding environment. The insulating materials could be water, air, and heated containers. Water insulation is the most popular way.

Adiabatic heat measurements are the most suitable for making a continuous heat of hydration curve under curing conditions close to mass curing. And also adiabatic hydration curves are the most appropriate starting points for temperature calculation in hardening structures.

Semi-adiabatic calorimeter is similar with the adiabatic calorimeter. But it allows a certain amount of heat loss to the environment. The maximum heat loss should be less than 100 J/(h·K). The calculated adiabatic curve from the semi-adiabatic test is lower than the curve from the true adiabatic test. The temperature development is lower than the sample in adiabatic test due to heat loss. Semi-adiabatic process is appropriate for pasts, mortars, and concrete samples. It is been generally used for determining the heat signature of concrete.

Cement hydration process is normally divided into five stages and that are shown in Figure 2.1. Once cement is mixed with water, a phase of rapid heat evolution (stage 1) takes place and stay about fifteen to thirty minutes. The rapid reactions outcome from ions dissolves in water and reacting between C_3A and gypsum. This phase is usually not confined by the calorimeter test due to its short reaction time.

The heat progression curves normally measured from the dormant period of cement hydration (stage 2). During the dormant period cement hydration process is ceased, slight heat is generated, and in this stage the material is flowable. While ion dissolution continues with time, the ion concentrations of C_3S and C_2S increase in the cementitious samples. This stage generally lasts less than five hours. At the end of the dormant period, the significant hydration starts again due to C_3S and C_2S hydration (stage 3). This phase of cement hydration is called the acceleration period. Concrete temperature increases rapidly in this stage. After the acceleration period the rates of heat generation gradually decrease (stage 4). In this stage, the thickness of the hydrated layer that covers unhydrated particles increases, and the surface area of the unhydrated portions decreases. The layer of cement hydrates acts as the diffusion area, which governs the permeability of the water and dissolved ions. Finally, cement hydration reaches the steady state nature (stage 5). Both stages 4 and 5 are known as the diffusion control phase.

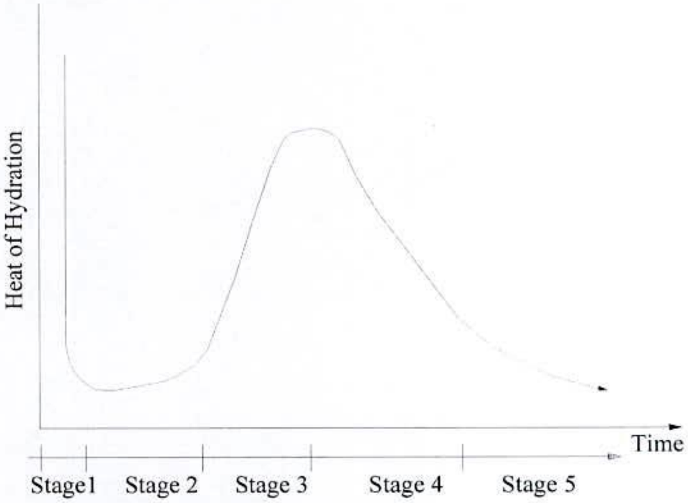


Figure 2.1: Heat Evolution at different stages of cement hydration process.

Cement with a high w/c ratio has more water and microstructural space available for hydration of cement, which in turn results in a higher ultimate degree of hydration. Since the heat of hydration is directly related to the degree of hydration, the heat generation is affected by the w/c ratio. As shown in Figure 2.2, at least six parameters (t_0, T_{max}, t_{max}, S_1, S_2, and A) are needed to describe a specific concrete heat evolution curve. These parameters are closely associated with concrete properties and performance.

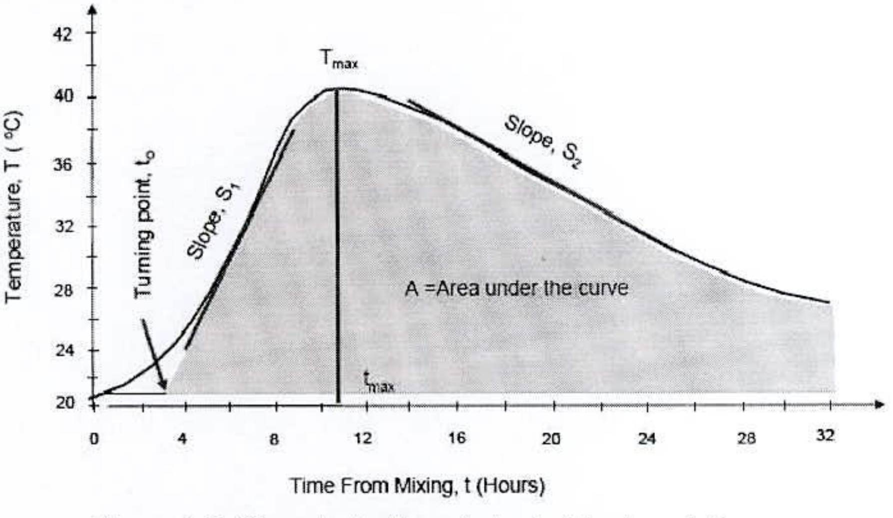


Figure 2.2: Characterization of a typical heat evolution curve

2.2.3 Factors that Affect the Heat of Hydration

The rate and quantity of the heat liberated greatly depends on the chemical and physical properties of the cement, water/cement ratio, supplementary cementitious materials (SCM), chemical admixtures, and curing conditions. These factors are discussed in the following section.

2.2.3.1 Fineness of cement

Fineness of cement affects the placeability, workability, and water requirement of a concrete mixture. It is normally measured in terms of specific surface area. The average Blaine fineness of modern cement ranges from 3000 to 5000 cm^2/g. Although cement with different particle distribution might have the same specific surface area, the specific surface area is still considered to be the most useful measure of cement fineness.

Since hydration occurs at the surface of cement particles, finely ground cement will have a higher rate of hydration. The finer particles will also be more fully hydrated then coarser particles. However, the total heat of hydration at very late ages is not significantly affected.

2.2.3.2 Water cement ratio

An important aspect during hydration is the decrease in porosity. The precipitated hydration products, which have lower specific gravities and larger specific volumes, cause cement grains to expand continuously as cement hydration proceeds. However, the volume of the hydration product is less than the total volume of the cement and water that reacted to form it. The hydrated product is not capable to fill the volume available for it. If external water is available, the cement will hydrate continuously until either the cement is completely hydrated or until the available space within the paste is completely filled. Complete hydration of cement is generally assumed to require a water/cement ratio of about 0.4 (Breugel, 1997). According to Young and Hansen (1987) hydration will stop when the amount of water is not enough to form a saturated C-S-H gel. A minimum w/c ratio of 0.42 is required for complete hydration. If external water is not available, the cement paste will dry as hydration proceeds. Additionally, when the internal relative humidity drops below about 80%, hydration will stop.

2.2.3.3 Type of cement

ASTM C150 standard describes 5 basic types of cement. Type I is designed for general use, while Type II offers a low level of resistance to sulphates. Type III is used when early strength is needed, and Type IV is designed for use with very large structures. Type V is designed for projects that require high sulphate resistance. Type of cement has some effect on heat of hydration due to the compositional variations. Detail of the cement types described below:

Type I: Portland cement is known as common or general purpose cement. It is generally assumed unless another type is specified. The typical compound compositions of this type are: 55% (C_3S), 19% (C_2S), 10% (C_3A), 7% (C_4AF), 2.8% MgO, 2.9% (SO_3), 1.0% Ignition loss, and 1.0% free CaO. A limitation on the composition is that the (C_3A) shall not exceed fifteen percent.

Type II: is intended to have moderate sulphate resistance with or without moderate heat of hydration. This type of cement costs is near about the same as Type I. It's typical compound composition is: 51% (C_3S), 24% (C_2S), 6% (C_3A), 11% (C_4AF), 2.9% MgO, 2.5% (SO_3), 0.8% Ignition loss, and 1.0% free CaO. A limitation on the composition is that the (C_3A) shall not exceed eight percent which reduces its vulnerability to sulphates. This type is for general construction that is exposed to moderate sulphate attack and is meant for use when concrete is in contact with soils and ground water.

Type III: It has relatively high early strength. Its typical compound composition is: 57% (C_3S), 19% (C_2S), 10% (C_3A), 7% (C_4AF), 3.0% MgO, 3.1% (SO_3), 0.9% Ignition loss, and 1.3% free CaO. This cement is similar to Type I, but ground finer to increases the specific surface typically 50-80%. The gypsum level may also be increased a small amount. This gives the concrete using this type of cement a three day compressive strength equal to the seven day compressive strength of types I and II. Its seven day compressive strength is almost equal to types I and II 28 day compressive strengths. The only shortcoming is that the six month strength of type III is the same or slightly less than that of types I and II. Therefore the long-term strength is sacrificed a little. It may be used in emergency construction and repairs or where early strength is required.

Type IV: Portland cement is generally known for its low heat of hydration. Its typical compound composition is: 28% (C_3S), 49% (C_2S), 4% (C_3A), 12% (C_4AF), 1.8% MgO, 1.9% (SO_3), 0.9% Ignition loss, and 0.8% free CaO. The percentages of (C_2S) and (C_4AF) are relatively high and (C_3S) and (C_3A) are relatively low. A limitation on this type is that the maximum percentage of (C_3A) is seven, and the maximum percentage of (C_3S) is thirty-five. This causes the heat given off by the hydration reaction to develop at a slower rate. However, as a consequence the strength of the concrete develops slowly. After one or two years the strength is higher than the other types after full curing. This cement is used for very large concrete structures, which have a low surface to volume ratio. This type of cement has not been made for many years, because Portland-pozzolan cements and ground granulated blast furnace slag addition offer a cheaper and more reliable alternative.

Type V: It is used where sulphate resistance is important. Its typical compound composition is: 38% (C_3S), 43% (C_2S), 4% (C_3A), 9% (C_4AF), 1.9% MgO, 1.8% (SO_3), 0.9% Ignition loss, and 0.8% free CaO. This cement has a very low (C_3A) composition which accounts for its high sulphate resistance. The maximum content of (C_3A) allowed is five percent for Type V Portland cement. Another limitation is that the (C_4AF) + 2(C_3A) composition cannot exceed twenty percent. This type is used in concrete that is to be exposed to alkali soil and ground water sulphates which react with (C_3A) causing disruptive expansion.

2.2.3.4 Sulphate content

During the final process of cement production, a small amount of gypsum is added and interground with the clinker to control the early reaction of tricalcium aluminate. With a low or over dosage of sulphate, the cement will have false or flash set. The proper amount of sulphate required for cement varies with the cement composition and fineness.

Lerch (1946) conducted a series of tests to study the effect of gypsum on hydration in terms of the heat liberation. It was found that heat liberated in 30 minutes, reduced by increasing SO_3 content regardless of the content of C_3A. This finding could be explained by the theory that alumina is less soluble in a lime-gypsum solution than in limewater (Lerch, et al., 1929). The addition of gypsum saturates the solution more quickly and the reaction of C_3A is retarded. Therefore, the heat of hydration is reduced.

2.2.3.5 Blended cements

In blended cement, a portion of the clinker is replaced with industrial by-products, such as coal fly ash (a residue from coal burning), blast furnace slag (a residue from iron making), or other pozzolanic materials. These products are blended with the ground clinker to produce a homogenous product known as blended cement. Blended cement has different properties than Portland cement, e.g., setting takes longer period of time along with ultimate strength (Cangiano, et al., 1992).

The relative importance of additive use can be expressed by the cement to carbon (C/C) ratio of the cement production in a specific country. Portland cement has a C/C ratio of 0.95, whereas blast furnace slag cement may have a C/C ratio as low as 0.35. Countries such as the United States, Canada, and United Kingdom have high C/C ratios, showing the dominance of Portland cement, whereas countries such as Belgium, France, and the former Soviet Union show lower C/C ratio, expressing relatively larger use of blended cements (Worrell, et al., 1995).

The future potential for the application of blended cement depends on the current application level, on the availability of blending materials, standards and legislative requirements. The global potential for CO_2 emission reduction through producing blended cement is estimated to be at least 5% of total CO_2 emissions from cement making (56 Mt of CO_2) but may be as high as 20%. The potential savings will vary by country and region. Worrell, et al. (1995) estimated the potential for carbon emission reduction on a national basis for 24 countries in the OECD, Eastern Europe, and Latin America. It was estimated that the minimum availability of blending materials on the basis of pig iron production and coal combustion. The potential emission reduction varied between 0% and 29%. The average emission reduction for all countries (producing 35% of world cement in the year of 1990) was estimated at 22%. It was negligible for countries with a large share of blended cement production (e.g., The Netherlands) or with a low availability of blending materials, i.e., countries without iron production or coal fired power stations (e.g., Costa Rica, Guatemala). It was high for countries with limited production of blended cements and a well-developed industry or fossil-based power industry (e.g., United Kingdom, United States). The C/C ratio for China was estimated at 85%. Considering the large iron production and coal use in power production in China, a large potential for blended cement may also be expected in the world's largest cement maker. According to Hendriks et al. (1999), no negative environmental effects of slag and fly ash addition in cement have been found.

2.3 RICE HUSK ASH

Critical economic and environmental situations of the current days encourage companies and researchers to develop and improve technologies intended to reduce or minimize industrial wastes. As a consequence, much effort has been expended in different areas, including the agricultural production. In recent years, studies have been carried out by different researchers using wastes generated from the agricultural and industrial activities as concrete-making materials. Wastes such as rice husk, sawdust, cork granules and coconut pitch have been used as filler or aggregate for concrete (Ramaswamy, et al., 1983; RCTT, 1979; Paramasivam and Loke, 1978; Cook, et al., 1977; Mehta, 1977).

Bangladesh is the forth highest paddy rice producing country all over the world and rice husk is abundantly produced. Recently RHA has attracted more attention to the researchers as an additive of cement. During growth, rice plants absorb silica from the soil and accumulate it into their structures. The accumulated silica concentrated by burning at high temperatures in RHA, which makes the ash valuable. The chemical composition of rice husk is found to vary from sample to sample due to the differences in the type of paddy, crop year, climate and geographical conditions (Chandrasekhar, et al., 2003).

Rice husk is the outer covering of paddy and accounts for 20% – 25% of its weight. It is removed during rice milling and is used mainly as fuel for heating in homes and rice milling industries in Bangladesh. Its heating value of 13 – 15 MJ/kg (Natarajan, et al., 1998; Jenkins, 1989) is lower than most woody biomass fuels. However, it is extensively used in rural Bangladesh because of its widespread availability and relatively low cost. In the major rice-producing countries, much of the husk produced from the processing of rice is either burnt or dumped as waste (Chindaprasirt, et al., 2009; Mathur, 2006; Chindaprasirt and Rukzon, 2006).

The RHA is usually producing through controlled and uncontrolled combustion process. Uncontrolled combustion process is used in most of the cases in Bangladesh. The characteristic of RHA depends on the combustion process and variation of temperature. The fine particulate matter which is carried away from the combustion zone by the flue gas produces fly ash. The ash produced with stoker and suspension fired boilers is closed to 100% amorphous.

The proportion of bottom ash to fly ash depends upon the boiler type and operating conditions. For example, McBurney Corporation offer a suspension fired boiler with pre-grinding of the husks. This produces approximately 10% bottom ash and 90% fly ash. Suspension fired boilers by other manufacturers, such as Fortum, are expected to produce similar proportions of ash. Combustion units with uncooled chambers, such as challenger units by Advanced Recycling Equipment Inc appear to produce nearer to 50% bottom ash and 50% fly ash. At least one manufacturer, Torftech UK Ltd. has a compact bed reactor (Torbed® reactor) which produces almost 100% fly ash (Dodson and Tortech, 2002).

2.3.1 Methods of Ash Analysis

Typically, the ash will contain some unburnt components as well as inert components of the husks. The unburnt component is predominantly carbon. It is typically measured by reheating a sample of the ash in an oven. The difference in mass of the sample before and after heating is referred to as the 'Loss on Ignition' (LOI). The LOI value is normally the same as the carbon content of the ash.

The carbon content of RHA varies according to the combustion process. The literature shows that the loss on ignition values of RHA vary from 1 to 35%. Typically, the carbon content varies from 5-7% in commercial RHA. The silica presents in the rice husks in molecular level and associated with water. It occurs in several forms (polymorphs) within the husks. In nature, the polymorphs of silica (SiO2) are: quartz, cristobalite, tridymite, coesite, stishovite, lechatelerite (silica glass), and opal; the latter two are being amorphous (Velupillai, et al., 1997).

RHA is a potential product to use as cement replacing material only when it is in amorphous nature. However, it has no value as cement replacing materials when it is in crystalline form. From the technical literature, two forms appear to predominate in combustion and gasification. These are lechatelerite (silica glass), an amorphous form, and cristobalite, a crystalline form. SiO_2 can also occur in a very fine, submicron form. The major and trace elements are conventionally expressed as their respective percentage of oxides and may not actually be present in this oxide form. SiO_2 is generally determined as 'total' SiO_2, since the proportion of crystalline to amorphous silica requires further costly analysis, usually by XRay Diffraction (XRD).

The colour of the ash generally reflects the completeness of the combustion process as well as the structural composition of the ash. Generally, darker ashes exhibit higher carbon content. Lighter ashes have achieved higher carbon burnout, whilst those showing a pinkish tinge have higher crystalline (tridymite or cristobalite) content.

2.3.2 Factors Influencing Ash Properties

Different researchers reported that the several parameters are influencing the properties of RHA. The major parameters are incineration temperature and duration along with geographical location.

2.3.2.1 Incineration temperature and duration

The most evaporable components are slowly lost and the silicates are left during burning. The characteristics of ash depend on the temperature and time of burning.

Hwang and Wu (1995) summarized the chemical composition of rice husk ash burned at different temperatures as shown in Table 2.1.

Table: 2.1: Chemical composition of RHA burnt at different temperatures

Elements		Temperature (^{0}C)				
		<300	400	600	700	1000
Element (%)	Si	81.90	80.43	81.25	86.71	92.73
	K	9.58	11.86	11.80	7.56	2.57
	Ca	4.08	3.19	2.75	2.62	1.97
	Na	0.96	0.92	1.33	1.21	0.91
	Mg	1.25	1.20	0.88	0.57	0.66
	S	1.81	1.32	1.30	1.34	0.16
	Ti	0.00	0.00	0.00	0.00	0.45
	Fe	0.43	1.81	0.68	0.00	0.68
Oxide (%)	SiO_2	88.01	88.05	88.67	92.15	95.48
	MgO	1.17	1.13	0.84	0.51	0.59
	SO_3	1.12	0.83	0.81	0.79	0.09
	CaO	2.56	2.02	1.73	1.60	1.16
	K_2O	5.26	6.48	6.41	3.94	1.28
	Na_2O	0.79	0.76	1.09	0.99	0.73
	Fe_2O_3	0.29	0.74	0.46	0.00	0.43

The burning temperature and cooling rate indicate the amorphous property of the rice husk ash. Within these processes, the physicochemical characteristics of RHA produced under controlled conditions generally differ on burning temperature (Cordeiro, 2006). For example, the burning temperature in the boiler, which should be less than 900°C to avoid the formation of cristobalite (a crystalline polymorph of quartz) (Hamad and Khattab, 1981), is not always effectively controlled. Moreover, if sufficient oxygen is not available, and if the residence time for the husk in the boiler is not long enough, organic material in the form of unburnt or partially burnt rice husk, will remain within the bulk RHA after the burning process. It was indicated by X-ray diffraction analyses (Yoganda and Jagadish,

1988) that RHA by-products from different parts of India presented silica in distinct phases.

The form of silica after combustion of rice husk depends on the temperature and duration of the combustion of rice husk. Mehta (1979) suggested that essentially amorphous silica can be produced by maintaining the combustion temperature below 500°C under oxidizing conditions for prolonged periods or up to 680°C with a holding time less than 1 min. However, Yeoh et al. (1979) reported that RHA can remain in the amorphous form at combustion temperature of up to 900°C if the combustion time is less than 1 hour, while crystalline silica is produced at 1000°C with combustion time greater than 5 min. Using X-ray diffraction, Chopra et al. (1981) observed that at burning temperature up to 700°C, the silica was in amorphous form.

An extensive investigation has been carried out in the manufacturing processes, including combustion and grind technologies to obtain high performances of RHA. The main factors in the various combustion and gasification processes that determine the type of ash produced are time, temperature and turbulence. These affect all chemical changes that occur in the combustion process including the way of ash morphology is altered.

Several studies mentioned that rice husks when burnt in controlled conditions between temperatures of 500°C to 700°C and ground to particle sizes of less than 10 μm will perform acceptable pozzolanic properties to apply in cement and concrete industries (Morsy, et al., 2008; Xiaoa and Falknerb, 2006; King, 2000). Uncontrolled combustion of poor quality of RHA produced high carbon content and high amount of loss on ignition at a temperature lower than 500°C (Morsy et al., 2008).

XRD patterns of ash combusted at a range of temperatures from 500°C – 1000°C have shown a change from amorphous to crystalline silica at 800°C, and the peak increased rapidly at 900°C. The change from amorphous to crystalline silica at 800°C was also found in other studies (Kashikar, 2000). In Vietnam, a series of experiments using a laboratory oven under conditions designed to simulate the conditions of combustion from a rural facility were carried out (Bui, et al., 2005).

SEM analysis of the ash found that the 'globular' amorphous silica increased in size from 5 – 10 μm to 10 – 50 μm with rising combustion temperatures from 500°C to 600°C. The transition to completely crystalline silica was completed by 900°C.

2.3.2.2 Geographical location

Hsu et al. (1996) reported that chemical variations in husk composition (and consequently ash composition) are influenced by such things as the soil chemistry, paddy variety and climate. A variation in colour and trace metal were found in ash from husks burnt in different regions, with ash produced from husks from Northern India resulting in a much darker ash than husks from the USA. The colour variation was not related to differences in the carbon remaining in the ash, although it is not known the precise regional features that affected the ash. According to Boateng and Skeete (1990) that the differences in mineral composition of ash can be attributed to fertilizers applied during rice cultivation, with phosphate having a negative effect on the quality of the ash in terms of its ability to act as a pozzolan. It has also been said that the high K_2O found in some ashes could be a consequence of K-rich fertilizers used during the paddy cultivation (Mehta, 1994). Sathy and Pramada (2006) noted that the chemical composition of rice husk was found to vary from sample to sample due to difference in type of paddy, crop year, climatic and geographical conditions.

2.3.3 Characteristics of amorphous silica

The Dictionary of Composite Materials Technology (Lee, 2010) defines amorphous silica as a naturally occurring or synthetically produced oxide of silicon characterized by the absence of a pronounced crystalline structure and whose X-ray diffraction patterns have no sharp peaks (Yalcin and Sevic, 2001; Kalapathy, et al., 2000; Riveros and Garza, 1986). This type of silica may be anhydrous or have a significant water of hydration in its structure.

The desirable physico-chemical and mechanical properties of amorphous silica, notably their high reactivity, excellent binding properties, relatively high purity and excellent mechanical strength make this material useful in a wide range of technologies. Although hosts of synthetic silica are produced commercially, the ones produced from plant origins such as rice husks have been noted to have some significant advantages over those from mineral and synthetic origins

(Zemnukhova, et al., 2006). A typical X-ray diffraction pattern of amorphous silica produced from rice husk combustion is shown in Figure 2.3 (Ikram and Akhter, 1988).

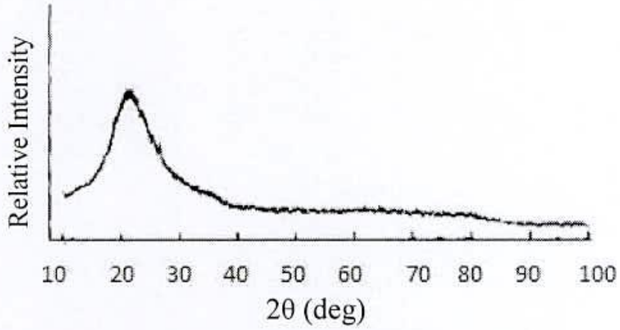


Figure 2.3: Typical XRD pattern of amorphous silica from RHA

The crystal structure of silica may determine its reactivity and degree of health danger. Whilst crystalline silica is less reactive and deemed carcinogenic, the amorphous silica is rather reactive and with no harmful effect. The major reflections or peaks of crystalline quartz from ICSD powder diffraction files (PDF) occur at Bragg 2θ angles of 20.856°, 26.636° and 36.541°. It can be seen that no defined peaks corresponding to these Bragg 2θ angles are found. A rather broad peak spanning 2θ angle range of 18 – 30° which is characteristic of amorphous structures is observed.

2.3.4 Uses of RHA

The utilization of ashes obtained from rice husk (RH) was considered as early as prior 1970s for partially replacing the Ordinary Portland cement (OPC). OPC is costly and unaffordable to a large section of the world's population. Since OPC is typically the most expensive constituent of concrete, the replacement of a part of it with RHA offers improved concrete affordability, particularly in developing countries. Substantial research has been carried out on the use of amorphous silica in manufacturing of concrete. There are two areas directly related with building construction for which RHA is used viz., in the manufacture of low cost building blocks and in the production of high quality cement.

The use of reactive RHA as supplementary cementitious material may lead to reduction of the emissions of carbon dioxide caused by the cement production. It can also improve the mechanical properties and durability of concretes (Zhang and Malhotra, 1996; Salas, et al., 1986; Metha, 1977). Moreover, the replacement of cement by RHA has another environmental advantage: the carbon remaining in the ash, which could be released to the atmosphere during a long storage period, is trapped in the concrete.

Studies have been carried out all over the world, such as in Guyana, Kenya and Indonesia on the use of low cost building blocks (Tuts, 1994; Boateng and Skeete, 1990). A study in Kenya showed that replacing of 50% Portland cement with RHA was effective, and the resultant concrete cost was 25% less (Tuts, 1994). The use of RHA in some specific applications is described below.

Due to the insulating properties of RHA, it has been used in the manufacture of refractory bricks (Confidential Report, 1998). Refractory bricks are used in furnaces which are exposed to extreme temperatures, such as in blast furnaces used for producing molten iron and in the production of cement clinker.

Rice husk ashes have been used effectively in blended cement binders and cementitious concretes. Up to 40% of RHA was blended in cement to manufacture mortar with high strength and good resistance of chloride penetration (King, 2000). Similarly, normal concretes using RHA to replace partly for cement have gained substantial good properties, such as strength and durability (Joshi, 1995).

Portland cement produces an excess of lime. The addition of a pozzolan, such as RHA, combines with lime in the presence of water results a stable and more amorphous hydrate (calcium silicate). It is stronger, less permeable and more resistant to chemical attack (Owens, 1999).

Small amounts of admixtures are often added with cement which improves the properties of the cement. Admixtures are either naturally occurring compounds or chemicals produced in an industrial process. Most admixtures are pozzolans. A pozzolan is a powdered material, which when added to the cement in a concrete mix reacts with the lime, released by the hydration of the cement, to create compounds which improve the strength or other properties of the concrete (King, 2000; Lohita and Joshi, 1995). Pozzolans improve the strength because they are smaller than the cement particles, and can be packed in between the cement particles and provide a finer pore structure. RHA is an active pozzolan. The type of RHA suitable for pozzolanic activity is amorphous rather than crystalline.

Studies on RHA for using as a pozzolan have been carried out during the last three decades (Sugita, 1994; James and Subba, 1986; Metha, 1977; Pitt, 1976). Most of these studies concern with ashes produced by controlled burning conditions, at specified temperature, time of burning, heating rate, type of furnace, and oxidizing conditions. In such conditions, a white highly reactive pozzolan with non-crystalline silica, small carbon content, and high specific surface area is produced.

A wide variety of environmental circumstances such as reactive aggregate, high sulphate soils, freeze-thaw conditions, and exposure to salt water, de-icing chemicals, and acids are deleterious to concrete. Laboratory research and field experience have shown that careful use of pozzolans is useful in countering all of these problems.

Recently, a large amount of rice husk has been used as fuel to operate the boilers in modern rice milling factories. It is used to produce steam, either for drying and parboiling of the rice grains or for the production of electricity in cogeneration systems.

Research in the University of Arkansas has focused on the manufacture of insulation from RHA was effectively possible. The material produced is highly lightweight with very low density.

So far, RHA has not been utilized yet in the construction industry, except for some repairing works in the USA where it was used in a dry-mix shotcrete to repair the Bowman Dam in northern California's Sierra Nevada Mountains, with positive results (Talend, 1997). The reason for not utilizing this material probably due to lack of understanding of the RHA blended concrete characteristics. Many researchers have already published on the properties of the blended RHA concrete such as strength and durability.

RHA was used as adsorbent since the main components of RHA is silica and carbon (Boveri, 2002; Calace, et al., 2002; Nakbanpote, et al., 2000). The RHA has more than 95% by weight of silica with high porosity and large surface area. (Boveri, 2002; Nakbanpote, et al., 2000; Williams and Nugranad, 2000).

2.4 POZZOLANS

Pozzolans comprised a part of the cement of ancient structures in Egypt, Greece and Rome. There is also evidence to suggest that crushed pottery was used during the early Minoan period (3000 - 1500 B.C.) to make lime mortars (Spence and Cook, 1983). Ancient engineers found that the use of fine powders of natural material or ground pottery shards could be used to make cement with very high quality. Recent examinations have shown that cement found in many parts of the great Pyramids is about 4500 years old and is still in good condition. This material has cracked and degraded in only about 50 years (Davidovits and Morris, 1988).

A concrete used to make an underground water storage tank from the ancient city of Camiros on the island of Rhodes was analyzed and found to contain cement consisting of volcanic earth and lime. This cement in the concrete, manufactured around 400 – 500 B.C., comprised about 20% of the mass of the concrete. In ancient concrete it appears that much attention was paid to the aggregate gradation and the ancient concrete that was tested had a gradation very close to the ideal that recognize for modern concretes (Efstathiadis, 1978).

Other evidence (Davidovits, 1987) confirms that pozzolans were used at the time of the Greeks, because X-ray diffraction shows the presence of a zeolitic material (analcime) which ranges from 10 to 40% by weight in the lime:mortars; this zeolite is often found in tuffs and other pozzolanic materials of Europe.

The term pozzolan came from USA simplification of pozzolana which evolved from the location Pozzuoli, Italy where the Romans found a reactive silica-based material of volcanic origin which they called pulvis puteolanus (Spence and Cook, 1983; Davis, 1950). Now a day both the terms pozzolan and pozzolana are used.

The Romans used the red or purple tuff found near Naples (Pozzuoli) later it was finely ground and mixed with lime or hydraulic lime and sand. If pozzolanic earth was not available, powdered tiles or pottery was used (Anon, 1988; Miles, 1974).

The 42 m span dome in the Pantheon, Rome, is one of several examples of Roman structures, many including pozzolans, that has survived nearly 2000 years and is made of lime-pozzolan concrete (Spence, 1980).

Early applications of pozzolan in ancient civilizations and contemporary uses in Europe, Asia and America have shown pozzolans to be useful materials. There may be more countries which contain pozzolanic materials and detailed scientific evaluations have not done yet. These countries may not have started the exploitation for various reasons or may not have brought the existence of such materials to the attention of the technical community.

The most common classification system used today is one which the primary division of pozzolans is divided into two classes: artificial and natural. Artificial pozzolans include materials such as fly ash, blast furnace slag, surkhi, siliceous and opaline shales, rice husk ash, burnt banana leaves, burnt sugar cane stalks and bauxite waste (Grane, 1980; Lea, 1970). If calcination was not required then they would be a natural pozzolan. Among the natural pozzolans are tuff, volcanic ashes, trass, rhyolitic pumicite, diatomite, gaize (Grane, 1980). The basic classification into natural and artificial has no real engineering or practical uses. With respect to economy and performance it does not matter whether the source is natural or not.

According to Mehta and Pitt (1976) rice hulls and rice straw are similar in composition and again do not easily lie in the natural or artificial category. These materials consist of 40% - 45% cellulose, 25% - 30% lignin, 15% - 20% silica and 8% - 15% moisture. When ignited at the appropriate temperature an ash of almost pure silica is produced.

The earliest test to estimate pozzolanic activity was the Lime Absorption Test proposed by Vicat in 1837. In this test 1 gm sample is added to 75ml of saturated limewater and shaken. At various ages 25m1 of solution is extracted and titration is performed to determine the lime absorption. Another early test by Rivot (1862) estimates reactivity by determining the residue of a pozzolan after heating with citric acid and then treating overnight with 10% KOH solution (Moran and Gilliland, 1950). Allen and Spence (1983) suggested that test method consists of compressive strength is sufficient to asses the reactivity of a pozzolan instead of chemical tests. Hammond (1983) notes a more simplified classification according to strength (activity) of mortars after curing for 8 days at 50°C. This is shown by the following Table 2.2.

Table 2.2: Classification of mortar according to strength

Indian Standerd		ASTM Standerd	
Activity	Strength (MPa)	Activity	Strength (MPa)
very inactive	<1.4	poor or inactive	< 2.6
inactive	1.4-2.8	intermediate	2.6-5.6
poor activity	2.8-4.1	active	> 7
intermediate	4.1-5.5		
active	5.5-6.9		
very active	>6.9		

The official definition of a pozzolan can be found in ASTM C618-89: pozzolans are "siliceous or siliceous and aluminous materials which in themselves contain little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties". However, the definition is lacking that it does not encompass all pozzolanic materials that can serve a useful purpose in building construction worldwide. The American Standards are specifically written for American construction practices and not for construction practices in developing countries. ASTM C618-89 Requirements for a Type N Pozzolan for Use as a Mineral Admixture in Portland cement concrete. The required specifications of Pozzolan are presented in Table 2.3.

The reactivity, and thus usefulness, of many inadequate natural pozzolans can be improved by simple grinding process. It is usually necessary to grind a natural pozzolan in order to obtain sufficient reactivity (U.S. Dept. of Interior, 1975).

Many pozzolans require grinding to increase fineness before use. If it is used with cement the pozzolan is usually interground with cement rather than blended - this type of pozzolan:OPC cement was used for the L.A. aqueduct in USA in 1910 (the pozzolan was a tuff). Recently, however, there has been more of a trend to add the pozzolan at the mixer because it allows better control (Davis, 1950).

According to Campbell, et al. (1982) to produce adequate pozzolanicity, many pozzolans must be ground to a Blaine of 5000 cm^2/g. If grinding is necessary, a careful series of pilot tests should be performed to determine how much grinding is required to satisfy sufficient fineness. Some research has surprisingly found that fineness has a more pronounced effect on strength at later ages (365 days) than at early ages (Hanna and Afify, 1976).

Table 2.3: Requirement for Pozzolan

Description	Values
SiO_2+Al_2O_3+Fe_2O_3, Minimum, %	70.0
SO_3, Maximum, %	4.0
Moisture content maximum, %	3.0
Loss on Ignition Maximum, %	10
Amount retained, wet-sieve on 45µm sieve, maximum, %	34
Pozzolanic activity index, Portland cement, at 28 days, minimum % of control	75
Pozzolanic activity index with lime, minimum MPa	5.50
Water requirement, maximum, % of control	115
Autoclave expansion or contraction, maximum, %	0.8
Specific gravity, maximum variation from average, %	5.0
Percentage retained on 45µm sieve, maximum variation, percentage points from average	5.0
OPTIONAL REQUIREMENTS	
Increase of drying shrinkage of mortar bars at 28 days, maximum %	0.03
Reduction of mortar expansion at 14 days in alkali expansion test, minimum %	75
Mortar expansion at 14 days in alkali expansion test maximum %	0.020

Rice husks are not pozzolanic unless they are fired. The firing temperature for rice husks is extremely critical in order to obtain a satisfactory material. The chemical composition of rice husks is similar to many other organic fibres and consists of: (a) cellulose $C_5H_{10}O_5$, a polymer of glucose; (b) lignin $C_7H_{10}O_3$, a polymer of phenol;

(c) hemicellulose $C_5H_8O_4$, a polymer of xylose; and (d) silica. The lignin and hemicellulose compositions may vary somewhat, depending on the species, but the ash composition (SiO_2) is generally 15 to 18% of the husk (Hwang and Wu, 1989). It was found that if the ash is fired at 700°C the colour changes from greyish to pinkish, with some spherical particles detected. X-ray analysis shows a definite tendency for the formation of crystalline material above 600°C-700°C firing temperature (Spence and Cook, 1983). This crystalline material is alpha-quartz and wollastonite between 700°C -800°C, and is tridymite, wollastonite, beta-Ca_3SiO_3, and beta-quartz at firing temperatures between 900°C-1000°C. After firing the ash need to be ground to a fineness of about 10000 cm^2/g (Spence and Cook, 1983). Cook and Suwanvitaya (1981), showed that rice-husk ash and rice-straw ash contained about 80% amorphous silica if fired at the appropriate temperature around 600°C; the surface area of this highly porous material was about 152 m^2/g. In another study, it was found that the optimum firing temperature for rice husk ash is in the region of 500-750°C (Cook, 1980). Rice husk burned at too low temperatures may have a substantial proportion of unburned carbon; it has been found that carbon content has a significant influence on the initial and final setting times of RHA but not on strength (Appropriate Technology International, 1983).

2.5 PROPERTIES OF CEMENTITIOUS MATERIALS

2.5.1 Workability

Usually typical concrete mixtures contain too much mixing water because of two reasons. Firstly, the water requirement and workability are significantly influenced by particle size distribution, particle packing effect, and voids present in the solid system. Typical concrete mixtures do not have an optimum particle size distribution, and this accounts for the undesirably high water requirement to achieve certain workability. Secondly, to plasticize a cement paste for achieving an acceptable consistency, much larger amounts of water than necessary for the hydration of cement have to be used because Portland cement particles, due to the presence of electric charge on the surface, tend to form flocks that trap volumes of the mixing water (Mehta, 1999; Mehta, 1997).

Studies by Jiang and Malhotra (2000) and Owen (1979) indicated that with high volume fly ash concrete mixtures, up to 20% reduction in water requirements can be achieved. However, there is the possibility of water reduction higher than 20% in the presence of RHA. This is because of fine particles of rice husk ash get absorbed on the oppositely charged surfaces of cement particles and prevent them from flocculation. The cement particles are thus effectively dispersed and trap large amount of water meaning that the system will have a reduced water requirement to achieve a given consistency.

The particle packing effect is also responsible for the reduced water demand in plasticizing the system (Mehta, 2004). Laskar et al. (2007) examined the effects of RHA on the rheological behaviour of high performance concrete. In their study RHA was used to replace cement on mass basis at the rate of 5%, 10%, 15% and 20%. Based on their test results, plastic viscosity increases tremendously with the increase in replacement level of RHA. RHA particles have the highest surface area and fineness and lower reaction ability than cement (Shetty, 2004). RHA particles fill into the spaces made by larger cement particle, decrease frictional forces of RHA-ordinary Portland cement (OPC) system and improve packing ability thereby reducing yield stress. The steep increase in plastic viscosity with the replacement levels suggests that fineness and shape of RHA play critical role. The more the fineness the more is the number of contacts among the particles and hence the more is the resistance to flow. In addition, any deviation from a spherical shape implies an increase in plastic viscosity for the same phase volume (Nedhi, et al., 1998).

A simple and often used flow table test (ASTM C 230) was selected as the basic test for the workability. Ikpong and Okpala (1992) studied the variation in workability of concrete with incorporation of RHA, concluded that, to attain the same level of workability, the mixes having rice husk ash required higher water contents than those containing only ordinary Portland cement as the binder. Ismail and Waliuddin (1996) reported the same of Ikpong and Okpalla (1992) and also concluded that the fineness of RHA did not have significant effect on workability. Bui et al. (2005) investigated the effect of RHA in concrete mix in presence of super-plasticizer and concluded that the workability of concrete is reduced in presence of RHA.

2.5.2 Setting Times

Initial and final setting time tests were shown to yield different results on plain cement paste and pastes having rice husk ash (Dakroury and Gasser, 2008). The studies showed that RHA increases the setting time of pastes (Ganesan, et al., 2008; Bhanumathidas et al., 2004; Cook, 1986). Just like other hydraulic cement, the reactivity of rice husk ash cement depends very much upon the specific surface area or particle size. The rice husk ash cement with finer particles exhibits superior setting time behaviour. Research has shown the increase in the initial setting time by raising the RHA level in the cement mixture over those of plain cement paste. Dakroury and Gasser (2008) mentioned that this may be due to the slower pace of heat induced evaporation of water from the cement–RHA.

Singh et al. (2002) examined the effect on setting time with RHA-blended Portland cement and reported that the both initial and final setting time was enhanced. Jaturapitakkul and Roongreung (2003) studied the normal consistency and setting time of cement materials with RHA and observed that the normal consistency of OPC was 23.9% and the consistency was higher when RHA. The consistency was 43.7% by mixing Calcium Carbide Residue (CCR) and increased to 62.0% depending on the percentage variation of RHA and CCR. The water requirement to maintain the same normal consistency increased with the increase of RHA content in the paste.

2.5.3 Strength

Cement was replaced by RHA in various percentages by Ikpong and Okpala (1992) and observed that at age of 90 days the compressive strength increased and the strength continued to increase with age for each of the mixes having RHA. The controlled concrete (0% RHA) attained a higher strength than the OPC/ RHA mixes at all ages. The compressive strength of OPC/RHA samples was compared with controlled samples.

Zhang and Malhotra (1996) investigated the effect of RHA addition in concrete as partial replacement of cement on compressive strength. The study observed that at 28 days, the RHA concrete had a compressive strength of 38.6 MPa compared with 36.4 MPa for the control concrete. At ages of 180 days, the compressive strength of

RHA concrete was found 48.3 MPa and the control one showed 44.2 MPa. At age 400 days the control concrete exhibited higher strength than the RHA concrete. Again the RHA concrete exhibited higher strength than control one at an age of 730 days.

Ismail and Waliuddin (1996) studied the effect of RHA on the compressive strength of High Strength Concrete up to 150 days and reported that at all ages (3, 7, 28 and 150 days) the control concrete exhibited slight higher strength than the RHA concrete at different levels of cement replacement. The test result showed that high strength concrete is possible to get economically using RHA and the optimum replacement of cement by RHA was around 10% to 20% with finely ground RHA. According to Ismail and Waliuddin (1996), the lower strength of concrete made with partially replacement of cement by RHA was because of higher w/c ratio in concrete. Wada et al. (1999) demonstrated that RHA mortar and concrete exhibited higher compressive strength than the control mortar and concrete. Zhang and Malhotra (1996) showed that the splitting tensile strength, flexural strength and modulus of elasticity of RHA concrete are higher or equal of control concrete and the result is shown in Table 2.4.

Table 2.4: Mechanical properties of concrete

Mix	RHA	W/cm ratio	Splitting Tensile Strength (MPa)	Flexural Strength (MPa)	Modulus of Elasticity (GPa)
1	0	0.4	2.7	6.3	29.6
2	10	0.4	3.5	6.8	29.6

Source: Zhang and Malhotra, 1996

Nehdi et al. (2003) made a comparative study on the compressive strength of concrete with RHA. The RHA was burnet at different temperatures (750^0C and 830^0C) with external jet of air. Results showed that in all cases the RHA concrete exhibited better result than control. Among the concrete samples higher result was observed when air jet was used for RHA production.

Sarkar (2006) examined the mechanical properties of heavy weight concrete in presence of RHA as partial replacement of cement. The RHA had a specific surface area of 5.6×10^6 mm^2/gm and the unit weight was 2.06×10^3 kg/m^3. The chemical composition of used RHA was 87.0% SiO_2, 1.75% Al_2O_3, 2.5% Fe_2O_3, 2.5% CaO, 2.3% MgO and 2.5% K_2O. Test was performed on 28 days ages and indicated that generally all the mechanical properties were increased with the increasing in RHA content up to 15%.

Joseph et al. (1989) investigated the compressive strengths variations of OPC and RHA mortars. At 35 % replacement, the RHA cement had gained early strength and, due to its higher percentage of silica, the RHA cement also had a higher compressive strength at later dates. Other studies also showed that at 28 days RHA cement had significantly higher compressive strength compared with OPC. Lucero et al. (1994) reported that highest compressive strength was obtained when 35% of Portland cement is replaced with RHA and the strength can be considerably reduced with 50% replacement of OPC.

Saraswathy and Song (2007) reported that when cement partially replaced by RHA then the compressive strength, splitting tensile and bond strength of concrete were increased. This research summarized that at 28 days strength of all concrete samples having different replacement levels of cement by RHA addition (5, 10, 15, 20, 25 and 30%) exhibited higher compressive strength and inclusion of RHA up to 25% did not affect the splitting tensile strength of concrete. All the RHA concrete showed higher bond strength values compared with the control one.

Gastaldini et al. (2007) considered the effect of chemical activators (K_2SO_4, Na2SO4, Na_2SiO_3) on the compressive strength of 20% RHA mixed concrete with different w/c and mixing ratios. Compressive strength was measured at different ages (7, 28 and 91 days) and concluded that at 28 and 91 days the RHA concrete showed higher strength than concrete with control sample for every water binder ratios (0.35, 0.50, and 0.65). The concrete mixtures having RHA and activated with 1% of K_2SO_4 showed the highest strength when compared without the activator.

2.5.4 Porosity

Sarawathy and Song (2007) investigated the effect of RHA addition with OPC cement on the porosity and water absorption of the concrete. Cement was replaced with 5%, 10%, 15%, 20%, 25%, and 30% RHA, porosity and water absorption test were carried out as per ASTM C642-97. From the test it was found that the porosity values decreased with the increment in RHA content because small particles of RHA improve the density of the blended cement. The coefficient of water absorption for rice husk ash replaced concrete at every replacement levels was found to be less when compared to control specimen.

2.5.5 Permeability

For reinforced concrete structures, one of the main forms of environmental attack is chloride ingress which leads to corrosion of the reinforcing steel. The strength, serviceability and aesthetics of the structures subsequently reduced due to the corrosion. This may lead to early repair or premature replacement of the structure. A general method of preventing such corrosion is to prevent chlorides from penetrating the structure by using comparatively impenetrable concrete.

The entrance rate of chlorides into concrete largely depends on the pore structure of the concrete. The penetrability of concrete is clearly related to the pore structure of the cement paste matrix. This will be influenced by the water-cement ratio of the concrete, the inclusion of supplementary cementing materials which serve to subdivide the pore structure and the degree of hydration of the concrete (McGrath and Hooton, 1996).

The rate of chloride penetration into concrete is affected by the chloride binding capacity of the concrete. A portion of the chloride ions reacts with the concrete matrix becoming either chemically or physically bound, and this binding reduces the rate of diffusion. However, if the diffusion coefficient is measured after steady-state conditions have been reached, then all the binding can be presumed to have taken place and this effect will not then be observed. If a steady state condition has not been reached, then all the binding will not be occurred and this will affect the results. The chloride binding capacity is controlled by the cementing materials used in the concrete. The inclusion of supplementary cementing materials affects binding, though the exact influence is unclear (Thomas, et al., 1995; Sandberg and Larrson, 1993; Rasheeduzafar, et al., 1992; Byfors, 1986). Also, the C_3A content of the cement influences its binding capacity (Hansson and Sorenson, 1990; Midgely and Illston, 1984; Holden, et al., 1983).

The chloride ion penetration resistance was examined by Zhang and Malhotra (1996) on concrete made with 10% RHA and 10% Silica Fume (SF). This test was conducted according to ASTM C1202. It was observed from the result that the use of RHA and SF have significantly reduced the chloride ion penetration in concrete and that is less than 1000 coulombs. According to ASTM C1202 when charge passed through concrete is less than 1000 coulombs, then the concrete has very high confrontation to chloride ion penetration.

A comparative study on rapid chloride permeability was investigated by Nehdi et al. (2003) on concrete made with different quality of RHA collected from Egypt and USA. The resistance to chloride penetration was assessed according to AASHTO T277-83 test method up to the age of 100 days. The result showed that the inclusion of RHA significantly reduced the permeability of concrete and it was 89% of the control concrete samples for 20% addition of RHA.

Rodriguez (2006) studied on the air permeability of concrete with RHA and the RHA was collected from two sources; a residual RHA from rice paddy milling industry in Uruguay and another produced in USA under controlled incineration process. Cement was replaced by RHA (10% and 20%) and water to binder ratio was 0.32 and 0.50. Air permeability was determined with "Torrent Permeability Tester" method (Torrent, 1999; Torrent and Frenzer, 1995) at the age of 28 days. After the test it was summarized that the permeability of RHA concrete with Uganda RHA was higher than the concrete prepared with RHA from USA. The permeability was also increased for both type of RHA concrete with the increase in water cement ratio. The percentage of reactive silica contained in the RHA collected from USA was 98.5% and that in Uganda RHA was 39.55%.

Saraswathy and Song (2007) looked into the effect of partial replacement of cement with 0%, 10%, 15%, 20%, 25% and 30% RHA on permeability of concrete according to ASTM C1202-94. It was found that the chloride charge passed through the concrete in coulombs were 1116, 1108, 653, 309, 265, 213 and 273 for concrete made with 0, 5, 10, 15, 20, 25 and 30% of cement replaced by RHA respectively. Charge passed through concrete is drastically reduced for the use of rice husk ash in concrete.

Gastaldini et al. (2007) studied the effect of chemical activators on the concrete having 20% RHA as cement replacing materials and concluded that at 28 and 91 days ages concrete exhibited a significant reduction in chloride ion penetration in presence of RHA with K_2SO_4. The other activators (Na_2SO_4 and Na_2SiO_3) also exhibited the same results for chloride ion penetration. The chloride ion penetration was measured according to ASTM C1202 (2000). Gjorv, et al. (1998) reported that RHA had used in the manufacture of concrete for the marine environment and replacing 10% Portland cement with RHA can improve resistance to chloride penetration.

2.5.6 Sorptivity

The sorptivity of concrete is a quantity that measures the unsaturated flow of fluids into the concrete (Hall, 1989). Sorptivity is a measure of the capillary forces exerted by the pore structure causing fluids to be drawn into the body of the material. While theoretically possible to consider the flow in any geometry, it is mathematically too complex to be of any practical use except where there are one dimensional flow conditions.

For one dimensional flow, it can be stated that as (Hall, 1989):

$$i = St^{1/2} \tag{2.3}$$

Where,

i is the cumulative water absorption per unit area of inflow surface,

S is the sorptivity and

t is the elapsed time.

In a laboratory condition where the concrete/mortar sample can be dried consistently and the flow conditions can be well defined, it is relatively easy to get a good fit line using least squares regression when plotting i vs. the square root of time.

Determining the sorptivity of a sample in the laboratory is a simple technique illustrated in Figure 2.4. According to the ASTM draft standard the sample is preconditioned to a certain moisture level. The sides of the concrete sample should be sealed to prevent the moisture movement. The gain in mass per unit area over the density of water is plotted against the square root of the elapsed time. The slope of the line of best fit of these points (ignoring the origin) is reported as the sorptivity.

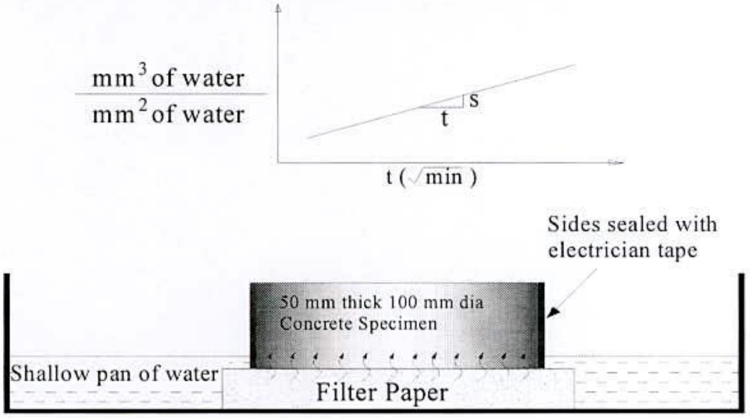


Figure 2.4: Laboratory Sorptivity technique

While sorptivity test avoid many of the difficulties of the RCPT and is able to evaluate concretes containing conductive materials, it does have its limitations. Mainly, it is only able to evaluate the surface of the concrete. The sorptivity of concrete is affected only by the surface conditions, at least in the time frame that is typically considered. Therefore, a sorptivity test will not give directly any information on the bulk properties of the concrete. Another difficulty is the dependence of sorptivity on the moisture content of the sample. This is not a problem in a laboratory situation, but for a field test the variable moisture content could drastically alter the results (Hall, 1989).

CHAPTER 3

MATERIALS AND METHODS

3.1 GENERAL

The research program comprised several experimental investigations. The particulars of production of suitable Rice Husk Ash from uncontrolled combustion process and different tests carried out on mortar specimens are discussed in this chapter. In the present study the effect of Rice Husk Ash on the mechanical properties and durability of mortar was studied in long term period, where the RHA was used as cement replacing material. Mortar mixes contained 0%, 5%, 10%, 15%, 20%, 25% and 30% Rice Husk Ash as a replacement of cement. Two types of fine aggregate viz., standard graded sand (ASTM C778) and locally available river bed sand suitable for concrete work having F.M. of 2.73 were used for the preparation of mortar. Cubical specimen of 5 cm size was prepared for compressive strength, salt crystallization, resistance to sulphate attack and fire performance test. Cylindrical specimen of 10 cm diameter and 20 cm height was fabricated for Sorptivity and permeability experiment.

3.2 MATERIALS

Same sets of materials have been used throughout the casting of samples for different proportion of RHA. Relevant tests in accordance with the ASTM Standard were carried out to determine the physical properties of the materials used in the work. The particulars of the materials along with their properties have been presented in the succeeding sections.

3.2.1 Cement

Cement is a vital element in mortar, the function of cement is not only to bind the sand but also to fill up the voids in between sand and any coarse grained particles to form a compact mass. Cement is the active portion of binding medium and is the only scientifically controlled ingredient in mortar. Ordinary Portland Cement (OPC) Type 1 was used throughout the tests. The physical properties and chemical composition of the cement are given in Table 3.1.

The particle size distribution of cement used in this study is shown in Figure 3.1 and the texture of cement obtained from SEM analysis is also shown in Figure 3.2. The cement particle is angular in shape and of different sizes.

Table 3.1: Chemical compositions and physical properties of ordinary Portland cement

Oxide Composition (%)		Physical Properties		
Oxide	Determined as	Description	Determined as	ASTM
SiO_2	21.62	Specific Gravity	3.07	About 3.15
Al_2O_3	5.24	Blaine Fineness (cm^2/gm)	3264	2800
Fe_2O_3	2.60	Setting Time:		
CaO	63.61	Initial (min)	78	≥45
MgO	2.30	Final (min)	309	≤375
K_2O	1.03			
Na_2O	0.15			
SO_3	2.78			

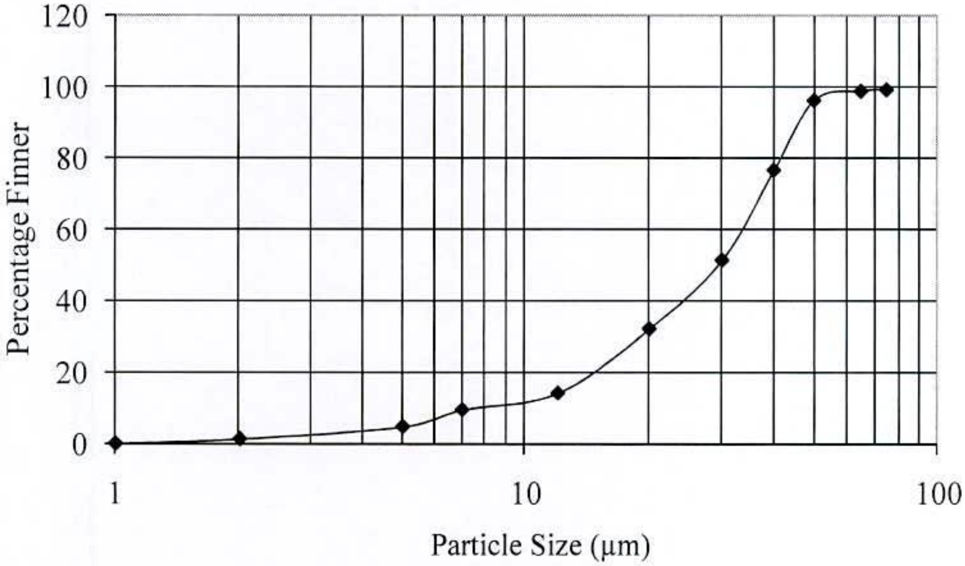


Figure 3.1: Particle size distribution of Ordinary Portland Cement

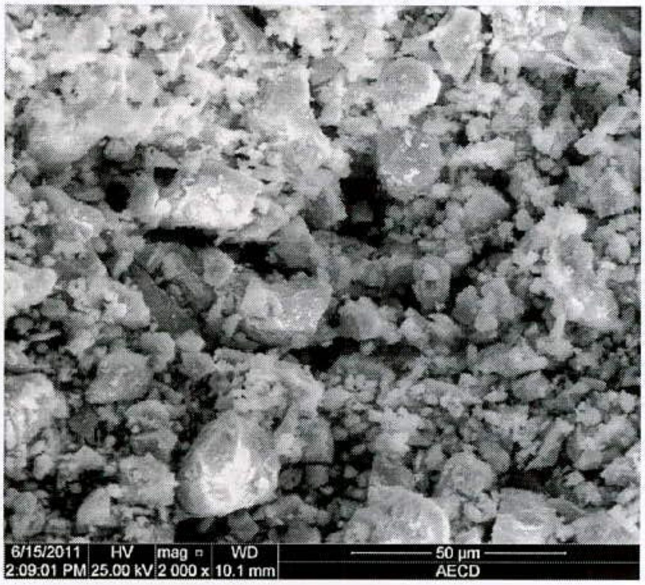


Figure 3.2: Texture of Ordinary Portland Cement

3.2.2 Fine Aggregate

The sand was characterized by means of various physical properties. In addition, the gradation of sand was observed by conducting the sieve analysis. Fine aggregate is defined as the one passing through 4.75 mm sieve. The fine aggregate is often termed as a sand size aggregate. Locally available river bed sand was used in the experimental program as fine aggregate. The physical properties of sand indicated that it is suitable to prepare mortar.

In this work two types of sand were used and that are

-ASTM Graded Sand

- Available river sand with F.M. 2.73

The properties of ASTM graded sand and available river sand are shown in Table 3.2.

Table 3.2 Properties of fine aggregate

Properties	Determined as	
	ASTM Graded Sand	Available Sand
Apparent Specific Gravity	2.61	2.58
Dry Specific Gravity	2.55	2.57
Absorption (%)	1.99	2.17
pH	7.2	7.2

The nominal maximum size and fineness modulus of concrete sand were 4.75 mm and 2.73 respectively. The fineness modulus indicated that the selected sand was appropriate for producing mortar for concrete mixtures. The fineness modulus of sand for use in concrete generally varies in the range of 2.4 to 3.2 (ACI 211.4R-93, 2004). Standard values for ASTM graded sand and the sand used in this study as ASTM graded sand are given in Table 3.3. Sieve analysis of available river sand with FM of 2.73 is given in Table 3.4.

Table 3.3: ASTM graded sand

Sieve No.	ASTM Graded Sand	
	Determined (% Finer)	Standard (% Finer)
No 16	100	100
No 20	100	100
No 30	97	96-100
No 40	71	65-75
No 50	25	20-30
No 100	3	0-4

Table 3.4: Sieve analysis of fine aggregate (locally available sand)

Sieve No.	Wt. Retained, (gm)	Cum. Wt. Retained,(gm)	Cum. Wt. Retained (%)	% Finer
No. 4 (4.75 mm)	0.00	0.00	0.00	100.00
No. 8 (2.36 mm)	22.50	22.50	4.50	95.50
No. 16 (1.18 mm)	85.50	108.00	21.60	78.40
No. 30 (0.60 mm)	179.00	287.00	57.40	42.60
No. 50 (0.30 mm)	165.00	452.00	90.40	9.60
No. 100 (0.15 mm)	41.50	493.50	98.70	1.30

Total cumulative % weight retained = 272.6 gm

Therefore FM of Sand = 2.73

The gradation of the selected sand was matched with the ASTM C33 gradation. Generally the ASTM graded sand is collected from mine of Ottawa, Illinois area in

USA. These are naturally rounded silica sands of nearly pure quartz. In this work river sand was collected and washed thoroughly and then sieved. After sieving the different sand sizes were mixed according to ASTM standard.

3.2.3 Water

Generally, potable water is acceptable to use in concrete/mortar preparation. Usually, water from lakes and natural streams that have marine life is suitable. Water containing sewage, mine water, or wastes from industrial plants should not be used without testing the tolerable level. Water from such sources should be avoided since the quality of the water could change due to intermittent discharge of harmful wastes into the stream. Water should be free from objectionable quantities of oil, acid, alkali, salt, organic matter, or other deleterious materials. Water which contains more than 0.25 % total solids by weight should not be used in cementitious work. Some properties of the used water are shown in Table 3.5.

Table 3.5: Properties of used tap water

Properties	Measured	Maximum Value
Total Solids (ppm)	7200	50000
Chlorides, as Cl- (ppm)	650	1000
Sulphates, as SO_4 (ppm)	1578	3000
pH	7.4	6.5-8.5

3.2.4 Rice Husk Ash

3.2.4.1 Rice husk collection

The rice husk used in this study was collected in November and December which was the peak time for paddy harvesting and at this time the major two species of paddy were available. The collected rice husk contains 7% to 11% of moisture. The collected husk was kept in sunny place for two days prior burning to remove the moisture from it and this process confirm the field burning condition of rural Bangladesh. After drying, the moisture content in the husk was observed to be 0.5% to 1.84%.

3.2.4.2 Rice husk ash production

Rice Husk Ash obtained from the uncontrolled incineration process was used as cement replacing materials in this study. Rice husk Ash samples were produced from three different types of incineration system. These were subjected to various tests to analyze the Blaine surface area, state (amorphous/crystaline), loss of ignition and chemical composition. A good quality of ash was chosen as cement replacing material after analyzing the ashes. Subsequently, these ashes were used for casting the specimen. There are mainly three types of burning process as follows:

(i) Heap Burning
(ii) Conventional Burning System
(iii) Laboratory Burning System

(i) Heap burning system

In this system, huge amount of Rice Husk were stored in a place and burnt with the help of rice husk briquette. There were no controlling systems present in this burning process. The heap was 2 m × 2 m and 0.5 m in height. Fired rice husk briquettes were placed in different point of the heap. The fired briquette was 150 mm long and 50 mm in dia. Schematic view of heap burning process is shown in Figure 3.3.

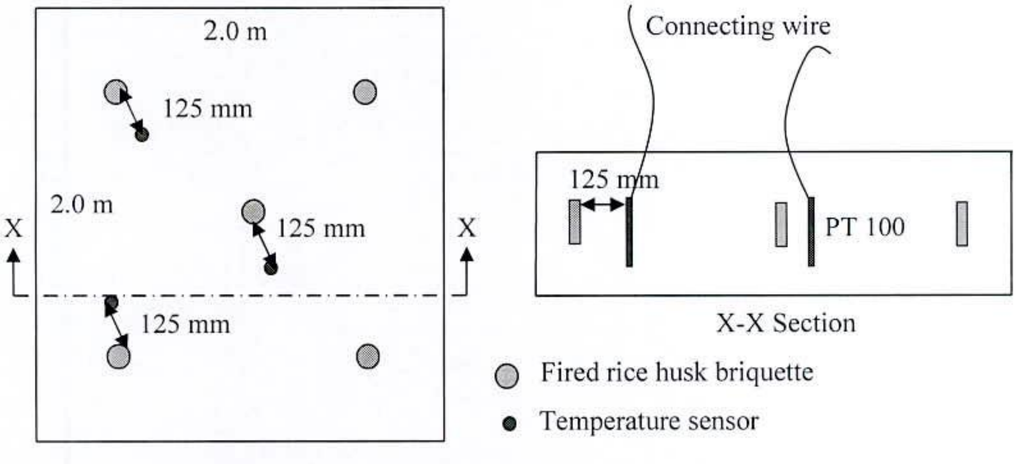


Figure 3.3: Heap burning system in laboratory

The burning of rice husk was allowed to start from the middle of the heap. Burning occurred from the fired husk briquette in all direction. It took almost four days for complete burning and simultaneous cooling of the sample. Temperature probes were placed at different locations on the heap to obtain the actual temperatures in respect to time. All the temperature sensors were placed at 125 mm away from the fired briquette and collected the temperature history of the husk heap as shown in Figure 3.3. The ash sample was collected and sieved through sieve No. 200 after grinding and denoted as RHA 1.

(ii) Conventional burning system

The parboiling system consists of mainly two parts, one of which is the steam generation unit (steam vessel and furnace) and other part is steaming bin for parboiling paddy. Steaming bin is connected with the steam generator with a steam pipe (Figure 3.4). This type of rice parboiling systems is mostly available in Bangladesh. In practical field, a part of the combustion chamber is situated below the ground level. There is opening in the side wall of combustion chamber for entry of air.

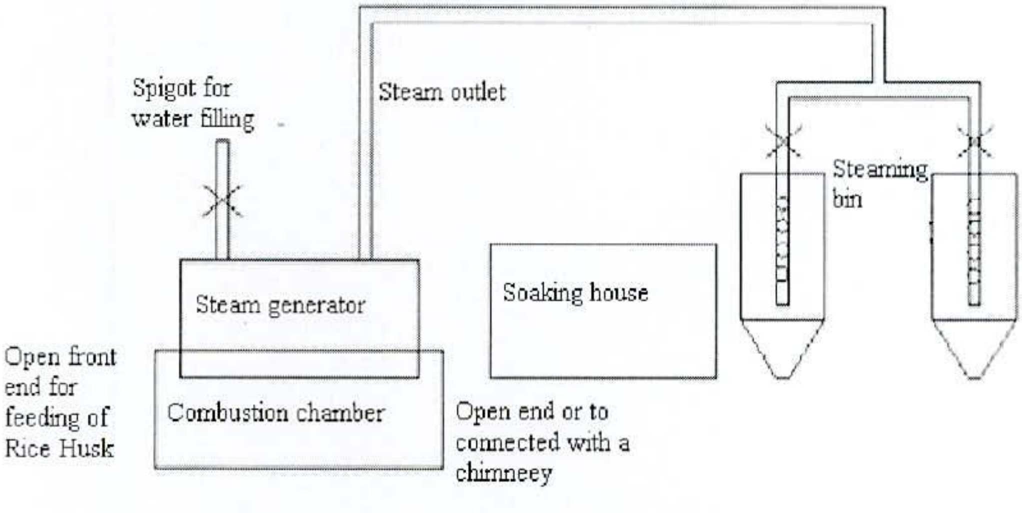


Figure 3.4: Schematic diagram of a conventional rice parboiling system

Rice husk was fired in the combustion chamber for the parboiling process of rice and finally ash produced by burning of rice husk is known as rice husk ash. The ash samples were collected from different locations of Khulna, Rajshahi and Dinajpur districts of Bangladesh. The colour of collected ash was light blackish grey. The collected ashes was kept in oven at 100°C for 6 hours and then ground in a laboratory ball mill for different durations of time. Subsequently the ash was sieved through No. 200 Sieve. The ash (RHA 2) passing through the sieve was collected for further laboratory investigations.

(iii) Laboratory Burning System

The rice husk ash produced in laboratory incineration system is designated as RHA 3. A rectangular enclosure of 2.05 m long and 0.9 m wide was divided into ignition and ash accumulation chamber by a steel wire mesh of 5 mm square opening. The ignition chamber was 0.65 m wide and 0.6 m deep and that of the accumulation chamber was 0.4 m and 0.4 m respectively. The wall thickness of the bottom portion was 0.375 m and that of the upper portion was 0.25 m. There were numbers of small opening (75 mm × 75 mm) in this wall. The detailed of this chamber is shown in Figure 3.5. The produced ash is deposited at the accumulation chamber and it was kept for long time (3, 6, 12, 24, 36, 48 and 60 hrs.) without any disturbance. At first, some small pieces of fired rice husk briquette were placed over the wire mesh and dried rice husk was continuously thrown over it. This throwing system was same as the rice parboiling industry in Bangladesh. The ignition system was developed within 20 to 30 minutes. In this laboratory ignition system the rice husk feeding process was slow in comparison to the existing system of Bangladesh.

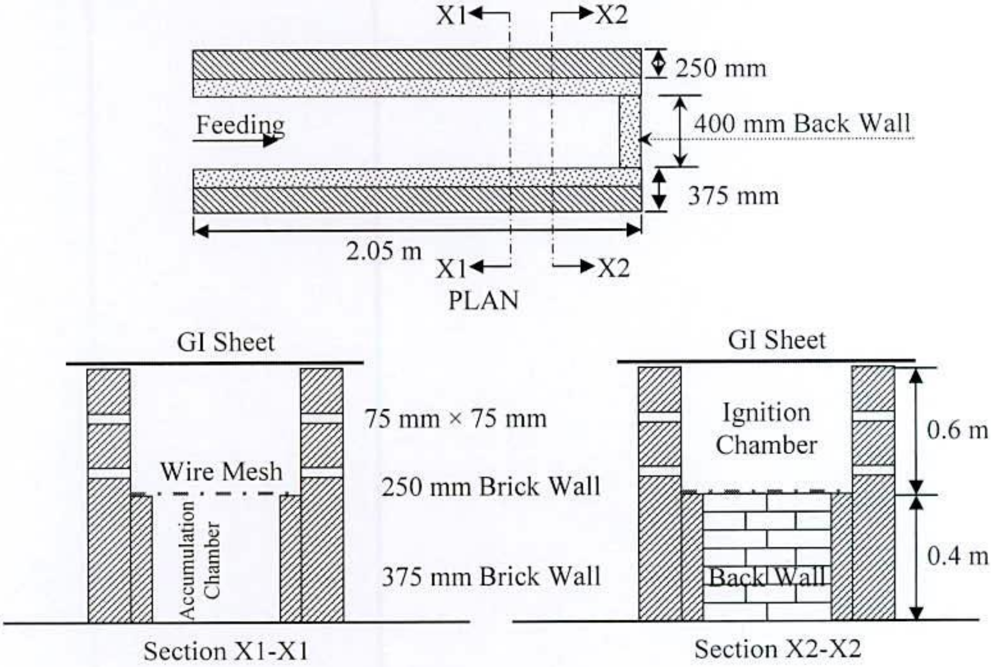


Figure 3.5: Diagram of laboratory burning system

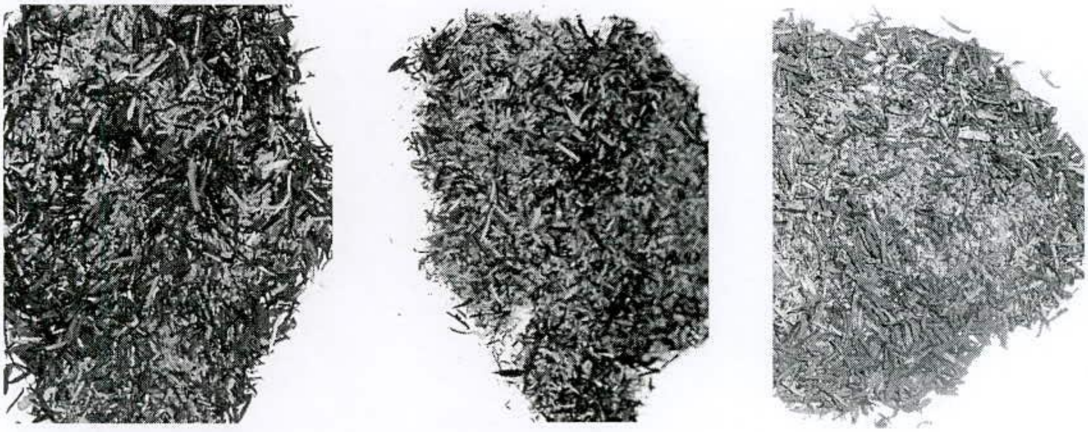
After some times of the firing, the fired husk stored in the accumulation chamber through the mesh. The rice husk size was shrinking after the firing. The top part of the kiln was closed by a steel sheet and the opposite side of the feeding of the kiln was partially closed to confirm the field condition. Before starting the firing operation, a series of thermal sensor of pt-100 type was placed at ignition and accumulation chamber. Average temperatures of ignition and accumulation chamber were termed as firing and cooling temperature. Temperature readings were continuously collected at regular interval.

3.2.4.3 Ash collection

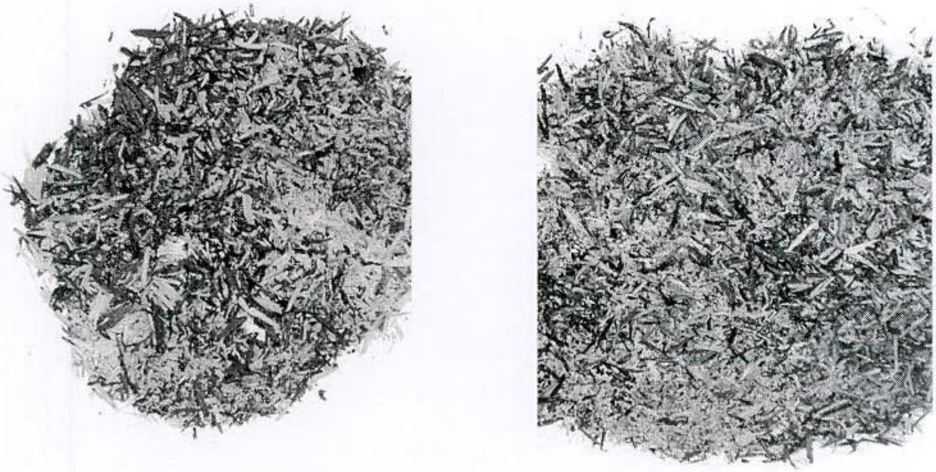
The RHA 1 produced in the heap burning system was collected when cooled down near by the ambient temperature. It was found that the top and bottom layer of the ash was blackish in colour with partial burning and the fully burnt ash in middle part was greyish in colour. The ash was collected from middle part removing one inch blackish top portion for this research work.

Rice Husk Ash (RHA 2) produced in conventional burning system was thrown to the open space from kiln without maintaining any specific duration. The ash sample was collected after cooling to the ambient temperature. Colour of this ash was greyish with some partially fired husk. It was observed that sometimes water is sprayed over the dumped ash. In this case the colour of the ash was black which was not collected for this study.

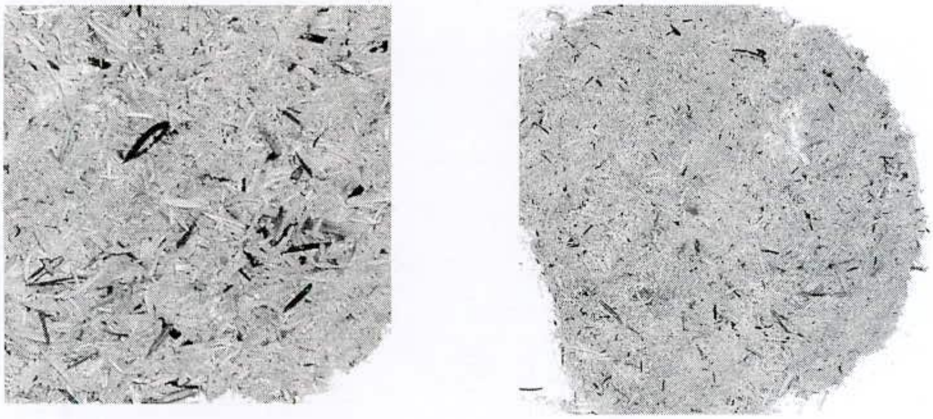
The laboratory burning system is more or less similar to the conventional burning system. The difference is that, after firing of the rice husk it was stored in an accumulation chamber and allowed to cool down without any disturbance. Openings in the side wall allowed air entry facility at the time of burning. The conventional parboiling process generally takes 3 days for one batch of parboiling of rice and ash is removed at any time within this period. Ash sample was collected at different retention time intervals of 3, 6, 12, 24, 36, 48 and 60 hours from the accumulation chamber to match with the field conditions. The effect of retention time on the ash quality was determined. The physical state of RHA through visual observation based on retention time is shown in Figure 3.6.



(a) 3 h stay, RHA 3 (b) 6 h stay, RHA 3 (c) 12 h stay, RHA 3



(d) 24 h stay, RHA 3 (e) 36 h Stay, RHA 3



(f) 48 h stay, RHA 3 (g) 60 h Stay, RHA 3

Figure 3.6: Ash collected from the accumulation chamber at different retention time

It was observed that the colour of the burnt rice husk ash was blackish for 3, 6, 12 and 24 hours of retention time which indicates the ash was partially burnt and having excess carbon content. At 36 hours retention time the ash had some different appearance from the earlier ash and at 48 and 60 hours retention time, the ashes were almost fully burnt and greyish colour. According to Boating and Skeete (1990) the whitish grey colour of the resulting ash is an indication of complete oxidation of the carbon in the ash.

3.2.4.4 Ash grinding

Grinding was done after collecting the rice husk ash from the different burning systems. Laboratory grinding mill was used for grinding purpose as shown in Figure 3.7. The sample of ash was equally divided in to four parts in order to use at different four grinding periods i.e. 45, 90, 135 and 180 minutes to find out the appropriate grinding time. After completion of each grinding operation, the ash was collected and screened with sieve No. 200. The ash finer than 75 μm was collected, weighed and fineness test was conducted.

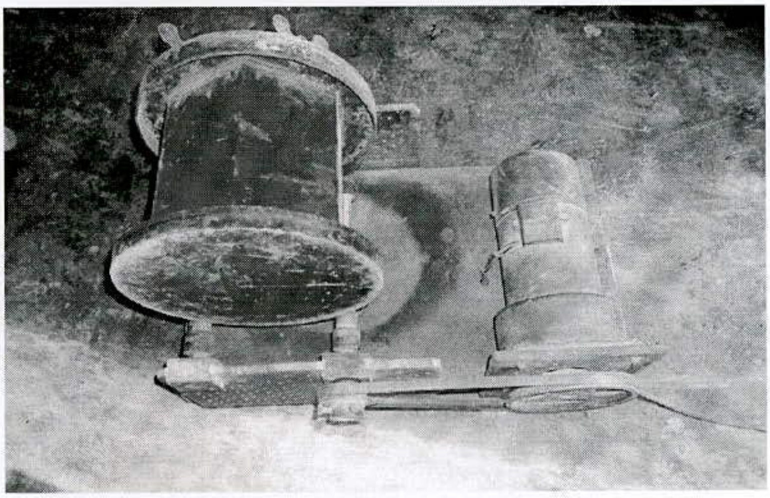


Figure 3.7: Laboratory grinding mill

3.3 EXPERIMENTAL METHODS

As described in the scope of this study, the main experimental objective is to study the sustainability of cement mortar made with a secondary material as cement replacing element. Major of the laboratory experimentation was done at the Khulna

University of Engineering & Technology. The XRD, FT-IR, SEM analyses were done out site of this University.

3.3.1 Specimen Preparations

The control mortar samples were prepared by sand with ordinary Portland cement (OPC) and other samples were prepared by sand and OPC partially replaced by RHA. The following procedure was followed to prepare the mortar sample:

1. The certain percentage of RHA was thoroughly mixed with ordinary Portland cement before mixing with sand to ensure the partially replacement of cement.

2. The sand and cement with or without RHA were allowed to mix till the mixture attained uniform colour. This process is shown in Figure 3.8.

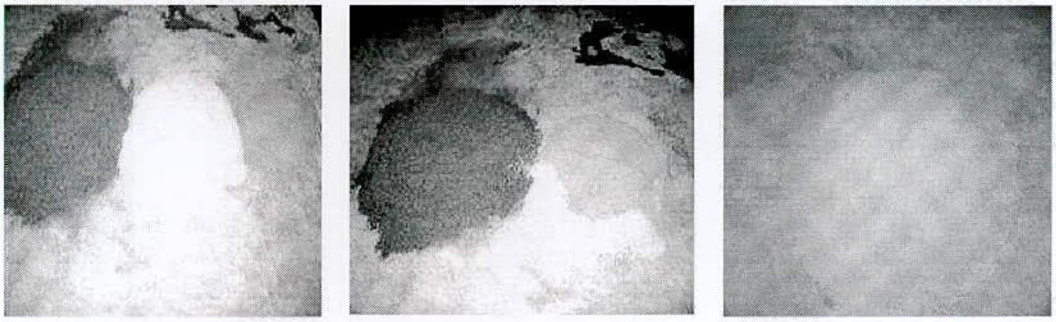


Figure 3.8: Photograph of mixed sample at different stages of mixing

3. Initially half of the prescribed water was added and thoroughly mixed with all other ingredients. Then, the rest amount of water spread over it and thoroughly mixed. The time required to complete the whole mixing process was about 2 to 3 minutes.

4. Addition of RHA in different percentages increases the water requirement for a constant workability of the cement mortar. Before preparation of mortar sample flow table test was performed to ensure a constant workability according to ASTM C230. The arrangement for flow table test is shown in Figure 3.9.

Figure 3.9: Photograph of flow table test arrangement for mortar sample

5. The water obtained from flow table test was used to prepare mortar. The mortar was placed in the 50 mm cube mould in two layers with sufficient tamping according to ASTM C109. For tamping seasoned oak wood rendered non-absorptive by immersion for 15 min in paraffin at approximately 200°C, have a cross section of about 13 mm by 25 mm and a convenient length of about 120 mm to 150 mm. The tamping face is flat and at right angles to the length of the tamper. Approximately one half of the depth of the mould was filled with mortar in all of the cube compartments. There were three cube compartments in each mould set. The mortar was tamped in each cube compartment by 32 times in about 10 seconds in 4 rounds, each round was to be at right angles to the other and consisted of eight adjoining strokes over the surface of the specimen. The tamping pressure was to be just sufficient to ensure uniform filling of the moulds. The 4 rounds of tamping (32 strokes) of the mortar was completed in one cube before going to the next. When the tamping of the first layer in all of the cube compartments was completed, the compartments were filled with the remaining mortar and then tamped as specified for the first layer. During tamping of the second layer, the mortar forced out on to the tops of the moulds was brought into after each round of tamping by means of the gloved fingers and the tamper upon

completion of each round and before starting the next round of tamping. Trowel was used to smooth the surface.

6. Some samples were prepared in cylindrical shape for water sorption and permeability test. The diameter and height of cylinder was 100 mm and 200 mm respectively. The cylindrical sample was cast in two layers in accordance with ASTM C31. The 10 mm diameter and 300 mm long tamping rod was selected for rodding the mortar in mould. Rodding of each layer was done with the rounded end of the rod using 25 numbers. The roddings was distributed uniformly over the cross section of the mould. For each upper layer, the rod was allowed to penetrate through the layer being rodded and into the layer below approximately 25 mm.
7. Mould with samples were placed over a wet cloth and covered by a polyethylene in the laboratory for 24 hours.
8. The samples were removed from the mould after 24 hours of casting and placed in a water chamber for curing at 25 ±2°C until the test.

3.3.3 Specimen Identification

For easy realization of the sample some identity mark was provided in this stage and the RHA is indicated as "A" and the detailed of specimen identification is given in Table 3.6.

Table 3.6: Identification of samples along with mix ingredients.

Sample ID	Type of RHA	Sample ID	Type of RHA	Sample ID	Type of RHA	OPC (%)	RHA (%)
A1-0	RHA 1	A2-0	RHA 2	A3-0	RHA 3	100	0
A1-10		A2-10		A3-10		90	10
A1-15		A2-15		A3-15		85	15
A1-20		A2-20		A3-20		80	20
A1-25		A2-25		A3-25		75	25
A1-30		A2-30		A3-30		70	30

3.3.4 Testing of Sample

The following tests were conducted to fulfil the objectives of this study:

- Workability
- Initial and final setting time
- Heat of hydration
- Short and long term compressive strength
- Fire performance
- Water sorption
- Permeability
- Salt crystallization
- Resistance to sulphate attack
- XRD, SEM and FT-IR

Detailed of the test procedure are outlined in subsequent sub-section.

3.3.4.1 Workability

Workability is one of the major issues for cement based products to confirm a constant flowability of RHA-mortar. Flow table test was performed according to ASTM C230 to attain the w/c ratio for constant workability of RHA mortar before casting. The flow table apparatus consists of an integrally cast rigid iron frame and a circular rigid table top 255 ± 2.5 mm in diameter, with a shaft attached perpendicular to the table top by means of a screw thread. The table top and shaft with contact shoulder were mounted on a frame in such a manner that it can be raised and dropped vertically through the specified height of 12.7 ± 0.38 mm for tables in used, by means of a rotated cam. The table top have a fine machined plane surface, free of blowholes and surface defects. The top is scribed with eight equidistant lines 68 mm long, extending from the outside circumference toward the centre of the table. The conical mould is made of bronze or brass for casting the flow specimen. The height of the mould is 50 mm. The diameter of the top opening is 70 mm and bottom diameter is 100 mm. The surfaces of the base and top are parallel and at right angles to the vertical axis of the cone.

Workability, strength, and durability are three basic properties of concrete. Amount of functional internal work necessary to overcome the internal friction to produce full compaction is termed as Workability. Size, shape, surface texture and grading of aggregates, cement replacing materials, water-cement ratio, use of admixtures and mix proportion are vital factors affecting workability. Owing to the high specific surface of RHA, the inclusion of RHA in OPC material might be lead to raise the amount of water requirement (Abdelmonem, 2000; Malhotra, 1993). The use of the different ashes prepared and collected previously, exhibit different water requirement for constant workability. Flow table test was performed to found out the constant workability.

3.3.4.2 Setting time

Initial and final setting time was examined using the manually operated Vicat apparatus according to ASTM C191 to observe the effect of rice husk ash addition with Ordinary Portland Cement. These methods determine the time of setting of hydraulic cement by means of the Vicat needle. The detailed of Vicat apparatus is shown in Figure 3.10.

A paste of cement with different percentages of rice husk ash was moulded, placed and allowed to start setting. Periodic penetration tests were performed on this paste by allowing a 1 mm Vicat needle to settle into this paste. The time of setting was measured as the difference between the time that a measurement of 25 mm penetration and the time of the initial contact between the cement and water. The final time of setting is computed as the time elapse from initial casting to hardening of paste in such manner that penetration of vicat niddle within 3 mm.

The Vicat apparatus consist of a frame, *A*, bearing a movable rod, *B*, weighing 300 g, one end, *C*, the plunger end, being 10 mm in diameter for a distance of at least 50 mm and the other end having a removable steel needle, *D*, 1 mm in diameter and 50 mm in length. The rod *B* is reversible, and can be held in any desired position by a set screw, *E*, and has an adjustable indicator, *F*, which moves over a scale (graduated in millimetres) attached to the frame, *A*. The paste is held in a conical ring, *G*, resting on a plate of similar planeness, corrosivity, and absorptivity to that of glass, *H*, about 100 mm square. The ring is made of a noncorroding, nonabsorbing material, and have an inside diameter of 70 mm at the base and 60 mm at the top and a height of 40 mm. Test specimen was prepared and placed on the mould according to ASTM C187 and ASTM C191 respectively.

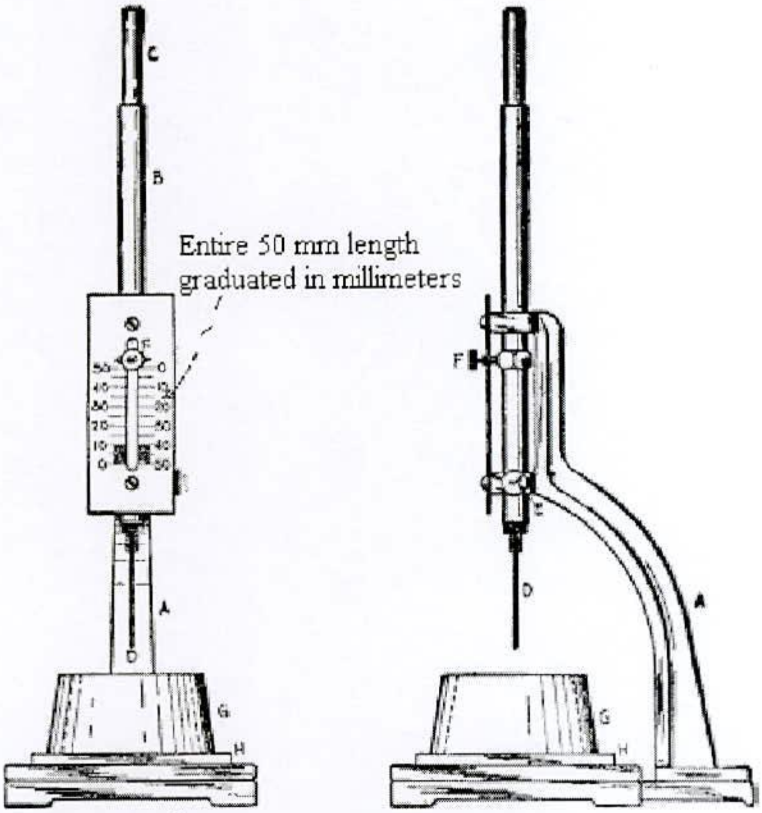


Figure 3.10: Vicat apparatus

Determination of setting time – Tests were conducted in the room at temperature and humidity of 25°C and 78% respectively. Samples were kept for 30 minutes after moulding without any disturbance. The penetration of the 1 mm needle was determined at this time and thereafter every 15 minutes until a penetration of 25 mm or less was obtained. For the penetration test, the needle *D* of the rod *B* was lowered until it rests on the surface of the cement paste. Each penetration test was performed at least 5 mm away from any previous penetration and at least 10 mm away from the inner side of the mould. The results of all penetration tests were recorded and the time for penetration of 25 mm is determined by interpolation. This is the initial setting time. The final setting time is when the needle does not sink visibly into the paste. This process was done on pure cement paste and cement paste having 10%, 20% and 30% RHA by replacing the same amount of cement by weight. Finally, the effect of RHA addition in cement on setting time was found out.

3.3.4.3 Heat of hydration

The heat of reaction which is released during the hydration of cement was measured by semi-adiabatic calorimeter method confirming to Nordest NT BUILD 388. In recent times, the calorimetry test is increasingly used because the heat of hydration is easily monitored by this process with time. This process has also been treated a heat signature or thermal fingerprint experiment since it determines a temperature connected property that is unique to a given mortar mix. In this study, semi-adiabatic calorimeter test was performed to find out the thermal fingerprint of the cement paste with and without Rice Husk Ash.

The heat progression curves normally measured from the dormant period of cement hydration. At the end of the dormant period, the significant hydration starts again due to hydration of C_3S and C_2S hydration which is called the acceleration period. Concrete temperature increases rapidly in this stage. After the acceleration period the rates of heat generation gradually slow down. In this stage, the thickness of the hydrated layer that covers unhydrated particles increases and the surface area of the unhydrated portions decreases. Finally, cement hydration reaches to the steady state. The last two stages are known as the diffusion control phase. Semi-adiabatic method is suitable for pasts, mortars, and concrete samples. It is been extensively used for determining the heat signature of concrete/mortar. In this study a 30 channel data logger with computer interfacing software, pt-100 thermocouple, semi-adiabatic calorimeter arrangement and electronic balance were used to collect the heat signature data for the cement paste with and without RHA.

3.3.4.4 Compressive strength

Compressive strength is the most important properties of cementitious materials. Portland cements with and without rice husk ash were mixed at specified water/cement ratios. Water/cement ratio was obtained from a flow table test for the mortar as described earlier. Cubical specimens of 50 mm were prepared as per ASTM standard. The cubes preparation and curing condition were described earlier.

For measuring the compressive strength, the specimens were cured for 7, 28, 90, 350, 600 and 900 days. Specimen surface was cleaned and ensured the saturated surface dry (SSD) condition before testing. Test was performed at 7days ± 1 hour, 28 days ± 5 hours, 350 days ± 1 day, 600 ± 1 day and 900 days ± 1 day of the sample ages which is within the permissible tolerance specified by ASTM C109 standards. The load rate applied to the specimen was kept within the range of 900 to 1800 N/s as mentioned in ASTM. The maximum permissible range between specimens from the same mortar batch, at the same test age is 8.7 % of the average when three cubes represent a test age. At least three samples were tested for every test slot and the average value was taken for analysis of results as presented in the results and discussions chapter. The compression testing machine along with the test specimen is shown in Figure 3.11.

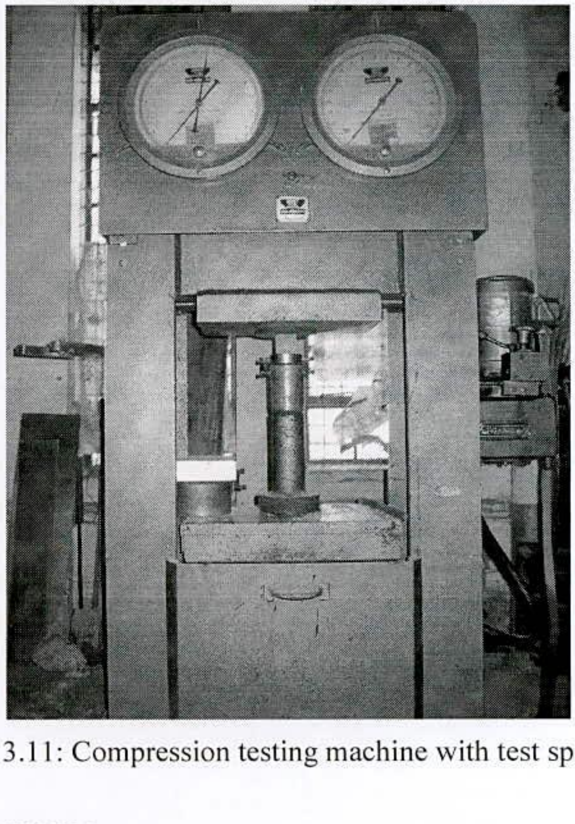


Figure 3.11: Compression testing machine with test specimen

3.3.4.5 Fire performance

Fire performance is one of the most important parameters for material durability. Before starting the firing test all samples were preconditioned. It was done by two steps. Firstly, the samples were kept in open air for 12 hours and then heated at

100°C for 12 hours. Then the samples were removed from oven and cooled down in open air for 12 hours. Afterwards the specimens were placed inside the electric muffle furnace for firing test. The internal chamber of furnace 30 cm × 30 cm × 30 cm. and the maximum heating capacity was 1200°C. Firing of samples is shown in Figure 3.12. Each sample was kept inside the furnace at a specified temperature for 30 minutes. The hot sample was removed from the furnace by mild steel pliers. Subsequently samples were cooled adopting two different processes. Three specimens were allowed to cool down freely to attain the room temperature (29°C to 32°C) in open air. Remaining three specimens of each type were quenched with water at 30°C for about 10 seconds. After this operation samples were cooled down freely to attain the room temperature. At the time of quenched with water huge amount of vapour was produced as shown in Figure 3.13. A very tiny time of submerging the specimens in water was assumed due to fear of their destruction as the result of thermal shock.

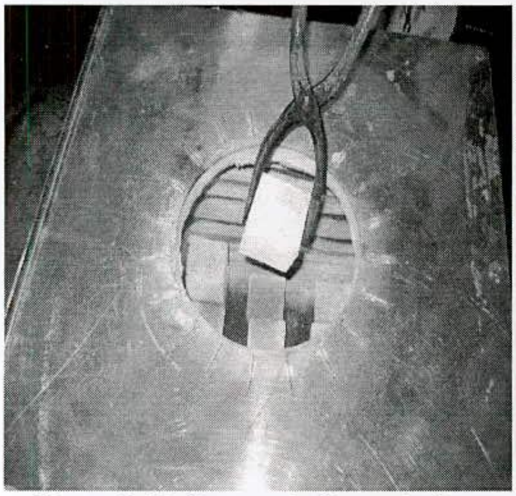


Figure 3.12: Removal of sample from muffle furnace

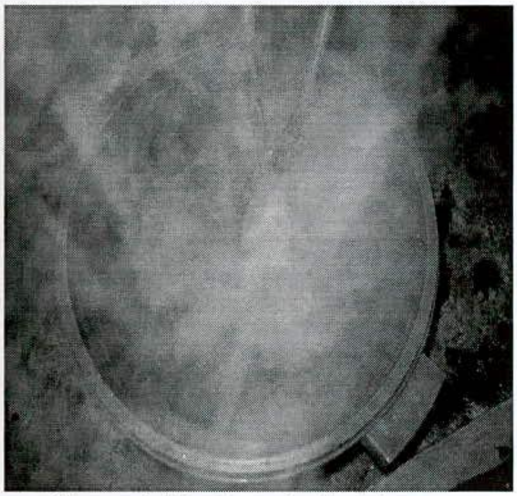


Figure 3.13: Quenched with water

Five different temperatures of 200°C, 300°C, 400°C, 500°C and 700°C were selected to observe firing effect. The temperature within the furnace was measured by two different thermocouples at different places and the average was taken. After cooling the sample was tested to find out its residual compressive strength and SEM analysis was performed to find out its performance.

3.3.4.6 Permeability test

In the AASHTO T277 (ASTM C1202) test, a water-saturated, 50 mm thick, 100 mm diameter mortar specimen was subjected to a 60 V (DC voltage) applied for 6 hours using the apparatus shown in Figure 3.14. The diffusion cell consists of two chambers, 3% NaCl solution were filled in one chamber and another chamber was filled by 0.3 N NaOH solution. The total charge passed was determined and it was used to rate the specimen according to the criteria mentioned in Table 3.7. The test originally developed by Whiting (1981), is commonly (though inaccurately) referred as the "Rapid Chloride Permeability Test" (RCPT). This test has been widely used in the literature (Goodspeed et al., 1996; Thomas and Jones, 1996; Saito and Ishimoiri, 1995; Samaha and Hover, 1992).

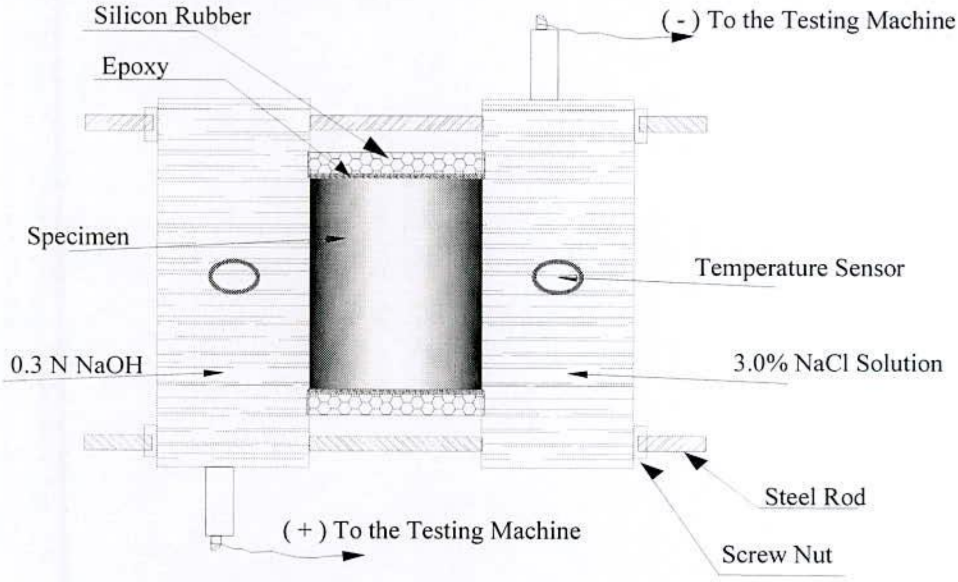


Figure 3.14: AASHTO T277 (ASTM C1202) test setup

Table 3.7: RCPT ratings (ASTM C1202)

Charged Passed (Coulombs)	Chloride Ion Penetration
>4,000	High
2,000-4,000	Moderate
1,000-2,000	Low
100-1,000	Very Low
<100	Negligible

In this experiment 3 numbers of samples were tested for each type of mix proportion and the average was presented in Chapter 4.

3.3.4.7 Resistance to sulphate attack

In order to evaluate the sulphate vulnerability of cementitious materials with and without RHA, an accelerated test method was undertaken. In the accelerated test method, the pH values and sulphate concentration throughout the test remained constant. According to Paulo et al. (2000) the conditions provided in accelerated test method are similar to field condition. Performance of the cementitious materials can be described based on the time how long it would be sustained in the solution and how it decreased its compressive strength.

Cubical specimens of 5 cm × 5 cm × 5 cm were cast with Ordinary Portland Cement (OPC) and OPC replaced by 10%, 15%, 20%, 25% and 30% of Rice Husk Ash (RHA), sand and water. Samples were kept in water bath at 23±2°C temperature up to 28 days age. Samples were removed from water bath and dried before it was sliced by rotary cutting device to make 12.5 mm × 12.5 mm × 12.5 mm cubical specimen. This dimension was chosen to maximize the surface-to-volume ratio, thus raise the potential for reaction with the sulphate solution. The lower the surface-to-volume ratio, the less likely the sulphate ions will permit throughout the specimen and potentially react to cause a strength reduction. These 12.5 mm cubes were stored in a circulating 4% Na_2SO_4 solution and the pH value of solution was maintained at 7.2. The pH value of sulphate solution was maintained at 7.2 which is closed to the field condition.

A diagram of the test setup is shown in Figure 3.15. Sulphate solution was put in a PVC container of 50 litres capacity and always agitated by a mechanical agitator. The samples were kept in the solution in a perforated PVC basket. The perforations allow all faces of the sample in contact with the Na_2SO_4 solution throughout the test time. The pH value of the Na_2SO_4 solution was controlled by adding 0.1 N H_2SO_4 from a container placed over the 50 litre PVC container. The pH value in the sulphate solution changed by leaching of CH from the sample and was minimized by adding 0.1 N H_2SO_4. Brown (1981) verified that controlling the pH by additions of sulphuric acid; it is required to make sure that the sulphate ion concentration of the solution remains steady over time. The conditions provided in this accelerated test method are more representative to field conditions.

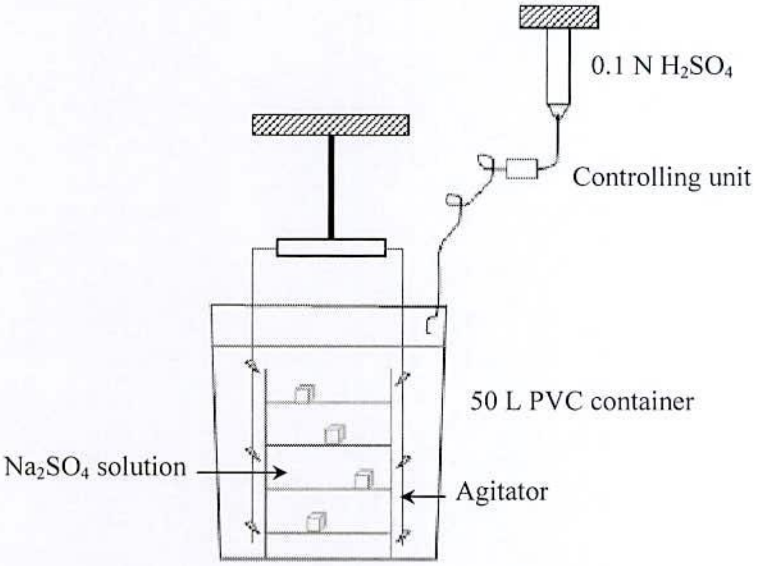


Figure 3.15 Diagram of sulphate resistance test setup

Sample without RHA were prepared with 50% water addition and the water added for preparing samples with the RHA was high. The water-to-cement ratio of 0.50 increases the permeability of the mortar cubes and allows for better comparison between all cementitious samples. After curing up to 28 days, samples were tested to measure compressive strength prior to sulphate immersion. For all compression testing, load was applied at same rate. Compressive strength was measured and compared to the initial 28 day strength after 28, 56, 84 and 112 days of immersion in sulphate solution.

3.3.4.8 Water sorption

This test method is used to determine the rate of absorption (sorptivity) of water by hydraulic cement concrete/mortar by measuring the increase in the mass of a specimen resulting from absorption of water as a function of time. In this case, one surface of the specimen is exposed to water. The exposed surface of the specimen is immersed in water and water ingress of unsaturated sample dominated by capillary suction during initial contact with water. The water sorptivity of mortar can be determined by using ASTM C1585. This test method was developed by Hall (1989) and the phenomenon is known as "water sorptivity".

The standard test specimen is a 100 ± 6 mm diameter disc, with a length of 50 ± 3 mm. Specimens were obtained from the middle of the cylinders prepared according to ASTM C31. The cross sectional area of a specimen was not varied more than 1% from the top to the bottom of the specimen.

The specimens were kept in an oven at a temperature of 50 ± 2°C for 3 days. After 3 days, each specimen was placed inside a separate sealable container. Precautions must be taken to allow free flow of air around the specimen by ensuring minimal contact of the specimen with the walls of the container. The container was kept at 23 ± 2°C for at least 15 days before the starting of the sorption test. The specimen was taken out from the storage container and weight of the conditioned specimen was taken to the nearest of 0.01 gm before sealing the side surfaces.

The contact area of the specimen was measured. The cylindrical peripheral surface was sealed with electric tape. The absorption test was performed at 23 ± 2°C with tap water conditioned to the same temperature.

The mass of the sealed specimen was taken nearest to the 0.01 gm and recorded it as the initial mass for water absorption calculations. The support device was placed at the bottom of the pan and filled the pan with tap water to maintain the water level of 1 mm to 3 mm above the top of the support device.

The timing device was started and the test surface of the specimen was immediately placed on the support device as shown in Figure 3.16. The time and date of initial contact with water were recorded.

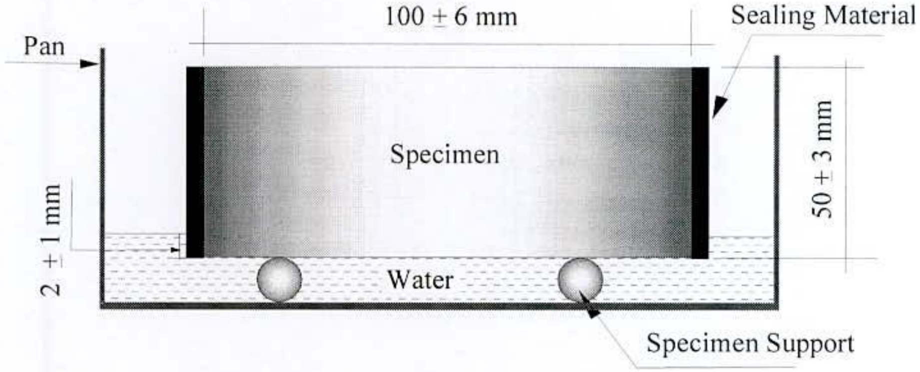


Figure 3.16: Schematic of the sorptivity procedure

Using the procedure described above the first reading was taken at 60 second and the second at 5 min ± 10 sec. Subsequent measurements were within ± 2 min of 10 min, 20 min, 30 min, and 60 min. The actual time was recorded to within ± 10 sec. The measurements were continued at every hour, up to 6 hours, from the first contact of the specimen with water. After the initial 6 hours, measurements were taken twice a day up to 9 days.

For each mass determination, the test specimen was removed from the pan and blotted off any surface water with a dampened paper, towel or cloth. After blotting to remove excess water, the specimen was inverted so that the wet surface does not come in contact with the balance pan.

Sorption means water entrance into pores under unsaturated circumstances due to capillary suction. According to ASTM C642 the sorptivity test measures the ability of cementitious materials to absorb water. Sorptivity (*S*) means the volume of water that is absorbed per unit of cross-section (*i*) in that particular time (*t*). Sorptivity *S* is measured by the following equation.

$$S = i/\sqrt{t} \tag{3.1}$$

Where, $i = [(W_t - W_d) \times 10^3]/A$ gm/mm^2

W_t = weight of sample at different time intervals

W_d = Dry weight of sample

A = cross sectional area

t = intervals in minutes.

3.3.4.9 Loss on ignition

Loss on Ignition (LOI) test was carried out to analyze the content of volatile organic compound inside the rice husk ash (RHA). The LOI of RHA was determined based on the SIRIM procedure (ISO 3262-1975). A one gram of dried sample was placed in a platinum crucible and ignited in the muffled furnace at 1000°C for 30 minutes to achieve constant mass, followed by cooling in desiccators. The loss of ignition, as a percentage by mass, is given by the formula:

$$\% \text{ LOI} = (m_o - m_1)/m_o \times 100 \qquad (3.2)$$

Where m_o is the mass of the sample and m_1 is the mass of sample after ignition

3.3.4.10 Salt crystallization test

The crystallization of soluble salts in the porous system of the mortar frequently produces deterioration. A salt will crystallize when the water evaporates and the activity of the ions in the solution overcomes that of saturation; but also when the relative humidity of the atmosphere in the surroundings of the material is inferior to that of equilibrium of a saturated solution of this salt. In this way, the accumulated salts in a porous system like in mortar will be crystallized and dissolved periodically depending on the relative humidity of the air. During the crystallization process high pressure is generated due to the growth of the crystals and its hydration. This process is known as salt crystallization. The following procedure was followed to find out the performance of mortar samples by salt crystallization test.

- The cured samples were immersed in a 14% solution of sodium sulphate decahydrate ($Na_2SO_4.10H_2O$) for four hours where density of this solution at 20°C was 1055 Kg/m^3.
- The samples were removed from solution and dried in an oven pre heated on 105°C for fifteen hours followed by cooling at room temperature for six hours.
- Weights of the sample were taken before recommencements of the soaking in salt solution. Samples were subjected to 20 such cycles.

3.3.4.11 XRD (X-ray Diffraction) test

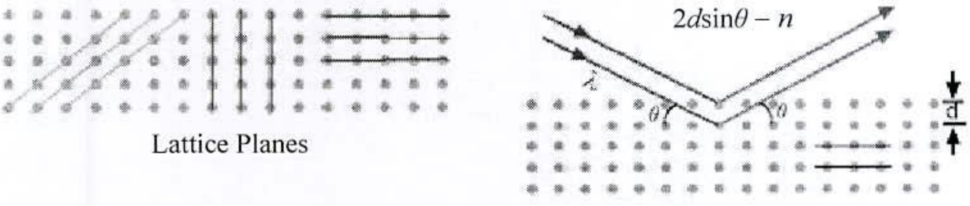
X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV. For diffraction applications, only short wavelength x-rays (hard x-rays) in the range of a few angstroms to 0.1 angstrom (1 keV - 120 keV) were used. Because the wavelength of x-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic x-rays can penetrate deep into the materials and provide information about the bulk structure.

In recent years synchrotron facilities have become widely used as preferred sources for x-ray diffraction measurements. Synchrotron radiation is emitted by electrons or positrons travelling at near light speed in a circular storage ring. These powerful sources, which are thousands to millions of times more intense than laboratory x-ray tubes, have become indispensable tools for a wide range of structural investigations and brought advances in numerous fields of science and technology.

X-rays primarily interact with electrons in atoms. When x-ray photons collide with electrons, some photons from the incident beam will be deflected away from the direction where they originally travel. If the wavelength of these scattered x-rays did not change (meaning that x-ray photons did not lose any energy), the process is called elastic scattering (Thompson Scattering) in that only *momentum* has been transferred in the scattering process. These are the x-rays that would be measure in diffraction experiments, as the scattered x-rays carry information about the electron distribution in materials. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows presuming the distribution of atoms in a material.

The peaks in an x-ray diffraction pattern are directly related to the atomic distances. The atoms, represented as green spheres, as indicated in the graph (Figure 3.17), can be viewed as forming different sets of planes in the crystal coloured lines in figure on left side. For a given set of lattice planes with an inter-plane distance of *d*, the condition for a diffraction (peak) to occur can be simply written as

$$2d\sin\theta = n\,\lambda. \tag{3.3}$$



Lattice Planes

Bragg's Law

Figure 3.17: Schematic diagram of X-ray diffraction pattern

The above equation (3.3) is known as the Bragg's law, W.L. Bragg, who first proposed it. In the equation, λ is the wavelength of the x-ray, θ the scattering angle, and n an integer representing the order of the diffraction peak. The Bragg's Law is one of most important laws used for interpreting x-ray diffraction data.

Powder XRD (X-ray Diffraction) is perhaps the most widely used x-ray diffraction technique for characterizing materials. As the name suggests, the sample is usually in a powdery form, consisting of fine grains of single crystalline material to be studied.

The term 'powder' really means that the crystalline domains are randomly oriented in the sample. Therefore when the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various *d* spacing in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. This phase identification is important because the material properties are highly dependent on structure.

Powder diffraction data can be collected using either transmission or reflection geometry, as shown below in Figure 3.18. Because the particles in the powder sample are randomly oriented, these two methods will yield the same data. In the MRL x-ray facility, powder diffraction data are measured using the Philips XPERT MPD diffractometer, which measures data in reflection mode and is used mostly with solid samples. This technique was done on Rice Husk Ash to find out its peaks with respect to intensity $2d\theta$.

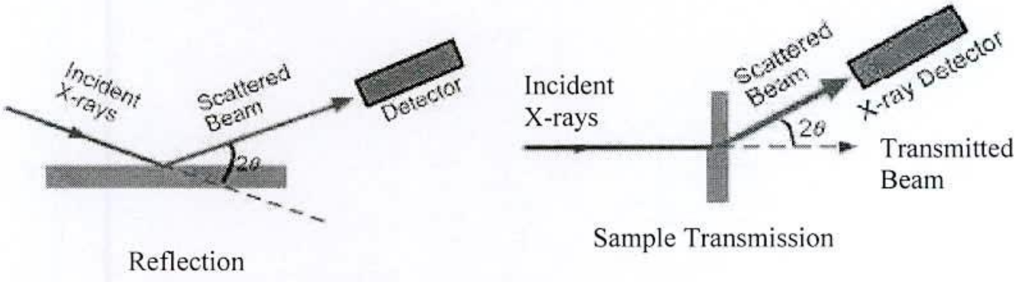


Figure 3.18: Powder diffraction data collection technique

3.3.4.12 SEM (Scanning Electron Microscope) test

The application of the SEM in petrographic analysis of cementitious materials and concrete microstructure is becoming increasing frequently (Bentz and Stutzman, 1993; Taylor, 1990; Struble and Stutzman, 1989; Scrivener, 1984). SEM imaging provides thorough images of the microstructure that augment those from stereo and optical microscopy. The primary advantages are the high-contrast images of the microstructure, the high spatial resolution of the images, and the ability to execute simultaneous imaging and chemical analysis.

The SEM (Figure 3.19) scans a focused beam of electrons across the specimen and measures any of several signals resulting from the electron beam interaction with the specimen. The most commonly used imaging modes are secondary electron, backscattered electron, and x ray. Images are monochrome since they reflect the electron or x-ray flux resulting from the beam⁄specimen interaction.

Secondary electrons (SE) are low-energy electrons produced as a result of an inelastic collision of a primary beam electron with an electron of an atom within the specimen (Goldstein, et al., 1992). Because of their low energy, they are readily absorbed and only those produced near the surface escape, producing the detailed images of surface topography. Specimens intended for secondary imaging benefit from a conductive coating of a heavy metal such as gold or gold/palladium to increase secondary electron flux, improving the imaging signal. SE images are used to study particle size, shape, surface roughness, and fracture surfaces.

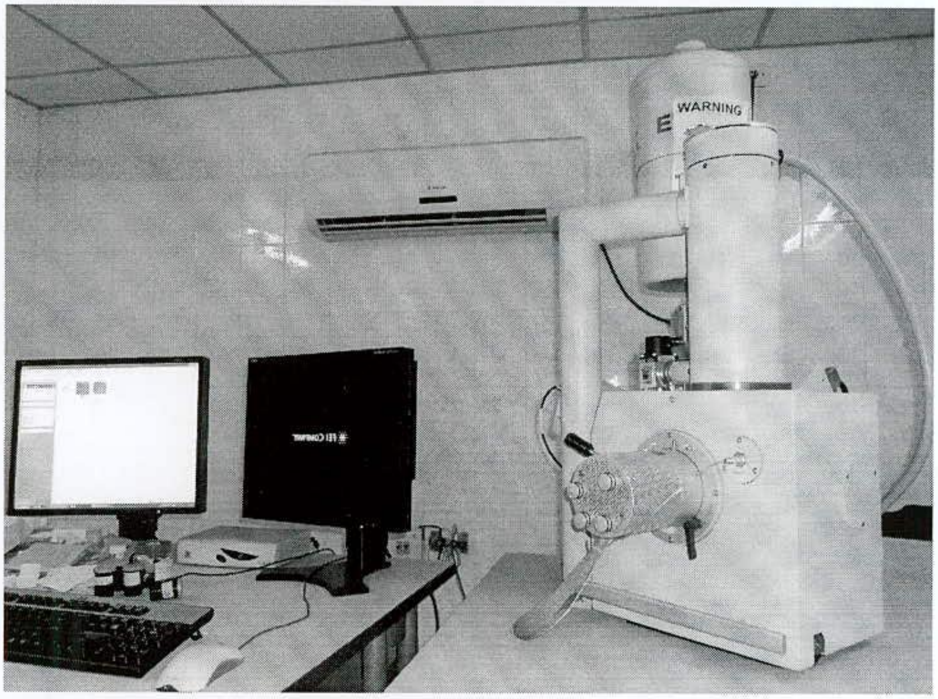


Figure 3.19: SEM Setup

The SEM may be used to examine Portland cement clinker, cement powder, cement pastes, mortars, and hardened Portland cement concrete. Specimen preparation uses an epoxy impregnated, polished section where the epoxy resin permeates the material's pore system or encases powder particles. The specimens are then cut or ground to expose a fresh surface and that surface is then polished by using a series of successively finer grades of diamond paste.

The cutting, grinding, and polishing steps are common to all preparations in order to expose a fresh surface. Diamond-blade slab or wayfaring saws, lubricated using propylene glycol, are suitable for exposing a fresh surface. This surface needs to be smoothed by grinding. Abrasive papers of 220, 320, 400, and 600 grits (silicon carbide paper) are also suitable for rapid removal of material by grinding. SEM technique was used to find out the particle size of cement and RHA. It is also used to find out the surface texture of mortar sample after and before in elevated temperature.

3.3.4.13 FT-IR (Fourier Transform Infra-Red) test

An FT-IR Spectrometer is an instrument which acquires broadband NIR to FIR spectra. Unlike a dispersive instrument, i.e. grating monochromator or spectrograph, a FT-IR Spectrometer collects all wavelengths simultaneously. This feature is called the Multiplex Advantage. FT-IR Spectrometers are often simply called FT-IRs. But for the purists, an FT-IR (Fourier Transform Infra-Red) is a method of obtaining infrared spectra by first collecting an interferogram of a sample signal using an interferometer, and then performing a Fourier Transform (FT) on the interferogram to obtain the spectrum. An FT-IR Spectrometer collects and digitizes the interferogram, performs the FT function, and displays the spectrum. In a dispersive spectrometer, wave-numbers are observed sequentially, as the grating is scanned. In an FT-IR spectrometer, all the wave-numbers of light are observed at once. When spectra are collected under identical conditions (spectra collected in the same measurement time, at the same resolution, and with the same source, detector, optical throughput, and optical efficiency) on dispersive and FT-IR spectrometers, the signal-to-noise ratio of the FT-IR spectrum will be greater than that of the dispersive IR spectrum. It shows different peak for different materials. In cement mortar this technique was performed to find out any change in the mortar specimen is available or not due to elevated temperature effect on the sample.

CHAPTER 4

RESULTS AND DISCUSSIONS

The results and discussions for this study are presented mainly into the three phases: Rice Husk Ash preparation and characterization, mechanical properties and performance, and durability of mortar. Most of the laboratory experimentations were done at the Khulna University of Engineering & Technology. The XRD, FT-IR, SEM tests were conducted at outside of this University.

4.1 RICE HUSK ASH PREPARETION AND CHARACTERIZATION

The properties of rice husk ash depend on incineration conditions and geographical locations of cultivation. Several researchers indicated that the rice husk ash produced by burning under suitable environment might exhibits active pozzolanicity, which would be satisfactory for limited replacement of Portland cement (Saraswathy and Song, 2007; Zhang and malhotra, 1996; Ismail and Waliuddin, 1996; Joseph, et al., 1989).

RHA has a highly microporous structure that is responsible for its very high surface area, which often exceeds that of silica fume (Moncef, 2003). Parameters that are influencing the surface area of ash samples are temperature, time of ignition and also the treatment of rice husk before burning. Rice husk ash adding to concrete/mortar has a propensity to pick up its compressive strength, resistance to chloride penetration and durability (Foletto, et al., 2005; Zhang, et al., 1996). However its workability may be negotiated due to its very much specific surface. Thereby, mixing of rice husk ash in cementing materials leads to reduce in cement consumption, whose production creates a serious environmental problem. Rice Husk Ashes produced from three different types of field conditions are analyzed for their reactivity and pozzolanic properties to identify the most possible technique to manufacture a reactive pozzolana as cement replacing material.

The comparison of RHA samples produced from different incineration process is discussed and suggested a viable method to manufacture good quality Rice Husk Ash in uncontrolled conditions in rural Bangladesh.

4.1.1 Temperature History

Temperature history of rice husk incinerations is presented for heap burning and laboratory burning system. Three sensors were placed at three different locations in heap burning system (Figure 3.3). All sensors exhibited very close reading and the maximum variation of temperature at a particular time was observed to be 10.3%. The average of three temperatures is presented in Figure 4.1.

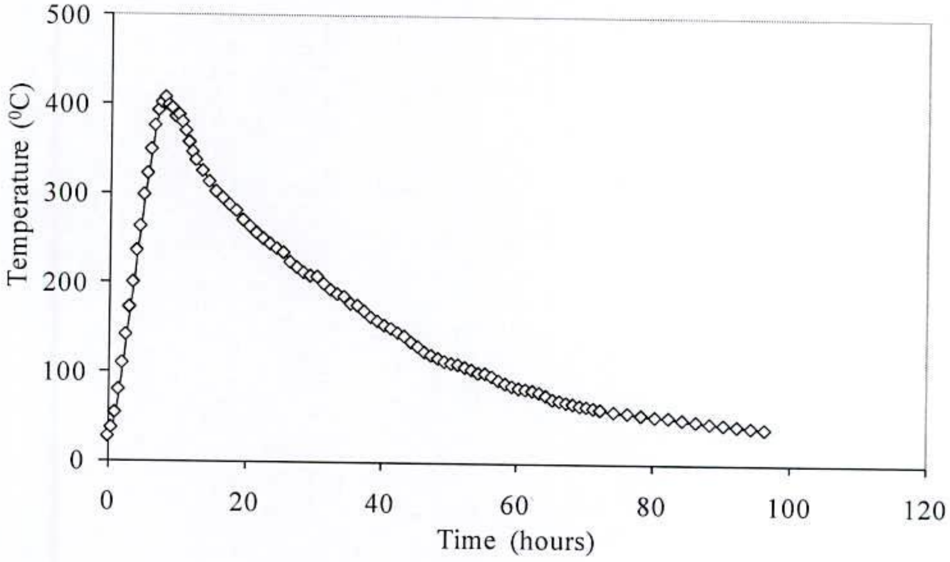


Figure 4.1: Variation of temperature with respect to time for heap burning

The maximum temperature of 407°C was found within 7.5 to 8.0 hours after ignition and then the temperature decreased rapidly up to 14.5 hours. After 15 hours of burning the temperature decreased gently up to 48 hours. A very low dropping nature was observed up to the end after 48 hours of burning.

The average temperature of ignition and accumulation chamber were termed as firing and cooling temperature and shown in Figure 4.2 and 4.3 respectively in case of laboratory burning. A little information is available in literature regarding the variation of firing and cooling temperature in conventional burning system. However, the highest temperature of conventional burning system was found to be 650°C to 730°C (Baqui, et al., 2007).

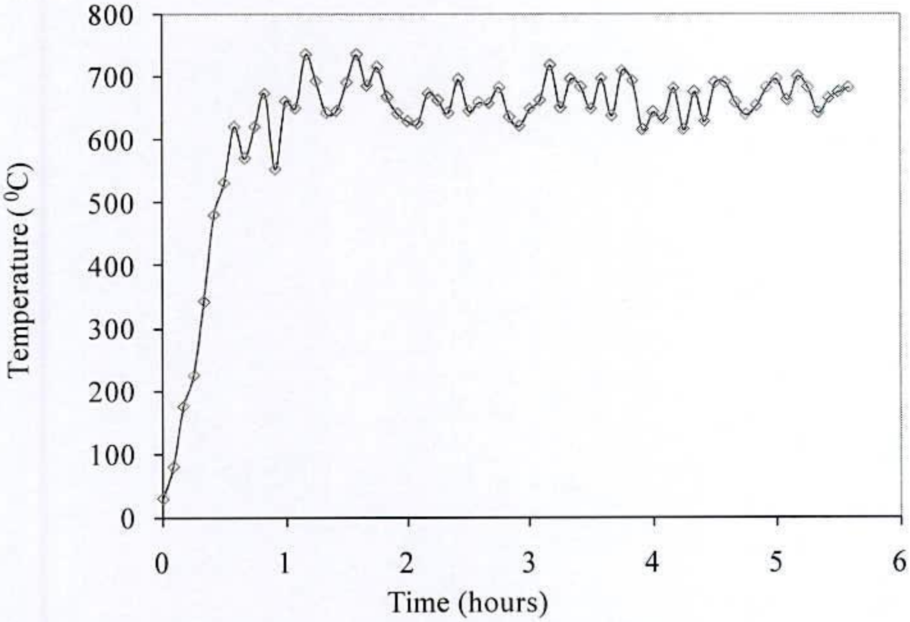


Figure 4.2: Temperature variation at ignition chamber with respect to time

Figure 4.2 shows that the average firing temperature after 45 minute was 663.6°C and the extreme high and low temperature in that period was 735°C and 553°C respectively. Cooling temperature of ash stored in accumulation chamber was measured after one and half hour from the time of firing. The plotted temperatures are the average of three different points that are described in Chapter 3 under the article 3.2.4.2. Temperatures were continuously collected at regular interval of 30 minutes.

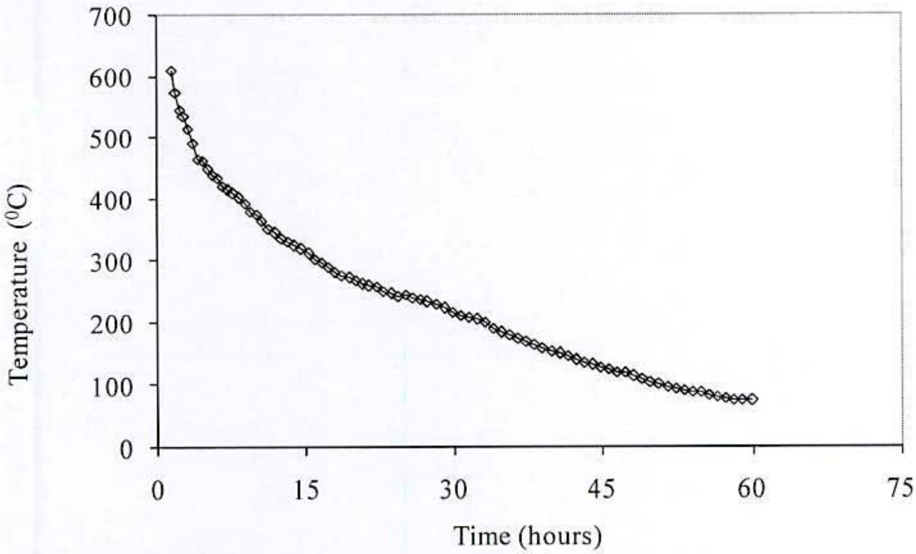


Figure 4.3: Temperature variation at cooling chamber with respect to time

Temperature was sharply dropped at a rate of 36.25°C/h within the initial four hours and after that cooling became slower. The rate of cooling was 12.97°C/h within 4 to 19 hours and it was 5.15°C/h at the last phase of 19 to 60 hours. The average ash temperature at 60 hours was observed to be 75°C which was much higher than the ambient temperature of 27°C.

4.1.2 Fineness of RHA

According to ASTM C204, Air permeability method was followed for measuring the fineness of the RHA. The incineration temperature, retention time and grinding time are the factors influence the Blaine fineness of the ash. Ashes were weighted prior to grinding and after sieving through sieve No. 200. The passed RHA through sieve was collected in a pan for use in this study.

Ash samples were collected from heap burning (RHA 1) exhibited the maximum fineness at 180 min grinding and it is 23.55% and 4.75% higher than 45 and 90 minutes grinding respectively. It was observed that the amount of ash passed through sieve was also higher (31.27%) at 180 minutes grinding and this value was higher by 19.35% with respect to the 45 minutes grinding. Amount of ash passed through sieve and the Blaine surface area are presented in the Table 4.1. The result indicates that the Blaine fineness had no significant variations after 45 minute grinding. The colour of this ash was light greyish as presented in Figure 4.7.

Table 4.1: Grinding time, fineness and amount of ash for heap burning system (RHA 1)

Grinding Time (minutes)	% of ash passing through Sieve No. 200	Blaine fineness	
		cm^2/gm	% increment
45	26.20	3083	00.00
90	29.46	3628	17.68
135	28.12	3656	18.59
180	31.27	3809	23.55

The RHA of conventional burning system (RHA 2) was collected from Khulna, Rajshahi and Dinajpur districts and termed as Khulna ash, Rajshahi ash and

Dinajpur ash. There are slight variations in Blaine fineness among these ashes. However, the amount of ash passing through sieve No. 200 varied for three different ashes. The results are shown in Table 4.2.

Table 4.2: Results of RHA 2 collected from Khulna, Rajshahi and Dinajpur districts.

Collection location	Grinding Time (minutes)	% of ash passing through Sieve No. 200	Blaine fineness	
			cm^2/gm	% increment
Khulna	45	36.50	2609	00.00
	90	36.07	2953	13.19
	135	39.77	3084	18.21
	180	40.25	3218	23.34
Rajshahi	45	45.28	3018	00.00
	90	45.78	3227	6.93
	135	46.54	3319	9.97
	180	48.15	3286	8.88
Dinajpur	45	34.73	2853	00.00
	90	37.21	3316	16.23
	135	37.94	3296	15.53
	180	38.17	3387	18.72

After 180 minutes grinding and sieving it was observed that 40.25%, 38.17% and 48.15% of ash were received from Khulna, Dinajpur and Rajshahi ash respectively. But the Blaine surface areas were observed very close to each other after 45 minutes grinding time. Table 4.2 shows a large variation in Blaine surface area for 45 minutes grinding time among the three ashes. The effects of grinding time on Blaine fineness of collected ashes from different locations are shown in Figure 4.4.

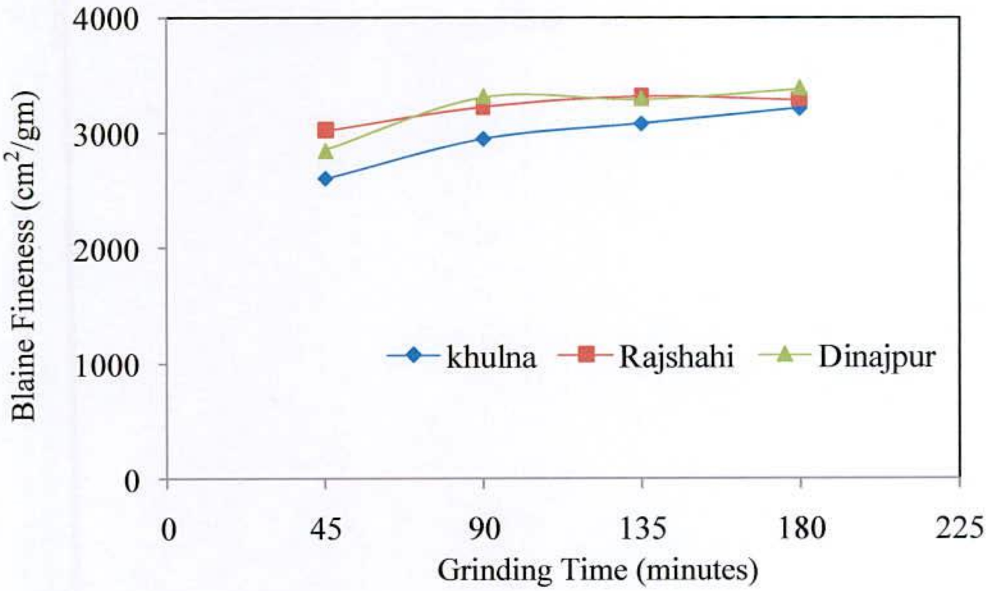


Figure 4.4: Variation of Blaine fineness with respect to grinding time for RHA 2

A mixed sample was prepared from the three different samples after 180 minutes grinding by taking equal amount of ash which is mentioned as RHA 2. After mixing it was found that the Blaine fineness of this sample was 3261 cm^2/gm, and used for the further investigation. The physical appearance of this ash is shown in Figure 4.7.

Ash was collected from laboratory incineration chamber (RHA 3) at different retention times of 3, 6, 12, 24, 36, 48 and 60 hours. There are considerable variations in Blaine fineness depending on the retention as well as grinding time. The ash was sieved through sieve No. 200 before measuring the Blaine fineness. The result is shown in Table 4.3.

Table 4.3 indicates that the amount of ash passing after grinding shows a little variation on grinding time. In case of retention time of 3 and 6 hours it was observed that the ash passing was less than 40% and 50% respectively. For other retention times the passing of ash was more than 50%. The results showed an insignificant effect of grinding time on the amount of ash passing through the sieve No. 200.

Table 4.3: Fineness of Rice Husk Ash (RHA 3) on grinding and retention time

Retention time (hours)	Grinding Time (minutes)	% Passing (through sieve 200)	Blaine fineness	
			cm^2/gm	% wrt. 90 minutes grinding
3	45	36.65	1738	-11.0
	90	37.17	1953	00.0
	135	38.27	2237	14.5
	180	39.42	2586	32.4
6	45	44.36	1926	-9.9
	90	47.92	2137	00.0
	135	46.14	2430	13.7
	180	48.25	2861	33.9
12	45	51.35	2180	-10.4
	90	54.26	2432	00.0
	135	52.37	2748	13.0
	180	54.50	3005	23.6
24	45	50.64	2486	-8.5
	90	51.92	2718	00.0
	135	53.08	2978	9.6
	180	53.61	3120	14.8
36	45	49.53	3521	-7.9
	90	53.81	3822	00.0
	135	53.34	4057	6.1
	180	54.72	4167	9.0
48	45	52.36	4818	-6.7
	90	52.81	5166	00.0
	135	53.40	5592	8.2
	180	54.00	5709	10.5
60	45	50.72	5968	-7.5
	90	49.27	6452	00.0
	135	50.81	6804	5.5
	180	51.62	6894	6.9

In case of Blaine fineness of the RHA 3, the retention time of ash in the accumulation chamber had a large effect. The Table 4.3 shows that the effect of retention time on fineness up to 24 hours is not significant. Blaine fineness of the RHA exhibited increasing values at 36, 48 and 60 hours of retention time as shown in Figure 4.5. The retention time has remarkable effect on fineness for 180 minutes grinding. The Blaine finenesses of RHA for 36, 48 and 60 hours retention time were observed 1.33, 1.83 and 2.21 times higher respectively at 180 minutes grinding when it was compared to the ash of 24 hours retention time. At 90 minutes grinding, the Blaine fineness of the ash had greater effect depending on the retention time as shown in Figure 4.6. At this time the finenesses of 36, 48 and 60 hours retention time ashes was observed 1.41, 1.9 and 2.37 times higher when compare with 24 hours retention time. From the above discussion it is clear that the retention time has a significant effect on the Blaine fineness of the ash.

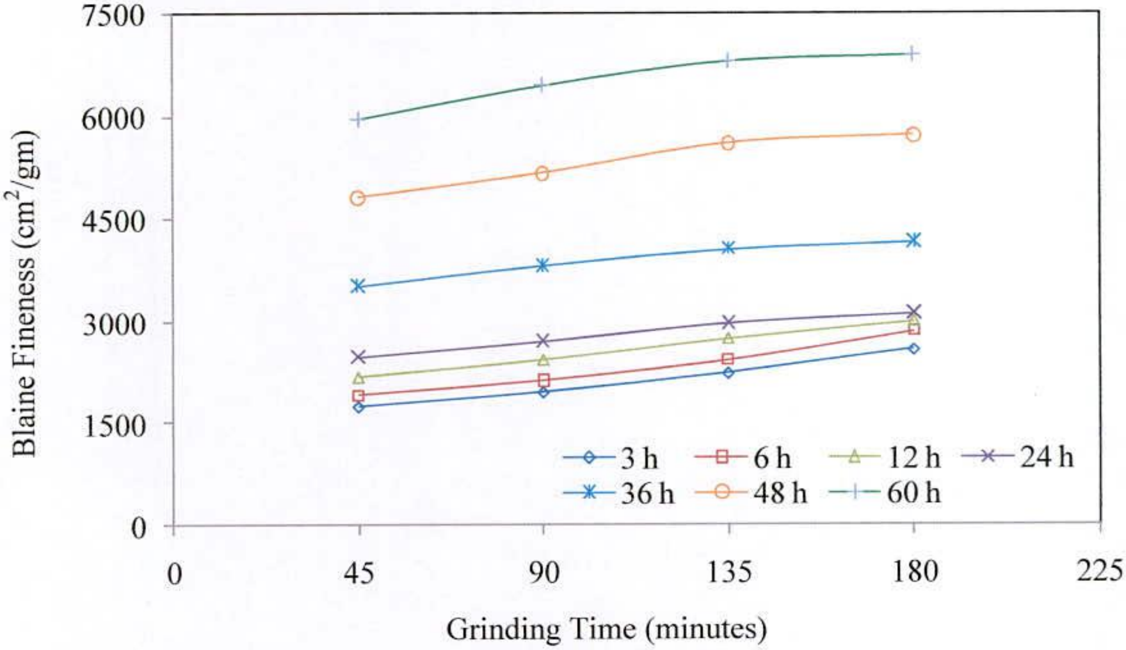


Figure 4.5: Grinding time and fineness of ashes for different retention time

It is observed from Figure 4.6, that 90 minutes grinding gives a good relation especially for the long retention time of ash with 135 and 180 minutes grinding. For retention time up to 12 hours the fineness is 24% to 34% higher of 180 minutes grinding time in respect of 90 minutes grinding. And for 36, 48 and 60 hours retention the fineness of 180 minutes grinding is higher by only 9%, 10.5% and 6.9% respectively with respect to 90 minutes grinding. It is concluded from here that the fineness of ash largely depend on the retention time and 90 minutes girding is suitable for a prolonged retention time.

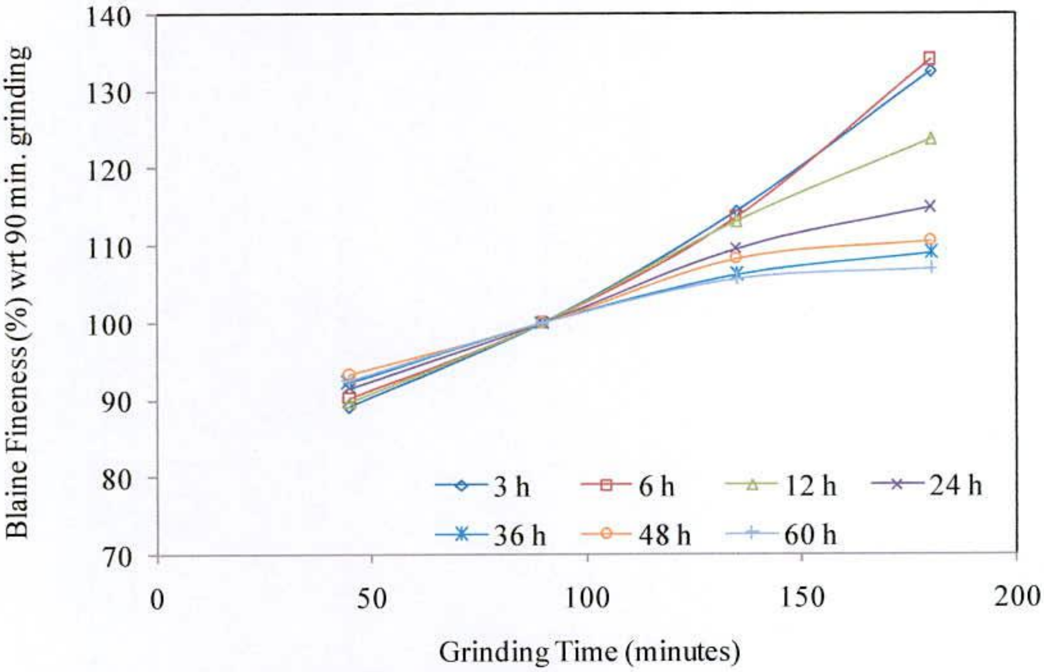


Figure 4.6: Blaine fineness with respect to 90 minutes grinding time

In case of the rate of ash collection after grinding and sieving operation, it was observed that the grinding time has no significant effect on the amount of ash production. Grinding time shows a remarkable effect on Blaine fineness. This is due to the RHA is turned into fine particles after initial grinding and subsequently finer due to prolonged grinding. If the size of the ash particles were not turned into fine at initial grinding time, might not further reduced at extended period of grinding. The physical appearances of the ash are shown in Figure 4.7.

From Figure 4.7 it is observed that the colour of ash was different. Colour of the ash was brighter in case of RHA 1 when it compared with RHA 2. It was observed in case of RHA 3 that the colour is directly depended upon ash retention time. The ash was blackish in colour up to 24 hours and the ash colour was changed to whitish from 36 hours retention time. Ash of 60 hours retention was whiter in colour than any other retention time. Blackish colour indicates the partial burning of the rice husk and generally unburnt carbon was present in the ash. Boating and Skeete (1990) stated that the whitish gray colour of the resulting ash was an indication of complete oxidation of the carbon in the ash.

RHA 1 RHA 2 RHA 3; 3h retention time

RHA 3; 6h retention time RHA 3; 12h retention time RHA 3; 24h retention time

RHA 3; 36h retention time RHA 3; 48h retention time RHA 3; 60h retention time

Figure 4.7: Physical appearance of the different RHA after grinding and sieving

4.1.3 Loss on Ignition

Normally, the ash contains some unburnt components and the unburnt component is predominantly carbon. The combustion process of rice husk has a significant influence on the carbon content of RHA. It was found from literature that the Loss on Ignition (LOI) of RHA varies from 1% to 35% (Velupillai, et al., 1997). It is typically obtained by reheating a sample of the ash in an oven. The difference in mass of the sample before and after heating is referred to as the Loss on Ignition. The LOI value is normally the same as the carbon content of ash. Loss on ignition affects on the performance of any materials. Different studies showed that the water demand of RHA blended cement was increased for the higher percentage of LOI values.

The loss on ignition for RHA 1, RHA 2 and RHA 3 with retention time of 36, 48 and 60 hours were determined. The loss on ignition of different ashes is present in Table 4.4.

Table 4.4: Loss on Ignition of different RHA

Description	Type of Rice Husk Ash				
	RHA 1	RHA 2	RHA 3		
			36 h	48 h	60 h
Loss on Ignition (%)	7.60	8.37	6.25	4.38	3.98

Table 4.4 shows that the highest LOI value of 8.37% was found for RHA 2 and the lowest value was 3.98% for RHA 3 for 60 hours retention time. According to ASTM C618-89, the maximum limit of LOI of a type N pozzolan for using as a mineral admixture in Portland cement is 10%. The results show that any of these three types of RHA can be used as cement replacing material.

4.1.4 Particle Size of RHA

The particle size distribution of Rice Husk Ash of laboratory incineration process (RHA 3) with 60 hours of retention time is shown in Figure 4.8. The ash was ground for 90 minutes in laboratory grinding mill and then sieved through sieve No. 200. It was observed that the fineness of this RHA 3 was more than two times of the OPC. This observation is quite similar to the Ganesan, et al. (2008).

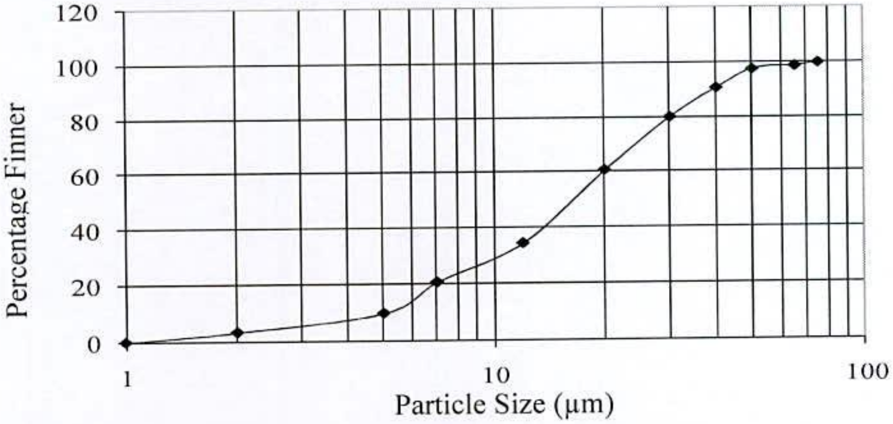


Figure 4.8: Particle size distribution of RHA 3 with 60 hours of retention

The particle size and texture of RHA 3 with 60 hours retention were analyzed with SEM and the observation is shown in Figure 4.9. It is clear from 500 and 2000 times magnification that the shape of the ash particle is angular in texture. The blackish portion of the SEM image is the base of the tape over which the ash particle was placed to complete the SEM analysis. A huge number of small particles are also observed in the SEM picture.

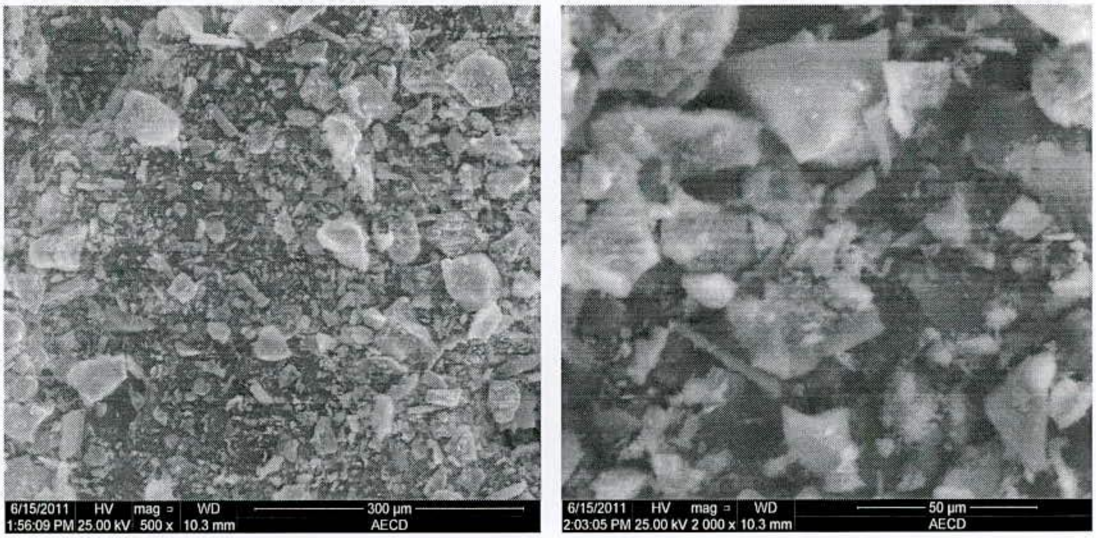


Figure 4.9: SEM image of RHA 3 of 60 hours of retention time

4.1.5 Characterization of RHA with XRD

XRD is a powerful technique for the qualitative and quantitative characterization of zeolite materials. XRD measurements can signify whether the catalyst is amorphous, crystalline, or quasi-crystalline, yield an estimate of average crystallite size, and yield *d*-spacing and lattice parameters, allowing identification of the present phases (Glusker, et.al., 1994). X-Ray diffractogram were acquired using Bruker D8 advance powder diffractometer with Cu-Kα as the radiation source with $\lambda = 1.5418$ Å at 40 kV and 40 mA. The sample was in fine powdered form lightly pressed to form a thin layer on sample holder. Samples were measured in the range of $2\theta = 10^{\circ} \sim 50^{\circ}$. The data analysis program automatically calculated the reflection position and *d* spacing.

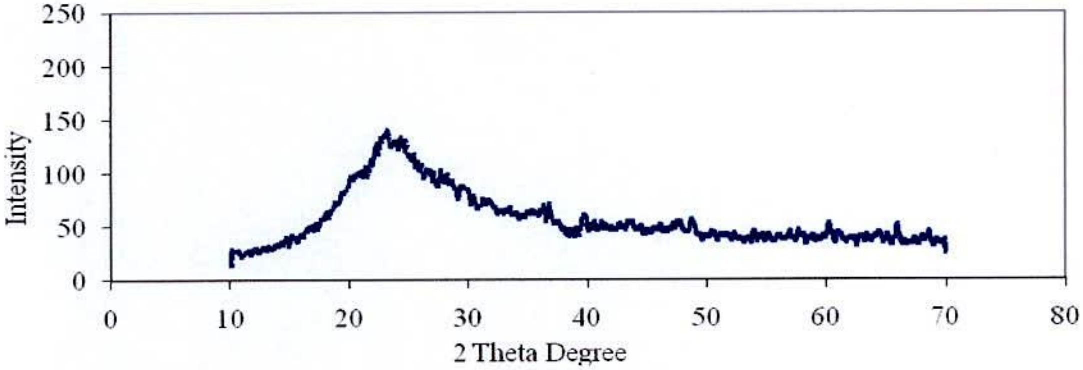
In case of all samples of rice husk ash, no sharp peak was observed in XRD analysis indicates that the ash is non crystalline form. The broad peak was found as Bragg 2θ angles are 23.21°, 26.07°, 25.51° and 23.43° for sample RHA 1, RHA 2, RHA 3 with 48 and 60 hours retention time correspondingly is shown in Figure 4.10. A rather broad peak spanning 2θ angle range of 18-30° which is characteristic of amorphous structures is observed. The XRD diffractogram of these RHA are in the range of $2\theta = 10°-70°$. Figure 4.10 shows XRD analysis of all samples.

Mehta (1979) reported that the noncrystalline silica can be formed by extended-time ignition at temperatures bellow 500°C in oxygen-rich atmosphere or by ignition at up to 680°C for less than 1 minute. However, the literature is departing on these values. Yeoh, et al. (1979) states that the noncrystalline silica is produced by ignition at up to 900°C for less than 1 hour and crystalline silica is obtained by ignition at 1000°C for less than 5 minutes (Della, et al., 2001). Researchers from India and Europe (Feng, et al., 2004; James and Rao, 1986) argued that the minimum ignition temperature must reach at least 402°C for the entire ignition of the organic portion of the rice husk to release the silica. In this research work ash sample of RHA 1 had faced maximum burning temperature of 405°C. Peak temperature for RHA 3 was observed 663.6°C and for RHA 2 was found 650°C to 730°C. From Figure 4.10 it is found that there is no sharp peak and the broad hump at 2θ is around 23° indicates these ashes are in amorphous stage.

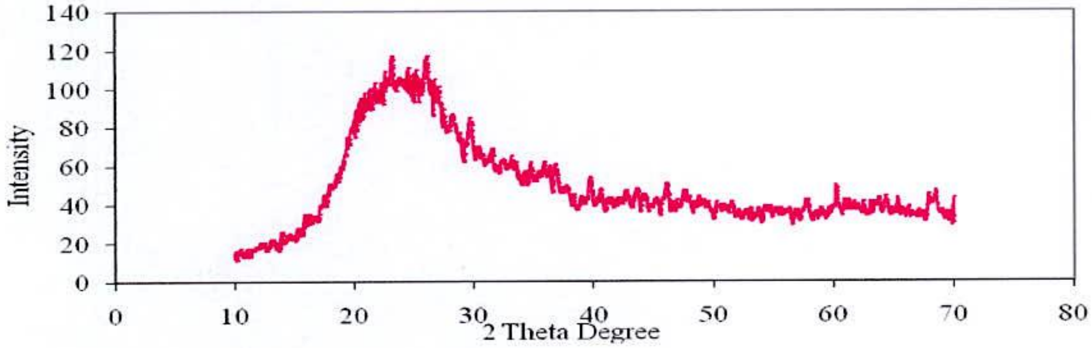
After chemical analysis it was found that the SiO_2 is 91.43% and the others compositions are shown in Table 4.5.

Table 4.5: Chemical Composition of RHA 3 for 60 hours retention time

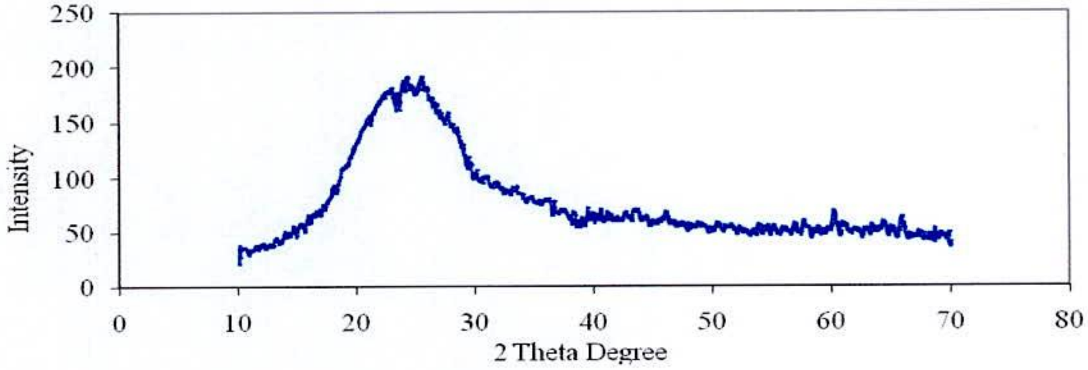
Constituents	% Composition
Fe_2O_3	1.28
SiO_2	91.43
Al_2O_3	0.76
CaO	0.91
MgO	1.12
L.O.I.	3.98



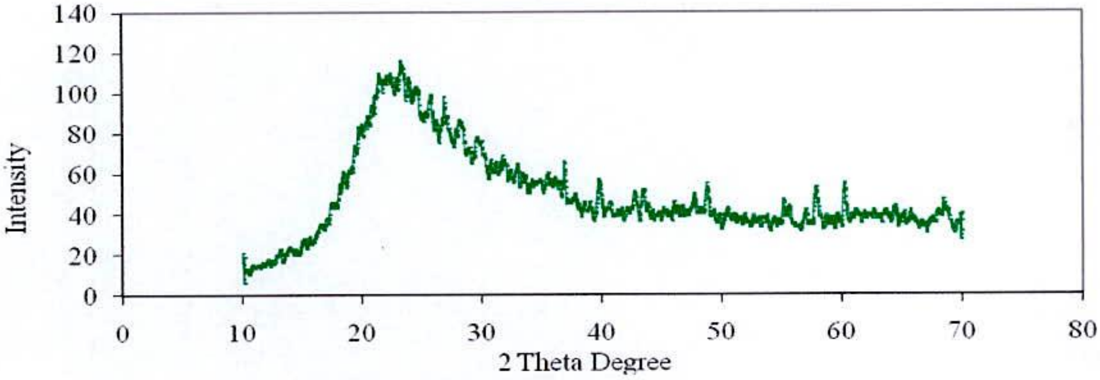
(a) XRD of RHA 1



(b) XRD of RHA 2



(c) XRD of RHA 3 - 48h



(d) XRD of RHA 3 – 60h

Figure 4.10: XRD analysis of RHA samples

Sample of rice husk ash (RHA 3) obtained from 60 hours retention time in accumulation chamber was whitish in colour. The silica content in RHA is 91.43%. Whereas, the percentage of LOI of RHA was about 3.86, represents the loss of volatile organic compounds and adsorbed water on the ash. Several researchers reported that RHA also consists of trace elements like Fe_2O_3, CaO, MgO, Na_2O, K_2O, and MnO (Chen and Yeoh, 1992; James and Subba, 1986). Some others elements except SiO_2 was observed in this RHA and shown in Table 4.5.

According to ASTM C618-89 requirements for a Type N Pozzolan for using as a mineral admixture in Portland cement concrete describe that the minimum amount of sum of SiO_2, Al_2O_3, and Fe_2O_3 is about 70%. From Table 4.5 it is observed that the sum of SiO_2, Al_2O_3 and Fe_2O_3 is 93.47%. This value is more than the minimum amount which confirm the material can act as a pozzolanic one.

4.2 MECHANICAL PROPERTIES AND PERFORMANCE OF MORTAR

4.2.1 Water Requirement for Constant Workability

The mortar samples were prepared with different ashes with various proportion exhibited different water requirement for constant workability. Flow table test provided the water requirement for constant workability. It was observed that the RHA 1 which was collected from open heap burning system needs more water than others two ashes.

The water requirement for constant workability of RHA 2 was also determined by flow table test. The results of RHA 1 and RHA 2 are presented in Figure 4.11.

The mortar contained 25% or more RHA 1 and RHA 2 exhibits cracks after 25 blows on flow table. Water requirement was increased by 32% and 34.4% for 20% replacement levels for RHA 1 and RHA 2 respectively. From Figure 4.11, it was observed that the water requirements for RHA 1 and RHA 2 followed an increasing trend with increase of RHA to fulfil the standard flow values according to ASTM C230.

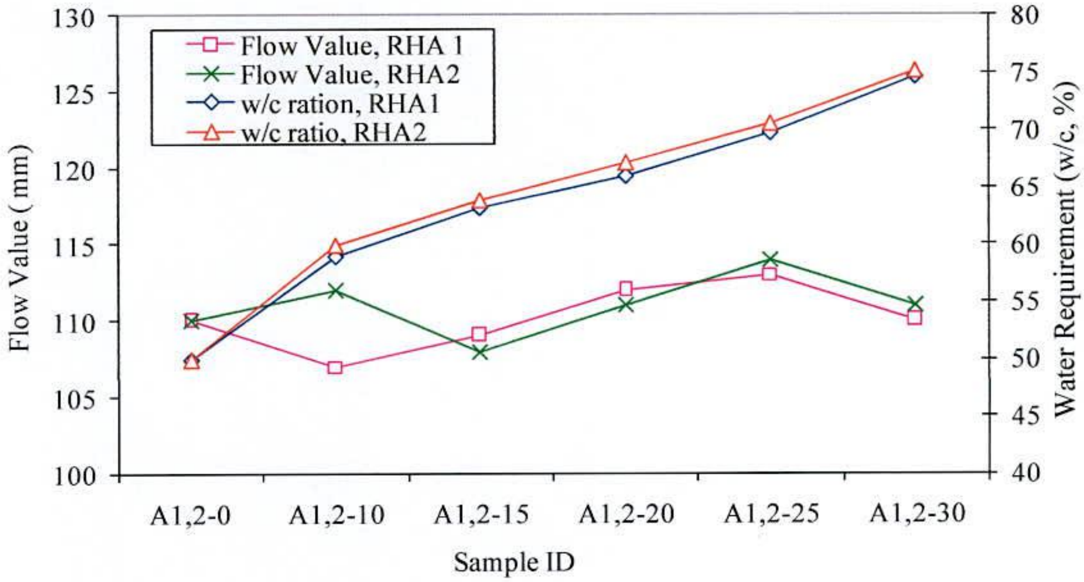


Figure 4.11: Water requirement for standard flow value of RHA 1 and RHA 2

Regarding the retention time and fineness have already presented in Table 4.3. The ashes of 36, 48 and 60 hours retention time with 90 minutes laboratory grinding were selected for finding out the water requirement to maintain the constant flow value. The water requirement for the standard flow value is shown in Figure 4.12 using the RHA 3 with retention time of 36, 48 and 60 hours.

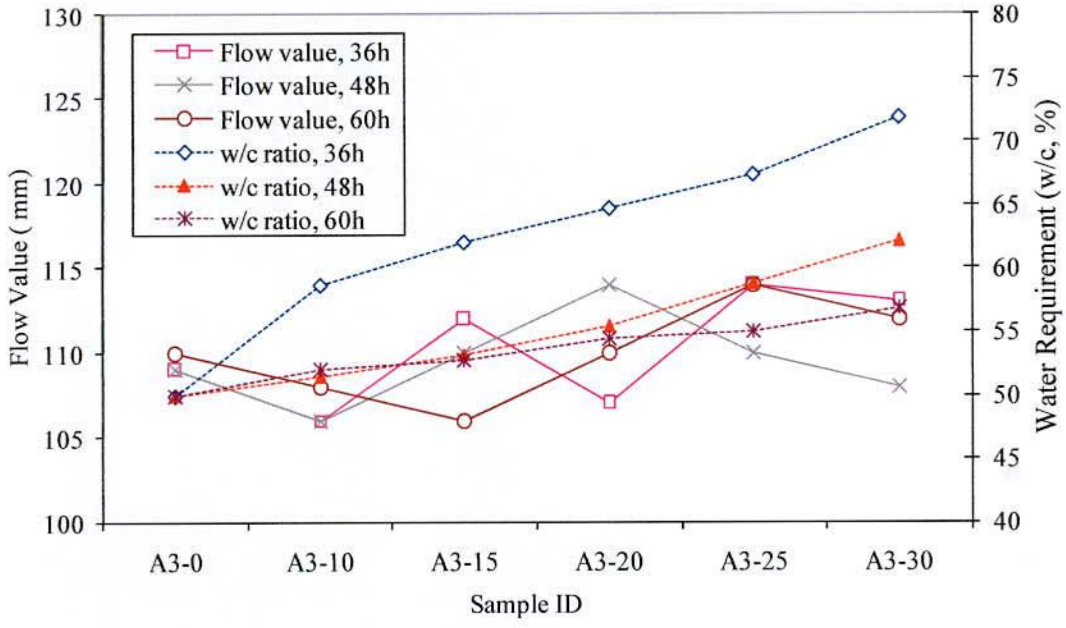


Figure 4.12: Water requirement for standard flow value of RHA 3

From the Figure 4.11 and 4.12 it was observed that the RHA 1, RHA 2 and RHA 3 of 36 hours of retention exhibited cracks at the time of flow table test with the replacement level of 25 and 30% (More results are presented in Annexure-A: Table A-1, A-2 and A-3). The Blaine fineness of ash RHA 1 and RHA 2 was very close to the cement fineness of 3264 cm^2/gm. The losses on ignition of these two ashes were also higher. Nehdi, et al. (2003) stated that the RHA is finer than cement and should be expected to play not only a pozzolanic role but also a microfiller effect to enhance the particle packing density of concrete.

In Figure 4.12, it is observed that water requirements of 48 and 60 hours ash are quite similar up to 20% replacement levels. The water requirement of 48 hours ash shows higher than the 60 hours ash at 25 and 30 % replacement levels. The ash of 36 hours of retention shows quite similar water requirement of RHA 1 and RHA 2. The flow value in all cases of retention times are considered within the standard range of 110±5 mm for RHA 3. From the above discussion it can be summarized that the ashes with retention time of 48 and 60 hours exhibit better results compared to other ashes.

The Blaine fineness is one of the important parameter for ash quality. It was observed that at 90 minutes grinding time the fineness of 60 hours ash was 25% higher than that of 48h ash. Therefore, the ash with 60 hours retention time is more suitable as cement replacing material in context of Blaine fineness, Loss on Ignition and workability. The Rice Husk Ash of 60 hours retention time designated as 'A3' was used for finding out the rheology of cementitious materials.

Rheology of cementitious materials is mostly defined by means of its flow characteristics, plastic viscosity (μ) and yield stress required to make flow (Hu and Larrard, 1996). It was considered enough to use an engineering approach for characterizing rheological properties of cementitious materials such as (flow time, slump and compacting density) to categorize the mixtures in terms of workability and to find out the amount of energy requisite to get a definite degree of compaction (Daczko, 2000; Hu and Larrard, 1996). Therefore, the rheology of OPC-RHA matrix in various levels of applied external stresses was analyzed in this study by means of flow table apparatus. This was done by measuring the instant flowability of OPC-RHA mixtures at definite uninterrupted number of blows. The number of blows were generated by the flow table was considered as an indicative parameter for the applied external stress on the samples to make it flow. The outcomes of this investigation are shown in Figure 4.13 in which the relationship between the number of blows and the corresponding immediate flowability of OPC along with rice hush ash, A3 having a range of 0 to 30% is plotted.

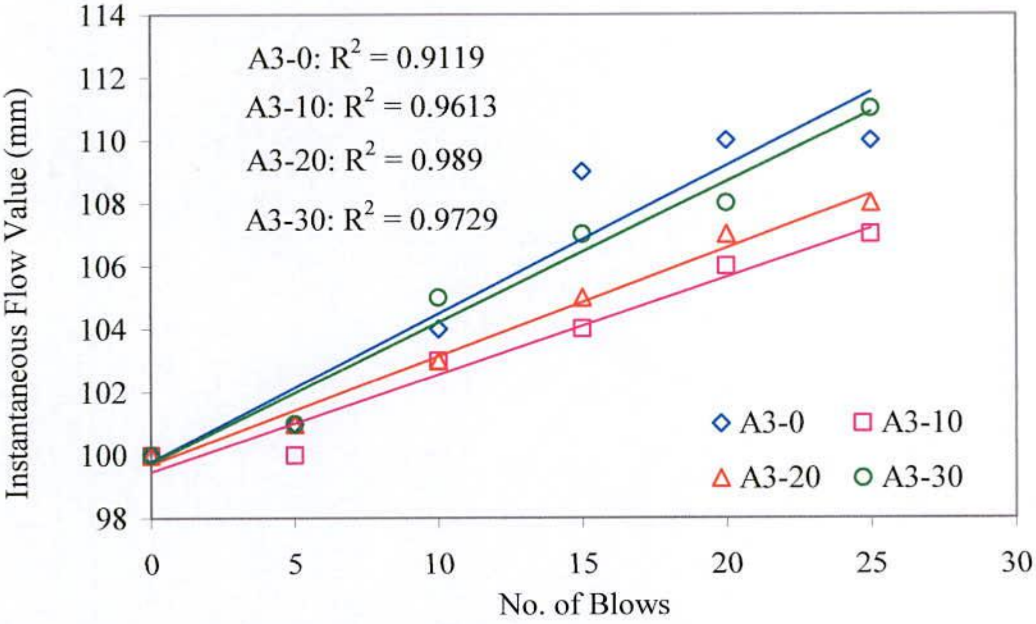


Figure 4.13: Instantaneous Flowability of mortar with external applied stresses

Figure 4.13 shows that a straight comparative correlation among the number of blows (applied external stress) and the consequence flowability of OPC-RHA mixture is established. These correlations appear to be more linear for OPC-RHA mixtures when evaluated to the controlled specimen. The correlation factors (R^2) of the trend-line are 0.9119 for controlled sample and 0.9613, 0.989, 0.9729 for OPC replaced by A3 at 10%, 20% and 30% respectively. This means that the addition of A3 in OPC mixes can change its behaviour under external applied stresses.

It also appears that this obtained relationship is quite similar to that shown in Bingham's material model. The intercept of the best-fit lines with the instant flow axis can be referred to yield stress (S_y), and the slopes of these trend-lines (θ') can be related to the plastic viscosity (μ). Both S_y and θ' are indicative qualitative measures for characterizing the rheological parameters of cementitious materials having RHA. Consequently, the values of θ' were estimated and found to be 27.8, 18.6, 20.0 and 26.1 for 0%, 10%, 20% and 30% of A3 addition in the mix respectively. It is also shown in the Figure 4.13 that the value of S_y is decreased with increasing A3 content up to 20% and for 30% of A3 the S_y value is close up to the controlled sample. These results pointed out that the rheological parameters (plastic viscosity and yield stress) of the cementitious material possibly altered due to the addition of rice husk ash.

4.2.2 Consistency and Setting Time

The percentage of cement substitute level by different Rice Husk Ash (RHA) against standard consistency is shown in Figure 4.14. The figure points out that the water requirement for standard consistency linearly raises with an increase of cement replacement levels by RHA and this is true for all types of ashes. As ashes are hygroscopic in nature and the specific surface area of RHA is higher than cement, it needs more water. Similar observation was found by Ganesan, et al. (2008).

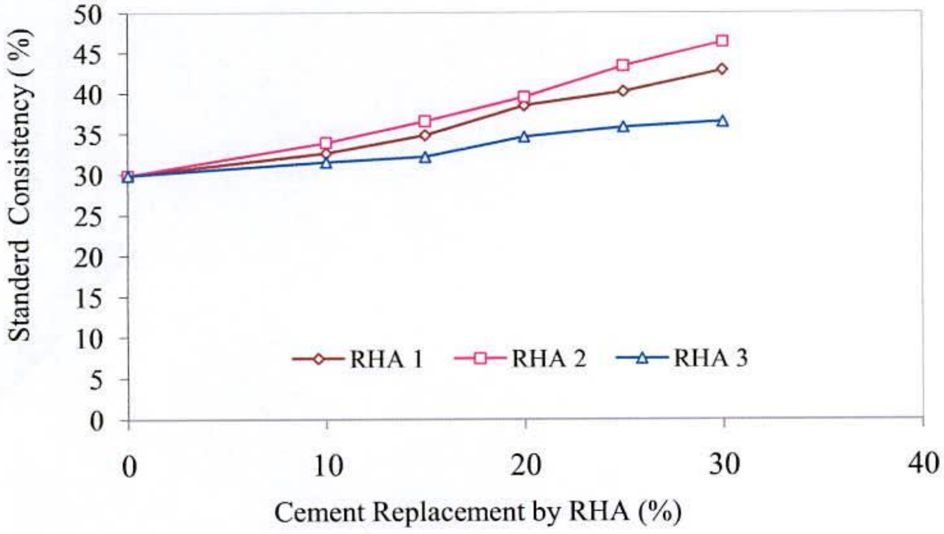


Figure 4.14: Standard consistency of RHA blended cement

The effect of addition of RHA on the initial and final setting time is shown in Figure 4.15. It is observed that the initial setting time increases with the addition of all type of RHA. The maximum initial setting time is observed at 10%, 20% and 15% replacement levels for RHA 1, RHA 2 and RHA 3 respectively. After reaching the maximum initial setting time at different replacement levels, all the samples exhibit a decreasing tendency in initial setting time. The initial setting time for all types of RHA blended cement up to 30% replacement levels is higher than the controlled samples.

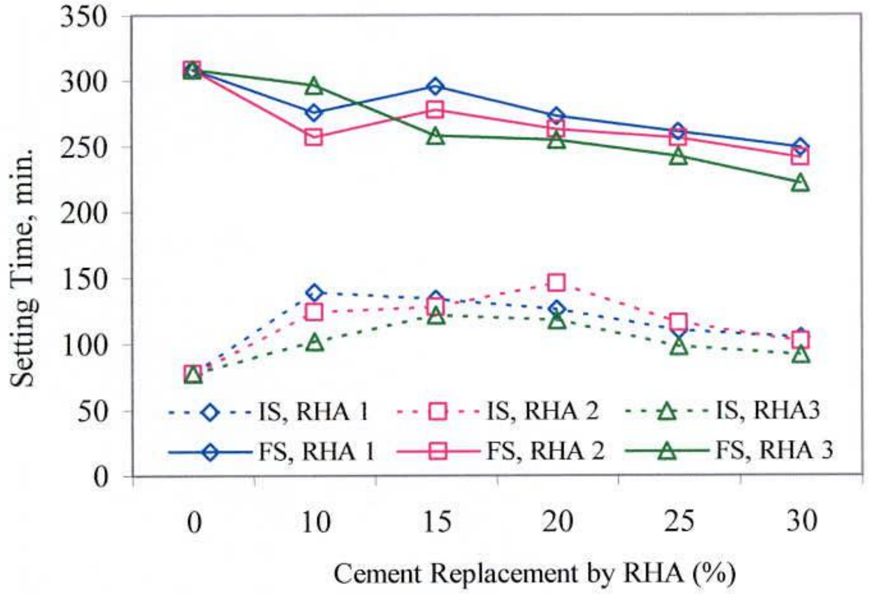


Figure 4.15: Initial setting (IS) and final setting (FS) time of RHA blended cement

On the other hand the final setting time declines with the increase of all types of RHA up to 30%. The final setting time observed for controlled specimen is 309 min. and the samples with maximum replacement levels (30%) was found to be 249, 241 and 222 minutes for RHA 1, RHA 2 and RHA 3 respectively. These values were well within the permissible limits as per ASTM C191. Ganesan et al. (2008); Bhanumathidas and Mehta (2004) and Cook (1986) also made similar observations.

4.2.3 Heat of Hydration

The rate of hydration directly influences the workability, setting behaviour, strength gaining rates and formation of pore structure of the cement mortar. The hydration was determined by measuring the generated heat by the calorimetric test. Test was performed to determine the effect of RHA addition as a replacing material of

Ordinary Portland Cement on cement hydration. The attainment of maximum temperature was delayed due to the addition of RHA.

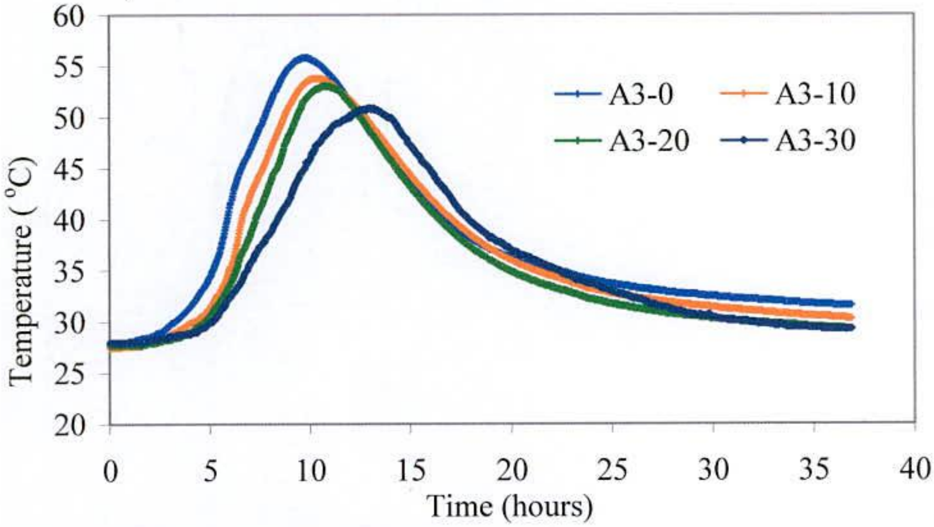


Figure 4.16: The variation of temperature with time due to hydration of cement past

The turning point for control sample and sample with 10, 20 and 30% RHA were 2.57, 3.68, 4.43 and 4.98 hours respectively. From this observation it is evident that the dormant period was prolonged due to addition of RHA in cement. The cementitious materials is flowable in dormant period which generally less than 5 hours. In this study the cement paste with 30% RHA exhibited maximum dormant period of 4.98 hours.

After dormant period, acceleration period started and heat is generated rapidly. The slope of the curve shows the rapidity of heat generation. It is found in Figure 4.16 that control sample and sample with 10% and 20% replacement levels observed same slope of 67.2°. Sample with 30% RHA exhibits 64.7° slope. The rate of heat generation for sample with 30% replacement levels is slower than other samples.

The maximum peak temperature of 27.9°C was found to the control sample at 9.83 hours from the time of water addition. The maximum temperatures were observed to be 26.3°C, 25.3°C and 23.7°C for the sample with 10%, 20% and 30% RHA at 10.26, 10.78 and 13 hours respectively. The sharpness of the peak was observed for control sample. The sharpness of the peak is gradually lost due to the addition of RHA.

Area developed under the temperature curve up to 37 hours of hydration period was the highest for the control sample among all other samples. The area under hydration curve was 468 unit for control sample while 432, 348 and 327 units for the samples with 10, 20 and 30% RHA.

The cumulative heat of hydration is shown in Figure 4.17. The development of cumulative heat of hydration of mortar decreased with the increase of RHA addition. The highest heat of hydration of 5692 kJ was developed for control sample. Conversely, the lowest value was obtained for mortar sample with 30% RHA.

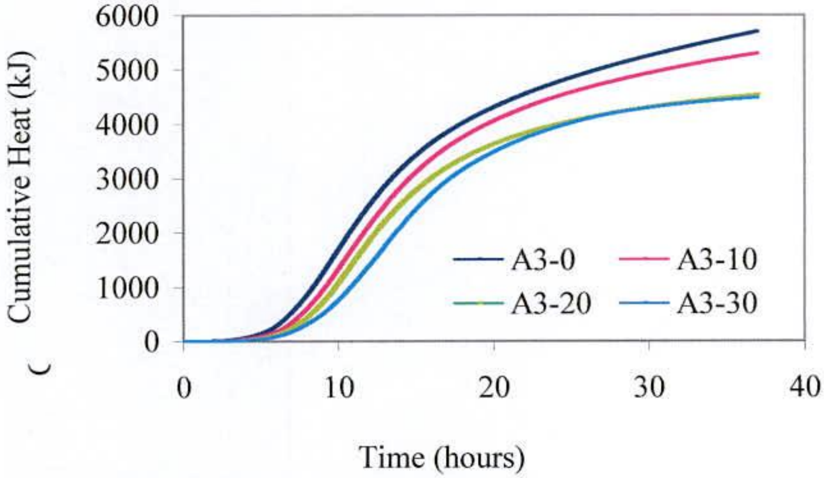


Figure 4.17: The effect of RHA addition on heat of hydration of cement paste

4.2.4 Compressive Strength

One of the most important properties of cementitious materials is its compressive strength. Numerous researchers tried to utilize Rice Husk Ash as a cement replacing materials. All the RHA used previously were collected or manufactured from controlled combustion system. Zhang and malhotra (1996) and Isamil and Waliuddin (1996) tried to investigate the effect of RHA addition in concrete as partial replacement of cement on compressive strength and observed a good relationship between the strength and replacement levels.

The compressive strengths of the prepared samples with different RHA were tested initially at 7, 28, 90 and 350 days. The suitable type of RHA was selected on the basis of compressive strength of 7, 28, 90 and 350 days. The selected type of RHA was used at various percentage of replacement to determine the long time strength at 600 and 900 days. The durability was investigated depending upon the results of compressive strength at different ages. The strength of mortar specimen prepared from OPC, RHA 1 and two different types of sand (ASTM Standard Graded Sand mentioned as S1; and local sand with FM 2.73 mentioned as S2) are given in Table 4.6(a) and 4.6(b).

Table 4.6(a): Compressive strength of mortar with RHA 1 and sand type S1

	Strength, MPa											
	7 Days			28 Days			90 Days			350 Days		
Sample ID	Strength	Average	% wrt. control	Strength	Average	% wrt. control	Strength	Average	% wrt. control	Strength	Average	% wrt. control
A1-0	27.14			33.77			36.96			39.55		
	26.19	26.16	100	33.17	33.08	100	36.10	35.75	100	37.22	37.82	100
	25.16			32.31			34.20			36.70		
A1-10	7.58			13.78			14.65			15.85		
	7.24	7.29	27.9	13.18	13.30	40.2	13.61	13.90	38.9	14.47	14.93	39.5
	7.06			12.92			13.44			14.47		
A1-15	7.41			13.61			19.38			16.89		
	6.89	7.06	27.0	13.35	13.15	39.8	18.52	18.55	51.9	15.68	16.05	42.4
	6.89			12.49			17.75			15.59		
A1-20	7.67			13.78			18.09			14.90		
	7.32	7.35	28.1	13.78	13.53	40.9	17.23	17.40	48.7	14.13	14.27	37.7
	7.06			13.01			16.89			13.78		
A1-25	5.94			12.06			14.82			13.61		
	5.69	5.77	22.1	11.20	11.49	34.7	14.30	14.30	40.0	13.44	13.21	34.9
	5.69			11.20			13.78			12.58		
A1-30	5.17			8.53			10.86			10.68		
	5.08	5.03	19.2	8.44	8.30	25.1	10.25	10.37	29.0	9.82	10.11	26.7
	4.82			7.93			9.99			9.82		

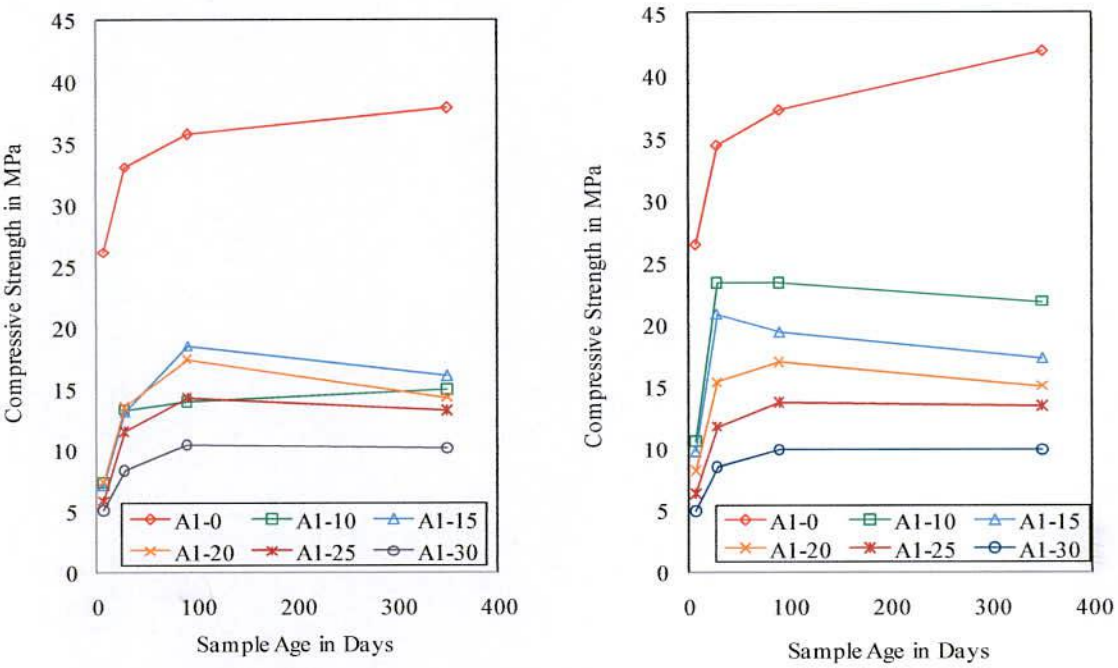
Table 4.6 (b): Compressive strength of mortar with RHA 1 and sand type S2

	Strength, MPa											
	7 Days			28 Days			90 Days			350 Days		
Sample ID	Strength	Average	% wrt. control	Strength	Average	% wrt. control	Strength	Average	% wrt. control	Strength	Average	% wrt. control
A1-0	27.22	26.42	100	35.93	34.38	100	38.43	37.19	100	43.68	41.93	100
	26.19			33.77			37.74			41.18		
	25.85			33.43			35.41			40.92		
A1-10	11.03	10.54	39.9	24.12	23.38	68.0	24.73	23.35	62.8	22.83	21.85	52.1
	10.51			23.43			22.74			21.71		
	10.08			22.57			22.57			21.02		
A1-15	9.99	9.68	36.6	21.54	20.85	60.7	19.99	19.38	52.1	18.09	17.29	41.2
	9.82			21.02			19.56			17.06		
	9.22			19.99			18.61			16.71		
A1-20	8.44	8.10	30.7	16.11	15.34	44.6	17.83	16.97	45.6	15.51	15.02	35.8
	7.93			14.99			16.71			15.16		
	7.93			14.90			16.37			14.39		
A1-25	6.55	6.26	23.7	12.23	11.75	34.2	14.39	13.73	36.9	13.96	13.44	32.1
	6.20			11.72			13.53			13.61		
	6.03			11.29			13.27			12.75		
A1-30	5.00	4.88	18.5	8.79	8.44	24.6	10.34	9.94	26.7	10.25	9.91	23.6
	5.00			8.27			9.82			9.99		
	4.65			8.27			9.65			9.48		

Table 4.6 (a) and 4.6 (b) show that the addition of RHA 1 in all replacement levels exhibit lower compressive strength than the control sample at 7, 28, 90 and 350 days. Compressive strength of control sample with standard sand at 28 days was 33.08 MPa (4800 psi) while the maximum strength was found to be 13.53 MPa (1963 psi) for 20% replacement levels which is 40% of the control sample strength. The strength of all samples having RHA 1 at 90 days was higher than 28 days but still lower than the strength of control sample. The strengths of all samples having

RHA 1 reduced at 350 days compared to 90 days strength except A1-10 sample. However, the compressive strength was in increasing nature for the control sample.

The compressive strength of controlled sample with S2 followed the same trend as S1. However, the trend of compressive strength for the samples with different percentage of RHA 1 did not follow the trend of compressive strength with S1. It is observed that the maximum strengths for A1-10 and A1-15 were at 28 days while for A1-20, A1-25 and A1-30 were at 90 days. The compressive strength in all cases was lower than the strength of control sample. It is also observed that in all replacement levels and ages, samples with sand type S2 exhibit higher strength than sand type S1.



(a) Sand S1

(b) Sand S2

Figure 4.18: Compressive strength with respect to control specimen at different ages (RHA1)

In Figure 4.18 it is observed that at 28 days strength the samples of 10 and 15% replacement levels exhibit higher values than any other days and this is valid only when sand type S2 (Local sand of FM 2.73) and RHA 1 was used. At later age (350 days) it is observed that samples with all replacement levels show lower compressive strength than 28 and 90 days results. The control samples exhibits higher strength than any other samples in all ages.

The strength of mortar specimen prepared from OPC, RHA 2 and two different types of sand S1 and S2 are given in Table 4.7 (a) and 4.7 (b).

Table 4.7 (a): Compressive strength of mortar with RHA 2 and stand type S1

	Strength, MPa											
	7 Days			28 Days			90 Days			350 Days		
Sample ID	Strength	Average	% wrt. control	Strength	Average	% wrt. control	Strength	Average	% wrt. control	Strength	Average	% wrt. control
A2-0	27.14			33.77			36.96			39.55		
	26.19	26.16	100	33.17	33.08	100	36.10	35.75	100	37.22	37.82	100
	25.16			32.31			34.20			36.70		
A2-10	11.37			22.23			21.54			19.30		
	11.11	11.11	42.5	21.37	21.42	64.8	20.50	20.68	57.8	18.95	18.72	49.5
	10.86			20.68			19.99			17.92		
A2-15	12.49			19.64			20.33			19.30		
	12.06	12.15	46.4	18.26	18.67	56.4	19.13	19.36	54.1	18.61	18.55	49.1
	11.89			18.09			18.61			17.75		
A2-20	11.89			17.92			18.01			17.58		
	11.72	11.72	44.8	17.75	17.52	53.0	16.89	17.20	48.1	16.54	16.77	44.3
	11.54			16.89			16.71			16.20		
A2-25	10.86			15.94			14.65			15.16		
	10.68	10.51	40.2	14.65	15.08	45.6	14.30	14.19	39.7	14.30	14.53	38.4
	9.99			14.65			13.61			14.13		
A2-30	9.30			12.58			12.41			11.37		
	8.62	8.85	33.8	11.80	12.03	36.4	12.06	12.00	33.6	10.68	10.74	28.4
	8.62			11.72			11.54			10.17		

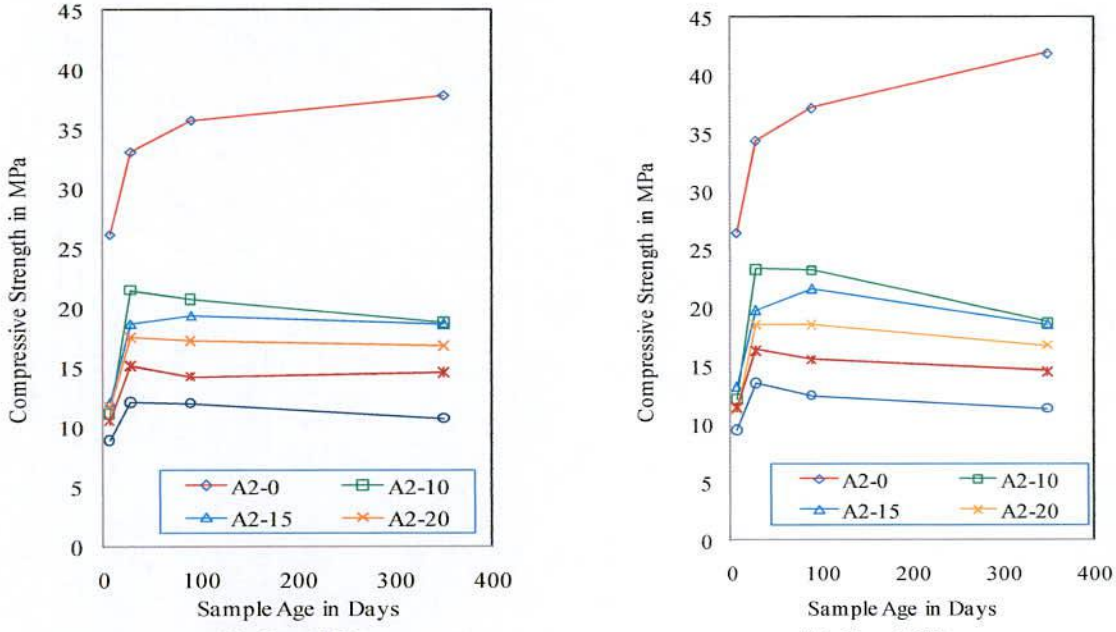
Table 4.7 (a) represents that the compressive strengths of mortar with RHA 2 in all replacement levels for sand type S1 were lower than the control sample. The sample with 10% RHA 2 shows higher strength at 90 days among the sample having

RHA 2. The compressive strength reduced in all replacement levels after 90 days. The control sample always exhibits higher strength than other samples. These observations are also true for the samples using sand type S2 which is presented in Table 4.7 (b).

Table 4.7 (b): Compressive strength of mortar with RHA 2 and sand type S2

	Strength, MPa											
	7 Days			28 Days			90 Days			350 Days		
Sample ID	Strength	Average	% wrt. control	Strength	Average	% wrt. control	Strength	Average	% wrt. control	Strength	Average	% wrt. control
A2-0	27.22			35.93			38.43			43.68		
	26.19	26.42	100	33.77	34.38	100	37.74	37.19	100	41.18	41.93	100
	25.85			33.43			35.41			40.92		
A2-10	12.66			24.12			24.30			19.30		
	12.06	12.18	46.1	23.35	23.32	67.8	23.09	23.20	62.4	18.95	18.72	44.7
	11.80			22.49			22.23			17.92		
A2-15	13.87			20.33			22.23			19.30		
	13.10	13.24	50.1	20.16	19.76	57.5	21.88	21.57	58.0	18.61	18.55	44.2
	12.75			18.78			20.59			17.75		
A2-20	11.80			19.13			19.30			17.58		
	11.03	11.23	42.5	18.70	18.52	53.9	18.52	18.52	49.8	16.54	16.77	40.0
	10.86			17.75			17.75			16.20		
A2-25	11.80			16.71			16.37			15.16		
	11.20	11.40	43.2	16.54	16.40	47.7	15.34	15.59	41.9	14.30	14.53	34.7
	11.20			15.94			15.08			14.13		
A2-30	9.91			13.78			13.01			11.98		
	9.48	9.51	36.0	13.78	13.58	39.5	12.23	12.49	33.6	11.03	11.40	27.2
	9.13			13.18			12.23			11.20		

The variation of compressive strength of mortar prepared with varying percentage of RHA 2 is presented in Figure 4.19. It is observed that at 28 days strength the sample of 10% replacement exhibits maximum compressive strength among the samples having RHA 2 as a replacement material. And this is only 67.8% strength with respect to the control sample at the same days. After 28 days all results show lower values. At 90 and 350 days it is observed that samples with all replacement levels show lower compressive strength than 28 days results. In all ages the control samples exhibit higher strength than any other samples. Numerous researchers already argued that the addition of RHA in cement shows better performance on compressive strength up to a certain levels (Ganesan, et al., 2008; Dakroury and Gasser, 2008; Gastaldini, et al., 2007; Feng, et al., 2004; Nehdi, et al., 2003; Mahmud, et al., 1996; Zhang, et al., 1996). The RHA which was used by these researchers was produced from controlled combustion process. In this study it may be concluded that RHA produced from open heap burning system and from the conventional milling system have no noticeable and acceptable performance on cement mortar. Therefore, further investigation is considered to be insignificant for RHA 1 and RHA 2 because strength is the major properties of the cementitious materials.



(a) Sand S1 (b) Sand S2

Figure 4.19: Compressive strength with respect to control specimen at different ages (RHA 2)

The strength of mortar specimen prepared from OPC, RHA 3 and two different types of sand S1 and S2 are given in Table 4.8 (a) and 4.8 (b). RHA 3 with 60 hours retention time is designated as "A3".

Table 4.8 (a): Compressive strength of mortar with RHA 3 and sand type S1

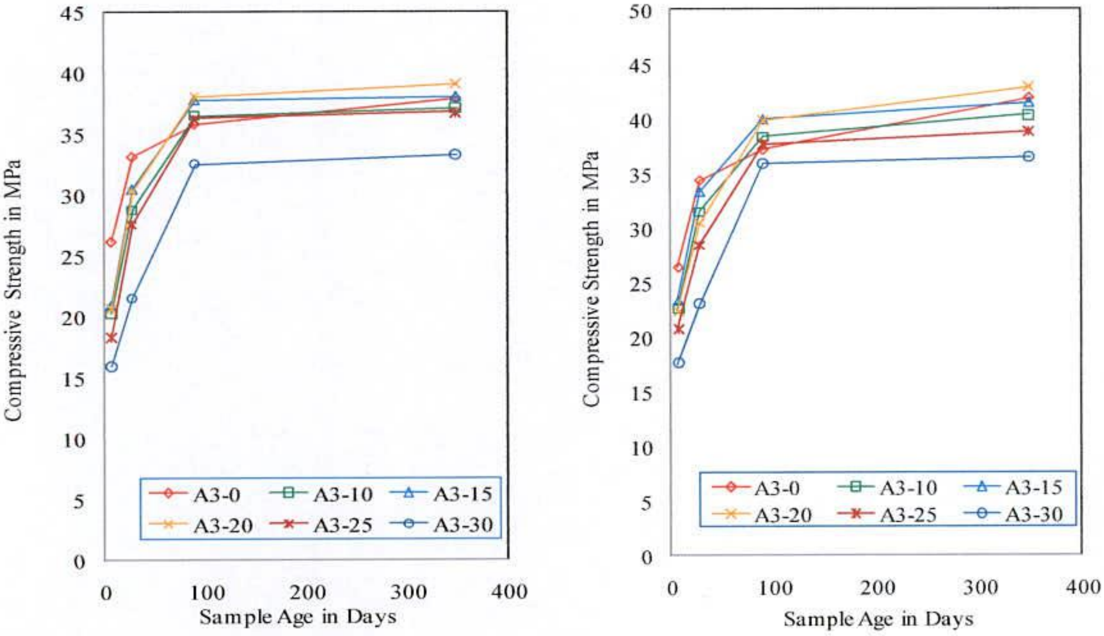
	Strength, MPa											
	7 Days			28 Days			90 Days			350 Days		
Sample ID	Strength	Average	% wrt. control	Strength	Average	% wrt. control	Strength	Average	% wrt. control	Strength	Average	% wrt. control
A3-0	27.14	26.16	100	33.77	33.08	100	36.96	35.75	100	39.55	37.82	100
	26.19			33.17			36.10			37.22		
	25.16			32.31			34.20			36.70		
A3-10	20.85	20.28	77.5	29.64	28.78	87.0	37.91	36.50	102.1	38.94	37.10	98.1
	20.68			28.86			36.44			36.53		
	19.30			27.83			35.15			35.84		
A3-15	21.54	20.94	80.0	31.02	30.47	92.1	39.80	37.74	105.6	39.80	37.99	100.5
	21.19			30.67			36.70			37.48		
	20.07			29.72			36.70			36.70		
A3-20	21.28	20.59	78.7	30.84	30.30	91.6	40.15	38.08	106.5	40.92	39.09	103.3
	20.85			30.58			37.05			38.25		
	19.64			29.46			37.05			38.08		
A3-25	19.13	18.21	69.6	28.86	27.54	83.2	38.08	36.21	101.3	37.74	36.76	93.0
	17.92			26.88			35.24			37.05		
	17.58			26.88			35.32			35.50		
A3-30	16.28	15.88	60.7	22.06	21.48	64.9	34.12	32.51	90.9	34.46	33.26	84.1
	16.02			21.88			32.05			33.17		
	15.34			20.50			31.36			32.14		

In case of RHA 3 the compressive strength of mortar with S1 significantly improved compare to RHA 1 and RHA 2. It is observed from Table 4.8 (a) that at 7 days the maximum strength for sample having RHA 3 is observed 80.03% of the control sample strength for 15% replacement levels and at 28 days that is 92.10% of the control sample for the same replacement levels. At 90 days of sample age the control sample having lower strength than the sample with RHA 3 addition up to 20%. In this age the maximum strength was observed at 20% replacement levels and this strength is 6.4% higher than the control sample. At 350 days the samples having RHA 3 is still in increasing trend but the rate is slower than the control sample. At this age samples having 15% and 20% replacement levels show higher compressive strength than the control sample. Samples with other replacement levels show lower strength than the control sample.

Table 4.8 (b): Compressive strength of mortar with RHA 3 and sand type S2

	Strength, MPa											
	7 Days			28 Days			90 Days			350 Days		
Sample ID	Strength	Average	% wrt. control	Strength	Average	% wrt. control	Strength	Average	% wrt. control	Strength	Average	% wrt. control
A3-0	27.22	26.42	100	35.93	34.38	100	38.43	37.19	100	43.68	41.93	100
	26.19			33.77			37.74			41.18		
	25.85			33.43			35.41			40.92		
A3-10	23.35	22.57	85.4	32.31	31.50	91.6	40.41	38.40	103.2	41.27	40.38	96.3
	22.57			31.88			37.56			41.10		
	21.80			30.33			37.22			38.77		
A3-15	24.30	23.41	88.6	34.63	33.31	96.9	42.04	39.92	107.3	43.16	41.44	98.8
	23.43			33.08			38.94			41.18		
	22.49			32.22			38.77			39.98		
A3-20	23.52	22.40	84.8	31.36	30.47	88.6	41.35	39.86	107.2	44.80	42.93	102.4
	22.14			30.33			39.46			42.47		
	21.54			29.72			38.77			41.53		
A3-25	21.37	20.71	78.4	29.46	28.43	82.7	39.20	37.71	98.4	40.75	38.88	86.2
	20.85			28.26			37.74			38.43		
	19.90			27.57			36.18			37.48		
A3-30	18.35	17.60	66.6	23.69	23.00	66.9	37.48	35.90	93.9	37.91	36.47	80.0
	17.58			23.26			35.24			36.18		
	16.89			22.06			34.98			35.32		

It is observed that the sample having sand type S2 shows same trend of strength as sample having sand type S1. In this case the strength has little variation from the results shown in Table 4.8 (a). The variation of compressive strength is shown in Figure 4.20.



(a) Sand S1 (b) Sand S2

Figure 4.20: Compressive strength with respect to control specimen at different ages (RHA 3)

In Figure 4.20, it is observed that at 7 and 28 days strength of the control sample showed higher strengths than the samples having RHA 3 in different percentages and also for different sand types. Sample of 90 days of curing up to 20% replacement levels of OPC by RHA 3 showed higher compressive strength than the control sample. At 350 days the compressive strength having 15% and 20% RHA 3 exhibited higher values than the control sample. The nature of strength in presence of RHA 3 was quite different from RHA 1 and RHA 2. Although the samples with 10%, 25% and 30% replacement levels showed lower strength compared to the control sample but still they were in increasing trend when compared to their strength at previous ages.

The strengths of control sample was lower than others samples with the replacement levels of 10%, 15%, and 20% of OPC by RHA 3 at 90 days curing. The results indicated that up to 20% replacement levels of OPC by RHA 3 have good performance at 90 days. At 350 days the control sample showed still lower value than the samples having 15% and 20% of RHA 3. But for sample having 10% replacement levels exhibited lower value than the control one, though it showed higher at 90 days time. This observation is quite similar to Feng, et al. (2004). According to the findings obtained by Gastaldini, et al. (2007) on compressive strength of RHA concrete with 20% rice husk ash and 0.50 w/c ratio provided same strength of control sample at 7 days and, compressive strength at 28 and 91 days were higher than those of the control samples.

Same results are also shown in Figure 4.18 (b) for 7 and 28 days strength, where the samples were prepared from OPC, RHA 3 and sand S2. At 90 days all samples having RHA 3 except the 30% replacement levels exhibited higher strength than the control sample. At the age of 350 days the compressive strength of all samples increased than 90 days strength. The rate of increase of strength having 25% and 30% replacement levels was very slow. However samples with 10%, 15% and 20% replacement levels showed similar trend to the control sample. At 350 days the sample having 20 % RHA 3 exhibited the highest result than all other samples including the control one.

Mahmud, et al. (1996) reported 15% cement replacement by RHA as an optimal level for achieving maximum strength. Zhang, et al. (1996) suggested that 10% RHA replacement exhibited higher strength than control OPC at all ages. Ganesan, et al. (2008) concluded that concrete containing 15% of RHA showed the highest compressive strength. Dakroury and Gasser (2008) reported that using 30% RHA as a replacement of cement could be considered optimum for all content of w/c ratios in case of mortars.

Some researchers concluded that the behaviour of cementitious products varies with the source of RHA (Malhotra, 1996; James, 1986). Gemma (2006) found out the compressive strength of concrete made from two different locations, one from the USA and the other from Uruguay. Author mentioned that at 7 days the concrete with Uruguay RHA showed higher strength than concrete with USA rice husk ash. And at

91 days, the result was different and in that age USA Rice Husk Ash concrete showed better result. Gemma (2006) used 20% addition of RHA with Ordinary Portland Cement and noted that in every case the control samples were some lower strength than the RHA concrete.

In the present study up to 20% replacement of OPC by Bangladeshi Rice Husk Ash (RHA 3) exhibits better strength for mortar specimen up to 350 days. Researchers observed a wide range of replacement levels of OPC by RHA. The observed results with addition of rice husk ash A3 in cement mortar had positive effect on the compressive strength. Replacement of OPC in mortar by this rice husk ash at 15% and 20% showed better result of strength than the control sample beyond 28 days.

The mortar specimens with rice husk ash A3 were further investigated for its long term performance. The long term performance of mortar with and without rice husk ash A3 based on compressive strength at 600 and 900 days are shown in Table 4.9.

Table 4.9: Long term compressive strength of mortar with rice husk ash A3.

Sample ID	600 days		900 days	
	Sand, S1	Sand, S2	Sand, S1	Sand, S2
	Average Strength (MPa)	Average Strength (MPa)	Average Strength (MPa)	Average Strength (MPa)
A3-0	37.96	42.10	39.17	43.17
A3-10	37.48	41.24	37.96	42.33
A3-15	38.45	42.24	38.69	43.22
A3-20	38.80	43.45	39.23	43.79
A3-25	34.38	35.81	33.40	34.21
A3-30	31.51	31.76	29.52	29.24

In the Figure 4.21 it is observed that the compressive strength of 30% replacement at 90 days is 51.3% higher with respect to 28 days. At 350, 600 and 900 days it was observed that the strength compared to 28 days were gradually declining. It was clear that the strength was decreasing after 90 days in case of 30% replacement levels at long time. Same observation was also shown in Figure 4.21 for 25% replacement levels.

The strengths for 10% and 15% replacement levels were slightly increasing with respect to 28 days strength while the strengths were increased to 26.8%, 23.8% and 28.9%, 24.7% respectively at 90 and 350 days with respect to 28 days strength. At later age rate of gain in strength was increased with a percentage of 30.25, 26.24 and 31.93, 26.97 respectively for replacement levels of 10% and 15% at 600 and 900 days respectively. For 20% replacement levels, the results exhibited nearly same of the 10% and 15% replacement levels up to 350 days.

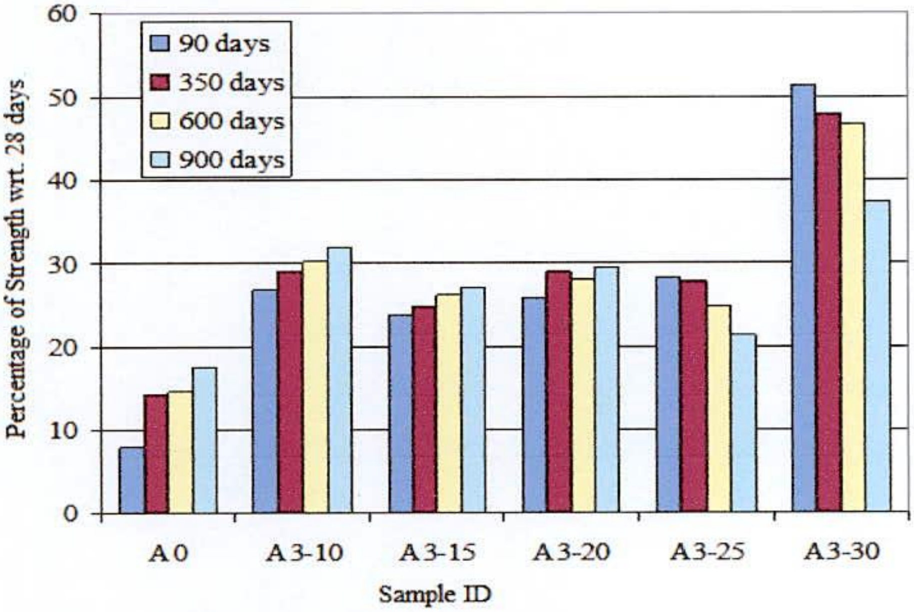


Figure 4.21: Increase in strength with respect to 28 days strength in percentage

From Figure 4.21 it is observed that the strengths for the samples having 25% and 30% replacement were dropped at 600 days age with respect to 350 days. On the other hand, samples of 10% and 15% replacement levels exhibited higher strength at 900 days than 350 days strength. For 20% replacement levels the variation of strength at 600 and 900 days were negligible. The strength for control samples at all ages exhibited increasing nature.

4.3 DURABILITY OF MORTAR

A durable concrete structure needs to be produced to accomplish more or less repair or maintenance free structures even though they are exposed to adverse environment. For reinforced concrete structures, chloride access and sulphate attack are the main parameters causing significant degradation of properties. Chloride entrance and sulphate attack leads to corrosion of the reinforcing steel and form etringite in the concrete. The strength, serviceability and aesthetics of the structures consequently reduced due to the environmental attack and may lead to early repair or premature replacement of the structure. A general method of avoiding such effect is to prevent chlorides penetration in the structure by using comparatively impenetrable concrete.

The penetration of chloride ions in the concrete, however, is a slow process. It cannot be determined directly in a time frame. Rapid chloride permeability test (RCPT) was adopted as a standard test. Structural concrete components will be degraded in sulphate rich environments with the attack of sulphate ions and their related cations on the products of hydration of Portland cement (Rasheeduzzafar, 1992; Lawrence, 1990; Cohen and Bentur, 1988; Calleja, 1980). The effect of permeability and sulphate ions on the performance of concrete is the influential subject in concrete durability.

Capillary absorption, hydrostatic pressure, and diffusion are the ways by which chloride ions can enter into concrete. The most familiar method is diffusion, the movement of chloride ions under a concentration gradient.

The following tests were performed to determine the durability of cement mortar incorporating rice husk ash.

- Permeability
- Sorptivity
- Salt crystalization
- Resistance to sulphate attack
- Performance under elevated temperature

4.3.1 Permeability of Mortar

For finding out the permeability of cement mortar, 100 mm diameter and 200 mm height cylinder was cast. The specimen was sliced according to the Figure 4.22 by diamond rotary blade. After cutting the face of the samples were rubbed to form a finished surface. Three samples of 50 mm thickness were made from one cylindrical specimen. Middle sample was used for determining the permeability and outer two samples were used to find out the sorptivity of the cement mortar. The average values of permeability results are presented in Figure 4.23. The permeability test was performed according to AASHTO T277 (ASTM C1202) as discussed in chapter 3.

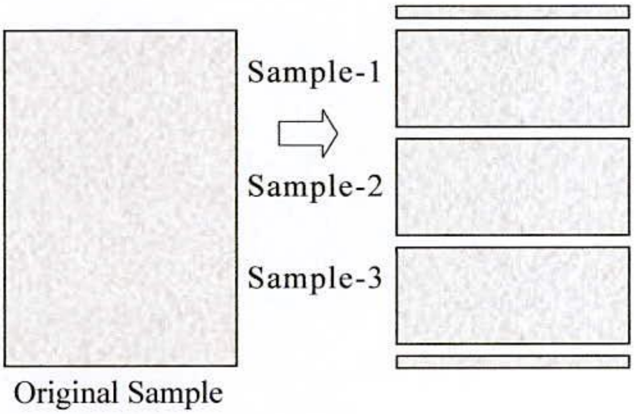


Figure 4.22: Sample preparation for permeability and sorptivity test

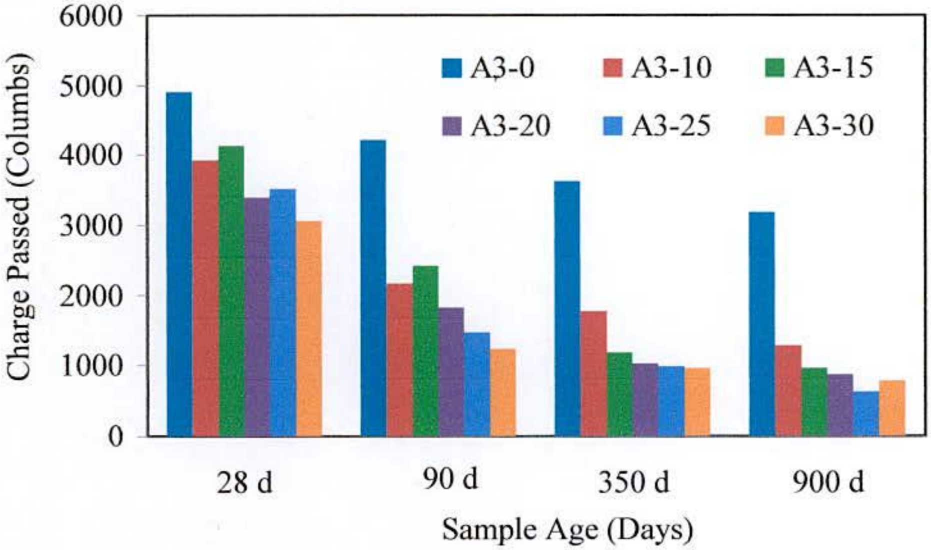


Figure 4.23: Total charge passing through different samples at different ages

From the above Figure 4.23 it is observed that the charge passing through the control sample has less affect on the samples ages compared to the samples having Rice Husk Ash (RHA). Control samples exhibit higher charge passing than others samples. For 28 days sample, permeability of controlled sample was significantly high and sample with 10 and 15% RHA was observed close to high permeability limit according to ASTM C1202. Samples having 20% to 30% replacement levels observed moderate permeability at the same age. At 90 days result it was observed that only the control sample shows high permeability and samples with 10% and 15% replacement levels exhibit moderate permeability. In the same age samples having 20% and onward replacement levels exhibit low permeability values. At later ages control samples are still in moderate permeability ranges but the charge passing through the all samples having RHA is decreasing nature. Very low permeability was observed in range from 15% to onward replacement levels at 900 days. The lowest permeability was obtained with 25% replacement of OPC by RHA. The comparison of permeability with respect to control sample is demonstrated in Figure 4.24.

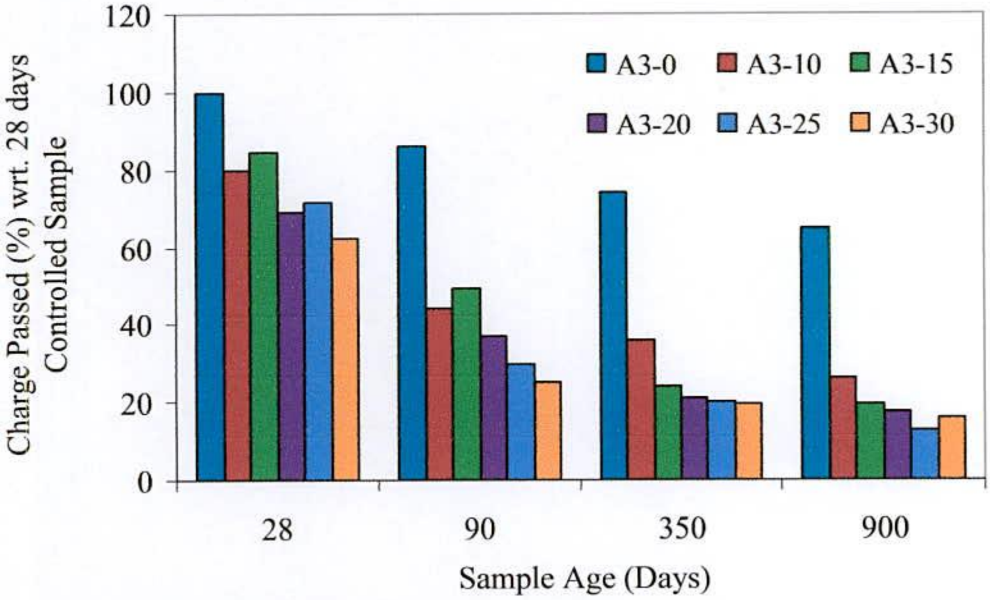


Figure 4.24: Total charge passing in % compared to 28 days control sample

In Figure 4.24 shows that the charge passing through samples decreased with respect to age. The decreasing rate was high for the samples having Rice Husk Ash with respect to the controlled sample. Higher decreasing rate was observed for 25% and 30% cement replacement levels by RHA. The results show that the permeability is decreasing with increase of RHA levels. It is obvious that the RHA addition in cement mortar as a partial replacement of OPC performs well in reducing permeability of mortar. The results obtained from this experiment are similar to the observation concluded by Rodrigues, et al. (2006) and Chindaprasirt, et al. (2005). The researchers concluded that incorporation of RHA in cementitious materials decreases the permeability.

It was observed that the temperature in anodic and also in cathodic cell was varied during the experiment. The rise of temperature during the experiment of permeability is shown in Figure 4.25. The maximum temperature observed at 6^{th} hours of the test. Among the all ages of mortar specimens it was observed that the highest rise of temperature was observed in control sample. Sample having 20% RHA exhibited the lowest temperature rise for 28 and 90 ages. However, the rise of temperature inversely varied with increase of RHA for 350 and 900 days except for 25% RHA at 900 days. This observation was found in case of samples with ASTM graded sand. Similar observation can be concluded for the sample having local sand with FM 2.73 for permeability and shown in Annexure B (Figure B1, B2 and B3).

Figure 4.25: Temperature rise during the permeability

4.3.2 Water Sorption

One of the main causes of deterioration of concrete structures is water absorption which influences the durability of the concrete and also has the threat of alkali aggregate reactions (Ithuralde, 1992). The more impermeable the concrete, the greater will be its resistance to deterioration. The most important methods involved in the progress of chloride ions through concrete are sorption and diffusion. Sorption drags the fluid carrying chloride ions into the concrete and diffusion travels the chloride ions as of regions of high concentration towards sections of low concentration. For mortar/concrete exposed to the air and subjected to wetting and drying, the capillary system of the cementitious material is usually only partially saturated, and thus sorption plays a significant role in the penetration of fluids into the mortar/concrete. For mortar/concrete in which the pore system remains saturated, sorption becomes negligible and the primary mechanism for chloride penetration is through concentration driven diffusion. The water sorptivity of concrete can be determined by using ASTM C1585/C642.

Due to the little initial surface tension and buoyancy effects, the relationship between cumulative water absorption (kg/m^2) and square root of exposure time $(t^{0.5})^{-1}$ show deviation from linearity during first few minutes (Tasdemir, et al., 1999). Thus, for the calculation of sorptivity coefficient, only the section of the curves for exposure period from 3 minutes to 60 minutes, where the curves were consistently linear, was used from Figure 4.26.

In this figure the coefficient of correlation is over 0.99 in most cases provide a very good fit to the data considered. This observation is same to Sousa (2003). Figure 4.26 shows that the coefficient of water absorption of mortar at all replacement levels was less than the control sample. The similar finding was also obtained by Saraswath and Song (2007). The sorptivity of mortar with different levels of RHA addition is presented in Figure 4.27.

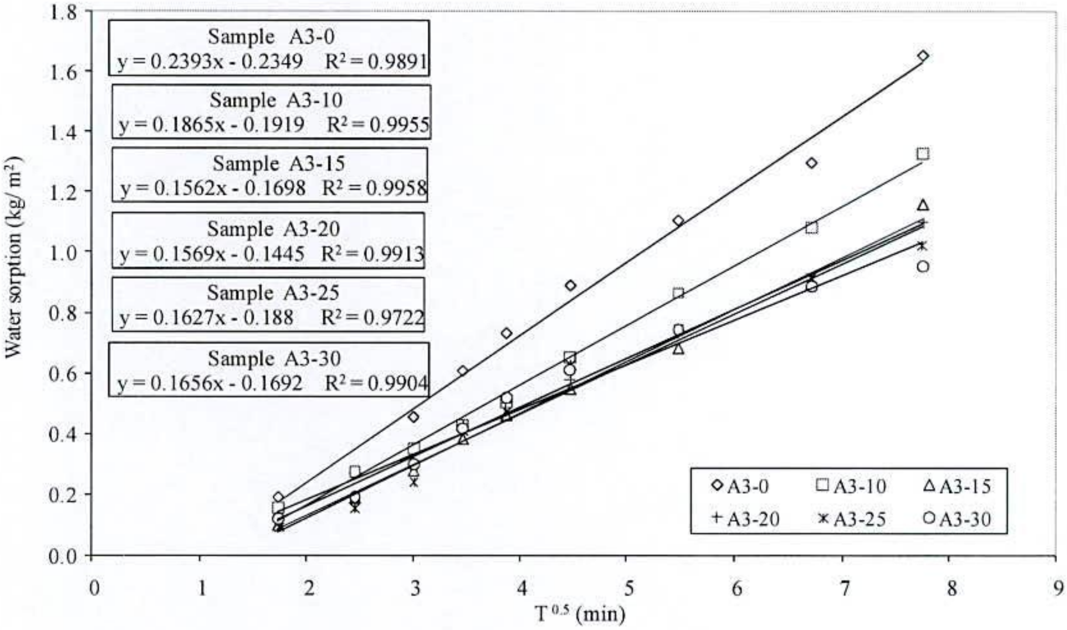


Figure 4.26: Linear regression for absorption by capillary action

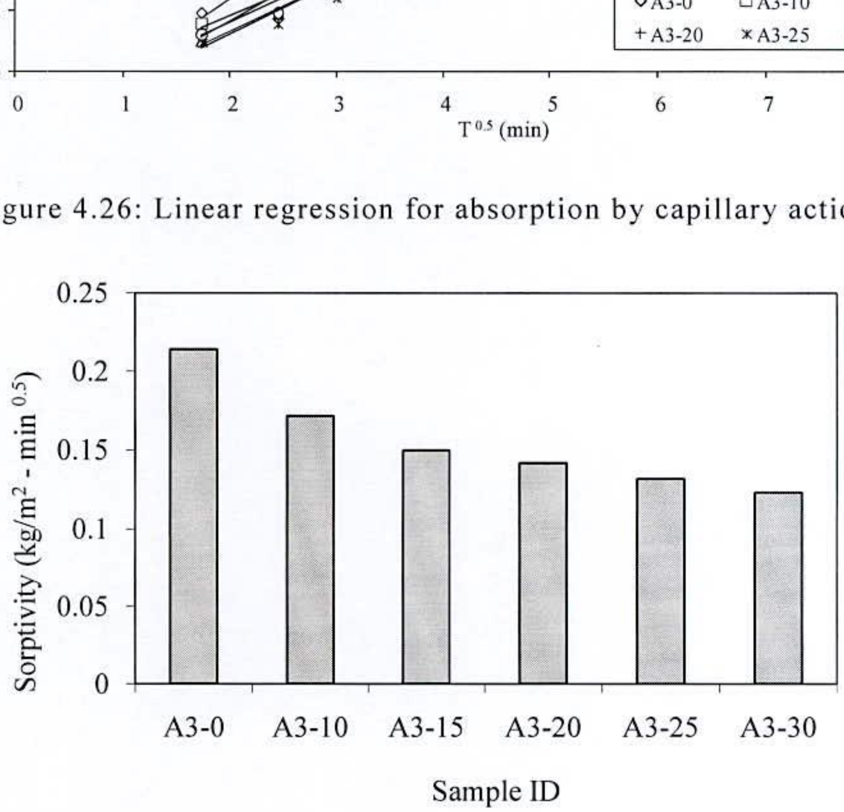


Figure 4.27: Sorptivity values of sample with different percentage of RHA

Figure 4.27 depicted that the sorptivity for samples having RHA shows lower values than the control sample. Sorptivity was observed minimum at 15% replacement level. An inverse relationship was observed between RHA content and sorptivity. The sorptivity was significantly reduced in case of RHA addition in the mortar samples. The incorporation of RHA may reduce the average pore size lead to less permeable paste. Several researchers also observed that the incorporation of pozzolans reduces the pore sizes of the cementitious materials (Rodrigues, et al., 2006; Chindaprasirt, et al., 2005). The similar observation was obtained for sand type S2 and is presented in Annexute B (Figure B4 and B5).

4.3.3 Salt Crystallization Test

The soluble salts migrate inside the exposed surfaces of cementitious members through moisture due to capillary rise and/or rain penetration. Salt crystallization behind the cementitious surfaces causes delimitation and breaking down of cement mortar. The effects of salt damage on cement mortar appear frequently as cracking or loss of materials. Salt crystallization test can help for choosing the most durable cementitious materials. The crystallization results are presented in Figure 4.28.

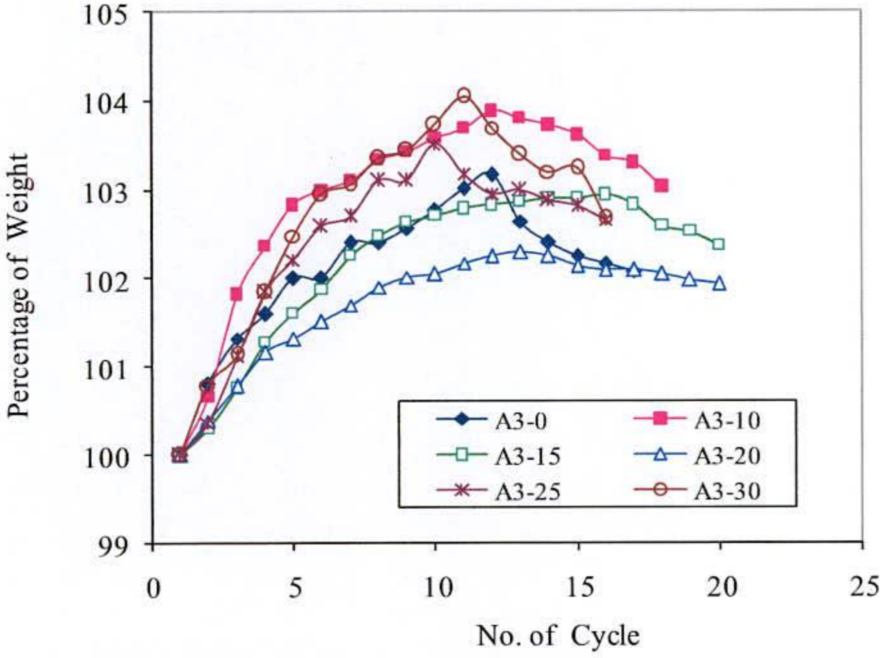
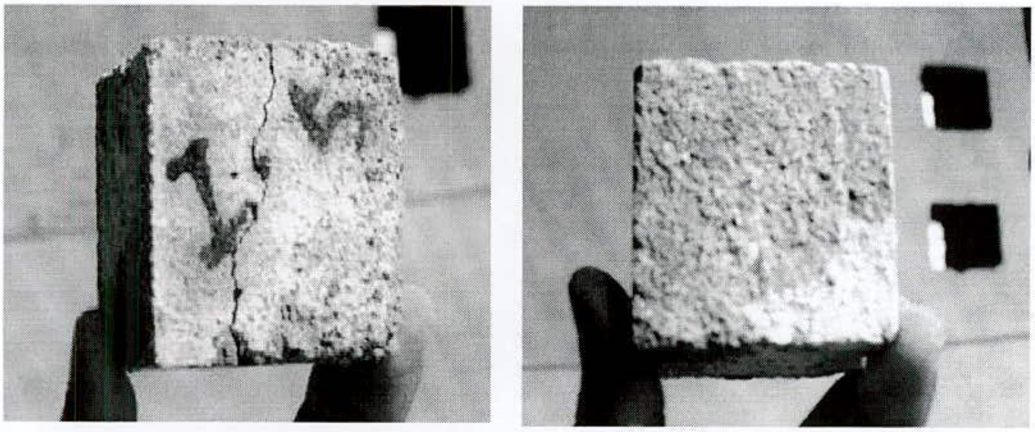


Figure 4.28: Variation of weight with respect to test cycles

Figure 4.28 illustrates that the control sample (A3-0) sustained in salt crystallization test up to 17 cycles. Only the samples having 15% and 20% RHA were sustained up to the 20 cycle of the test. Mortar sample having 10%, 25% and 30% of RHA replacement level completed 18, 16 and 16 cycles respectively. It means that the optimum level of replacement of OPC with RHA is within 15% to 20% for durability against the salt crystallization. Samples were not considered for further cycle, when cracks were observed or breaking of any portion of the tested specimens. The crack on sample is shown in Figure 4.29 (a). The reason of decreasing weight of samples after certain cycles of experiment is due the loss of some particles from its surface. In this stage when cracks or ruptures of any portion of the sample were found discarded from further test. The loss of particles from the specimen surface is shown in Figure 4.29 (b).



(a) Crack observed (b) Surface was roughed

Figure 4.29: Crack and loss of particles of sample due to salt crystallization

The sustainability of mortar in crystallization test and gain of weight due to crystallization are demonstrated in Figure 4.30. The control sample (A3-0) and sample with 10% replacement level (A3-10) show maximum weight at 12th cycle of the test and crack was observed in these samples at 17th and 18th cycle of salt crystallization test, respectively. Samples made of 15% and 20% RHA sustained against the standard 20 test cycles and exhibit maximum weight at 14 and 13 cycles respectively. The samples with 25% and 30% replacement, maximum weight was observed at 10 and 11 test cycles and sustained up to 16 test cycles.

The sustainability of RHA-mortar with locally available sand with FM 2.73 (Sand type S2) against the crystallization was found almost same as mortar with ASTM graded sand. The results are presented in Figure B-6 and B-7 of Annexure B.

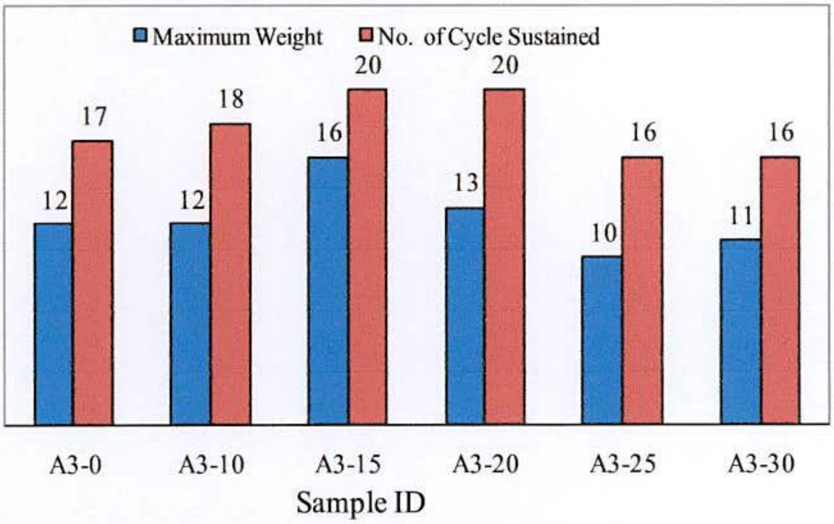


Figure 4.30: Sustainability and gain of weight due to crystallization

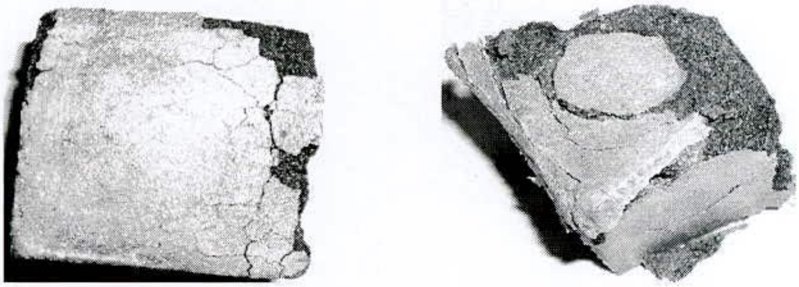
4.3.4 Resistance to Sulphate Attack

The sulphate attack of concrete guides to expansion, cracking, and deterioration of numerous structures exposed to sulphate surroundings such as piers, bridges, foundations, concrete pipes, etc. Sulphate ions come in a group with other ions such as sodium, potassium, magnesium and calcium ions from the soil, ground water, and seawater (Nabil and Akhras, 2006; Ouyang, et al., 1988; Mehta, 1983; Brown, 1981). The sulphate ions react with C_3A and $Ca(OH)_2$, to create expansive and softening forms of deterioration. The sulphate attack in marine location gives increase to expansive ettringite, gypsum, and brucite and sometimes is associated with calcite formation (Hossain and Lachemi, 2006; Frigione and Sersale, 1989). The development of gypsum and ettringite show the way to expansion, cracking, deterioration, and disruption of concrete structures.

In this investigation, the sulphate resistance of Portland cement with and without RHA was assessed using the accelerated test method proposed by Mehta and Gjorv (1974). The pH and sulphate concentration of the solution were kept constant throughout the experiment and changes in strength were considered as a measure of sulphate resistance rather than the expansion of the mortar. Compressive strength was measured after 28, 56, 84 and 112 days of immersion in sulphate solution and compared to the 28-day strength.

After 28 days of curing age of the samples were immerged in sulphate solution and compressive strength test was performed after different time of immersion. The experimental results are tabulated in Annexure A (Table A-4 and A-5). At least 3 nos. of sample were tested from each mixing compositions and the average values were shown. The samples were not considered for testing which exhibited noticeable defects (e.g., surface defects, cracks or voids).

Sample with 30% RHA exhibits cracks at 56 days in sulphate solution and no spalling was observed in this stage. This sample was not considered to test due to surface cracks and kept in the solution. After 84 days immersion in solution, sample exhibits enormous spalling shown in Figure 4.31.

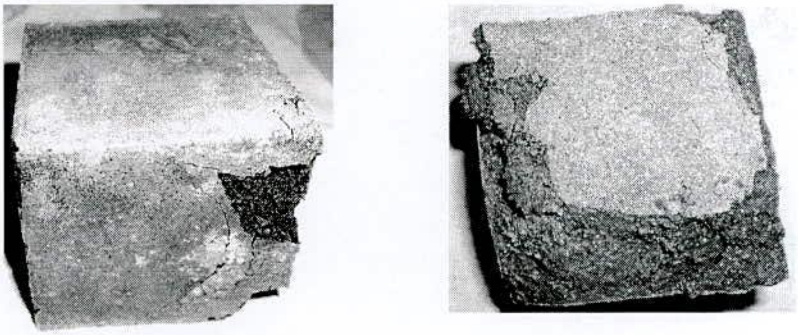

(a) Controlled Sample (A3-0)

(b) A3-30 Sample

Figure 4.31: Spalling of samples after 84 days immersion in sulphate solution

The surface spalling was observed to control samples and A3-30 sample after 84 days of immersion in sulphate solution. At this stage others samples exhibited no spalling and severe surface cracks. Control samples and samples of A3-30 were removed from the sulphate tank in this stage and other samples were kept for next step.

Figure 4.32 shows the samples having 10 and 25% of RHA after 112 days in sulphate solution. Both samples showed spalling and crack in their surface. Samples having 15 and 20% RHA were still in good condition and tested.



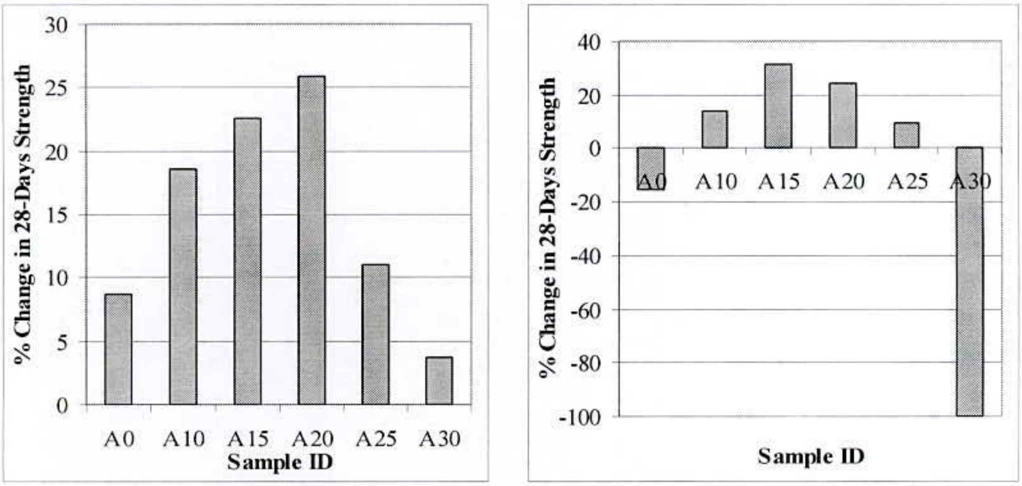
(a) A3-10 Sample (b) A3-25 Sample

Figure 4.32: Samples immerged for 112 days in Sulphate solution

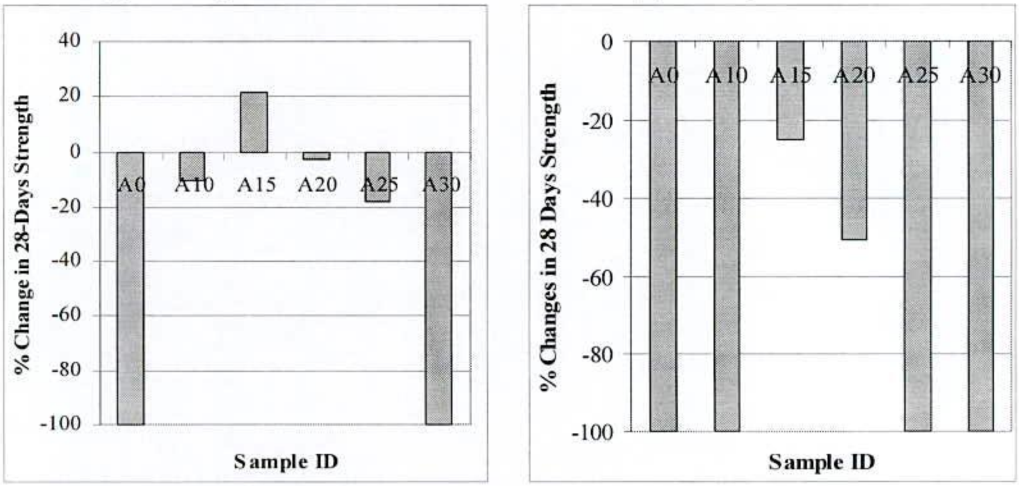
Figures 4.33 shows the relative change in average compressive strength measured after 28, 56, 84 and 112 days of exposure in 4% Na_2SO_4 solution. The change in result is calculated as percentage of the strength of each samples measured after 28 days curing in water.

Loss in strength during the exposure time can be due to the effect of cracking by expansion of ettringite and gypsum formation and the loss of C-S-H. Various cements may prolong to hydrate in the sulphate solution and may experience an increase in strength. Susceptibility to sulphate attack can simply be interpreted through strength loss. Increases in strength do not provide any information about sulphate resistance; such results only show that the cement continues to hydrate in sulphate solution over the test period.

The strength of all samples increased after 28 days of sulphate exposure. Sample having 30% RHA showed the lowest increase in strength i.e. 3.67% and the control sample showed 8.68%. Others samples having 10%, 15%, 20% and 25% of RHA exhibited 18.56%, 22.52%, 25.87% and 10.94 % of increase in strength at this stage as indicated in Figure 4.33 (a). For 56 days of immersion in sulphate solution, sample with 30% of RHA exhibited cracks on the surface and discarded for testing. At this age control sample strength was lowered by 15.63% than the 28 days hydrated strength. Sample having 15% of RHA showed the highest compressive strength and increased by 31.57% with compared to its 28 days strength. Others replacement levels (10%, 20%, 25%) still in decreasing nature and presented in Figure 4.33(b).



(a) 28 Days Immersion (b) 56 Days Immersion



(c) 84 Days Immersion (d) 112 Days Immersion

Figure 4.33: Variation of strength at different periods of sulphate immersion

For 84 days of immersion the control sample showed spalling and rejected for further testing. The strength of all the samples decreased at 84 days immersion compared to 56 days of immersion. However, the strength of sample with 15% replacement levels was still higher than others. The results are plotted in Figure 4.33 (c). At later ages of 112 days exposure in sulfate solution, when the sample actual age was 140 days, observed that samples with 10% and 25% replacement levels also lost total strength because of surface spalling. Sample having 15% and 20% of RHA shows no sign of crack and spalling on their surface. However, their strengths reduced by 24.98% and 50.71% respectively with respect to 28 days strength. It might happen due to the attack of sodium sulphate on mortar for the reaction of Na_2SO_4 and $Ca(OH)_2$ to form gypsum and the reaction of the formed gypsum with calcium aluminate hydrates to form ettringite (Hekal, et al., 2002; Massazza, 1993). The ettringite exerted expansive force inside the mortar causes reduction of strength or formation of crack (Hossain and Lachemi, 2006).

From the above discussions and observations it is concluded that mortar with 15% rice husk ash A3 exhibits better performance against sulphate compared to all other replacement levels as well as control sample.

4.3.5 Performance at Elevated Temperature

The performance of mortar incorporation with rice husk ash under the influence of high temperature on microstructure and mechanical properties are discussed in this sub-section. Fire is one of the most serious risks and create critical problem in structures. A concrete structure exposed to high temperature is weakened which is not clearly understood. The important part of the fire on concrete is degradation of mechanical properties of concrete. Nijland and Larbi (2001) reported that concrete heated by fire might lead to a variety of structural failure such as cracking, spalling, debonding of aggregate from mortar, expansion, loss of strength and mineralogical/chemical changes. Hence the performance of structural elements under fire recently becomes more and more important. In this study traditional cement mortar made from OPC and modified cement mortar from OPC and RHA was used. The mortar sample with RHA of 90 days age was considered for this experiment because this sample showed higher compressive strength in previous experiment.

The heating rate of mortar specimen is shown in Figure 4.34 shows quite similar to the ASTM E119 up to 700°C. The maximum test temperature was 700°C and the temperature increasing rate was followed according to ASTM standard. The temperature inside the furnace was collected by two different thermocouples at different places and determined the average of these two. The standard and developed temperature in furnace is shown in Figure 4.34. According to ASTM standard, the temperature of 538 and 704°C should be raised at 5 and 10 minutes respectively while the same temperatures were observed in the furnace at 4.96 and 9.45 minutes respectively. So the tested temperature was developed in furnace is very close to the ASTM standard.

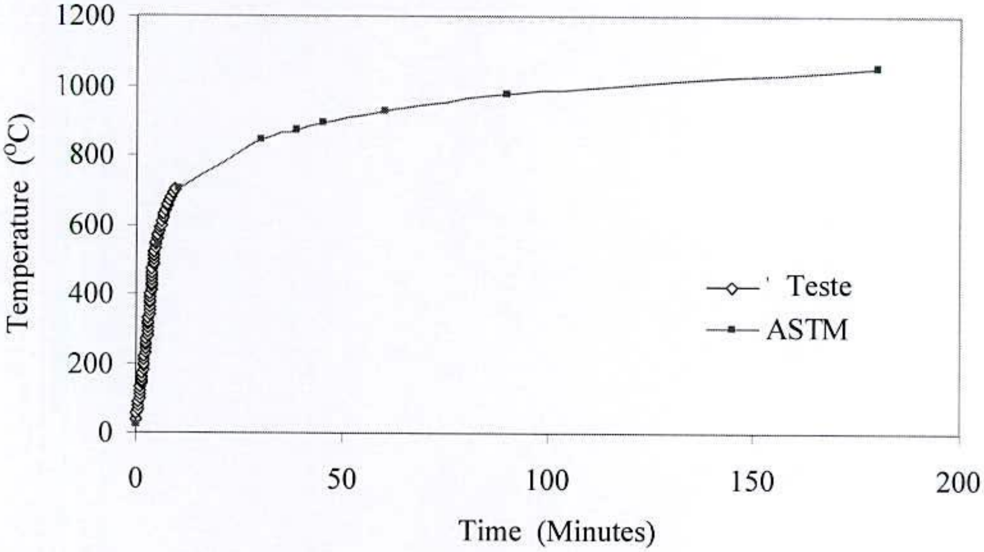
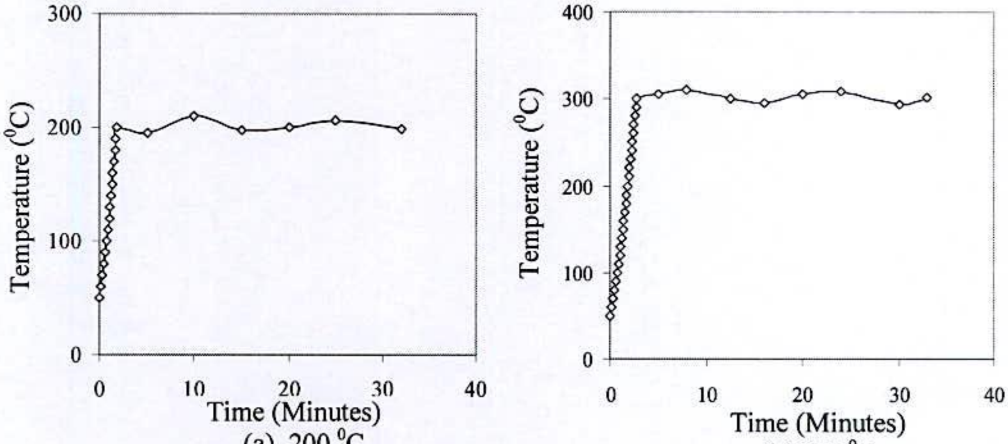


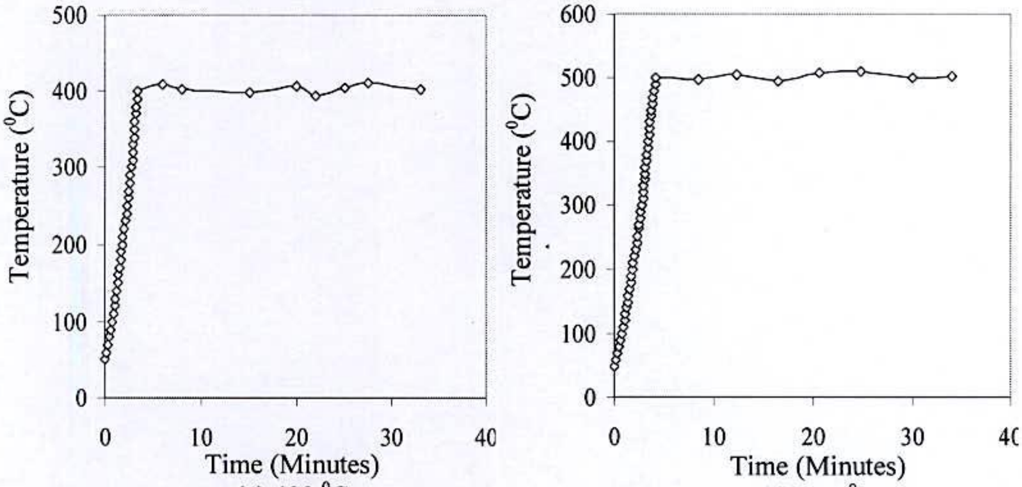
Figure 4.34: The rise of temperature with respect to time

The experiment was conducted at 200°C, 300°C, 400°C, 500°C and 700°C shown in Figure 4.35. The samples were kept in the furnace for 30 minutes at experimental temperature. After this the samples were removed from the furnace and cooled in two different ways as described earlier in article 3.3.4.5.



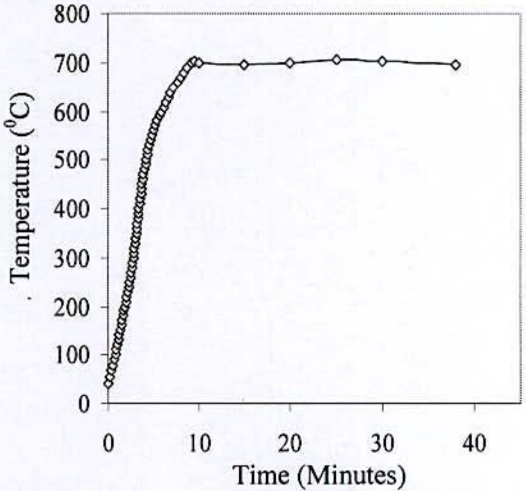
(a) 200 ^{0}C

(b) 300 ^{0}C



(c) 400 ^{0}C

(d) 500 ^{0}C



(e) 700 ^{0}C

Figure 4.35: Applied temperatures during the experiment

The loss of weight of each specimen was measured. It was found that the percent weight loss was increased with increasing amount of RHA. This might be due to the loss of moisture absorbed by the RHA. It is clear that moisture absorbing capacity increased with the increase of amount of RHA. Figure 4.36 shows the variation of percent weight loss with respect to temperature for different percent of RHA replacement. The loss of weight for all samples followed same trend. A maximum of 22.2% weight loss was observed for 30% RHA replacement. Initially 10% - 15% weight loss was due to preconditioning of samples and this changed the graphs sharply. Then the loss maintained a gradual slope for all percentage of RHA replacement. It is important to note that 4% - 6% of weight loss occurred within the temperature range of 200°C - 700°C for A3-10 to A3-30 type samples. On the other hand it was 9% for controlled samples.

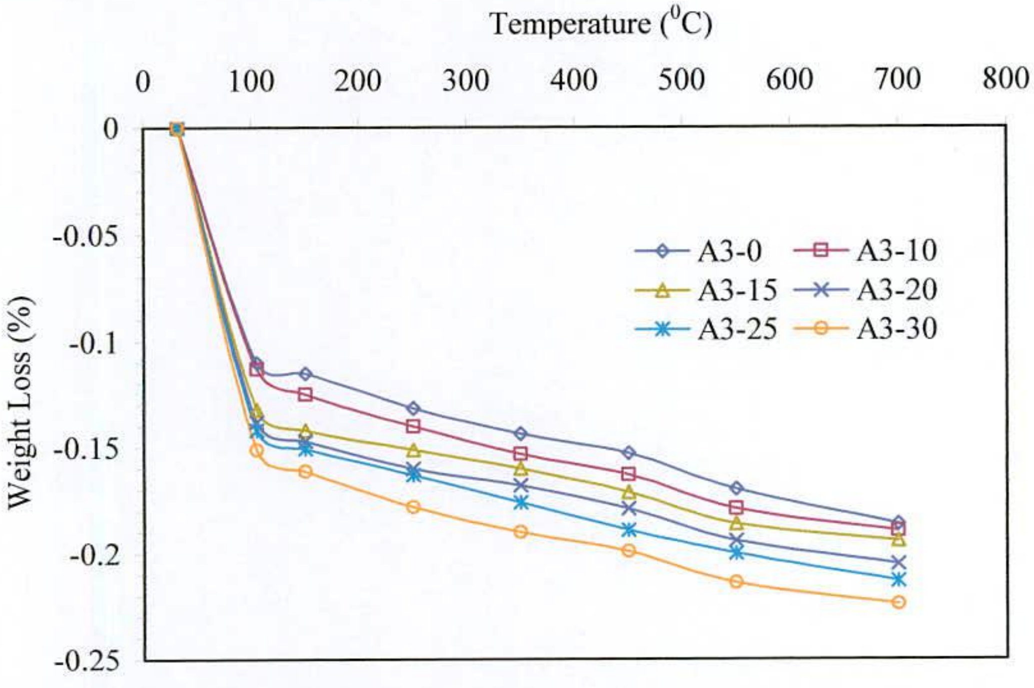


Figure 4.36: Temperature with respect to percentage of weight loss

The compressive strength test of mortar sample was carried after cooling of sample by two different ways. The control specimen showed higher strength than 25% and 30% replacement levels and 10%, 15% and 20% replacement of OPC by RHA showed higher strength than the control sample for non-heated samples. Strength of samples heated at elevated temperature exhibit different pattern from the strength of non-heated samples. At 200°C the control sample showed the highest strength than any other samples when cooled in open air and 10% replacement levels exhibited higher compressive strength among all the samples when the samples were quenched with water and then cooled in open air. The strength of all samples heated at different temperature and cooled in open air and quenched with water are presented in Figure 4.37 and 4.38.

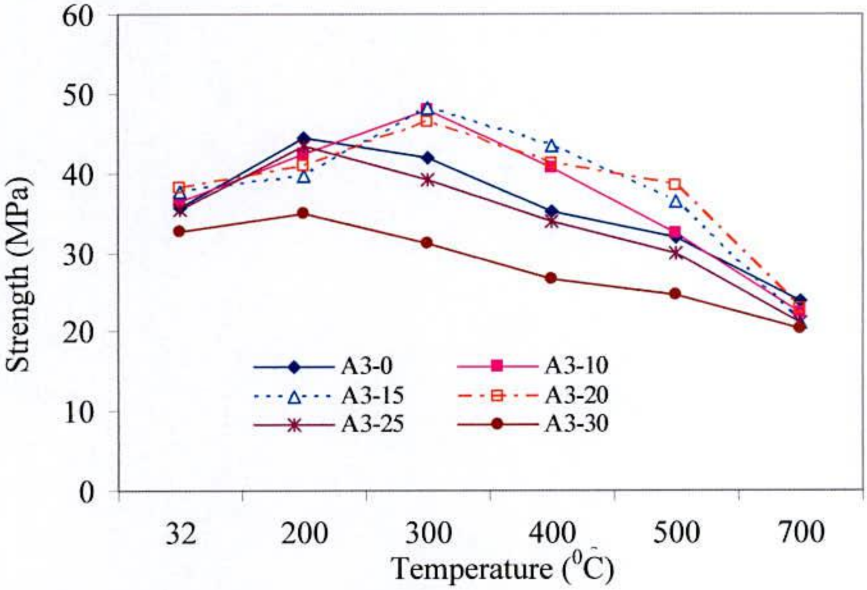


Figure 4.37: Strength of mortar at different temperature levels (cooled in open air)

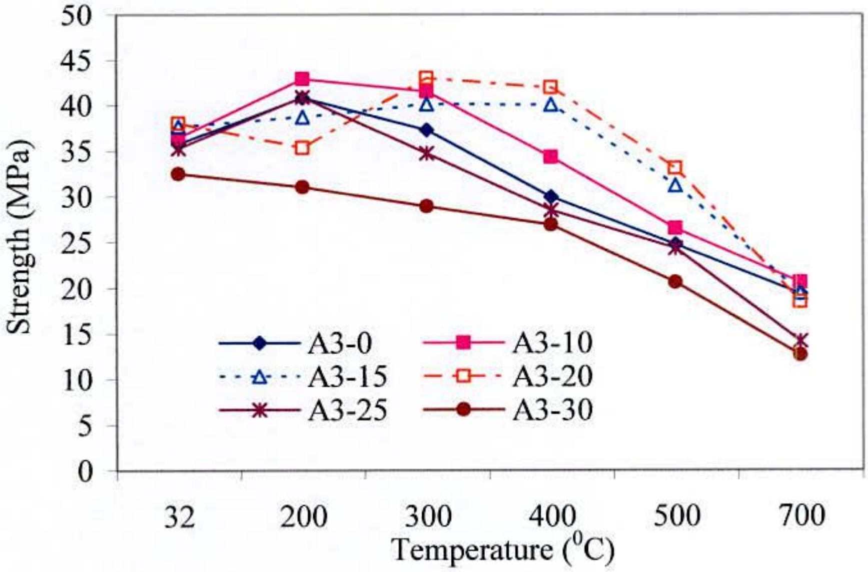


Figure 4.38: Strength of mortar at different temperature levels (quenched with water)

The highest compressive strength of 48.26 MPa (7002 psi) was obtained for 15% replacement of OPC heated at 300°C and cooled at room temperature in open air while the highest compressive strength of 43.02 MPa (6241psi) was obtained for 20% replacement of OPC cooled by quenching with water. It is also observed that the compressive strength of samples with 10%, 15% and 20% rice husk ash A3 were higher than the strength of control sample in case of open air cooling as well as cooling by quenching with water. The strengths of all samples were higher than the non-heated sample except 30% RHA sample when cooled in open air. On the other hand, only 25% and 30% RHA samples were lower than the non-heated sample when cooled by quenching with water.

In case of cooling in open air and quenched with water the controlled sample at 400°C exhibited lower strength than the non-heated sample. At this temperature the strength of samples with 10%, 15% and 20% RHA were still higher than non-heated samples when cooled in open air. Whereas, in case of quenched with water samples with 15% and 20% of RHA exhibited higher strength. All other samples at this elevated temperature lost strengths in compare with the non-heated sample.

At elevated temperature of 500°C, the strength of all samples were lower than the non-heated sample when cooled in open air except 20% RHA sample. However, the strength of all sample at elevated temperature of 500°C were less than non-heated sample when cooled by quenched with water. All samples showed the lowest strength at 700°C for both cooling processes.

The compressive strength of mortar with rice husk ash A3 at different temperature levels with respect to non-heated control sample cooled in open air and quenched with water are presented in Figure 4.39 and 4.40.

The Figure 4.39 shows that the highest strength 24.4% increased for control sample at 200°C for cooling in open air when compared with non-heated sample (32°C). The sample with 25% RHA showed the highest increase of strength (21.8%) among the other samples with RHA when normally cooled in open air. However, the highest strength of 20.1% was obtained by 10% RHA sample for cooling by quenched with water shown in Figure 4.40.

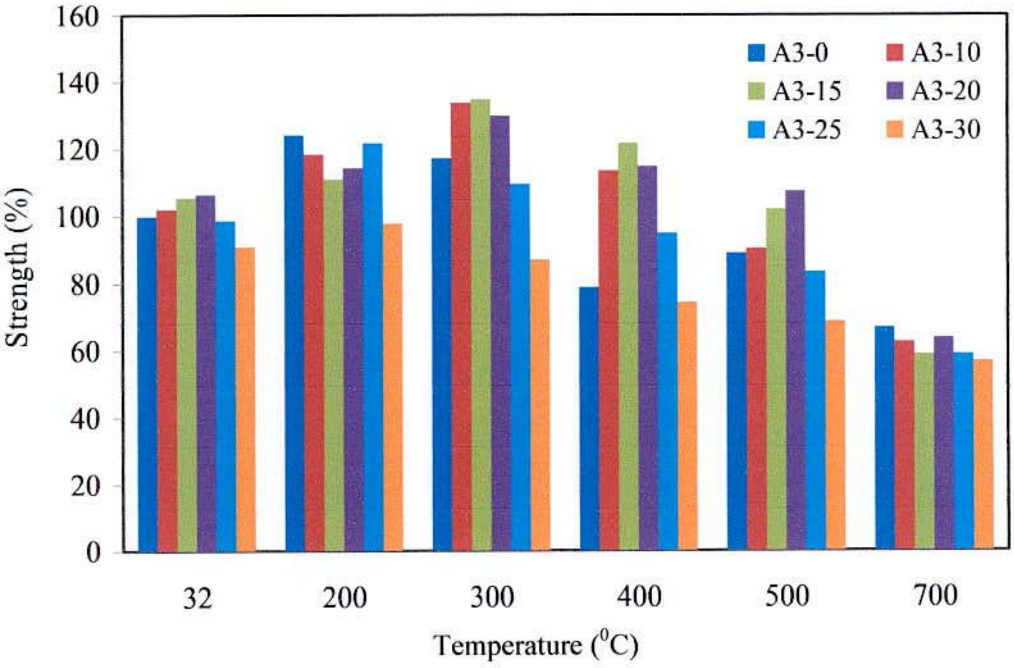


Figure 4.39: Compressive strength with respect to control sample (cooled in open air)

Furthermore, at the elevated temperature of 300°C, the highest strength of 35% was gained by sample with 15% RHA for open air cooling while sample with 20% RHA for cooling by quenched with water gained 20.3% strength. It is also observed that the 35% increase of strength of 15% RHA sample is the highest among the all samples in both cooling processes. The 15% and 20% RHA samples also showed the highest increase of strength of 21.7 and 17.3% when cooling in open air and quenched with water respectively after heating at 400°C. In case of heating at 500°C temperature, the strength slightly increased only for 15% and 20% RHA samples in open air cooling process. However, all the samples lost strength compared to non-heated control sample. There was no increase in strengths for all samples were found for further increase of temperature up to 700°C in both cooling process. At higher temperature beyond 500°C samples with RHA exhibited lower performance than the control sample.

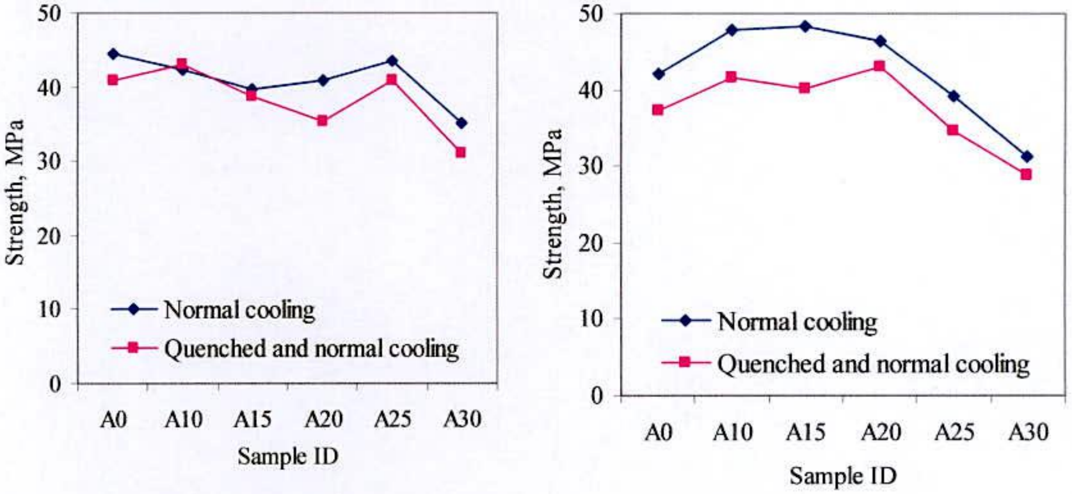
In case of cooling in open air, the samples were brought out from furnace after heating to experimental temperature and allowed to cool down at ambient temperature in a open space. The highest strengths of 47.84, 48.26 and 46.44 MPa (6941, 7002 and 6738 psi) were found for samples with 10%, 15% and 20 % RHA respectively at a temperature of 300°C.

level beyond 200°C. The highest strength gaining by the A3-0, A3-10, A3-15, A3-20, A3-25 and A3-30 samples were 14.26, 17.65, 6.50, 12.96, 15.88 and 0.00% respectively compared to the non-heating strength of each sample. Furthermore, the highest and lowest strength gaining were found by 10% and 30% RHA sample though the highest strength was obtained by 20% RHA sample. On the other hand, lose of strengths for sample A3-0, A3-10, A3-15, A3-20, A3-25 and A3-30 were found to be 52.65, 52.10, 51.67, 57.10, 65.33 and 61.16 % respectively at 700°C.

Effect of cooling conditions on strength after heating to an elevated temperature is shown in Figure 4.41. From Figure 4.41 it is observed that at 200°C and 400°C temperature, samples of A3-10 and A3-20 show higher strength when quenched with water and then air cooling process compared to the open air cooling. However, all other samples including the control sample exhibit lower strength for quenching with water and then cooled in open air after applying different levels of elevated temperature.

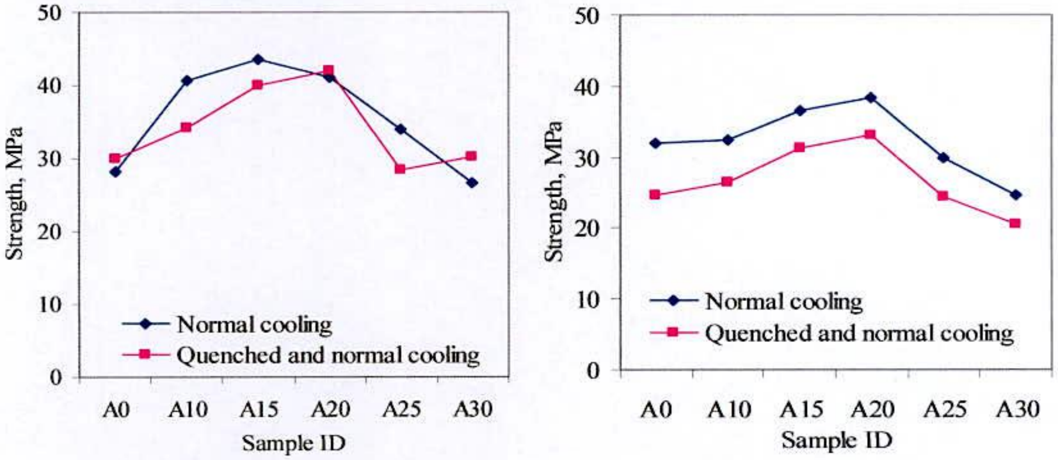
The degradation of strength at elevated temperature is quite similar to that observed by Sarshar (1989) and Nassif, et al. (1999) on concrete cylinder. Specimens were heated up to 500°C and cooled by quenching with water by Bazant and Kaplan (1996) mentioned that the compressive strength is much lower than specimens not quenched but allowed to cool slowly.

Finally the strength was reduced to 67% when heated at 700°C and cooled in open air process for control sample and 12.6% more strength lost in case of quenched with water and then air cooling process (Annexure A: Table A-6 and A-7). Samples having 10% and 15% RHA exhibited only 4.9% and 4.3% strength loss for quenched with water when compared to the open air cooling process. After that the variation of strength was increased up to 23.8% for 30% RHA level.



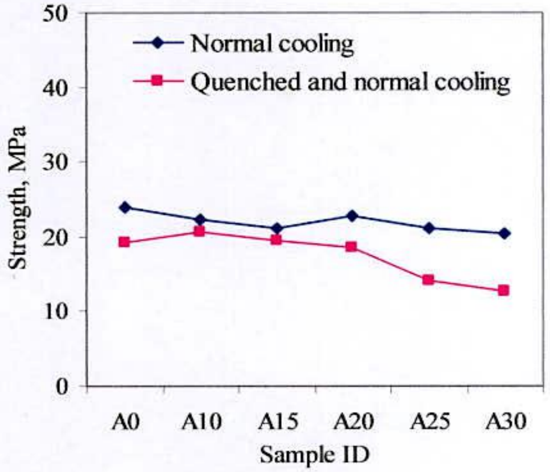
(a) Sample at 200^0C

(b) Sample at 300^0C



(c) Sample at 400^0C

(d) Sample at 500^0C



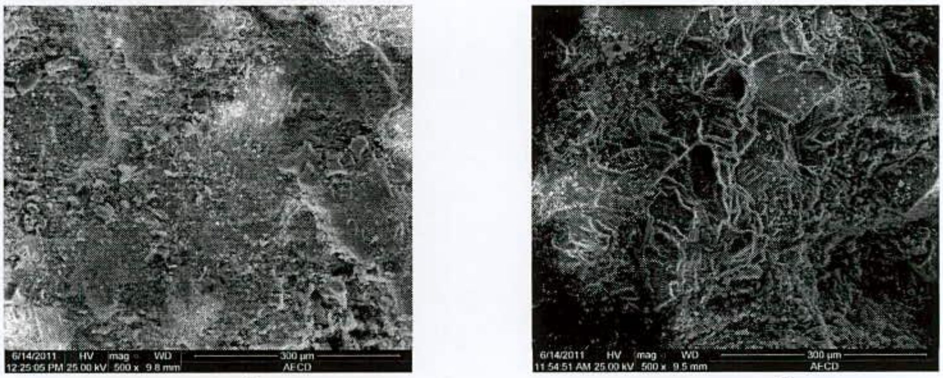
(e) Sample at 700^0C

Figure 4.41: Effect of elevated temperature and cooling conditions on sample

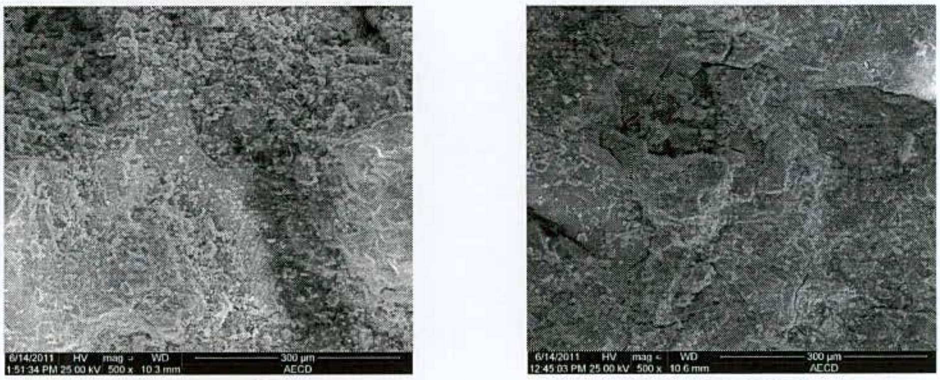
Concrete samples up to 450°C show different trend of compressive strength (Diederichs, et al., 1995; Hammer, 1995; Furumura, et al., 1995; Diederichs, et al., 1989; Diederichs, et al., 1988). The investigations showed that some samples show lower strength up to 200°C and after that the strength was in reverse trend when compared to ambient temperature strength. Some researchers mentioned that crack or spalling was occurred at elevated temperature on concrete specimen. However, in present study no sign of spalling was observed up to the 700°C as mentioned by Khoury and Algar (1999). Also Castillo and Durrani (1990) reported explosive spalling present is about one third of the specimens being heated to 700°C. It may be happened due to presence of excess free lime or other impurities in cement.

The influence of elevated temperature on the performance of cement mortar in presence of RHA as a supplementary material of cement was investigated with the help of SEM. For SEM analysis the cubical specimen was reduced to small size of 20 mm × 20 mm and 12 mm in thick. At first the 50 mm cubical samples were divided in 4 nos. of slices. The inner two slices have 12 mm thick and each of these slices was segmented by 4 equal size and confirming 20 mm × 20 mm × 12 mm sample. The prepared samples had one or two original surfaces out of 6 surfaces. One surface of these samples was polished for testing with the SEM. Before testing with the SEM, the samples were kept in furnace to attain the test temperature. SEM images of the samples are present in the Figures 4.42, 4.43 and 4.44.

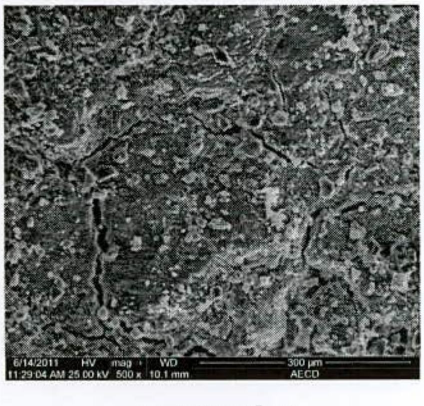
The control mortar sample at ambient temperature and also sample heated to 200°C, 300°C, 500°C and 700°C were tested with SEM to measure the length and width of micro-crack as the effect of temperature. No crack was observed in SEM image for mortar sample heated to 200°C. The sample exhibited micro cracks after 200°C. The total crack length was 1547 μm and the maximum width was 2.30 μm which was 10% of total crack length for sample heated at 300°C. The width of the remaining length was 1 μm to 2 μm. At 500°C, the micro-crack length was increased to 2581 μm and width increased to 4.80 μm which was 20% of the total crack length.



A3-0 (32°C) A3-0 (200°C)



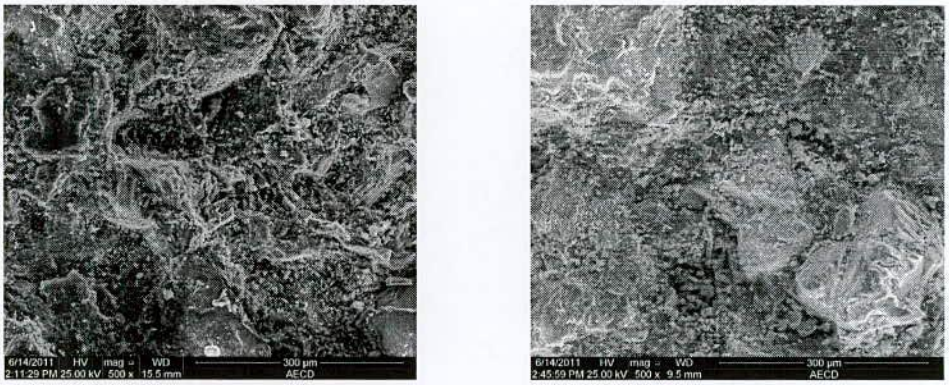
A3-0 (300°C) A3-0 (500°C)



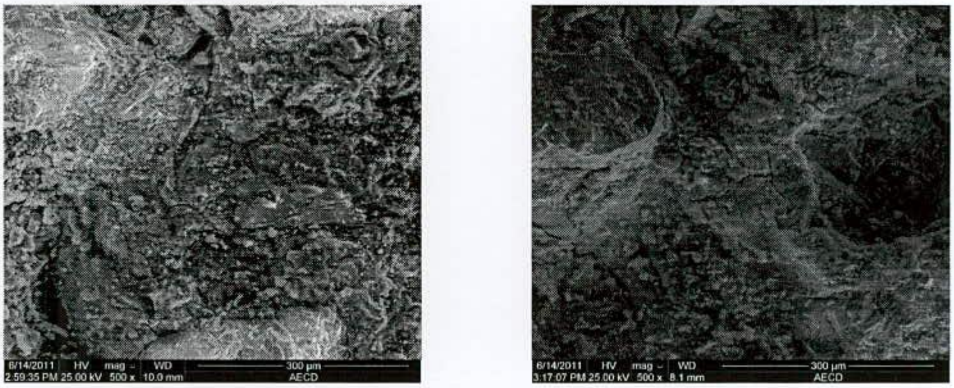
A3-0 (700°C)

Figure 4.42: SEM image of control sample heated to different temperatures

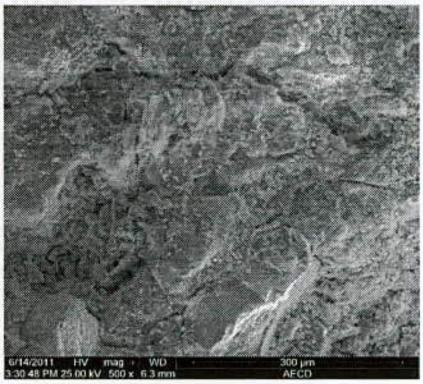
The width of remaining length varied from 1.50 µm to 2.85 µm. However, crack length was reduced to 2356 µm at 700°C. Whereas, micro-crack width was further increased to 11.50 µm, which is 45% of the total length. The 20% length was with 6 µm to 8 µm width and rest of the crack was 3 µm widths. The difference in crack length at different elevated temperature may be occurred due to the heterogeneous nature of mortar.



A3-20 (32°C) A3-20 (200°C)



A3-20 (300°C) A3-20 (500°C)

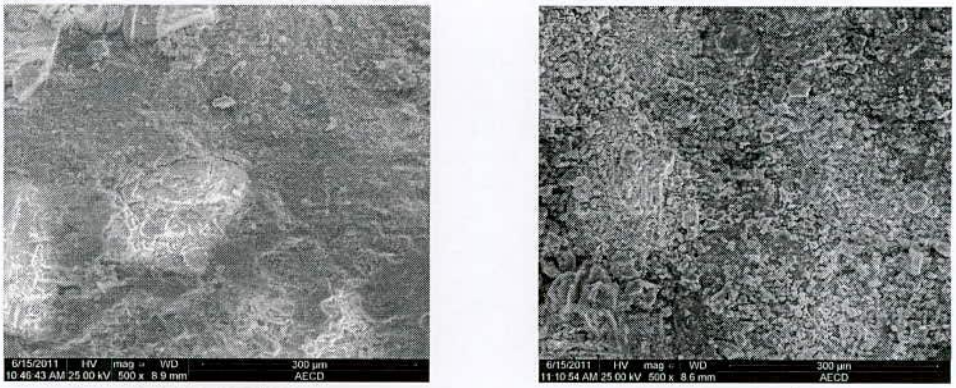


A3-20 (700°C)

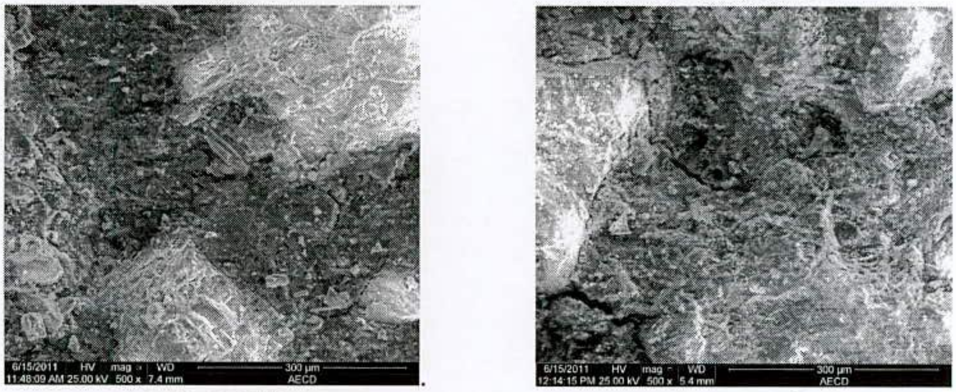
Figure 4.43: SEM image of mortar with 20% RHA heated at different temperatures

No crack was observed in SEM image for 20% RHA sample (A3-20) at 32°C and 300°C (Figure 4.43). At 200°C the sample exhibited micro cracks of 657 µm length with very minor width. The total crack length was 3567 µm and the maximum width was 3.05 µm which is 17% of total crack length for sample heated at 500°C. The width of the remaining length was 1.1 µm to 2.9 µm. Again, for 700°C, the total micro-crack length was found to be 3630 µm. The width of crack was found to be

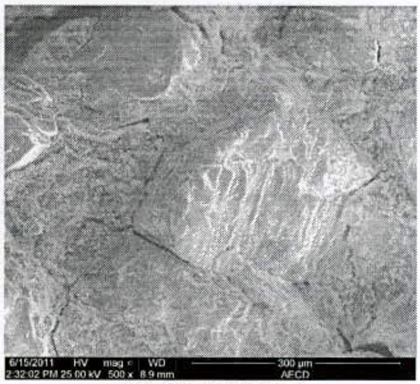
7.9 µm which is 80% of the crack length and the rest of the crack was 2 µm to 6 µm width.



A3-30 (32°C)   A3-30 (200°C)



A3-30 (300°C)   A3-30 (500°C)



A3-30 (700°C)

Figure 4.44: SEM image of mortar with 30% RHA heated at different temperatures

From Figure 4.44, no crack was observed in SEM image for mortar sample having 30 % RHA up to 200°C temperature. Total length of the crack was 1619 µm and most of the crack width was equal or below to 0.12 µm at 300°C. Only 10 % length of the crack was 0.25 µm width. A3-30 (500°C) showed the total crack length of 1610 µm which is similar to the length of samples in 300°C. Crack width was increased and about 45 % of the crack was at least 1.95 µm widths. In this case the length of the crack was observed equal for all samples while the width of the crack was increased at 300°C. It was observed that the total crack length was 2668 µm at 700°C. Crack width was increased and about 68 % of the crack was at least 2.8 µm widths. According to Ali et al., (2004) and Kalifa et al., (2000), the effects of high temperatures on concrete are generally visible in the form of surface cracking. Omer (2007) noticed that the surface cracks became visible when the temperature reached to 600°C.

4.3.6 FT-IR Spectrum Analysis

A potassium bromide (KBr) pellet was prepared by grinding the sample with KBr at high pressure in dry condition to perform the FT-IR spectrum with the help of FT-IR 8400 Shimadzu Spectrometer. KBr was chosen because it is transparent to infrared radiation. At first finely 1 µg of ground sample was mixed with 100 µg of KBr and prepared the pellet. A lower concentration of sample was taken to prepare thin pellet like a liquid film. The noisy spectra might form by complete absorbing or scattering of the IR beam when pellet is thicker or cloudy. The prepared pellet is transparent as like a glass that is essential for the FT-IR spectrum test.

The main goal of IR spectroscopic analysis is to determine the presence of chemical functional groups in the sample. Different functional groups absorb different characteristic frequencies of IR radiation. IR spectroscopy is an important and popular tool for structural clarification and compound identification. To ascertain the formation of new compound, OPC sample and sample with 10%, 20% and 30% RHA were studied in a range of wave number 4000 - 500 cm^{-1}. A total 30 numbers of scan were completed with a resolution of 2 cm^{-1}. The FTIR spectrum for mortar sample at normal temperature with and without RHA addition is presented in Figure 4.45 and the FTIR spectrum for mortar sample heated at 300°C is presented in Figure 4.46.

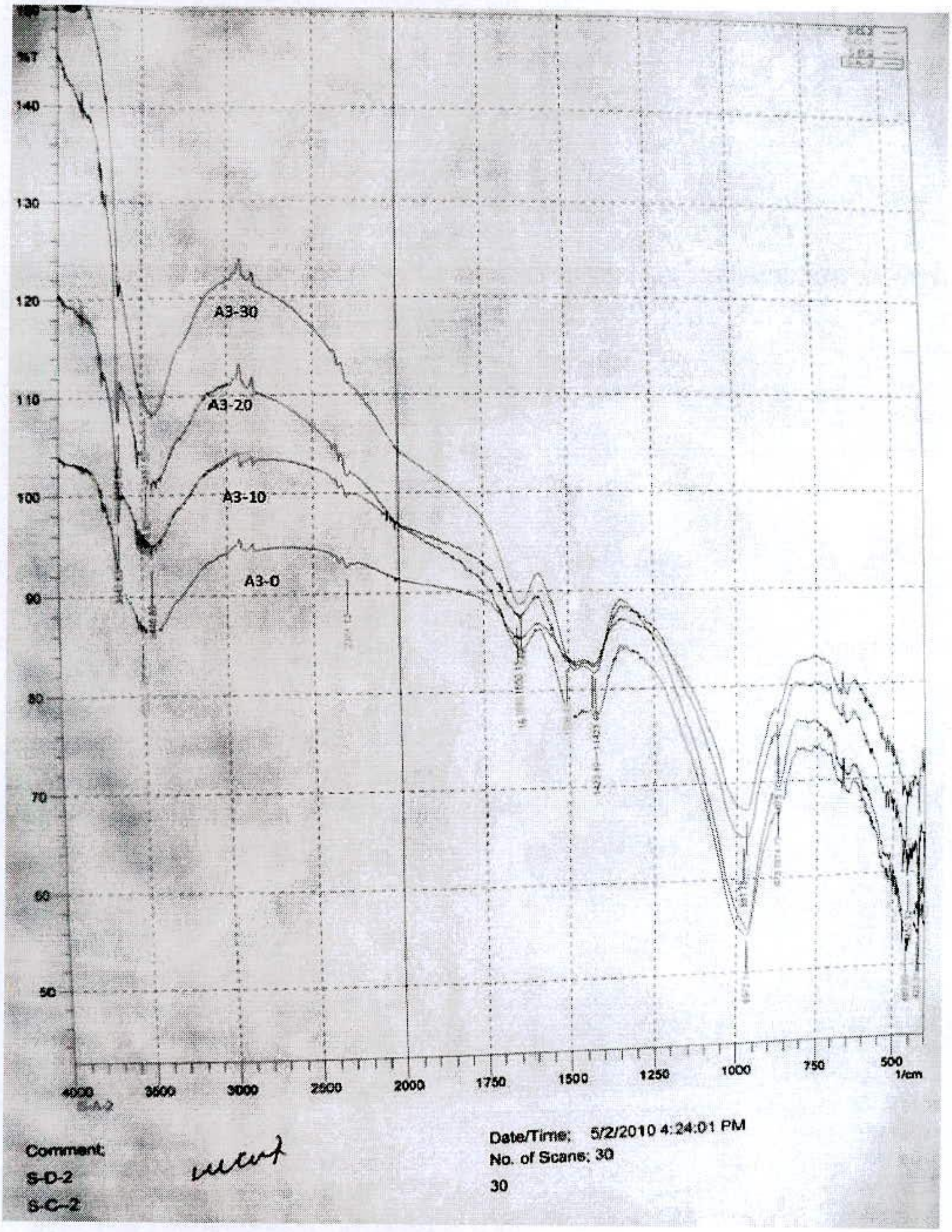


Figure 4.45: FT-IR spectra of non-heated mortar sample with different percentage of RHA

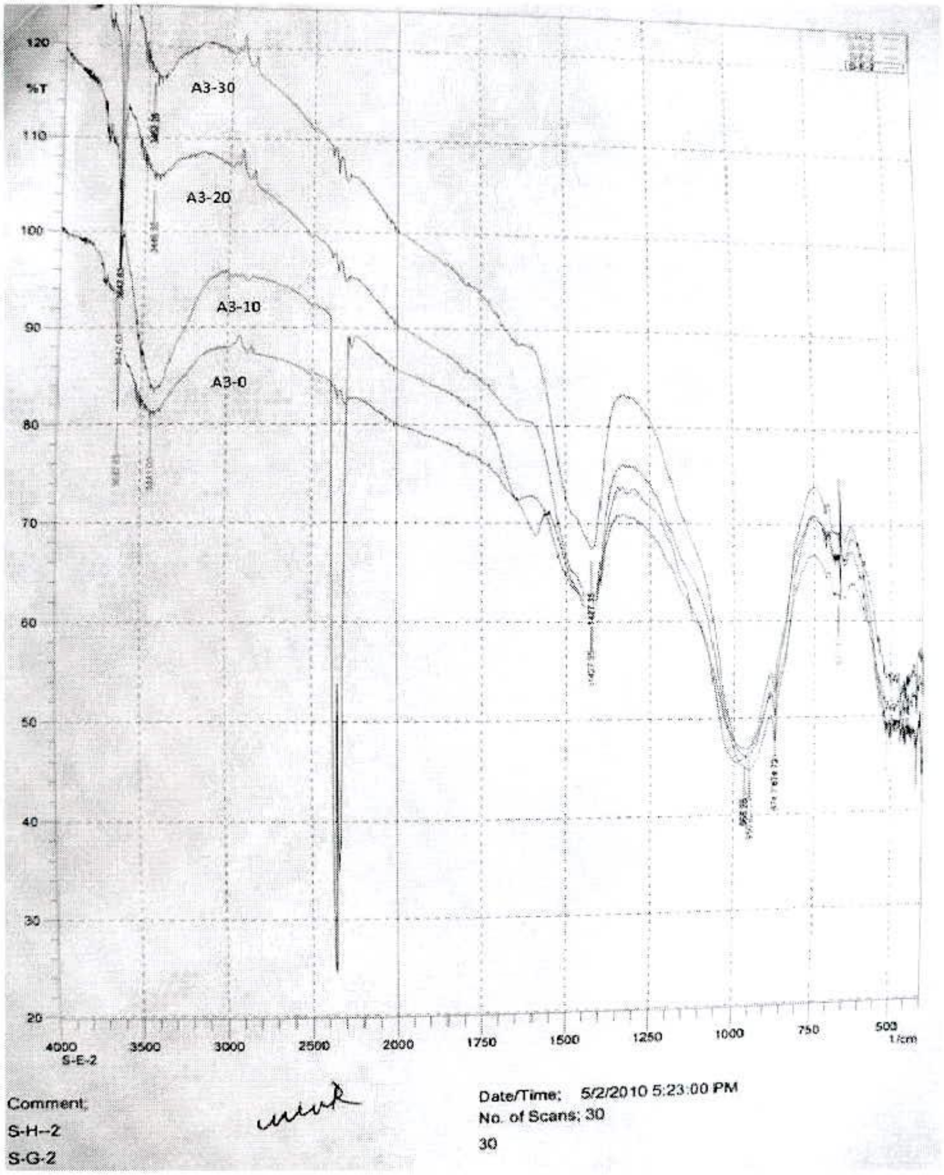


Figure 4.46: FT-IR spectra of heated (300°C) mortar sample with different percentage of RHA

Figure 4.45 and 4.46 indicate that the functional groups for the sample with and without RHA addition provide similar peak values. This signifies that the absence of new functional group in cement mortar with or without RHA at normal as well as elevated temperature. In Figure 4.46 a sharp dropping is observed at wave number 2350 indicates the unwanted presence of CO_2 in sample A3-10. From this observation it may be concluded that the addition of RHA with OPC act as a micro-filler, and this observation is similar to Nehdi, et al. (2003).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The experiments were conducted for the development of sustainable cement mortar incorporating rice husk ash in this study. Seven specific objectives of this study and scope of the work are mentioned in Chapter 1. To fulfil the requirement of the objectives the experiments were conducted and subsequent results are presented in Chapter 4. On the basis of the extensive experimental observations and discussions the following conclusions are drawn.

i. Rice husk ash was produced from laboratory burning system with 60 hour retention time exhibits better performance than the conventional and heap burning systems. Retention time has a significant effect on the Blaine fineness and rate of ash production. The laboratory burning produced the best quality RHA with maximum fineness.

ii. Grinding time of 90 minutes is reasonably satisfactory for optimum fineness of rice husk ash produced in laboratory burning with 60 hours retention time.

iii. The RHA obtained from laboratory burning is in amorphous state and the texture is angular in shape.

iv. Loss on ignition is less for RHA obtained from laboratory burning system with 60 hours retention time compared to the RHA produced from heap and conventional burning system.

v. Rice husk ash from laboratory burning with 60 hours retention and 90 minutes grinding time satisfied the requirement to use as a pozzolanic material according to ASTM Standard.

vi. A notable reduction of flowability is obtained with incorporation of RHA in cement mortar. The water requirement for standard flowability is directly increased with the increase of rice husk ash addition in cement mortar.

vii. The addition of RHA increases the initial setting time of cement mortar. Conversely, the final setting time of cement mortar gradually decreases due to the addition of RHA.

viii. The rheology of the cementitious materials is significantly altered due to addition of RHA as a cement replacing material in mortar.

ix. The compressive strength of control sample exhibits higher values up to 28 days curing than all other samples having RHA.

x. The mortar samples having RHA of conventional and heap burning show lower compressive strength than the control sample as well as the sample having RHA obtained from laboratory burning at all replacement levels.

xi. The mortar sample with 20% RHA exhibits the highest strength at 90 days and onward. Moreover, the cement mortar with 15% RHA reveals second highest compressive strength at the respective sample age. The compressive strength of mortar at 15% and 20% replacement is almost same at the highest age. The optimum replacement level of ordinary Portland cement by rice husk ash might be 15% or 20% by considering other parameters.

xii. Permeability of mortar sample decreases with the increase of RHA addition and also the sample age. The highest permeability is obtained for control sample while mortar having 30% RHA shows the lowest permeability from 28 to 350 days. The sample having 25% RHA exhibits the lowest permeability at 900 days.

xiii. Water sorption of mortar samples having RHA exhibits lower values than the controlled sample. An inverse relationship is observed between RHA content and sorptivity.

xiv. Samples with 15% and 20% RHA exhibit the best performance against salt crystallization than any other percentages of replacement levels along with the control sample. Only these two samples complete the standard 20 test cycles.

xv. All samples immerged in sulphate solution for 28 days after initial curing of 28 days provides higher compressive strength in comparison to the strength of samples obtained after 28 days of normal curing. The sample having 15% RHA lost 25% strength after 112 days immersion in sulphate solution. However, the sample with 20% RHA lost 51% strength for same 112 days of immersion. The controlled sample collapsed after 56 days of immersion in sulphate solution.

5.2 RECOMMENDATIONS

The present study was conducted to develop a sustainable cement mortar incorporating RHA. However, there are many scopes to work with RHA considering other parameters that were not under the scope of this study. The following additional studies are recommended that can be conducted for the further development in commercial scale production and commercialization of the product, which are proposed below:

i. An investigation can be conducted to improve the quality of RHA considering aeration and rice husk feeding rate in the combustion chamber for the commercial production of RHA.

ii. The performance of mortar and concrete can essentially be investigated for RHA blended cement considering lower fineness modulus of fine aggregate.

iii. In depth investigation can be carried out to find out the mechanisms of strength gaining at later ages as well as elevated temperature for the addition of RHA with OPC.

iv. Detail study can be carried out to obtain the behaviour of lime mortar and concrete with the addition of RHA.

v. The effect of blending of RHA with clinker in cement kiln can be investigated for commercial production of RHA blended cement.

vi. Detail economical and environmental aspects may be performed to develop an environment friendly cementitious material production industry by incorporating RHA in ordinary Portland cement.

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ANNEXURE

Annexure - A

Table A-1: Water requirement for standard flow value of RHA 1

ID No	Replacement level	Water Demand (W/C Ratio, %)	Flow Value (mm) (110±5 mm)
RHA1-0	0	50.0	110
RHA1-10	10	59.0	107
RHA1-15	15	63.2	109
RHA1-20	20	66.0	112
RHA1-25	25	69.80	113*
RHA1-30	30	74.6	110*

* Crack was observed

Table A-2: Water requirement for standard flow of RHA 2

Sl No	Replacement level	Water Demand (W/C Ratio, %)	Flow Value (110±5 mm)
RHA2-0	0	50.0	111
RHA2-10	10	60.0	112
RHA2-15	15	63.8	108
RHA2-20	20	67.2	111
RHA2-25	25	70.6	114*
RHA2-30	30	75.1	111*

* Crack was observed

Table A-3: Water requirement, flow value and replacement of cement by RHA 3

Sl No	Retention time (h)	Replacement level	Water Demand (W/C Ratio, %)	Flow Value (110±5 mm)
1	36	0	50	109
2		10	58.6	106
3		15	62	112
4		20	64.7	107
5		25	67.4	114*
6		30	71.9	113*
1	48	0	50	109
2		10	51.5	106
3		15	53.2	110
4		20	55.4	114
5		25	58.8	110
6		30	62.2	108
1	60	0	50	110
2		10	52	108
3		15	52.8	106
4		20	54.5	110
5		25	55	114
6		30	56.8	112

* Crack was observed

Table A-4: Strength after immerged in sulfate solution at different ages with S1.

Sample ID	Strength, MPa								
	28 days moist cured	28 days in sulphate solution		56 days in sulphate solution		84 days in sulphate solution		112 days in sulphate solution	
	Aver.		Aver.		Aver.		Aver.		Aver.
A3-0	33.09	37.57	35.96	30.33	27.92	--	--	--	--
		35.84		26.88		--		--	
		34.46		26.54		--		--	
A3-10	28.78	36.19	34.12	35.84	32.74	27.92	25.73	--	--
		34.12		32.05		25.16		--	
		32.05		30.33		24.12		--	
A3-15	30.47	38.94	37.34	42.73	40.09	39.63	37.11	24.12	22.86
		37.22		39.63		36.53		24.12	
		35.84		37.91		35.15		20.33	
A3-20	30.30	41.36	38.14	40.67	37.68	31.71	29.52	17.23	14.93
		36.88		37.91		29.64		14.13	
		36.19		34.46		27.23		13.44	
A3-25	27.54	31.71	30.56	31.36	30.10	24.81	22.52	--	--
		30.67		29.64		22.40		--	
		29.29		29.29		20.33		--	
A3-30	21.83	25.16	22.63	--	--	--	--	--	--
		21.37		--		--		--	
		21.37		--		--		--	

Table A-5: Strength after immerged in sulfate solution at different ages with S2.

Sample ID	Strength, MPa								
	28 days moist cured	28 days in sulphate solution		56 days in sulphate solution		84 days in sulphate solution		112 days in sulphate solution	
	Aver.		Aver.		Aver.		Aver.		Aver.
A3-0	34.38	36.70	34.73	25.94	24.44	--	--	--	--
		34.33		24.47		--		--	
		33.17		22.92		--		--	
A3-10	31.51	34.12	33.34	27.83	25.25	--	--	--	--
		32.74		24.47		--		--	
		33.17		23.44		--		--	
A3-15	33.31	36.45	35.10	36.70	34.18	29.47	27.69	18.44	17.00
		34.04		33.69		26.63		16.80	
		34.81		32.14		26.97		15.77	
A3-20	30.47	34.46	32.89	32.14	30.10	24.47	23.38	--	--
		33.17		29.64		23.44		--	
		31.02		28.52		22.23		--	
A3-25	28.43	30.67	28.81	28.52	27.06	21.28	20.51	--	--
		28.35		26.54		20.85		--	
		27.42		26.11		19.39		--	
A3-30	23.01	25.33	23.44	--	--	--	--	--	--
		23.78		--		--		--	
		21.22		--		--		--	

Table A-6: Variation of Strength (MPa) due to Elevated Temperature and air cooling.

	Temperature					
	32°C	200°C	300°C	400°C	500°C	700°C
	Strength MPa					
A3-0	35.76	44.47	41.96	34.20	31.85	23.85
A3-10	36.50	42.35	47.84	40.62	32.31	22.39
A3-15	37.74	39.73	48.26	43.52	36.47	21.03
A3-20	38.08	40.92	46.44	41.06	38.42	22.79
A3-25	35.30	43.56	39.21	33.97	29.83	21.06
A3-30	32.51	34.99	31.13	26.63	24.61	20.35

Table A-7: Strength variation due to Elevated Temperature and quenched with water

Sample ID	Temperature					
	32°C	200°C	300°C	400°C	500°C	700°C
	Strength MPa					
A3-0	35.76	40.86	37.32	29.98	24.72	19.35
A3-10	36.50	42.95	41.55	34.33	26.47	20.59
A3-15	37.74	38.79	40.18	40.10	31.22	19.42
A3-20	38.08	35.35	43.02	41.93	33.05	18.47
A3-25	35.30	40.90	34.73	28.48	24.32	14.18
A3-30	32.51	31.05	28.89	26.91	20.57	12.63

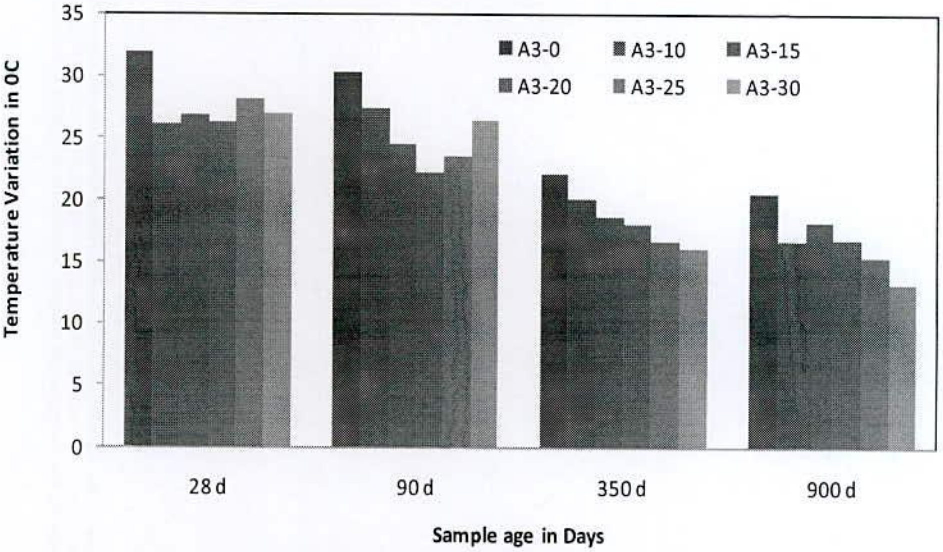
Table A-8: Percentage of Strength wrt. to control sample at ambient temperature

Samples are normal cooling after elevated temperature						
Sample ID	Temperature					
	32°C	200°C	300°C	400°C	500°C	700°C
A3-0	100.0	124.4	117.3	78.8	89.1	66.7
AS-10	102.1	118.4	133.8	113.6	90.3	62.6
A3-15	105.5	111.1	135.0	121.7	102.0	58.8
A3-20	106.5	114.4	129.9	114.8	107.4	63.7
A3-25	98.7	121.8	109.6	95.0	83.4	58.9
A3-30	90.9	97.9	87.1	74.5	68.8	56.9

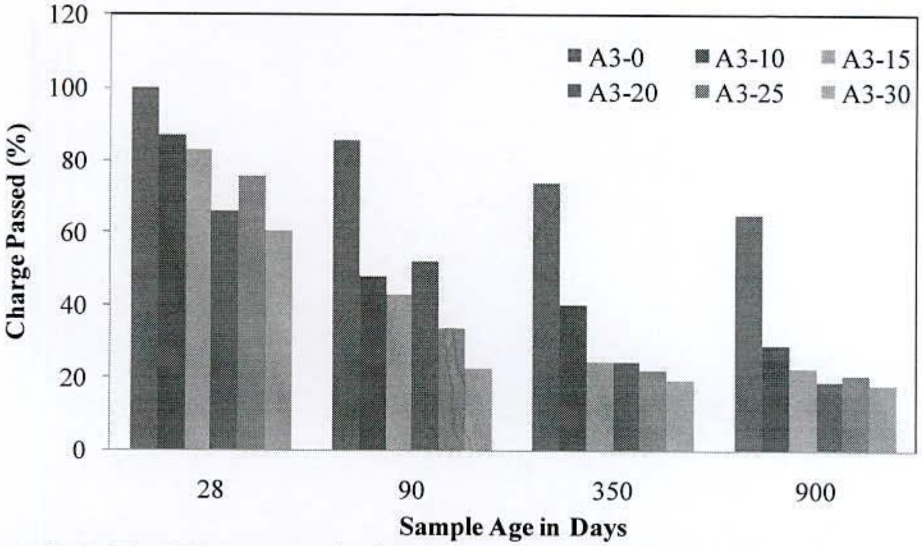
Table A-9: Percentage of Strength wrt to control sample at ambient temperature

Samples are quenched and normal cooling after elevated temperature						
Sample ID	Temperature					
	32°C	200°C	300°C	400°C	500°C	700°C
A0	100.0	114.3	104.4	83.8	69.1	54.1
A10	102.1	120.1	116.2	96.0	74.0	57.6
A15	105.5	108.5	112.4	112.1	87.3	54.3
A20	106.5	98.9	120.3	117.3	92.4	51.6
A25	98.7	114.4	97.1	79.6	68.0	39.6
A30	90.9	86.8	80.8	84.2	57.5	35.3

Annexure - B



FigureB-1: Total Charge passing through different samples at different ages for sand type S2.



FigureB-2: Total Charge passing in % compare to 28 days control sample for sand type S2.

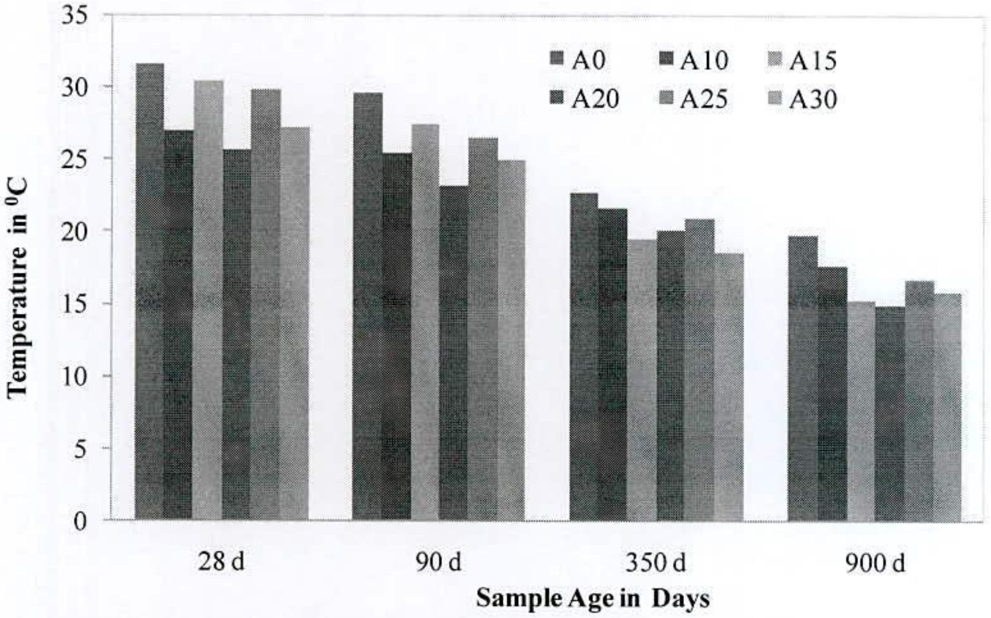


Figure B-3: Temperature rise during the experiment for sand type S2.

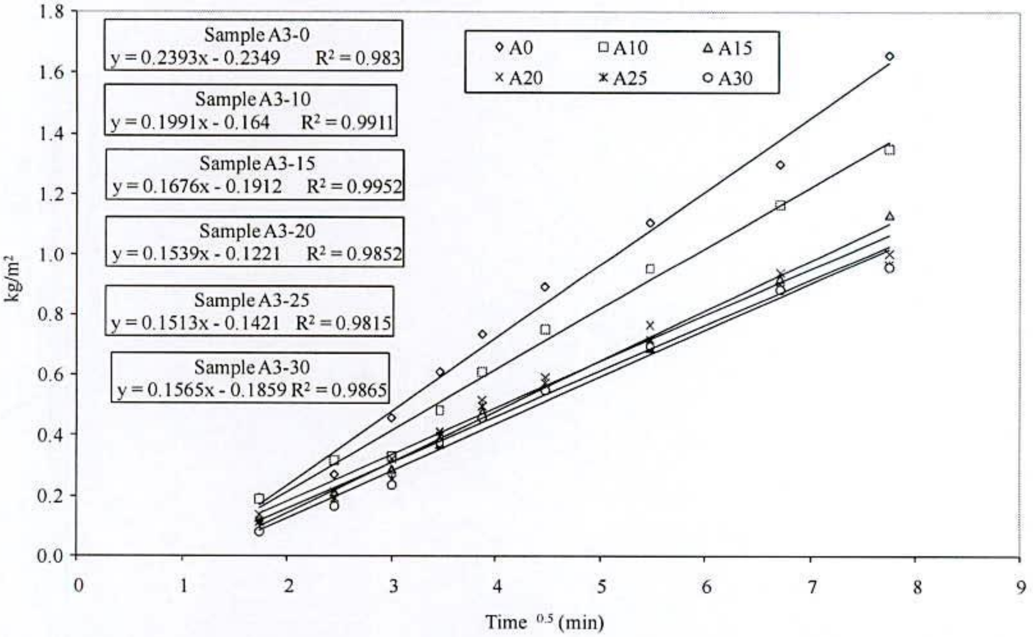


Figure B-4: Linear regression for absorption by capillary during 6 hours for sand type S2

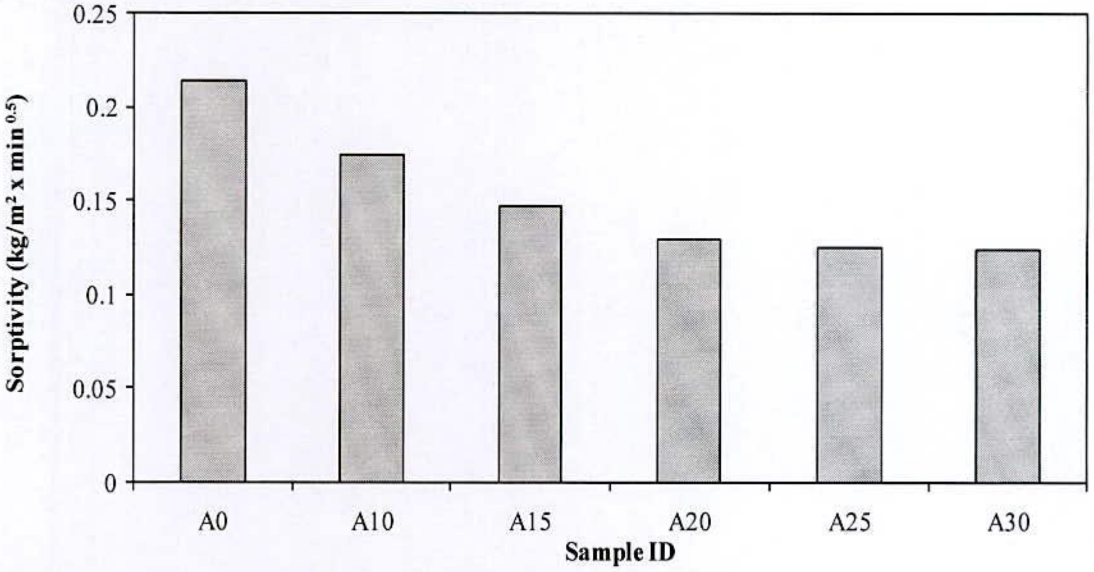


Figure B-5: Sorptivity values of mortar with different proportion of RHA for sand type S2.

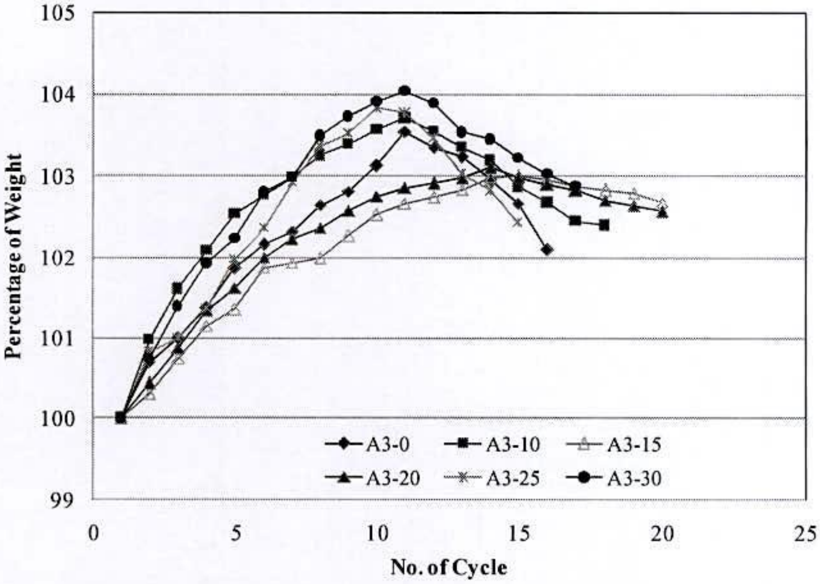


Figure B-6: Variation of weight with respect to test cycle for sand type S2

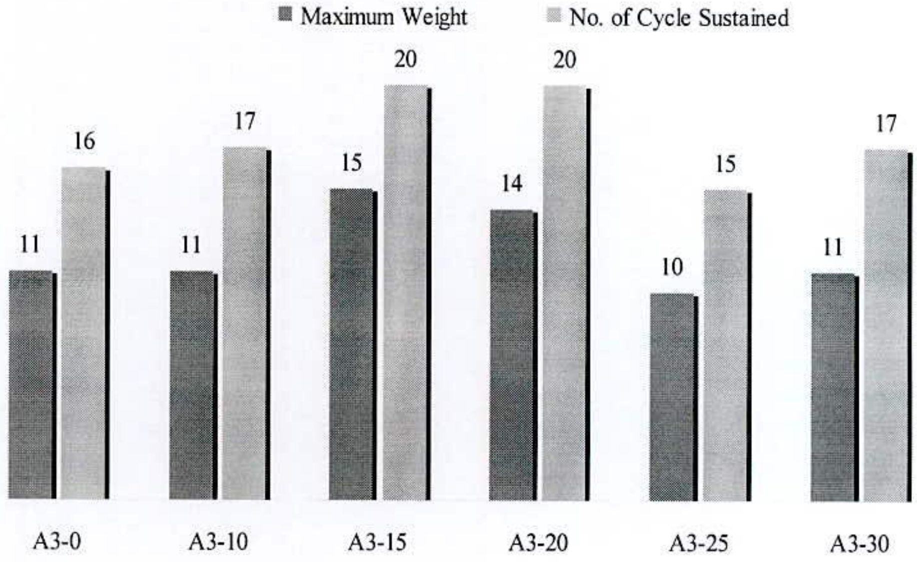


Figure B-7: sustainability and gain of weight due to crystalization with sand type S2.

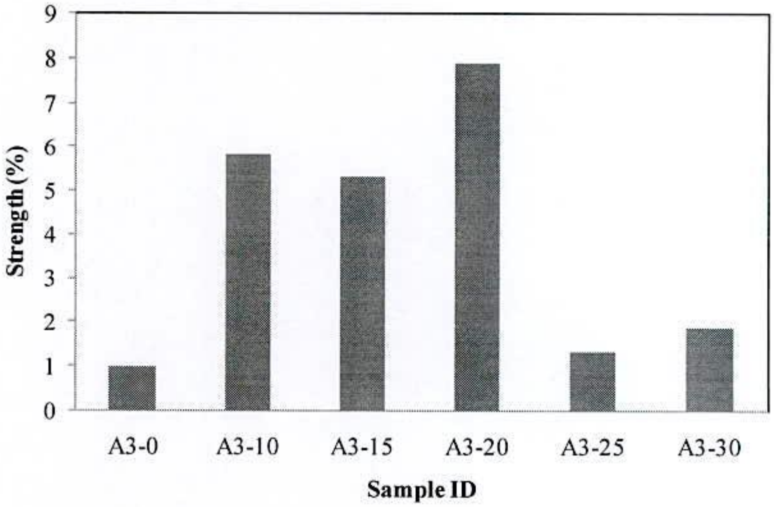


Figure B-8: Variation of strength at 28 days immersion of sulphate immersion with sand type S2.

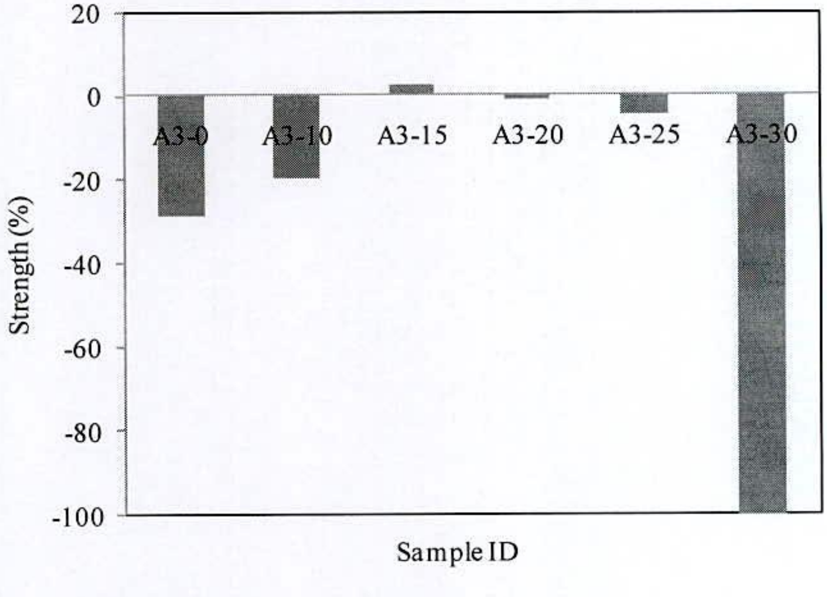


Figure B-9: Variation of strength at 56 days immersion of sulphate immersion with sand type S2.

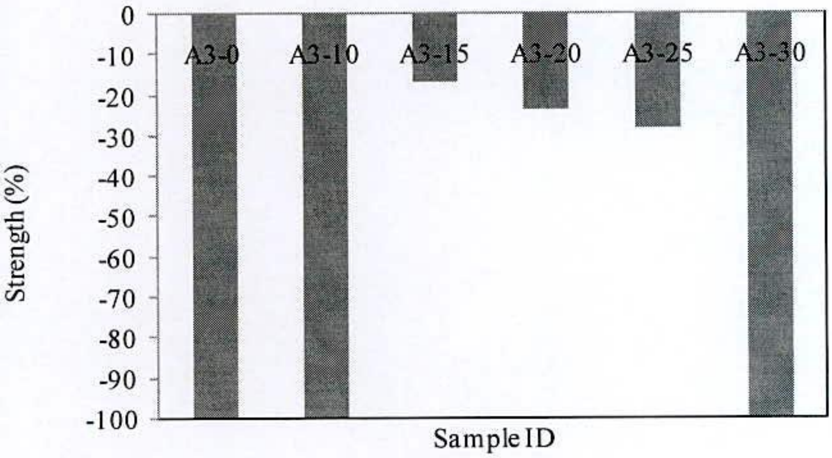


Figure B-10: Variation of strength at 84 days immersion of sulphate immersion with sand type S2.

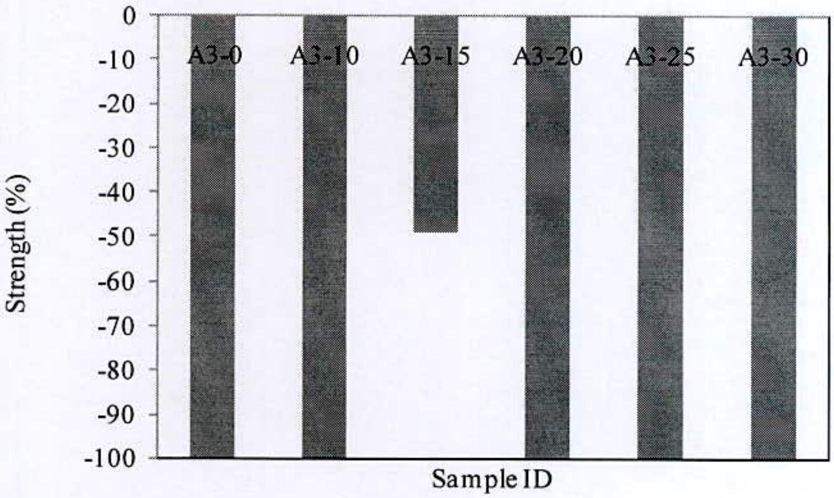


Figure B-11: Variation of strength at 112 days immersion of sulphate immersion with sand type S2.