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Date : 30 June 2008

TITLE PAGE

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Rice Husk Ash: Burning Procedures and Its Effects On Cementitious Properties of Paste and Mortars

By

Mohamed Kassim Bin Jahaber

A THESIS

SUBMITTED TO THE POSTGRADUATE STUDIES PROGRAMME

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DEGREE OF MASTERS OF SCIENCE IN CIVIL ENGINEERING

BY RESEARCH

BANDAR SERI ISKANDAR,

PERAK

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

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Rice Husk Ash: Burning Procedures and Its Effect on Cementitious Properties of Paste and Mortars

Abstract

Rice husk ash (RHA) is a waste material that needs costly disposal to avoid environmental pollution. Nevertheless RHA has basic oxide contents that have some cementitious properties. By and large through normal burning procedures, RHA contains about 80%-85% amorphous SiO_2, which is a vital cementitious element. The focus of this research is to establish a burning procedure to derive highly active amorphous silica from rice husk so that its pozzolanic reactivity can be enhanced. Numerous burning procedures have been employed for this purpose. Finally two methods of burning were established. Even though the temperatures of burning varied between the two procedures, both were based on the same principle of thermal combustion in three stages. In the first stage the burning temperature was capped at 280°C, which was less than the ignition temperature of rice husk in the presence of air. In the second stage, the temperature was maintained between 280°C and 520°C. The presence of air is essential to oxidize the residual carbon from the rice husk. In the third stage, the temperature was increased to 550°C but in the absence of air. The two procedures with burning duration of 184 minutes and 176 minutes yielded silica content of 93.1 % and 94.3% respectively. The XRD Test further confirmed that the silica was in amorphous form. The cement paste cubes containing RHA replacements of 2.5%, 5%, 7.5%, 10%, 12.5%, 15%, 17.5% & 20% were tested and their compressive strengths were compared with control cement cubes. It was found that the percentages replacement of 5% and 7.5% of RHA with water/cement (w/c) of 0.28 and 0.32 respectively produced higher compressive strength compared with its control mix. The optimum w/c for cement paste cubes containing 2.5% RHA in order to get high strength was 0.25. For other replacement ratios of 5%, 7.5%, 10%, 12.5%, 15%, 17.5% & 20% RHA, the corresponding w/c were 0.28, 0.32, 0.32, 0.35, 0.36, 0.37, and 0.39 respectively. Test on pozzolanic activity index of RHA was carried out and compared with RHAs that were obtained from other methods of burning. The pozzolanic activity index of this RHA was found to have higher value compared to RHA from ferrocement incinerator. The effect of RHA on porosity of cement cubes containing RHA was also investigated in this research and was found that RHA replacement with low w/c reduces porosity.

Abu Sekam Padi: Procedure Pembakaran Dan Effek Dalam Ciri-Ciri Mortar Simen.

Abstrak

Abu sekam padi adalah bahan buangan yang memerlukan kos pembuangan yang tinggi untuk mengelakan pencemaran alam sekitar. Walau bagaimana pun abu sekam padi mempunyai ciri-ciri simen. Dengan kaedah pembakaran biasa, abu sekam padi mengandungi lebih kurang 80%-85% bahan silika (SiO_2) amorfus yang merupakan elemen penting dalam simen. Tinjauan utama penyelidikan ini adalah untuk mencari suatu tatacara pembakaran sekam padi untuk menghasilkan silika amorfus yang aktif supaya aktiviti pozolanik dalam simen dapat digalakkan. Pelbagai tatacara pembakaran telah dikaji serta dijalankan untuk tujuan ini. Akhirnya dua cara pembakaran telah dipastikan. Walaupun suhu pembakaran adalah berbeza bagi kedua-dua tatacara pembakaran. Kedua-duanya adalah berdasarkan kepada prinsip pembakaran terma yang diasingkan dalam tiga peringkat. Dalam peringkat pertama,dengan kehadiran udara suhu pembakaran dihadkan pada 280°C, iaitu yang lebih rendah dari suhu pencucuhan sekam padi. Dalam peringkat kedua, suha pembakaran dikawal serta dikekalkan diantara 280°C dan 520°C. Kehadiran udara adalah penting untuk mengoksidakan baki karbon dalam sekam padi. Dalam peringkat ketiga pula, suhu pembakaran ditingkatkan ke 550°C tanpa kehadiran udara. Kedua-dua peringkat pembakaran dengan masa pembakaran 184 minit dan 176 minit dapat masing-masing menghasilkan abu sekam padi yang mengandungi silika sejumlah 93.1 % dan 94.3%. Uji-kaji XRD telah dijalankan dan membuktikan silika yang dihasilkan adalah dalam bentuk amorfus. Kuib simen yang mengandungi peratusan gantian simen dengan abu sekam padi sebanyak 2.5%, 5%, 7.5%, 10%, 12.5%, 15%, 17.5% & 20% telah diuji, dan kekuatan mampatan kiub simen telah dibandingkan dengan kiub kawalan. Didapati kiub yang mempunyai peratusan gantian 5% dan 7.5% abu sekam padi dengan masing-masing nisbah air simen (a/s) 0.28 dan 0.32 menghasilkan kekuatan mampatan yang lebih tinggi berbanding dengan kiub kawalan. Nisbah optima a/s untuk bancuhan kiub simen mengandungi 2.5% abu sekam padi untuk menghasilkan kekuatan mampatan yang tinggi adalah 0.25. Untuk nisbah gantian simen yang lain seperti 5%, 7.5%, 10%, 12.5%, 15%, 17.5% & 20% abu sekam padi, nisbah a/s yang diperlukan adalah masing-masing 0.28, 0.32, 0.32, 0.35, 0.36, 0.37, dan 0.39. Uji-kaji indeks aktiviti pozolanik abu sekam padi telah dijalankan dan dibandingkan dengan abu sekam padi yang dihasilkan oleh tatacara pembakaran yang lain. Indeks aktiviti pozolanik abu sekam padi yang dihasilkan dengan tatacara yang disyorkan dalam kajian ini didapati mempunyai nilai yang lebih tinggi berbanding dengan abu sekam padi yang dihasilkan dengan alat pembakaran ferosimen. Kerana keliangan kiub simen yang mengandungi abu sekam padi telah dikaji dalam penyelidikan ini, dan didapati abu sekam padi dalam simen dengan a/s yang rendah akan menghasilkan keliangan yang rendah.

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CHAPTER ONE

1.1 Introduction

Rice husk is an agricultural waste that is being produced in large amount in Malaysia and else where. In Malaysia, annual production of rice husk is about two million tones per year. A small fraction of the waste rice husk is used for cattle feed and as burning fuel. The rest of the bulk amount is disposed off. The disposal of rice husk by open surface burning is problematic because it can pollute the atmosphere due to presence of high carbon content present in the smoke. This problem could be resolved by properly utilizing the rice husk as value added material.

When the rice husk is burnt, about 17% - 25% of its weight remains as ash, which is rich in silica. This silica content in ash has great significance as the silica rich ash can partially replace cement in concrete. At present the understanding on pozzolanic material for producing durable concrete is quite well deliberated and pozzolanic materials like fly ash, slag, and silica fumes, etc., are being used as partial substitutes for cement in concrete industry.

2.1.1 Background of Study

The existence of the rice husk is due to the morphological development of the rice plant, which resulted in the evolution of a protective envelope, which must be removed to gain access to the edible rice grain. The protective cover is the husk. Rice husk is composed of organic constituents, cellulose, fibre, etc., The rice husk in the mills is a waste material, which occupies a large space and requires to be cleared even now and then. Despite being used as a conventional fuel and cattle feed, still abundant is left to decay. An easy solution to mill owners is to burn it. However, the open field burning creates pollution to the environment. So, it became necessary to find a better use of the rice husk.

Research work on rice husk started in 1924. These researches led to the discovery that when the rice husk was burnt about 17-25% of its initial weight was silica rich ash. Initially a conventional method of open heap burning had been employed to derive the ash. The ash derived from this method of burning is in crystalline form and chemically non reactive. Further this rice husk ash had shown non-uniformity in structure, characteristic properties and composition. The nature of uncontrolled combustion in open heap burning had resulted in attributing these draw backs to rice husk ash. It drew the attention of many researchers to invent a new method to derive chemically reactive amorphous ash from rice husk. Since then many people conducted researches and came out with various methods of obtaining silica in the amorphous form. Many special methods were designed and special equipment was invented to obtain homogenous silica. Those methods involved careful pyro processing of rice husk under controlled conditions of heat and air.

1.2 Problem Statement

2.1.1 Depletion of Resources

Due to extensive use of conventional concrete in construction industry, demand for cement production is increasing, hence the raw materials used for cement manufacturing such as limestone, shale etc., are depleting. Therefore there is a great need to find alternative materials, which can partially substitute the portion of Portland cement in concrete.

2.1.2 Agricultural Waste Disposal Problem

Due to the ever-expanding population and food production, the agricultural wastes also tend to increase annually. This has created an ever increasing problem of disposal of such wastes. The available space to dump them is limited and costly. It is necessary to find ways and means to dispose them without any pollution problem and financial burden to rice millers. For an example, it is estimated that the production of rice husk in Malaysia is two million metric tons a year. The amount of RHA generated by rice millers is estimated to be 400,000 tones per year. So, these agricultural wastes are required to be converted into value added product by extensive R&D activities.

2.1.3 Environmental Pollution

The open burning is a conventional way of disposing such type of agricultural wastes. Although, by regulation it is prohibited to burn such wastes in open fields, however, it is much difficult to implement in rural areas. This open burning spreads hazardous carbon particles and other gases into atmosphere in the form of smoke that is harmful for clean environment.

2.1.4 Issues Related to Concrete Durability

Since many decades ago, durability of concrete has become one of the concerns amongst researchers. The deterioration mechanisms in concrete are due to the permeability problems faced by concrete cover which basically allows ions, gasses and solutions to be transported into the concrete. This problem can be prevented by enhancing the properties of concrete at the cover zone. Silica rich pozzolanic materials have good track record to tackle such issues.

1.3 Objectives

The principal objectives of this research are

a) To develop a burning procedure for thermal combustion of rice husk to maximize the retrieval of active amorphous silica.

b) To determine the optimum percentage of RHA in replacing OPC.

c) To identify the optimum water cement ratio.

1.4 Scope of this Study includes

a) To burn the rice husk in accordance with burning procedure and determine the chemical composition of ash.

b) To carry out x-ray diffraction on RHA for qualitative analysis to determine major and minor phases.

c) To carry out x-ray fluorescence on RHA for elemental composition.

d) To determine the compressive strength of cement paste with various % inclusion of RHA. The results are compared to the results with normal OPC.

e) To carry out pozzolanic activity index test on ashes. Compare and analyze the results.

f) To carry out porosity test on cement paste cubes samples with and without addition of RHA as replacement material on various proportions.

CHAPTER TWO

Literature Review

2.1 Rice Husk – An Introduction

Rice husk is an agricultural by-product that is available abundantly all over the world. Only in Malaysia, the annual production of rice husk is about two million tones per year. A small quantity of which is used for cattle feed and burning as a fuel where as bulk of the quality remained unused. The rest of the quantity is left unused. The disposal of rice husk by the conventional method of burning causes pollution to the atmosphere due to presence of high carbon content in the smoke.

Upon burning of rice husk, it yields about 17% - 25% ash, which is found rich in silica[2]. This silica has a great significance in concrete production. Currently the understanding of producing durable concrete exposed to very aggressive environment has much improved. Pozzolanic materials like fly ash, slag, and silica fumes are being used as partial substitutes for cement in concrete. Literature review shows that the rice husk ash has also shown to have better pozzolanicity[2].

2.1.1 Morphology

The existence of the Rice husk is due to the morphological development of the rice plant, which resulted in the evolution of a protective envelope, which must be removed to gain access to the edible rice grain. The productive cover is the husk. Rice husk is composed of organic matter such as cellulose lignin, fibre and small amounts of crude protein and fat. Among these organic constituents, cellulose is a major constituent. In addition, rice husk consists of a range of minerals, which include silica, alumina and iron oxide. The composition of rice husk by proximate analysis (% dry fuel) is obtained as fixed carbon (16.22%), volatile matter (63.52%) and ash (20.26%). But According to ultimate analysis (% dry fuel), rice husk contains carbon (38.83%), hydrogen (4.75%), oxygen (35.47%), nitrogen (0.52%), sulfur (0.05%), chlorine (0.12%) and ash (20.26%) (Refer Table 2.1) When the rice husk is burnt, about 17% - 25% of its weight remains as ash, which is rich in silica. The ash will also contain as much as 10% alkalis, traces of iron, aluminum, and calcium

Table 2. 1: Composition, heating values and alkali index of typical rice husk.

Proximate analysis (% dry fuel)	Ultimate analysis (% dry fuel)	Elemental composition of ash (%)	Higher heating value (constant volume)	Alkali index (as Oxide)
Fixed Carbon = 16.22	Carbon = 38.83	SiO_2 = 91.42	15.84 MJ / kg	0.50 kg Alkali / GJ
Volatile mater = 63.52	Hydrogen = 4.75	Al_2O_3= 0.78	6811 Btu / lb	1.17 (lb alkali / MM Btu)
Ash = 20.26	Oxygen (diff.)	TiO_2 = 0.02		
Total = 100	= 35.47	Fe_2O_3 = 0.14		
	Nitrogen = 0.52	CaO = 3.21		
	Sulfur = 0.05	MgO =<0.01		
	Chlorine = 0.12	Na_2O = 0.21		
	Ash = 20.26	K_2O = 3.71		
	Total = 100.00	SO_3 = 0.72		
		P_2O_5 = 0.43		
		CO_2/other		
		Total = 100.64		
		Undetermined = -0.64		

2.1.2 Mineral Admixtures

Admixture is one of the ingredients of concrete, which is used to improve certain properties of concrete. Generally, admixtures can be broadly classified into two major categories that are chemical and mineral admixtures. Chemical admixtures can be further classified by their functions such as air entraining admixtures, water reducing admixtures, retarding admixture, accelerating admixtures and super plasticizers.

Mineral admixtures are generally the by product of natural materials. Based on their chemical properties such as CaO, CO_2, Al_2O_3, Fe_2O_3 they are classified as cementitious materials or pozzolans.

A pozzolan is a siliceous or alumino siliceous material that is by itself possesses little or no cementitious property but will in finely divided form and in the presence of water, chemically react with the calcium hydroxide released by the hydration of Portland cement to form compounds possessing cementitious properties. rice husk ash, palm oil husk ashes, Ground Granulated Blast furnace Slag, Fly ash, Silica fumes are such examples.

2.2 Physical Properties of Cementitious Material

2.2.1 Fineness

Fineness of cement is a vital property. The rate of hydration depends on its fineness. High fineness is necessary for rapid strength development. This property is expressed in terms of surface area per unit mass of the material[1]. As per ASTM and British standards, the minimum required specific surface of ordinary portland cement (OPC) Type 1 is 225m^2/kg. All mineral admixtures especially commercially available admixtures such as silica fume, fly ash and slag are much finer than the OPC. It is the total surface area of cement that represents the material available for hydration.

Tzong-Horng Liew stated that at a heating rate of 5^o C/min, the specific surface areas of both the carbon/silica and pure silica powders from rice husk were 261 and 235 m^2/kg and the average pore diameters were 2.2 and 5.4 μm respectively. It is also reported that leaching of rice husks with an acid solution before their combustion would yield silica powder of high specific surface area. However, if the acid leaching was performed after combustion, the specific surface area of silica would be poor[10].

N.B.Singh and Sarita Rai have used RHA of 387 m^2/kg Blaine surface area in their research. The compressive strength of cement ($280m^2/kg$) was compared with compressive strength of cement with 10% RHA addition. The strength of RHA cement except for the age of one day was found to be higher.

2.2.2 Grindability

The grinding time relates directly to the nature of the silica in the ash. To produce ash of the same fineness, the grinding period can be as long as seven hours for highly crystalline ash, and as little as 15 minutes in a continuous grinder for ash containing amorphous silica. Many researchers have found that the amorphous ash is much easier to grind than the crystalline ash[25]. N.Bouzoubaa and B.Fournier had established a correlation between grinding time and particle size distribution using ball mill grinder. The particles size of the RHA decreased with increasing grinding time. The median particle size for the RHA decreased from 40 to 8.3μm and 7.5μm after 140 and 200 seconds of grinding respectively. Particle size reduction was most significant during the first 140 seconds of grinding. After 140 seconds of grinding, most of the large particles had been crushed so that all the particles were less than 45μm and more than 55% of the particles were less than 10μm. Further extension in the grinding time was less effective in increasing the fineness of material[25].

2.3 Compressive Strength of Cement Pastes

Fresh cement paste is a plastic network of cement particles in water. Total water added with cement to make cement paste is available in paste in one of the three forms: combined water, gel water and capillary water. Combined water, which is non evaporable water in fully hydrated cement and combined chemically or physically with the products of hydration, represents about 23% of the mass of dry cement. Capillary water is water present in capillary pores. The capillary pores available in paste are about 18.5% of original volume of dry cement. It is necessary for capillary pores to contain enough water to carry out hydration processes. Hence capillary water facilitates hydration by providing high internal relative humidity in paste. If cement is partly hydrated due to insufficient water, the paste contains an interconnected system of capillary pores. The effect of this is a lower strength and increased permeability[1].

Compressive strength of concrete is one of the important properties of concrete. Generally, addition of mineral admixture as replacement retards the heat of hydration so that it results in low early strength. Three major physical factors that can affect the compressive strength of concrete are 1) Cement dilution effect 2) Particle size distribution 3) Heterogeneous nucleation[7].

2.3.1 Cement Dilution Effect

The cement dilution effect is equivalent to the effect that was caused by an increase in the water cement ratio of that concrete. Cement dilution effect is inversely proportional to replacement rate of mineral admixtures. The increase of replacement rate involves a decrease of the amount of cement[12]. At early stage; the mineral admixture does not participate in cement hydration process due to its slow pozzolanic reaction. This leads to a decrease of the total amount of hydrates without significantly changing the degree of hydration[12]. This problem can be solved by adding highly reactive form of mineral admixture in concrete.

Several compressive strength tests to monitor the performance of RHA derived from uncontrolled combustion process have been conducted[26]. In this research the performance of 10% RHA was compared with control mix and 10% silica fume replacement. The compressive strength of RHA cement mixture was lower than other two types but it showed some improvement over other two types at 90 days. Nehdi[5] has investigated the performance of amorphous RHA, which was produced from Torbed Reactor under controlled combustion. It was found that the compressive strength results for the various concrete mixtures containing 7.5%, 10% and 12.5% of RHA showed increased compressive from day one onward[5].

2.3.2 Particle Size Distribution

The particles size and amount of the mineral powder used influence the initial porosity and strength of the concrete mix. Chopra studied the effect of crystalline RHA in high strength concrete obtained by intense grinding of RHA in ball mill. From the research results, he concluded that the fineness of RHA might activate the pozzolanic property of RHA even in crystalline form[19]. Mohamed Shoaib Ismail also concluded this in his research.

2.3.3 Heterogeneous Nucleation

Nucleation process is the onset of the phase transition in a small region. The phase transition can be the formation of crystal from a liquid. Nucleation normally occurs at nucleation sites on surface containing liquid or vapour. Suspended particles or minute bubbles also provide nucleation sites. This is called heterogeneous nucleation. When mineral admixtures are dispersed in cement paste, it generates large number of nucleation sites for the precipitation of the hydration products. This mechanism makes the paste more homogeneous and dense thereby improving compressive strength of pastes.

2.4 Pozzolanic Reactivity

2.4.1 Definition

A pozzolan is defined as a siliceous or siliceous and aluminous material, which in itself possesses little or no cementing property but will in a finely divided form and in the presence of moisture, chemically reacts with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties. The capability of a pozzolan to react with calcium hydroxide, especially the rate of reaction is defined as pozzolanic reactivity. The term pozzolanic activity index is used to quantify pozzolanic reactivity.

2.4.2 Significance

The addition of RHA, whose particles are finer than those of Portland cement, will result in dispersion of RHA in cement paste matrix and they generate a large number of nucleation sites for the precipitation of the hydration product of the cementitious paste[7]. Therefore, this mechanism makes the paste more homogenious and dense due to pozzolanic reactions between the amorphous silica of the RHA addition and calcium hydroxide produced by the cement hydration reactions. This shall result in formation of C-S-H gel. In addition, the filler effect of the fine grains of the RHA caused denser packing within the cement and reduces wall effect in the transition zone between the paste and aggregates. This weaker zone is strengthened due to higher bond between these two phases improving the concrete microstructure and properties. Therefore, the addition of RHA increases the mechanical strength and durability when compared to the plain paste because of the interface reinforcement. G.C. Isaia[7] also agreed to this concept and emphasized that the filler effect is at least, equally important or even more significant than pozzolanic effect.

2.4.3 Testing Methods

Pozzolanic reactivity can be evaluated using the method specified in ASTM C-1240 & BS EN 13263 – 2005. Mehta[69] had proposed a method to evaluate silica activity index. Silica activity index is a measure of the degree of amorphousness of silica.

In this method, the index is determined by calculating the percentage of available silica that dissolves in excess of boiling 0.5N sodium hydroxide in three minutes extraction. It is done in a stainless steel beaker on a minus 325 mesh sample. The higher the amount dissolved the more would be the amorphousness of the silica.

Shah further proposed a simpler method to evaluate silica activity index that recommends titrating a solution containing one gram of the ash in a 25ml of distilled water against methylene blue. The amount of methylene blue required to produce a colour change is used as an index of the state of the silica in the ash.

Another method proposed by Luann[6] is the conductivity method. In this rapid evaluation method, the conductivity levels of saturated $Ca(OH)_2$ solution with RHA indicate amorphousness of the RHA. The change in the conductivity levels of saturated $Ca(OH)_2$ solution with and without RHA, is the measure of amorphousness of RHA.

2.4.4 Methods Enhancing Reactivity

Qingge Feng has employed a method in order to enhance pozzolanic reactivity of RHA in which the rice husk was subjected to hydrochloric acid pretreatment before combustion[6]. In this method, rice husk was immersed in 1N hydrochloric aqueous solution. After immersion the rice husks were washed repeatedly with water until hydrochloric acid was undetected in the filtrate. Then it was air-dried at room temperature. After combustion, the RHA derived from this pretreated rice husk was found to have better pozzolanic activity[6].

Table 2. 2: Chemical composition and physical properties of pretreated and untreated RHA[6]

	Pretreated RHA	Untreated RHA
Loss on ignition (%)	2.65	2.31
SiO_2 (%)	96	92.40
Al_2O_3 (%)	0.1	0.03
Fe_2O_3 (%)	0.2	0.04
CaO (%)	0.2	0.70
MgO (%)	<0.1	0.30
Na_2O (%)	0.03	0.07
K_2O (%)	0.16	2.54
SO_3 (%)	-	-
P_2O_5 (%)	0.18	0.51
MnO (%)	0.02	0.11
Cl (%)	0.01	0.11
Specific gravity (g/cm^3) (%)	2.12	2.10
Specific surface (m^2/kg) (%)	311	110
Median grain size (μm)	7.2	7.4
Change in electrical conductivity (mS/cm)	8.43	4.75

2.5 Chemical Properties

2.5.1 Heat of Hydration

Heat of Hydration is the heat generated when cement and water react. The amount of heat generated is depending chiefly upon the chemical composition of the cement. C_3A, C_2A are primary compounds responsible for high heat evolution. The water cement ratio, fineness of cement and temperature of curing are the other factors that affect hydration[45]. Generally, the rate of heat generated of commercially blended cements is low during early stages, due to dilution of cement with mineral admixture and slow pozzolanic activity of mineral admixtures. This property of mineral admixtures with low heat of hydration makes it suitable for mass concrete production or construction such as the raft foundation and gravity dams.

Nazia Pathan[26] had studied the pattern of heat generation and the resultant temperature rise in concrete made with RHA and Silica fume against control mix. The Percentages of replacement were 5% and 10% of RHA and silica fume respectively. The research focused on evolution of heat from concrete for three minutes. The results were in support of the general belief that the pozzolans added in the concrete liberated low heat compared with control mix during the early stages. But the total amount of heat dissipated from concrete containing RHA was increased compare to concrete with OPC[19].

M.S. Ismail and A.M.Walludin[19] had concluded this fact in their research as well. The enhancement of hydration rate, which tends to increase with powder fineness, usually counteracts a part of the negative effect of cement dilution resulting from the replacement of cement by mineral admixtures[12].

Relating to this topic, N.B. Singh and Sarita Rai[14] have also studied on hydration of ordinary Portland cement in the presence and absence of 10% RHA by employing different techniques[14]. The results showed that in the case of OPC with RHA hydration values are lower up to three days. But from 7 days onwards, the values are higher as compared to that of OPC cement. The lower values may be due to the dilution effect in the presence of RHA. Besides, pozzolanic reaction might have not started up to three days of hydration. However after three days of hydration, the pozzolanic reaction might have occurred and more C-S-H gel was formed. This caused an increase in hydration rate.

2.5.2 X-Ray Diffraction (XRD)

X- ray diffraction is a useful technique for qualitative analysis and for the determination of major and minor phases. In X-ray diffraction analysis, X-rays are used to determine crystalline compound in a given sample. The analysis is based on that x-Ray will be diffracted by crystal planed and minerals can be identified by measuring the diffraction at different angles. The diffraction pattern of unknown material is compared with that of the reference database in order to identify its chemical compound. Each crystalline compound has its unique characteristic X-ray pattern, which may be used as fingerprint for its identification.

X-ray diffraction is based on Bragg's law

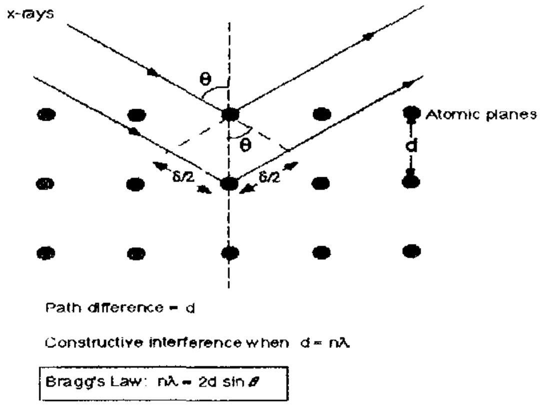


FIG 2.1: X-Ray diffraction pattern

X-ray radiation most commonly used is that emitted by copper, whose characteristic wavelength for the K radiation is 1.5418 Å. When the incident beam strikes a powder sample diffraction occurs in every possible orientation of 2 theta. The diffracted beam may be detected by using a moveable detector such as a Geiger counter, which is connected to a chart recorder. In normal use, the counter is set to scan over a range of 2 theta values at a constant angular velocity. Routinely, 2 theta ranges of 5 to 70 degrees are sufficient to cover the most useful part of the powder pattern. Refer FIG 2.1 for standard striking pattern of incident beam on sample and diffraction pattern after striking.

2.5.3 X-Ray Fluorescence (XRF)

When a primary X-ray excitation source from an X-ray tube or a radioactive source strikes a sample, the X-ray can either be absorbed by the atom or scattered through the material. The process in which an x-ray is absorbed by the atom by transferring all of its energy to an innermost electron is called the "photoelectric effect." During this process, if the primary X-ray had sufficient energy, electrons are ejected from the inner shells, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells. During the process the characteristic X-ray whose energy is the difference between the two binding energies of the corresponding shells is given off. Because each element has a unique set of energy levels, each element produces X-rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample. The process of emissions of characteristic X-rays is called "X-ray fluorescence," or XRF. Analysis using X-ray fluorescence is called "X-ray fluorescence spectroscopy." In most cases the innermost K and L shells are involved in XRF detection. A typical x-ray spectrum from an irradiated sample will display multiple peaks of different intensities as shown in FIG 2.2.

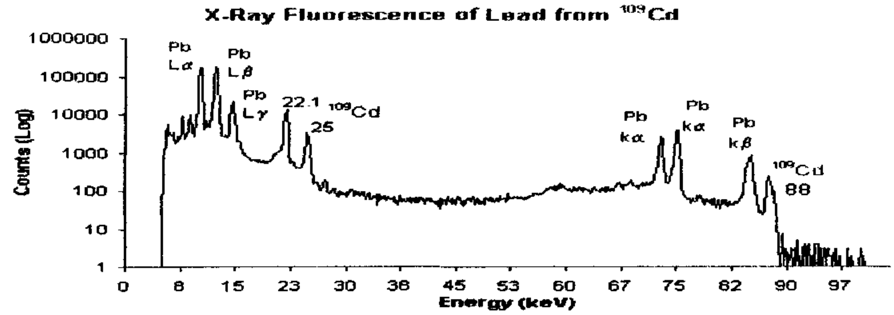


FIG 2. 2: Spectrum taken using Amptek XR-100CR 25mm^{2}X500μm X-Ray Detector (20μs shaping time) and Amptek MCA8000A Multichannel Analyzer.

The characteristic X-rays are labeled as K, L, M or N to denote the shells they originated from. Another designation alpha (a), beta (b) or gamma (g) is made to mark the X-rays that originated from the transitions of electrons from higher shells. Hence, a

Ka X-ray is produced from a transition of an electron from the L to the K shell, and a Kb X-ray is produced from a transition of an electron from the M to a K shell, etc. Since within the shells there are multiple orbits of higher and lower binding energy electrons, a further designation is made as a1, a2 or b1, b2, etc. to denote transitions of electrons from these orbits into the same lower shell.

The XRF method is widely used to measure the elemental composition of materials. Since this method is fast and non-destructive to the sample, it is the method of choice for field applications and industrial production for control of materials. Depending on the application, XRF can be produced by using not only X-rays but also other primary excitation sources like alpha particles, protons or high-energy electron beams.

2.5.4 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope, or SEM, is an incredible tool for seeing the unseen worlds of micro space. Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image. A scanning electron microscope works by scanning an electron beam across the surface of an object. This type of microscope can magnify up to 100,000 times. A light microscope can only magnify up to1,000 times. Because the scanning electron microscope takes such clear images, it is a good tool to use in studying biological, geological, and anthropological specimen.

The SEM creates the magnified images by using electrons instead of light waves. The SEM shows very detailed 3-dimensional images at much higher magnifications than is possible with a light microscope. The images created without light waves are rendered black and white Samples have to be prepared carefully to withstand the vacuum inside the microscope. Biological specimens are dried in a special way that prevents them from shriveling. Because the SEM illuminates them with electrons, they also have to be made to conduct electricity. Scanning electron microscopy examines structure by bombarding the specimen with a scanning beam of electrons and then collecting slow moving secondary electrons that the specimen generates. These are collected, amplified, and displayed on computer monitor. SEM is typically used to examine the external structure of objects that are as varied as biological specimens, rocks, metals, ceramics and almost anything that can be observed in a dissecting light microscope.

2.6 Concrete Durability

2.6.1 Definition

Concrete durability is defined as its ability to resist weathering action, chemical attack and abrasion without changing its shape, appearance and major engineering properties during the expected service life.

2.6.2 Causes of Loss of Concrete Durability

The loss of durability is usually caused by the attack of external agents present in the surrounding environment or by the attack of internal agents resided within the concrete. These causes can be categorized as physical, mechanical and chemical. Physical causes are mainly due to the action of frost or due differences in the thermal properties of aggregate and of the cement paste. Mechanical causes are mainly due to abrasion. Chemical causes are due to chemical attack, acids, sea water and also by chlorides. In chemical causes, since the attack takes place within concrete mass, the attacking agent must be able to penetrate throughout the concrete. The transport of attacking agents can be carried out by three phenomenon that are permeation (pressure gradient), diffusion (concentration gradient) and sorption (capillary suction).

Permeation is the penetration of substances through a solid. Permeation in concrete increases mainly through inter connected capillary pores with sizes of at least 120 nm. Permeability of concrete depends on capillary porosity, which in turn depends on water cement ratio and degree of hydration. Decrease in water cement ratio reduces permeability of concrete. The permeability of aggregate used in concrete also influences the permeability of concrete.

Diffusion is movement of the particles from area of high concentration to area of lower concentration until equilibrium is reached. Generally, permeability and diffusivity are interrelated and they are roughly proportional to each other. Curing generally controls the permeability and diffusivity. Good and prolonged curing is essential to reduce diffusivity. The soluble chlorides in deicing salts or those occurring naturals in soils, seawater and ground water can penetrate into the concrete by absorption through its surface.

2.6.3 Chloride Ion Penetration

Deterioration of concrete due to corrosion of steel is the most serious durability problem faced by construction industry. The chloride ions present in concrete destruct the thin oxide layer on the steel surface that was formed due to high alkanity of hydrate cement paste. Subsequently it results in corrosion of steel reinforcement.

Many researchers have widely agreed and proven with results of many research papers that, the use of pozzolans or supplementary cementing materials can reduce permeability by 7 to 10 times. The control on ingress of chloride ions in concrete and increase of resistance to chloride can be achieved by addition of pozzolans due to two principal aspects. Firstly, use of mineral admixtures will result in a denser pore structure in the cement paste matrix and thus the change in mineralogy of the cement hydrates leads to a reduction in the mobility of chloride ions. Secondly, the chemical reaction of lime crystals with mineral admixtures increase paste density, resulting in reduced porosity over time and will enhance the matrix chemicals resistance to many aggressive species.

O.E.Gjorv and M.H.Ngo[24] of Norwegian University of science and technology have investigated the ability of Rice husk ash in improving the resistance to chloride penetration. In their research 10% of OPC was replaced by RHA in the different levels of concrete quality with the compressive strength varying from approximately 40 to 70 Mpa. Both the capillary suction and accelerated chloride diffusivity were distinctly improved by the addition of RHA[24].

N.Bouzoubaâ and B.Fournier[25] have proven the general belief that RHA improves resistance of concrete against chloride penetration. In their extensive research, they have considered the cement replacement of 7.5%, 10% and 12.5% RHA with and without air entrainment agents. The resistances are compared with silica fume replacement and control mix. It was found that for the replacement of 7.5%, 10% and 12.5% RHA in non-entrained concrete, the chloride ion penetrabilities at 28 days is 1210 coulombs, 830 coulombs and 600 coulombs respectively. These values are lower than the control mix (2472 coulombs) and higher than 7.5% silica fume replacement (430 coulombs)[25].

Nazia Pathan[26] has employed electrical component to identify the concrete ability to resist ion penetration (ASTM C 1202). With a 60-volt current supply, the test consists of monitoring the total charge in Coulombs passed through 95 cm thick section of 10 cm diameter cylinder over a period of 6 hours. The results were 3791 coulombs, 1535 coulombs and 1162 coulombs for control mix, 10% RHA and concrete 10% silica fume respectively. Again it has been proven that the ability of chloride ion penetration of concrete with RHA lies between control mix and concrete with silica fume. Concrete deterioration due to reinforcement corrosion in concrete with mineral admixture is reduced. Resistance to chloride ion penetration varies and depends on the types of mineral admixture used.

2.7 Alkali-Silica Reactivity

2.7.1 Definition

The chemical reaction between the active silica constituents of the aggregate and the alkalis in the cement can damage the concrete. This process is known as alkali-silica reaction (ASR).

2.7.2 Causes

The reactive forms of silica are Opal amorphous), Chalcedony (Crystalline fibrous) and Tridymite (Crystalline). These materials occur in several types of rocks such as Opaline or Chalcedonic cherts, siliceous limestones, rhyolites and rhyolitic tuffs, dacite and dacite tuffs, andesite and andesite tuffs and phyllites. But chemically stable aggregates in concrete do not react chemically with cement in a harmful manner. The reaction starts with the attack of the siliceous minerals in the aggregate by the alkaline hydroxides derived from the alkalis (Na_2O and K_2O) in the cement. The alkalis- silicate gel formed attracts water by absorption or by osmosis and then tends to increase in volume. Since the gel is confined by the surrounding cement paste, internal pressures resulted and eventually led to expansion, cracking and disruption of the cement[1].

2.7.3 Mechanism

It is well known that the replacement of small percentage of cement with a pozzolanic material reduces the expansion that occurs when alkali hydroxides react with silica containing aggregates. The mechanism that prevents expansion due to alkali silica reactivity by adding pozzolanic material in concrete is as follow

1. Pozzolans reduce permeability, thereby preventing the ingress of water and transport of alkali and hydroxyl ions;

2. Pozzolans increase strength and stiffness resulting in better resistance to cracking and less expansion.
3. Replacing a portion of cement with a less alkaline pozzolanic material decreases the total amount of alkali present; and
4. Pozzolans react with calcium silicate (CS) to form calcium silicate hydrate (C-S-H) with a low Cao/ SiO_2 (C/S ratio). Formation of this C-S-H depletes CH and the low C/S ratio enables the entrapment of alkalis, both of which reduce the amount of hydroxyl ions available to participate in the alkali-silica reaction (ASR).

2.7.4 Preventive Measures

The following are the parameters to be considered to prevent alkali-silica reaction.

1. Prevent contact between the concrete and external source of moisture.
2. Use Portland cements with an alkali content of not more than 0.6% expressed as Na_2O.
3. Use a blend of ordinary Portland cement and Ground Granulated Blast furnace Slag with a minimum of 50 % of slag.
4. Use a blend of OPC and PFA with a minimum of 25 % of PFA.
5. Limit the alkali content of the concrete to 3 Kg / m^3.

2.8 Ash Preparation and Equipment

2.8.1 Temperature

The temperatures at which rice husks are subjected to thermal combustion are essential in order to get highly reactive silica for rice husk. Generally, as the temperature increases, the phase diagram of silicon dioxide indicates that a transition from the amorphous to crystalline forms known as tridymite and crystobalite takes place at high temperature. Prolonged heating at high temperature produces crystalline silica. According to Mehta, when rice husk is first heated, weight loss occurs up to 100° C due to evaporation of absorbed water. At 350°C, the volatiles ignite, causing further weight loss and the husks commence to burn from 400°C to 500°C. The residual carbon oxidizes and the majority of the weight loss occurs in this period. The silica in ash is still in an amorphous form. The temperature beyond 800°C produces crystalline silica. The Amorphous form of silica is most suitable to be used as supplementary cementious material. Amorphous form of silica is chemically reactive in nature and reacts with $Ca(OH)_2$ in cement paste to form C-S-H gel. In other words it enhances pozzolanic reactivity of Rice husk ash. Crystalline silica is chemically inert and not effective in early hydration processes. It gives only filler effect due to its fineness.

2.8.2 Duration

Duration of thermal combustion play a key role in the virtual realization of obtaining active amorphous silica from RHA. The increased hours of thermal treatment may reduce the activeness of silica. Mehta states that totally amorphous silica can be produced by maintaining the combustion temperature below 500° C under oxidizing conditions for prolonged periods. Shuichi Sugita patented his methods of producing rice husk ash in which one of his claims is to have more than 48 hours thermal treatment.Another research at the Annamalai University, India treated the RHA for two and a half hours at 600° C but their product was not suitable for reinforced concrete works due to low Pozzolanic activity. Therefore it is understood that by manipulating duration of treatment and temperature, different kinds of pozzolan can be achieved.

2.8.3 Equipment

A set up of apparatus is a key factor to derive highly active RHA in amorphous form. This set up should be capable of facilitating uniform combustion of Rice Husk. Many researchers have resorted to conventional open heap burning to sophisticated apparatus burning. A few methods, which were commonly used for deriving RHA, are given below.

The inventor Norman Pitt from Los angels had invented a process and apparatus for the incineration of organic material. His invention was mainly focused on converting potential useful fuel value of agricultural waste materials into useful energy. It consists of exposing the material to elevated temperature in an excess of air in a cylindrical furnace. The furnace has tangential inlet at the bottom and discharge consists of concentric hollow cylinder projecting into the bottom portion of the furnace. Refer FIG 2.3 for apparatus set up. The process could be conducted under conditions whereby a highly reactive amorphous form of silica is produced.

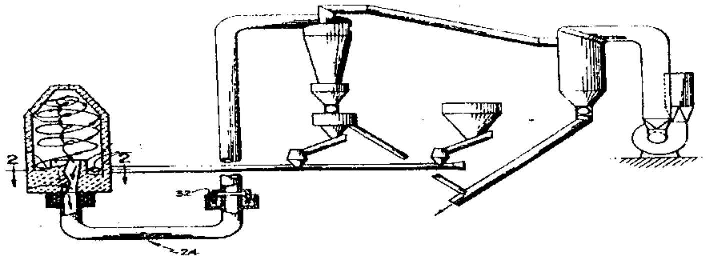


FIG 2. 3: Norman Pitt's apparatus for the incineration of organic material

In 1988, the inventor Frans L. Halfhide from Netherlands had filed a patent for his invention of particulate fuel burner and its operation method. The FIG 2.4 illustrates Frans L. Halfhide's particulate fuel burner. This invention relates to a burner comprising two coaxially mounted tubes. The outer tube is provided with means to introduce both air and particulate matter in the space between both tubes. Opening provides transfer of gases resulting from gasification of the solid material to the inner space of the inner tube. This invention aimed to obviate the draw back of uneven burning of waste material by other methods. Also aimed at all the materials that could be burnt in fluidized bed. It was designed so as to burn mixtures of materials, in which the individual components have different specific weight. Using air as fluidizing agent has resulted a nonuniform distribution[66].

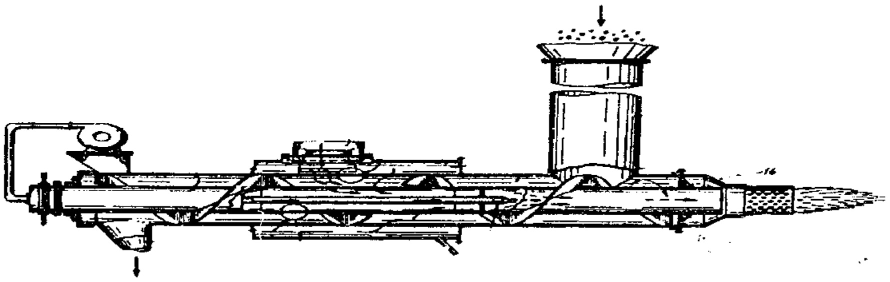


FIG 2. 4: Frans L. Halfhide's particulate fuel burner

Inventor Shuichi Sugita from Japan had been granted patent on 19th July 1994 for methods of producing active rice husk ash by two new apparatus set up. The first method which includes placing a hollow platform having many holes of a size too small for rice husk to enter on an enclosed floor slab, erecting a chimney on the hollow platform in communication with the interior of the hollow platform, forming a cone of rice husk around the chimney to completely cover the hollow platform, igniting the rice husk at the small holes for smolderingly incinerating the rice husk into carbonized rice husk to self burn into ash. The FIG 2.5 illustrates Shuichi Sugita's apparatus. However, it was found that performance of this apparatus is not very encouraging due to its simplicity. The long time required to complete one cycle of thermal combustion is a disadvantage. Although this inventor claimed that no heat source other than that of ignition required, he also admitted that the burning was uneven. This is another disadvantage. In the second method another apparatus had been used to produce active rice husk. The apparatus in which down stream rotary kiln was connected with upstream rotary kiln in tandem. This method suggests heating the up stream rotary kiln to a controlled temperature for carbonizing rice husk, heating the down stream rotary kiln to a controlled temperature for burning rice husk into ash. After the supply of rice husk into up stream rotary kiln, the rice husk is subject to smoldering incineration to get carbonized rice husk. Then this carbonized rice husk is transferred to down stream rotary kiln to get burnt into ash. Thereby resulting active rice husk is being discharged from down stream rotary kiln. The experimental results of compressive strength of concrete incorporating rice husk ash in various percentages against plain concrete by graphical presentation were also shown in this patent. This patent concludes that the compressive strength of concrete increases with increasing rice husk ash content.

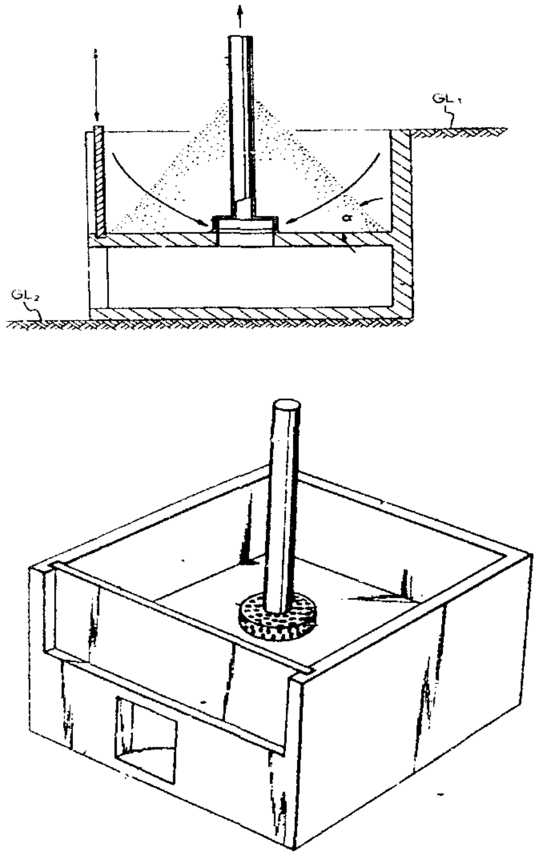


FIG 2. 5: Shuichi Sugita's apparatus

A research project that was funded by Indian government was carried out in Annamalai University, India with the objective of producing a substitute or partial substitute for cement to meet the growing demand of cement for construction. A specially designed brick furnace, cylindrical in shape, was used for this purpose. This furnace was constructed with firebrick, insulation bricks and red bricks at the inner, middle and outer layers respectively. It was provided with M.S distributor plate with drilled holes of ¼ inch diameter at 1 ½ inch pitch and was placed 0.5m above ground to aid uniform distribution of air. Three caps were provided for distribution of material. Five thermocouples were placed at a distance of 30 cm to observe the temperature. A water manometer was provided at the bottom of the distributor plate to develop air draught. A blower coupled with a motor was used to develop the necessary air draught. The waste lime and husk were mixed in the ratio of 20% CaO and 60% SiO_2 and charged from top and burnt in the kiln. This ratio was found to be optimum after several trials. The duration of process was 2 ½ hours at the temperature of 600^0C. After withdrawal, this calcined product was cooled, mixed with about 5% gypsum and ground in a ball mill to have the standard fineness as needed for the Portland cement. Rice husk was also being used in furnaces and boilers as a fuel. This resulted in a lot of half burnt husk ash, the disposal of which was a big problem to mill owners. So, another effort was made to utilize this half burnt husk ash for commercial purpose in which husk ash was ground to fineness and mixed with waste limestone clinkers and ground again. 5% gypsum was used as an admixture. The resulting material was tested for cementious properties. But in many cases the cubes disintegrated when cured in water due to lack of binding property. This project report concluded that a cementitious material having a compressive strength of 100 kg/cm^2 can be successfully prepared by burning paddy ash and lime in the ratio of 1:6 by weight at 600^0C in a properly designed furnace and controlling the combustion with thermostat controls and regulating the pressure with a manometer. This cement having cementitious properties adequate for use as mortar binder in masonry works. But not suitable for reinforced concrete works as its performance under serviceability conditions such as cracking and deflection was unsatisfactory[23].

CHAPTER THREE

METHODOLOGY

3.1 Materials

3.1.1 Rice Husk Ash

Rice husk was collected from a rice mill located at Semanggol, Perak that was dry and possessed no damage to skeletal structure. The collected rice husk was burnt in carbolite furnace in accordance with the burning procedure as developed in this research. After the burning, RHA was ground in Los Angeles machine in order to attain the required fineness.

3.1.2 Cement

Ordinary Portland cement (similar to ASTM C150 Type 1) with specific gravity of 3.15 and Blaine fineness of 325 m^2/Kg was used. Chemical and physical properties of cement are shown in Table: 3.1

Table 3.1: Chemical and physical properties of cement

Chemical analyses (%)		Physical tests	
CaO	65.59	Specific gravity	3.15
SiO_2	20.33	Specific surface (Blaine)	325 m^2/Kg
Al_2O_3	4.99	Compressive strength	
Fe_2O_3	3.14	7 days	29.6 N/mm^2
SO_3	2.61	28 days	40.4 N/mm^2
MgO	1.83	Setting time	
Cl	0.028	Initial setting	104 sec
Total alkali	0.09	Final setting	136 sec
LOI	1.15	Soundness by Le' Chatelier test	1.2 mm

3.2 Experimental Details

The experiments that were conducted on RHA in this study are given in Table 3.2. This includes the two burning procedures and the experiments to determine physical and chemical properties of RHA. Pozzolanic activity index test and compressive strength test were also included to evaluate the chemical reactivity of RHA and its performance in cement paste respectively.

Table 3.2: Experimental details

No	Experiments	Sample	Standard	Measurable	Unit
1	Burning procedure	RH	-	Amorphousness& Chemical composition	%
2	Pozzolanic activity index test	Mortar cubes	ASTM C-1240	Chemical reactivity of RHA	-
3	Moisture content	RHA	ASTM C-1240	Moisture	%
4	Loss on ignition	RHA	ASTM C-1240	Carbon content	%
5	Normal consistency	Cement paste	ASTM C-187	Water cement ratio	-
6	Fineness	RHA	ASTM C-204	Surface area	m^2/kg
7	Density	RHA	ASTM C-1240	Particle density	g/cm^3
8	Porosity	Cement paste	-	Porosity	%
9	Compressive strength Test	Cement paste	ASTM C109/C109M	Compressive strength	N/mm^2
10	XRD	RHA	-	Amorphousness RHA	-
11	XRF	RHA	-	Chemical composition	%
12	Scanning electron microscope	RHA	-	Micro pore structure	-

Mix proportions for cement pastes with various replacement ratios of RHA in this study are given below

Table 3.3: Mix proportion for cement pastes with various replacement ratio of RHA

percentage of RHA	W/C	Cement (gm)	RHA (gm)	Water (ml)
0%	0.235	750	0	176.25
	0.25	750	0	187.5
	0.26	750	0	196.88
	0.28	750	0	210
	0.32	750	0	240
	0.35	750	0	262.5
2.5%	0.235	731.25	18.75	171.84
	0.25	731.25	18.75	182.81
	0.28	731.25	18.75	204.75
	0.3	731.25	18.75	219.38
	0.325	731.25	18.75	237.66
5%	0.235	712.5	37.5	167.44
	0.25	712.5	37.5	178.13
	0.28	712.5	37.5	199.5
	0.295	712.5	37.5	210.19
	0.32	712.5	37.5	228
7.5%	0.235	693.75	56.25	163.03
	0.28	693.75	56.25	194.25
	0.33	693.75	56.25	228.94
	0.31	693.75	56.25	215.06
	0.35	693.75	56.25	242.81
10%	0.325	675	75	219.38
12.5%	0.35	656.25	93.75	229.69
15%	0.36	637.5	112.5	229.5
17.5%	0.372	618.75	131.25	230.11
20%	0.393	600	150	232.8

3.3 Establishing the Burning Procedure of Rice Husk

Two trial burning procedures consisting of 3 stages were adapted in order to obtain the good quality ash that can exhibit high pozzolanic characteristics. Details of the two burning procedures are tabulated in Table 3.4 & Table 3.5 respectively.

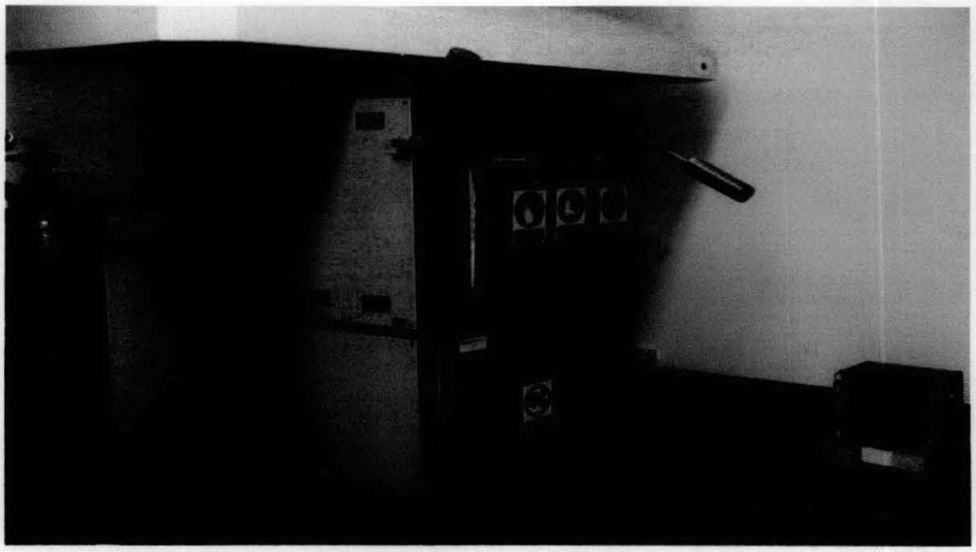
Table 3.4: Burning Procedure 1

	Temperature (° C)	Duration (Minutes)	Remarks
1st STAGE	24-200	10	No Smoke
	200	10	No Smoke
	200-250	5	No Smoke
	250	5	No Smoke
	250-280	5	No Smoke
	280	10	Smoke evolves
2nd STAGE	280-310	9	Smoke evolves
	310	10	Black smoke evolves
	310-360	7	Black smoke evolves
	360	5	Black smoke subsides
	360-480	28	
			Open the door for 10 minutes to allow oxygen in
	440		Temp. reduces to 440
	440-480	19	
	480-520	34	
3rd STAGE	520-550	12	
	550	15	
Total		184 mins	White colour ash was obtained.

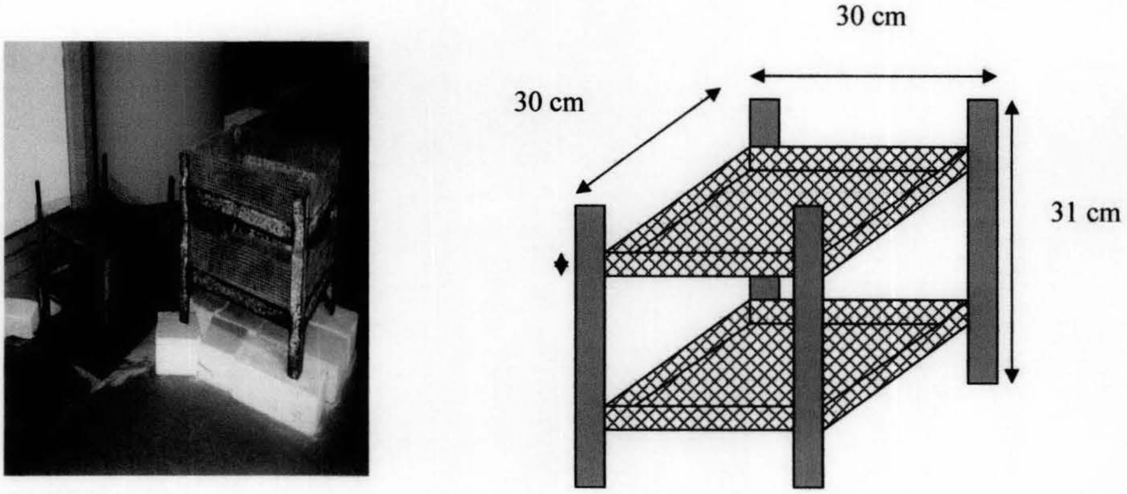
Table 3.5: Burning Procedure 2

	Temperature (° C)	Duration(Minutes)	Remarks
1st STAGE	27-280	15	No smoke
	280	10	Smoke evolves
	280-320	5	Smoke evolves
2nd STAGE	320	15	Black smoke evolves
	320-360	5	Black smoke evolves
	360 – 380	5	Black smoke evolves
	380	30	Black smoke subsides
	360-480	12	
			Open the door for 10 minutes to allow oxygen in
	467		Temp. reduces to 467
	467-500	17	
	500	10	
	500-520	15	
	520	10	
3rd STAGE	520-550	12	
	550	15	
			176 mins
Total			

A carboite furnace installed in mechanical engineer dept, UTP that controls the temp increment at the rate of 20^0 – 40^0 C / minute was used for burning. In order to achieve the uniform burning under oxidizing condition, the rice husk was placed in two layers specially designed BRC trays. (Refer FIG 3.1). It helped to avoid heap burning and allowed the air to flow freely between rice husks. The layer thickness of husk in BRC tray was limited to two inches only. There was adequate gap between two layers of trays that can facilitate proper circulation of air.



(a): Carbolite furnace



(b) BRC trays

FIG 3. 1: Carbolite furnace and BRC trays

3.4 Grinding

Rice husk ash obtained by burning was ground using *Los Angeles machine.* (Refer FIG 3.2). The machine consisted of a hollow steel cylinder with both ends closed. The cylinder is mounted on stub shafts attached to the ends of the cylinder but not entering it, and should be mounted in such a manner that it may be rotated with the axis in a horizontal position within a tolerance in slope of 1 in 100. An opening in the cylinder was used for charging the ash and then solid steel balls were introduced for the purpose of grinding. After charging the RHA, the machine was rotated at the speed of 30-33 rpm for 30 minutes.

FIG 3. 2: Los Angelevs grinding Machine

3.5 Accelerated Pozzolanic Activity Index Test

The purpose of the test was to evaluate the pozzolanic reactivity of RHA in cement in comparison with control mixture. The test was conducted in accordance with ASTM C 1240[63]. For this two different mixes control and test mix were prepared as detailed below

Control Mixture:

1. 250 gm of Portland cement
2. 687.5 gm of graded standard sand
3. 121 ml of water

Test Mixture:

i. 225 gm of Portland cement
ii. 25 gm of RHA
iii. 687.5 gm of graded standard sand
iv. Y ml of water required for flow of 100 to 115% of control mixture.

The test was conducted in following sequences

i. Mix the predetermined amount of cement and standard sand in mechanical mixer followed by water for control mixture.
ii. Determine the flow of cement mortar by using flow test method. (ASTM C109)
iii. Mold the specimens from a control mixture in mortar test cubes.
iv. After 24 hour of initial curing in the moist room (23 + 1.7° C and relative humidity of not less than 95%), place the cubes in air tight glass container and store in oven at 65 + 1.7° C for six days.
v. Mix the cement and RHA until a homogeneous mixture was attained. Then add standard sand followed by water for test mixture. The amount of water is adjustable so as to get flow of 100 to 115% of control mixture.
vi. Repeat the procedure 3 and 4 for test mixture.
vii. Determine the compressive strength of three specimens of the control mixture and test mixture at 7 days after molding.

3.6 Moisture Content

The purpose of this test was to determine the moisture content of RHA. This test was carried out in accordance with ASTM C 311. The procedure of test was as follows

i. The weighed sample (B) was placed in a crucible and was dried in the oven at 105 to 110°C.
ii. The sample was taken out and weighed at constant time interval until the difference in weight between two successive weighing was not more than 0.1%.
iii. The final weight of the sample was then recorded. (A)

Calculate the percentage of moisture as follows

Moisture Content, = (A/B) X 100 %

Where

A= Mass loss during drying, and

B= Mass of sample before drying

3.7 Loss on Ignition (LOI)

The purpose of this test was to determine the loss on ignition of RHA samples. The loss was assumed to represent CO_2 in RHA. The procedures adopted were in accordance with ASTM C 311

i. 1 gram of the RHA sample was weighed (B) in a porcelain crucible and dried to constant weight in an oven at 105 to 110° C.
ii. The crucible was ignited in a furnace at a temperature of 750 ± 50° C.
iii. The initial heating period was allowed for 15 minutes and at least 5 minutes for all subsequent periods until the difference in weight between two successive weighing was not more than 0.1%.

The percentage of loss on ignition was calculated as follows:

Loss on ignition, = (A/B) X 100 %

Where

A= Loss in mass between 150 and 750° C

B= Mass of moisture free sample used.

3.8 Preparation of Cement Pastes

The standard practice recommended in ASTM C 305-99 was followed to prepare the cement pastes for making cubes. The recommended practice for preparation of paste was as follows

i. The required amount of cementitious material and water were prepared.
ii. All the water for mixing was mixed in the bowl.
iii. The cementitious material was added to the water and was allowed for 30 seconds for the absorption of the water.
iv. The mixer was then turned on and the mix was mixed at low speed (140± 5 r/min) for 30 s.
v. The mixer was stopped for 15 s to allow the paste that may have collected on sides of the bowl to be scraped.
vi. The mixer was then engaged at medium speed (285 ± 10r/min) and the mixer was mixed for one minute.
vii. After one minute, the paste was cast into cube moulds.

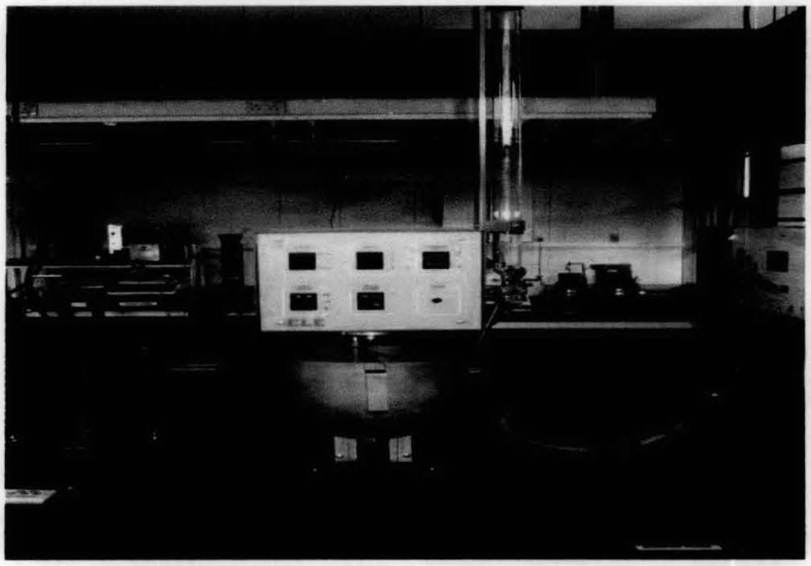


FIG 3. 3: Mechanical cement paste mixer

3.9 Normal Consistency of Hydraulic Cement Pastes

The standard consistency was measured by the penetration of a cylindrical plunger, 50mm long and 10mm in diameter into a sample of the fresh paste being tested. The standard consistency of a paste was obtained when the plunger penetrates into paste. The paste was made of normal consistency when the rod settles to a point 10 +/- 1mm below the original surface in 30s after being released.

The proportion of water required to produce a mix of standard consistency was obtained from a series of tests on trial and error basis. The correct proportion of water is expressed as a percentage by mass of cement.

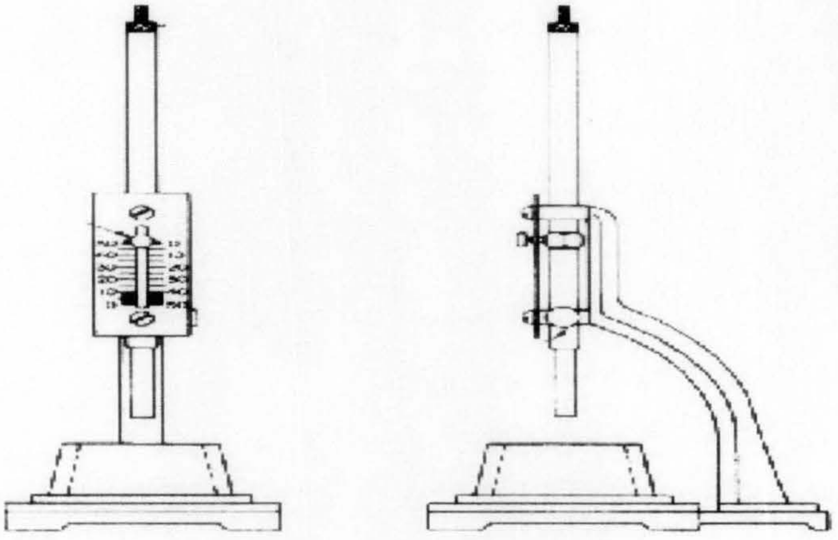


FIG 3. 4: Vicat Apparatus

3.10 Determination of Fineness

This test was done to determine the fineness of RHA, using the Blaine air-permeability apparatus shown in FIG 3.5. This test was done according to ASTM C 204.The procedure adopted was as follows

i. The quantity of cement, m_1, was calculated from the equation:

$m_1 = 0.500\rho V$

Where ρ is the density of the cement equals to 3.15 g/cm^3, as was obtained from the density test

V is the volume of the cement bed (cm^3)

ii. A perforated disc was placed at the bottom of the cell and was placed on a new filter paper disc. The filter paper disc ensured fully covers the perforated disc and is flat pressing with a clean dry rod.

iii. The weighted cement was placed in the cell and the cell was tapped to level the cement. The new second filter paper disc was then placed in the cell. The plunger was pressed gently until the lower face of the cap was in contact with the cell. The bed was then compacted and ready for permeability test. The plunger was slowly withdrawn.

iv. The conical surface was inserted into the socket at the top of the manometer. The top of the cylinder was closed with a suitable plug. The stopcock was opened with gentle aspiration raised the level of the manometer liquid to highest etched line. The stopcock was then closed.

v. The plug was removed from the top of the cylinder. The manometer liquid began to flow. The timer was started as the liquid reaches the second etched line. The timer was stopped when the liquid reached the third etched line. The time was recorded.

vi. The result was expressed in specific surface:

$$S = \frac{524.2\, K \times \sqrt{t}}{p}$$

Where K is the apparatus constant.

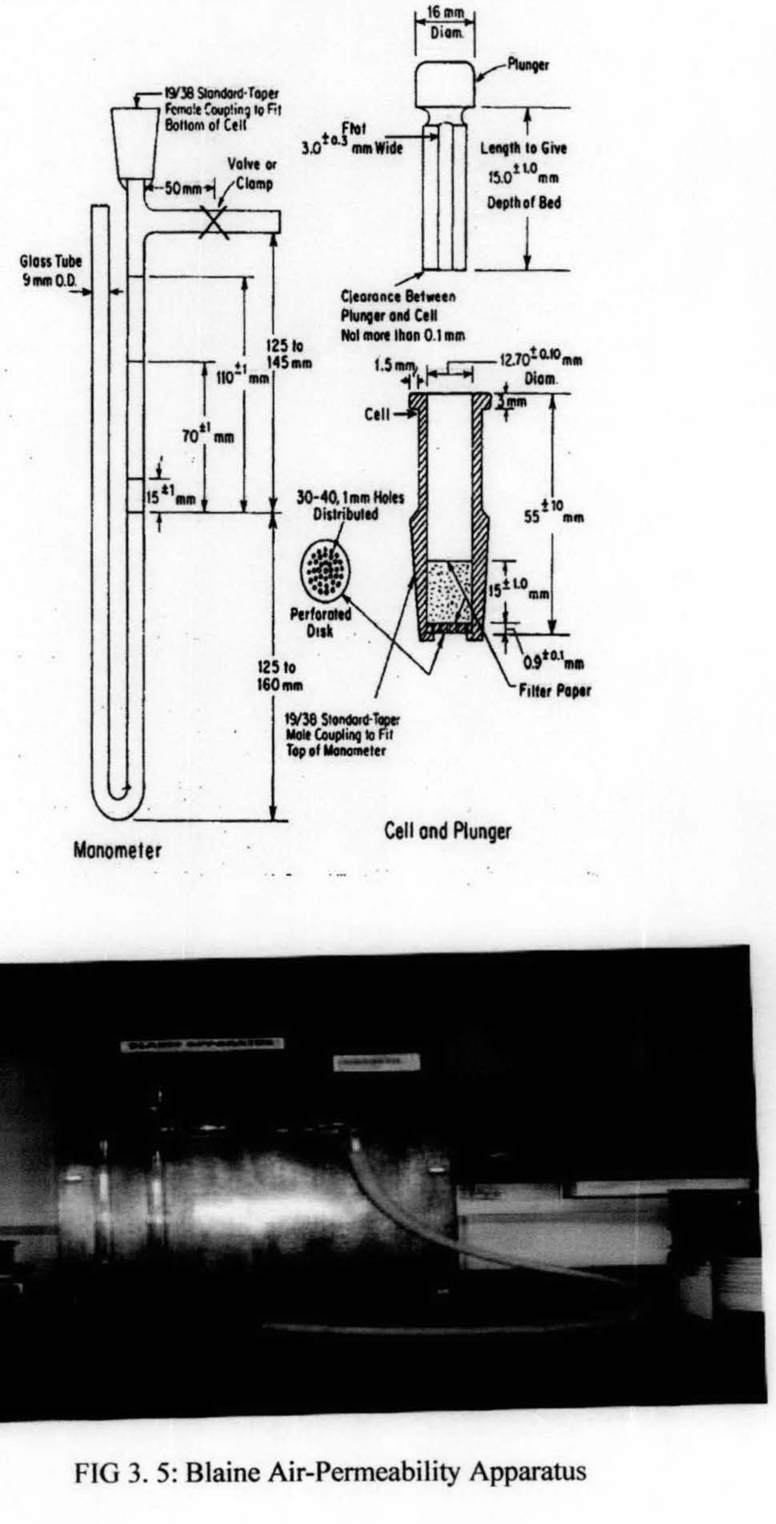


FIG 3. 5: Blaine Air-Permeability Apparatus

3.11 Determination of Density of RHA

In order to determine the density of RHA, a test based on the test method covered under ASTM C 188, was adopted. A conical flask of 100ml capacity and kerosene having a density of greater than 0.73 g/ml were used in density determination. Initially, the conical flask was filled with kerosene and inside of the flask was dried above the level of liquid after pouring. The first reading was taken at this point after the flask has been immersed in the water bath. A known quantity of RHA, Weighed to the nearest 0.05g, was introduced in small increments at the same temperature as the kerosene. Care was taken to avoid splashing and to ensure that RHA did not adhere to the inside of the flask above the kerosene. After all the RHA has been added, the level of the liquid was raised to final position. Final reading was taken after the flask has been immersed in the water bath. The differences between the first and final readings represented the volume of liquid displaced by the mass of RHA

The particles density, ρ was calculated as follows:

Particle density = mass of cement (g)/ displaced volume (cm^3)

3.12 Porosity

The purpose of this test was to determine the porosity of cement pastes of various combinations. The standard testing procedure is given below.

i. The desicator was filled up with water until the entire cement cube samples were submerged in water.
ii. The sambles were left for 6 hours with the vacuum pump activated.
iii. Then vacuum pump was stopped and the samples were left for 24 hours.
iv. The samples were then removed from the desicator and wiped with dry cloth.
v. The samples were then weighed in air (W_a) and water W_{sw}
vi. Then the samples were placed in an oven at 100^0 C for 24 hours.
vii. Subsequently the oven dry samples were weighed (W_d)

Porosity equation is given by

$P = [(W_a - W_d) / (W_a - W_{sw})] \times 100$

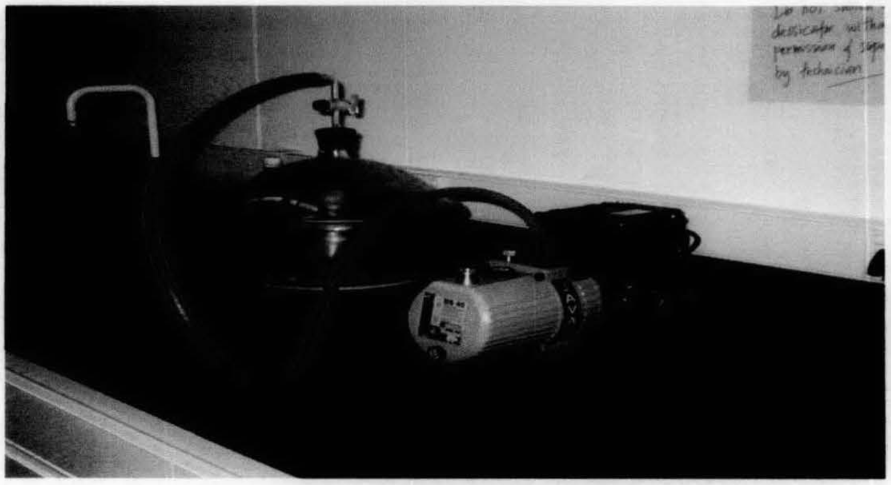


FIG 3. 6: Porosity Apparaus

3.13 X- Ray Diffraction (XRD)

The X-ray diffractometer machine was used for the qualitative analysis of RHA samples and the X-ray diffraction analysis was used to determine the crystalline compound in a given sample. This useful technique was used for the determination of major and minor phases of RHA sample. The test was carried out as described below

1. Firstly, the sample was prepared by grinding the burnt RHA samples.
2. Then, the sample was placed in a small plate and inserted into the XRD machine.
3. The degree of shooting according to the chosen parameter and started the machine.
4. The duration of the test was adjusted in accordance with the degree of shooting.

FIG 3. 7: X-Ray Diffractometer Machine

3.14 X-Ray Fluorescence (XRF)

The XRF method was used to measure the elemental composition of the RHA sample. This test results indicated the oxide content and chemical composition of RHA samples. The testing procedures were done as follow:

1. The burnt RHA sample was ground.
2. The sample was mixed with boric acid and made in the form of pill shape with the help of compressor.
3. The sample was then inserted into XRF machine.
4. XRF machine was then turned on for examination.
5. X rays from X-Ray tube started striking on sample.
6. From the emissions of characteristic X ray, the elements were identified.

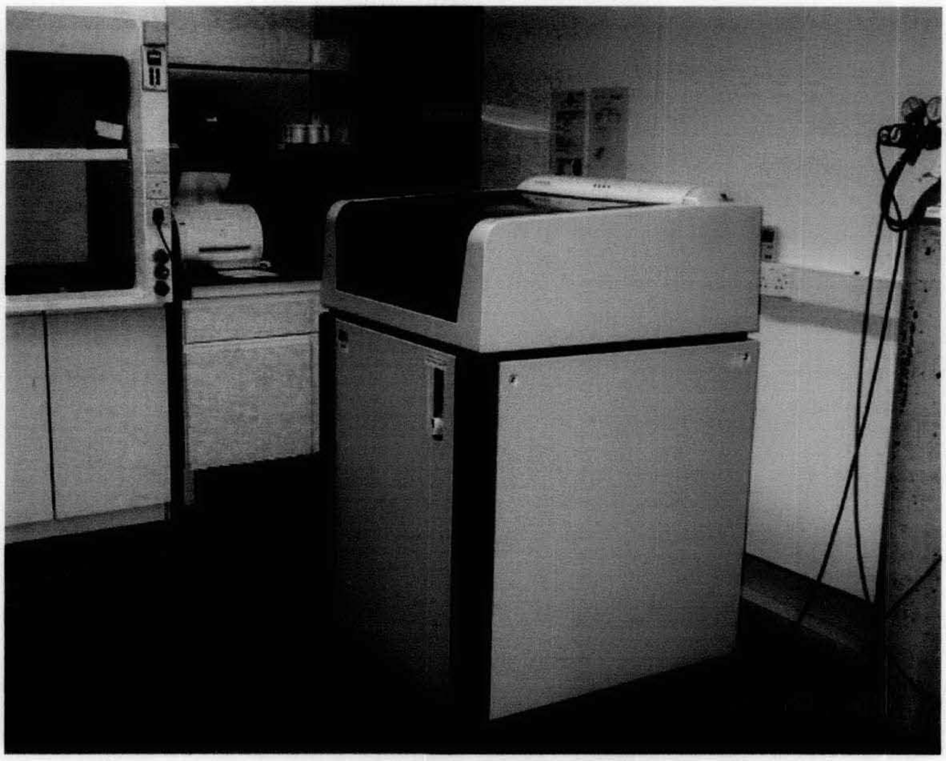


FIG 3. 8: XRF machine

3.15 Scanning Electron Microscope

The Scanning electron microscope was used to get micro space structure images of cement pastes at higher magnifications. The Scanning electron microscope has created images using electrons instead of light waves. The images created without light waves were rendered black and white. The following procedures were followed to carry out this test.

i. The Samples were prepared carefully to withstand the vacuum inside the microscope.
ii. The sample was placed inside the microscope's vacuum column through an air-tight door.
i. After the air was pumped out of the column, an electron gun [at the top] emits a beam of high energy electrons.

ii. This beam traveled downward through a series of magnetic lenses designed to focus the electrons to a very fine spot.

iii. Near the bottom, a set of scanning coils moved the focused beam back and forth across the specimen.

iv. As the electron beam hit each spot on the sample, secondary electrons are knocked loose from its surface. A detector counts these electrons and sent the signals to an amplifier.

v. The final image was built up from the number of electrons emitted from each spot on the sample.

vi. These images were displayed on computer monitor.

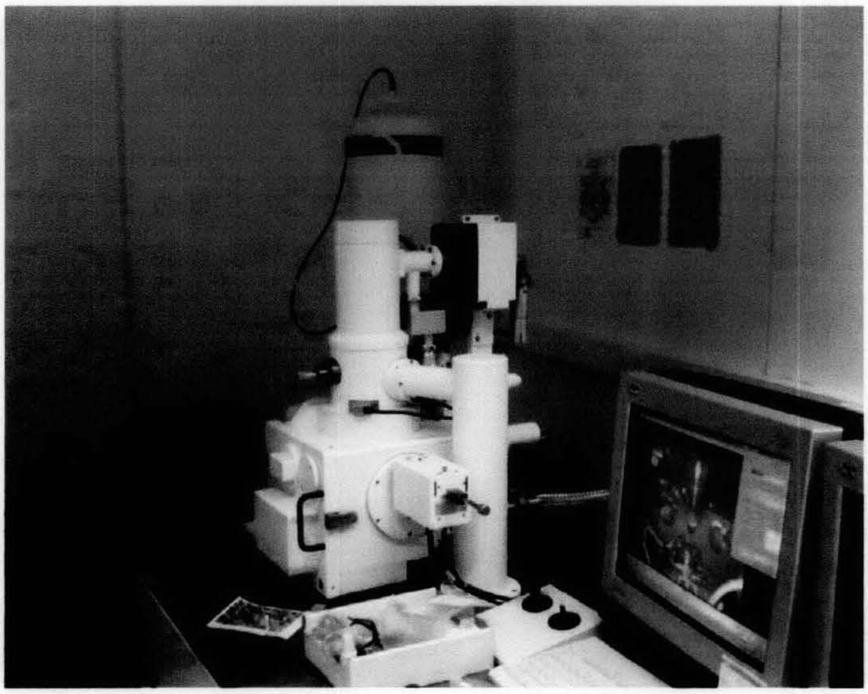


FIG 3. 9: Scanning Electron Microscope

CHAPTER FOUR
RESULTS & DISCUSSIONS

4.1 Burning Procedure

The sample of the rice husk (RH) was collected from a rice mill located at Semanggol, Perak. The sample of RH was placed in a carbolite furnace at room temperature. The temperature was gradually raised to about 200°C during which the evaporation of the absorbed water took place. Loss of weight occurred and the husk became crispy enough and started to smolder. The temperature was further raised to 250°C and maintained for few minutes, before rising to the next level of 280°C. At this stage, smoke started to evolve whereby ejecting out the volatile substances like cellulose, lignin, fibre etc present in the husk. The next level of temperature was 310°C where it was maintained for 10 minutes to ensure that the entire sample started smoldering uniformly. A further increase to 360°C ignited the husk and thick black smoke evolved. Ignitions of husk tend to increase the temperature without a need from the external source. Care was taken that the temperature did not exceed 380°C, by not allowing fresh air to flow into the system. This stage lasted until all the thick black smoke subsided. At the end of the first combustion stage, a weight loss about 70% had occurred. The second stage was meant to oxidize residual carbon in the presence of air. The temperature was raised to about 480°C simultaneously allowing air to flow through the system. Care was taken that the temperature did not go beyond 520°C. The duration of this stage lasted to about 30 to 35 minutes. At third stage, the temperature was raised and maintained between 520°C to 550°C in the absence of air in the system. Any flow of air may cool down the ash. This stage ensured the formation of uniformly structured amorphous silica from the RH. The RHA obtained at this stage was white in colour.

In the second procedure, the sample of rice husk from similar source was placed in the carbolite furnace. Unlike the first procedure, the temperature was directly raised to 280°C in a time span of 15 minutes. At 280°C, the temperature was maintained for 10 minutes. During which smoke started to evolve. Again it was raised to 320°C and maintained for 15 minutes. When temperature was raised to 360°C thick black smoke was driven off. The temperature 380°C was the ignition point where it was maintained for 30 minutes until the smoke subsided. The rest of the procedure was similar to the first procedure. This second procedure was tried out just to reduce the duration of heat treatment in comparison with the first procedure.

Samples obtained from two burning procedures were all amorphous. Before establishment of these burning procedures, the drawbacks of other common methods were identified and efforts were taken to rectify those in these methods. The advantages of this method over other methods are given below.

1. The silica content of RHA derived from the two burning procedures type I & II were 93.1% and 94.3% respectively. On the other hand, the silica content of RHA from industrial furnace was 90.7% and that of ferrocement incinerator was 88.8%. The RHA from Suchita sugita's apparatus has 90% silica content. But it had no uniformity in burning. So, these methods achieve higher silica content in RHA. (Refer Table 4.1).

Table 4.1: SiO_2 content of various burning procedures

References	Apparatus	SiO_2 (%)
Bouzabaa, (2001)	Industrial furnace	90.7
Thailand research board, (1980)	Ferrocement incinerator	88.8
Shuichi sugita, (1994)	Shuichi Sugita's innovative apparatus	90
Kassim, (2007)	Carbolite furnace	93.1 and 94.3

2. Duration of burning plays a major role in obtaining highly active silica. Although the burning temperature does not exceed the temperature 700°C, the longer duration may reduce degree of amorphousness of RHA. The duration of burning

procedures proposed by this method type 1 & 2 were 184 and 176 minutes respectively. Comparatively the durations of burning proposed by Shuichi Sugita[67] were 24 to 48 hours. The duration in ferrocement incinerator was 48 hours. Although another patented method proposed by Norman Pitt[65] was a continues process, the carbon content of RHA was very high. Shorter duration of burning in Type 1 & 2 method helped in getting highly reactive silica. The results of Pozzolanic activity index test may be used to evaluate degree of amorphousness of RHA. It is noted that Pozzolanic activity index of RHA obtained from this method was much higher than other RHAs. (Refer Table 4.2).

Table 4.2: Temperature variation and duration of various burning methods

Method		Temperature variation	Duration	Remarks
Shuichi Sugita's patent method[67]		370°C – 750°C	24 –48 hours	Uncontrolled combustion
Thailand research board[40]		< 700°C	48 hours	Uncontrolled and uneven combustion
Norman Pitt's patent Method[65]		1149°C	Continuous process	Carbon content is high
Kassim's Method[70]	Type 1	24°C – 550°C	184 mins	Controlled combustion
	Type 2	200°C - 550°C	176 mins	

3. The heating rate of burning has effect on specific surface, pore volume, pore diameter and removal of metallic ingredients from RHA[4]. In view of those, this burning procedure have adopted optimum heating rate of 20°C– 40°C /min thereby the presence of metallic ingredients as oxides were reduced without need of pretreatment of RH to achieve the same. The method of leaching RH with acid solution to yield silica of high surface area may also be eliminated by adoption of this burning procedure.

4. The removal of residual carbon from RHA is an important process. In fluidized bed method, increasing the temperature inside bed can control any excess of carbon content in RHA. It may lead to some negative effects such as reduction of degree of amorphousness of RHA. To eliminate this, the removal of residual carbon by oxidation in the presence of air is taken place at second stage. The temperature at this stage was maintained between 480°C–520°C only. Since the temperature did not exceed more than 800°C, it may not affect the degree of amorphousness. (Refer Table 4.4)

5. A white silica powder is preferable as supplementary cementitious material in concrete. The addition of black or dark brown silica powder in silica may lead to discoloration of concrete that is not desired by engineers. An idea of dividing total burning procedure into three temperature zones was initiated to obtain white silica at the end of the burning process. During the third stage, where the temperature was maintained between 520°C & 550°C in the absence of air, was aimed to get uniform structure amorphous white silica. This helped to over come the problem of obtaining dark brown ash as experienced by P.K. Mehta's method[69].

4.2 Particle Density for Cement and Rice Husk Ash

Particle density of RHA derived from Type 1 & 2 burnings was found to be 2.1 g/cm^3. The particle densities of RHAs that were derived from other sources like industrial furnace, pretreated RH with hydrochloric acid and ferrocement incinerator are given in Table: 4.3. These results showed that particle density of RHAs from different sources remained close to each other irrespective of burning conditions. The particle density depends mainly on grinding method and duration of grinding. Generally, the amorphous RHA requires lesser grinding time than crystalline RHA to achieve an equivalent density.

Table 4.3: Particle Density of RHA from Various Sources

Sample	Particle density (g/cm^3)	Reference
RHA by method Type 1 & 2	2.1	Kassim, (2007)
RHA from industrial furnace	2.16	Bouzoubaa, (2001)
Pretreated RHA with hydrochloric acid	2.12	Qingge feng, (2004)
RHA from ferrocement furnace	2.1	(Thailand research board, 1980)

4.3 Determination of finesses

The results obtained from the Blaine Air permeability Test is shown as below:

Time (t) for cement

1) 18s
2) 19s
3) 20s

Average Time = 19 second

Time (t) for RHA

1) 38.3
2) 36.2
3) 36.7

Average time = 37.1 second

Given:

$$S = \frac{524.2\,K \times \sqrt{t}}{P}$$

For cement specific surface area

$$S = \frac{524.2\,(1) \times \sqrt{19}}{2.93}$$

$$= 779.84\,cm^2/g$$

For RHA specific surface area

$$S = \frac{524.2\,(1) \times \sqrt{37.1}}{2.34}$$

$$= 1364.48\,cm^2/g$$

The result shows that the surface area of RHA was higher than cement surface area. High surface area of RHA will cause an effect on water absorption in concrete. High surface area will absorb more water and this will increase the requirement of water during mixing. High surface area also would result in high pozzolanic reaction.

4.4 Pozzolanic Activity Index

Pozzolanic activity index is a measure of the degree of amorphousness of RHA. The pozzolanic activity index of RHA through Type 1 & 2 burning procedure was 105. This indicates that RHA is chemically reactive so that it could take part in the chemical reaction even at early stages. As such, the silica in RHA has reacted with $Ca(OH)_2$, which was produced from hydration process, to form C-S-H gel at early stages. This is the main cause for early strength development. The RHA from torbed reactor (refer Table 4.4) derived at maximum temperature of 750°C has pozzolanic activity index of 88 and another sample from same source at a maximum temperature of 830°C has a pozzolanic index of 105 at 7 days. Another sample from industrial furnace has a pozzolanic activity index of 99 at a corresponding duration of 7 days while the sample produced by ferrocement incinerator has a pozzolanic activity index of 92 only at the end of 28 days.

Table 4.4: Pozzolanic activity index of various RHAs

References	Max. Temperature	Pozzolanic activity index	
		7 days	28 days
Nehdi ,(2003)	750°C	88	-
	830°C	105	-
Bouzoubaa (2001)	700°C	99	-
Thailand research board, (1980)	700°C	-	92
Kassim, (2007)	550°C		105

4.5 Moisture Content

The moisture content value in percentage indicates the moisture available in RHA. The American standard specification for silica fume for use as mineral admixture (ASTM C 1240 –97b) allows maximum moisture content of 3%. The RHA obtained from Type 1 & 2 burning procedures had moisture content of 1.5% only. This complies with the ASTM specification requirements of moisture content for mineral admixtures

A= Mass loss during drying and

B= Mass of sample before drying

Moisture content, = (A/B) X 100 %

= (0.075/5) X 100 %

=1.5%

4.6 Loss on Ignition (LOI)

Loss on ignition is an indicative of residual carbon present in RHA. ASTM C-1240 specification for silica fume allows loss on ignition up to 6%. The loss on ignition of RHAs from two burning procedures was 2.5%. The loss on ignition of RHA from other sources is given in Table 4.5. The removal of residual carbon from RHA is imminent. The second stage of the burning procedure mainly focuses on this. Increasing the burning temperature to a higher level helps in the removal of carbon but it does not result in a white RHA. Two samples of RHA from fluidized bed burner one from top and other from the bottom of the furnace were tested to be having carbon content of 2%. But they were not white in colour. The samples of RHA from torbed reactor were found to be having higher carbon content with the increase in temperature. But this method did not produce white RHA due to insufficient duration of heating. The sample from Norman Pitt's apparatus was found to have carbon content of 12 – 14 % that is very high because the maximum carbon content allowable by ASTM specification is 6%. Another innovative method proposed by Ajiwe[8] who suggested pre carbonising RH before burning in electric furnace at 600 °C. The RHA derived from this method had a carbon content of 2% only. So, RHA from Type 1 & 2 burning procedures satisfies the ASTM specification requirements of LOI less than 6%.

Table 4.5: Loss on ignition of RHAs of various sources.

References	Apparatus	Samples	LOI (%)
Sheng Huang, (2001)	Fluidized bed	Carry over ash	2
		Furnace ash	2
Nehdi, (2003)	Torped reactor	RHA (750°C)	1.8
		RHA (830°C)	2.3
		RHA (750°C + air)	3.7
		US RHA	7
Norman Pitt, (1976)	Norman Pitt's innovative apparatus	RHA	12 -14
Ajiwe, (2000)	Pre carbonized in stove and burnt in electric furnace at 650° C	RHA	2
Kassim ,(2007)	Carbolite furnace	RHA	1.5

4.7 Porosity

Control mix mortar cubes, cement paste cubes with RHA replacement of 2.5%, 5% & 7.5% were cast to analyse its effect on porosity. The graphical illustrations of the results are shown in FIG 4.1, FIG 4.2 & FIG 4.3. The results showed that the increase in water cement ratio had increased the porosity of the cubes irrespective of RHA replacements. It was observed that the porosity of control mix cubes with higher w/c was high on all 3, 7 & 28 days when compared with the corresponding cement cubes with RHA replacement. These results proved two factors namely the porosity increases with increased water cement ratio and the porosity decreases with increased RHA replacement in cement paste cubes. The addition of RHA disperses homogeneously in cement paste matrix thereby increasing the density of cement paste consequently decreasing the porosity of the cement paste.

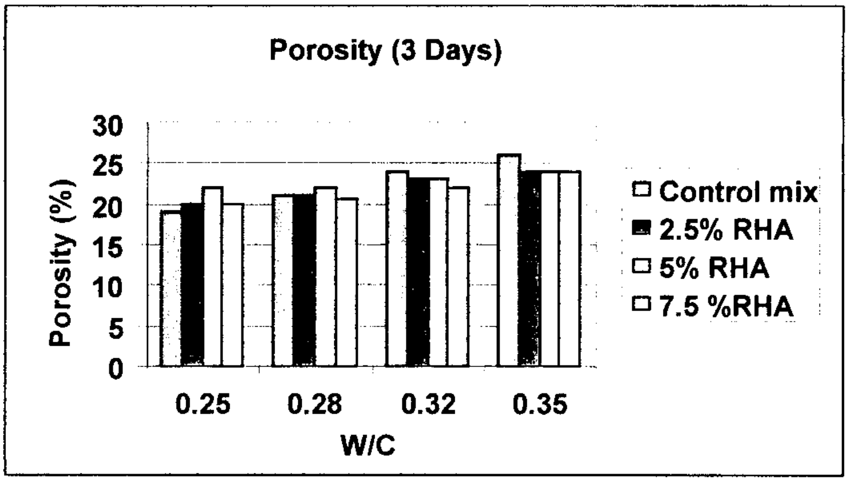


FIG 4.1: Porosity of paste cubes on various w/c (3 days)

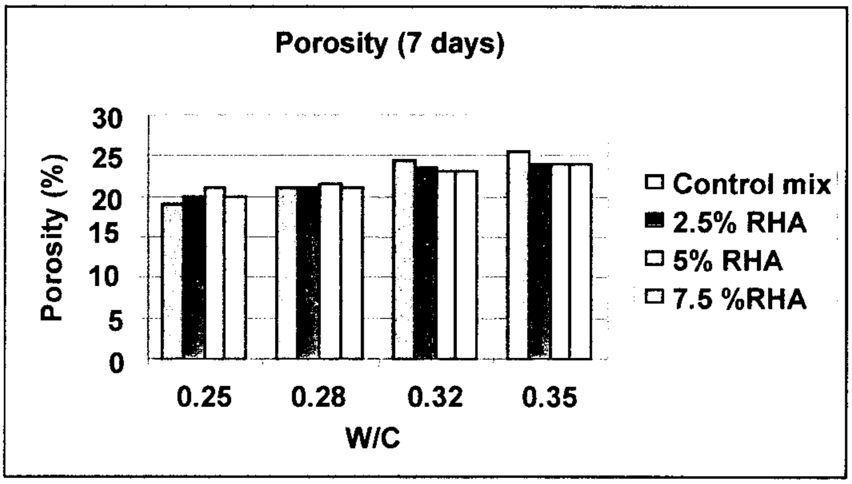


FIG 4.2: Porosity of paste cubes on various w/c (7 days)

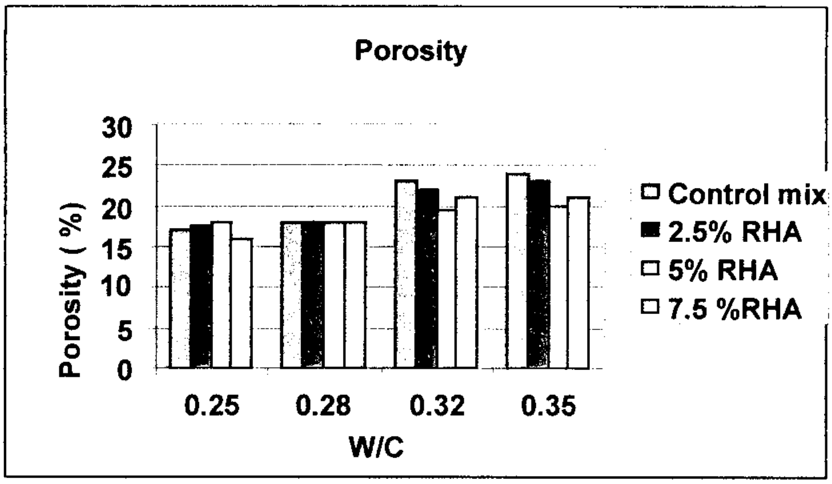


FIG 4.3: Porosity of paste cubes on various w/c (28 days)

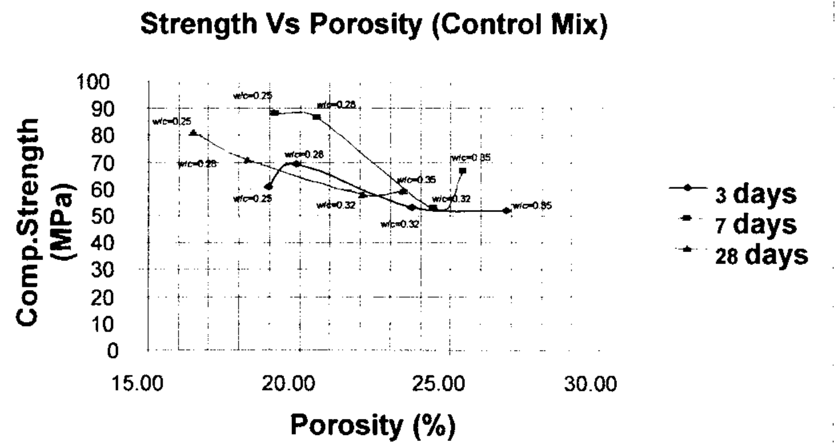


FIG 4. 4: Comparison of Compressive Strength with Porosity (Control mix)

The FIG 4.4 shows that strength of control mix cement paste decreasing as the porosity increases. This means that low porosity will result in high strength.

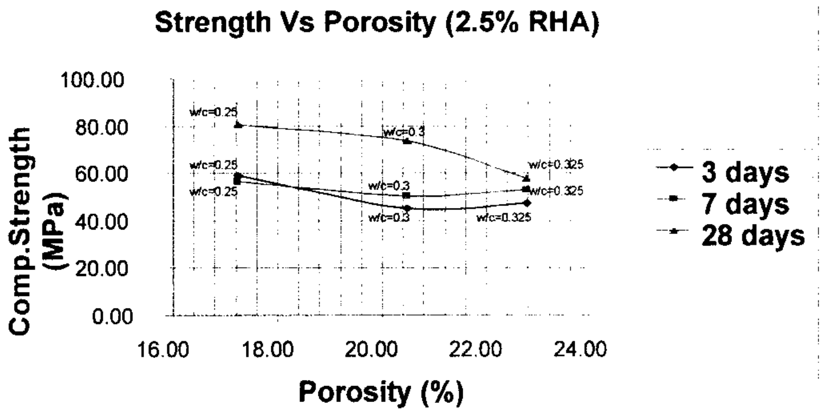


FIG 4. 5: Comparison of Compressive Strength with Porosity (2.5% RHA)

Decreasing of strength is shown as porosity increase in 2.5 % RHA (Refer FIG 4.5). The decreasing of strength as porosity increase is only shown at 28 day. At early age pozzolanic reaction was causing different kinds of results.

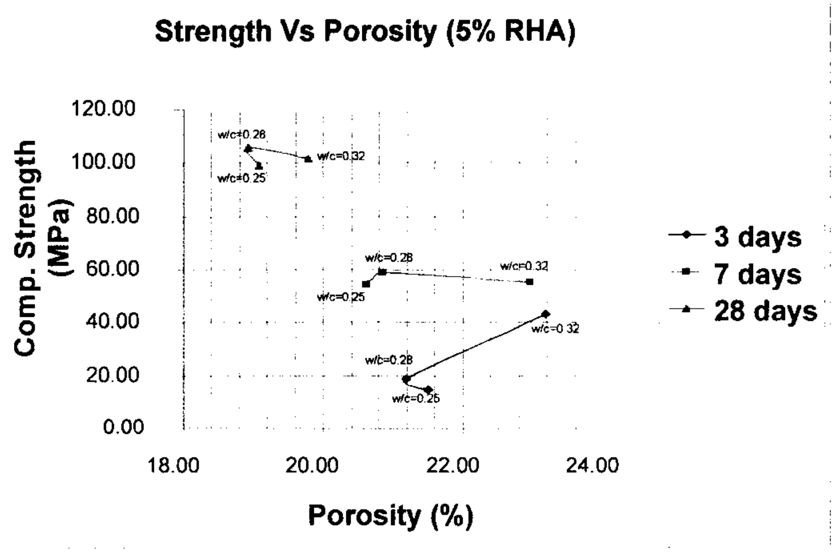


FIG 4. 6: Comparison of Compressive Strength with Porosity (5% RHA)

From the FIG 4.6, highest strength and low porosity is not achieved by lowest water cement ratio paste. w/c of 0.28 gives highest strength and low porosity to the paste.

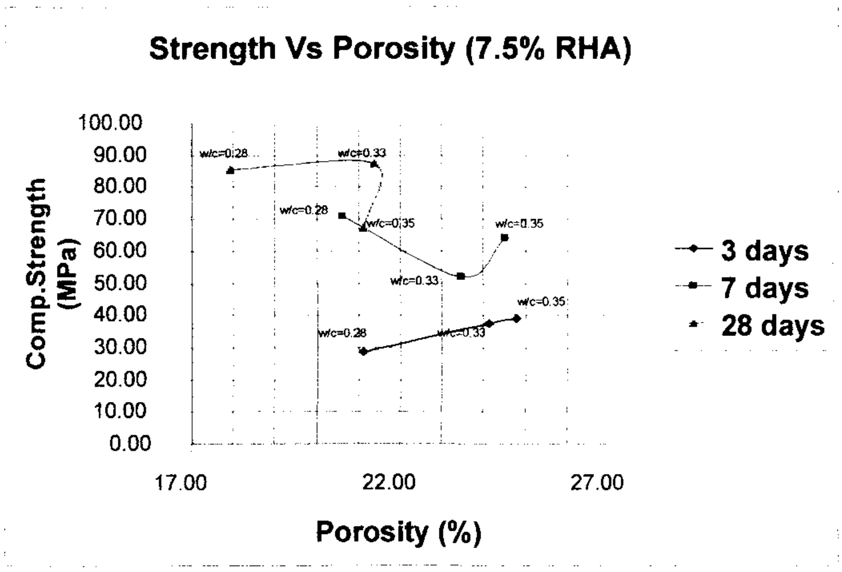


FIG 4. 7: Comparison of Compressive Strength with Porosity (7.5% RHA)

For cement paste cubes with 7.5% RHA replacement, water cement ratio at 0.33 showed the highest strength but with high porosity. At low water cement ratio of 0.28, it gave high strength and lowest porosity but slightly lower in strength than paste with 0.33 water cement ratio.

4.8 Compressive strength of Cement pastes:

Totally 108 numbers of 50mm X 50mm cement paste cubes with RHA replacement that varies from 2.5% - 20% were cast to determine compressive strength. For comparative analysis, control cement paste cubes were also made. Firstly, control cement paste of standard consistence was prepared. Consistence was determined by the vicat apparatus, which measures the depth of penetration of a 10mm diameter plunger under its own weight. The water requirement for control cement paste of standard consistence was 23.5%. By keeping the W/C constant, cement paste cubes with RHA replacement of 2.5 %, 5% and 7.5% were made respectively. w/c of 23.5 was too low for cement cubes containing RHA more than 7.5%. This was due to higher water requirement of RHA. As the replacement ratio of RHA increases, water requirement also increases due to its higher surface area. The compressive strength of control mix was higher compare with replacement of 2.5%, 5% & 7.5%. Especially, the strength of cement paste cubes containing 7.5% replacements was low due to inadequate water to complete hydrationprocess. (ReferFIG4.8)

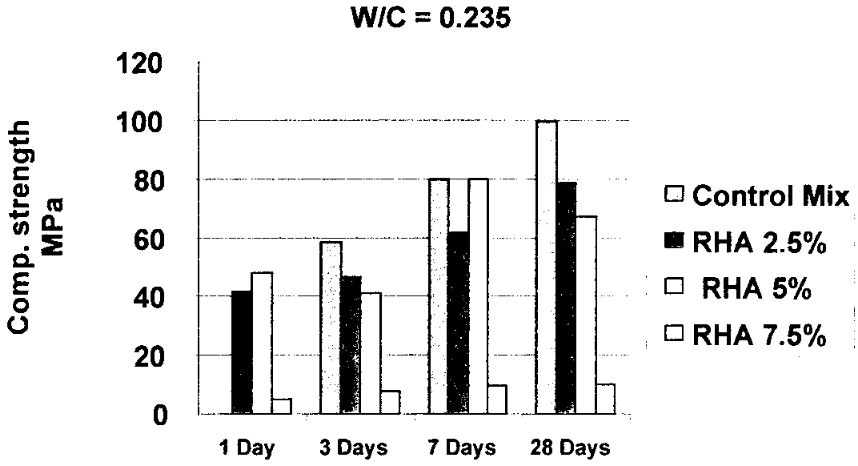


FIG 4. 8: Compressive strength (w/c = 0.235)

For second batch, w/c ratio was increased to 0.25, in which cement paste of control mix, RHA replacement of 2.5% and 5% were made. In this case, 28th day strength of control mix cubes and cubes containing 2.5% RHA replacement were lower compared with previous batch due to high water cement ratio. But, the strength of paste cubes containing 5% RHA replacement had increased about 32% compare with cubes made with w/c 0.235 due to sufficient water available for heat of hydration.(Refer FIG 4.11).

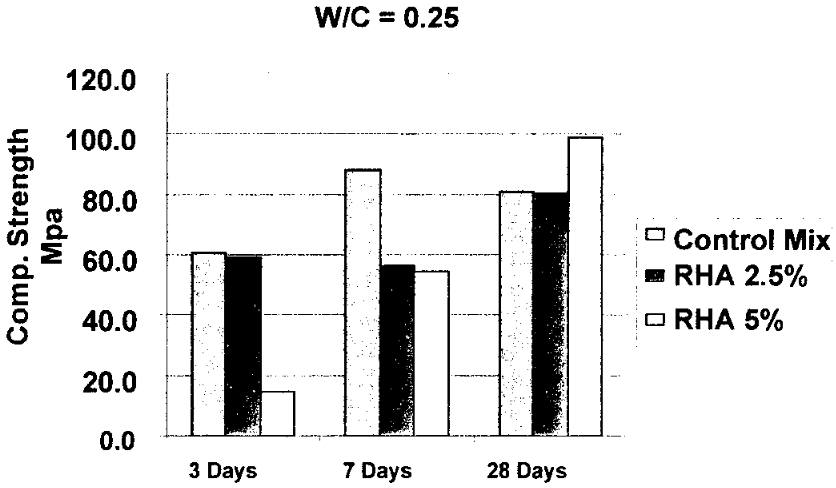


FIG 4. 9: Compressive strength (w/c = 0.25)

In third batch, W/C ratio of 28 was selected. The compressive strength of cement paste cubes containing 5% and 7.5% RHA replacement have shown higher values. It is important to notice that strength of control mix was reduced in comparison with values of other w/c ratios. It proved that higher w/c ratio lowers the strength.(Refer FIG 4.10).

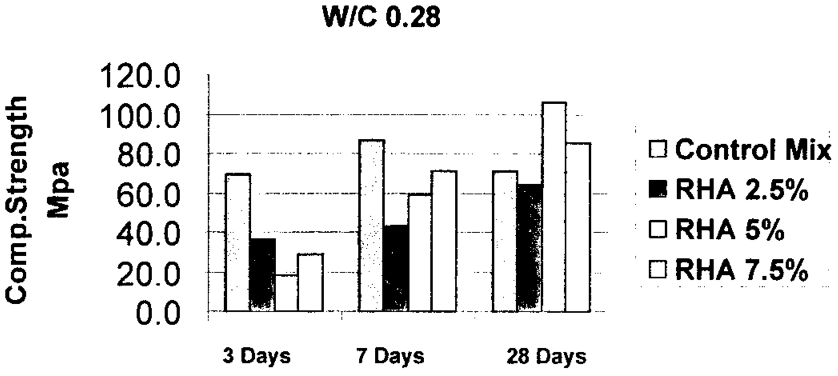


FIG 4. 10: Compressive strength (w/c = 0.28)

For w/c 0.32, cement paste cubes with 5% replacement has shown higher values of all. But the value was lower about 3.85% in comparison with corresponding cubes with w/c of 0.28%. The strength of control mix was lowered further due to higher w/c.(Refer FIG 4.11)

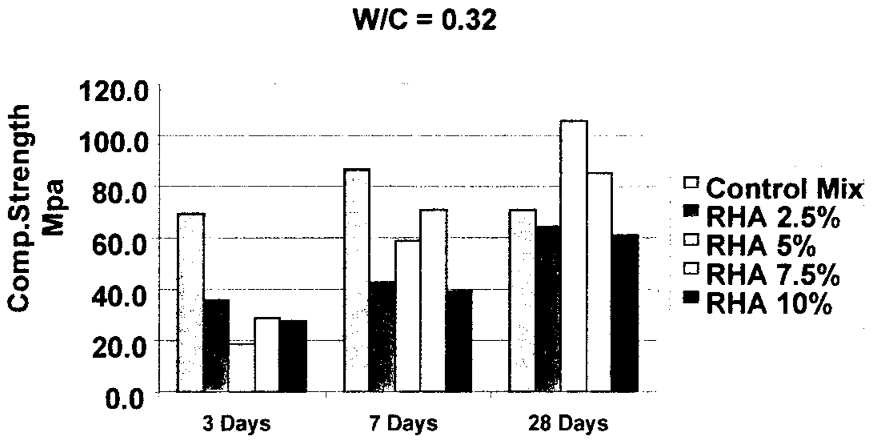


FIG 4. 11: Compressive strength (w/c = 0.32)

For w/c 0.35, the compressive strength of control mix, cement paste cubes with 7.5% RHA & 12.5% RHA were found to be lower due to higher water cement ratio and cement dilution effect. (Refer FIG 4.12)

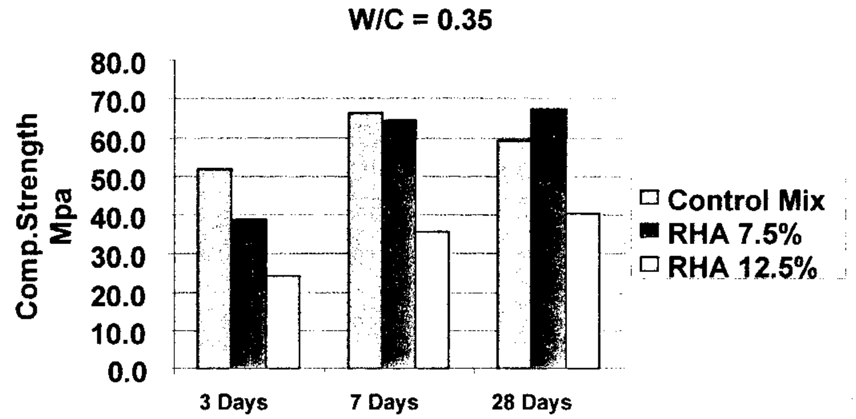


FIG 4. 12: Compressive strength (w/c = 0.35)

The cement paste cubes with RHA replacement of 10%, 12.5%, 15%, 17.5% & 20% were made with w/c ratios of 0.32, 0.35, 0.36, 0.37 & 0.39 respectively. The control paste cubes with w/c of more than 0.35 could not be made due to higher w/c. So that no comparisons were made for cement pastes containing RHA replacement of 15%, 17.5% & 20%.

The compressive strengths of control mix cubes are given in Table 4.6. The optimum w/c ratio for cement paste cubes to get higher 28 day strength was 0.235. (Refer FIG: 4.13). It was also observed that all other w/c ratios except optimum w/c ratio have given lower strength. Even though the amount of water added with cement paste of optimum w/c is sufficient for chemical reactions, there would have been no water available in capillary pores. Since the cement paste cubes were immersed in water for curing, there could be ingress of water from outside. That water helped to maintain high internal relative humidity and achieve full hydration.

Table 4.6: Compressive strength of control mix (MPa)

AGE	W/C				
	0.235	0.25	0.28	0.32	0.35
3	58.51	60.64	69.14	52.94	52
7	79.65	88.04	86.58	52.54	66.38
28	99.25	81.04	70.66	57.88	59.14

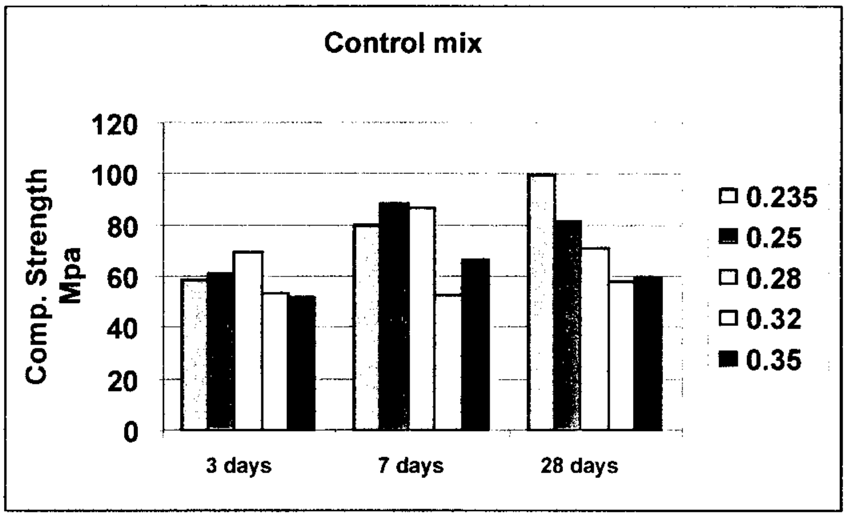


FIG 4. 13: Compressive strength (Control Mix)

For replacement ratio of 2.5% RHA, the highest strengths were achieved at w/c of 0.25. The w/c of 0.235 might be insufficient to carry out full hydration process. So, it resulted in lower strength. The other w/c of 0.28 & 0.32 were also given lower strength due to higher water cement ratio.

Table 4.7: Compressive strength of RHA – 2.5 % (MPa)

AGE	W/C			
	0.235	0.25	0.28	0.32
3	36.03	46.57	45.12	47.28
7	43.07	61.35	50.42	52.7
28	64.26	78.43	73.28	57.62

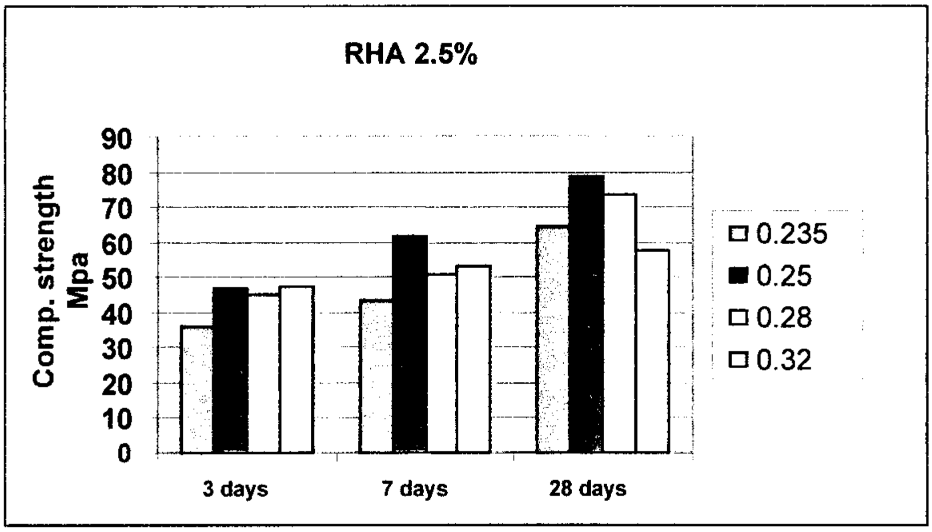


FIG 4.14: Compressive strength (RHA 2.5%)

For replacement ratio of 5% RHA, the highest strengths were achieved at W/C of 0.28. The increase in addition of RHA required additional amount of water for full hydration. The reduction in strength for cement paste cubes with w/c of 23.5 due to insufficient water for hydration thereby formation of interconnected pore system. These inter connected pores might have weakened the cement paste. The compressive strengths of cement paste cubes of various w/c are given in Table 4.8. Please refer Table 4.8 for graphical illustration.

Table 4.8: Compressive strength of RHA – 5.0 % (MPa)

AGE	W/C			
	0.235	0.25	0.28	0.32
3	41.24	14.36	18.36	42.8
7	79.65	54.34	58.66	54.98
28	66.85	98.7	105.64	101.62

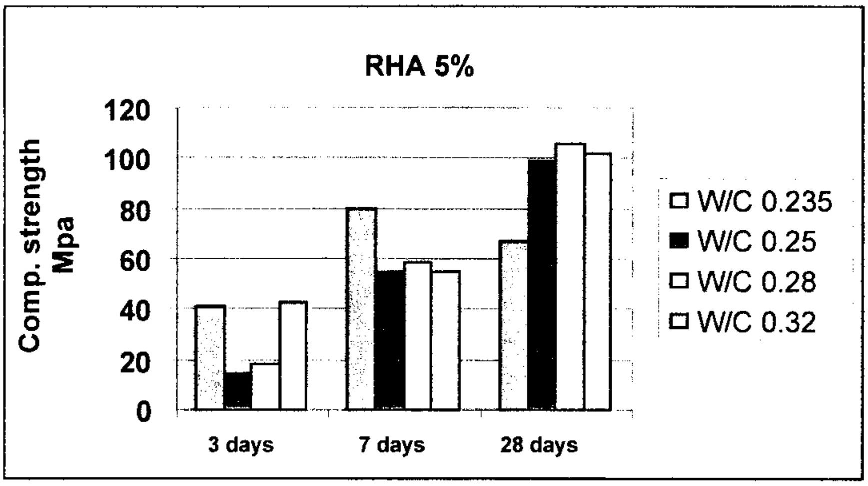


FIG 4.15: Compressive strength (RHA 5%)

For replacement ratio of 7.5 % RHA, the highest compressive strength was achieved with w/c of 0.32. The cement pastes made with w/c of 0.235 gave lower strength. This explains that w/c of 0.235 is insufficient for heat of hydration process to be carried out. The other water cement ratio of 0.35 seemed to be higher for 7.5 % RHA replacement. (Refer Table 4.9 & FIG 4.18)

Table 4.9: Compressive strength of RHA – 7.5 % (MPa)

AGE	W/C			
	0.235	0.28	0.32	0.35
1	5.19			
3	7.75	28.62	37.02	38.6
7	9.43	70.88	51.84	64.22
28	9.85	85.26	87.2	67.14

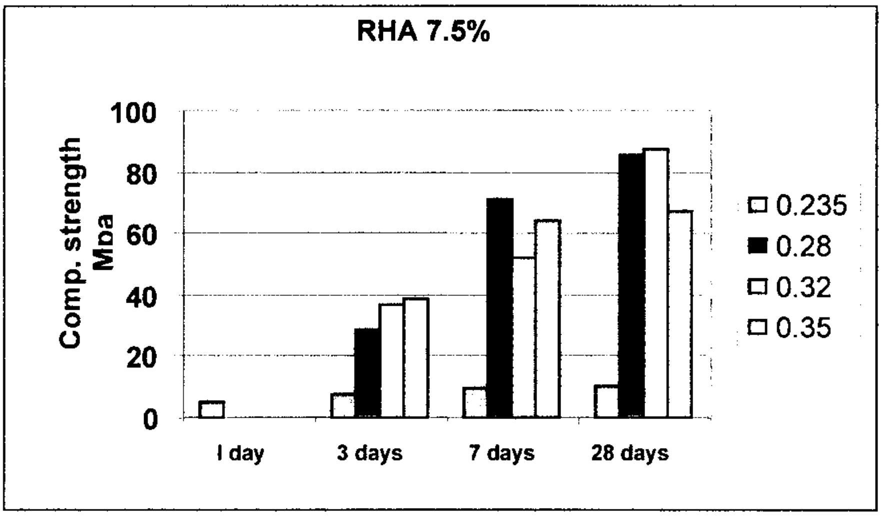


FIG 4. 16: Compressive strength (RHA 7.5%)

For cement paste cubes made with 10 % RHA replacement, the w/c was maintained at 0.32. The cement paste cubes made with lesser w/c were found to be not workable. The compressive strengths of these cement paste cubes are given in Table 4.10. The comparison of compressive strengths of these cubes with control mix are shown in FIG 4.19

Table 4.10: Compressive strength of RHA – 10.0 % (MPa)

AGE	W/C
	0.32
1	
3	27.29
7	39.21
28	60.76

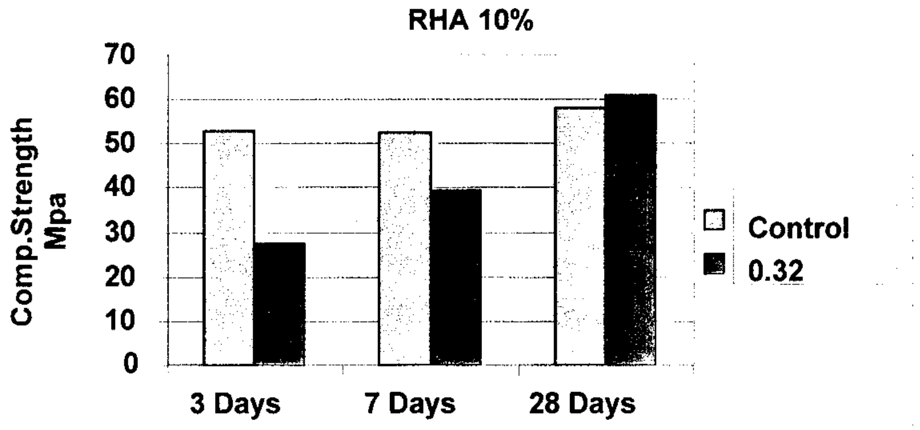


FIG 4.17: Compressive strength (RHA 10%)

The cement paste cubes with 12.5 % RHA replacement required higher water cement ratio of 0.35 due to high percentage of RHA addition. But the compressive strengths of these cubes were lower compared with control mix. (Refer Table 4.11 & FIG 4.20)

Table 4.11: Compressive strength of RHA – 12.5 % (MPa)

AGE	W/C
	0.35
1	
3	24.45
7	35.44
28	40.45

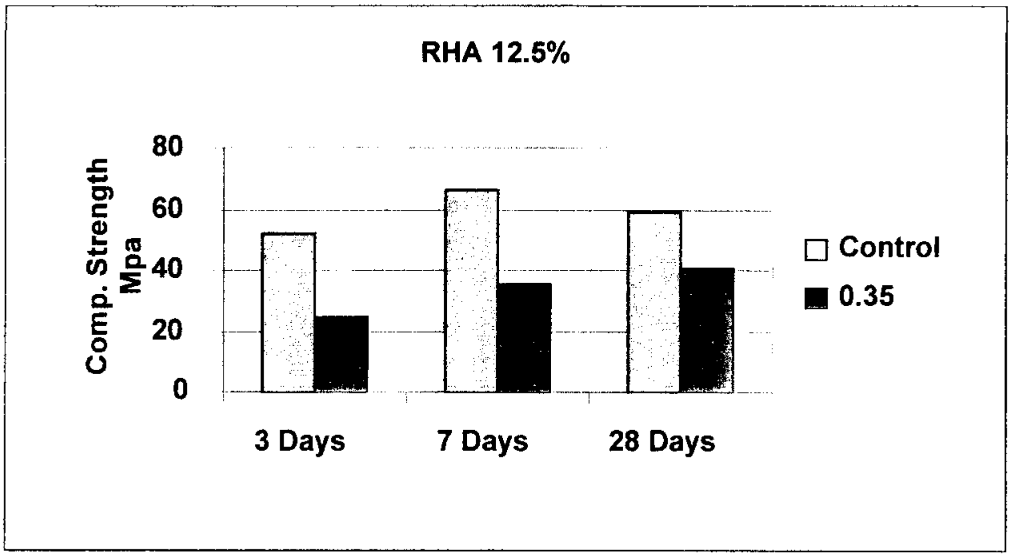


FIG 4.18: Compressive strength (RHA 12.5%)

For replacement ratio of 15 % RHA, the water cement ratio was increased to 0.36. The control cement paste cubes could not be made due to high water cement ratio. The compressive strengths of paste cubes are shown Table.

Table 4.12: Compressive strength of RHA – 15.0 % (MPa)

AGE	W/C
	0.36
1	-
3	20.80
7	30.51
28	35.44

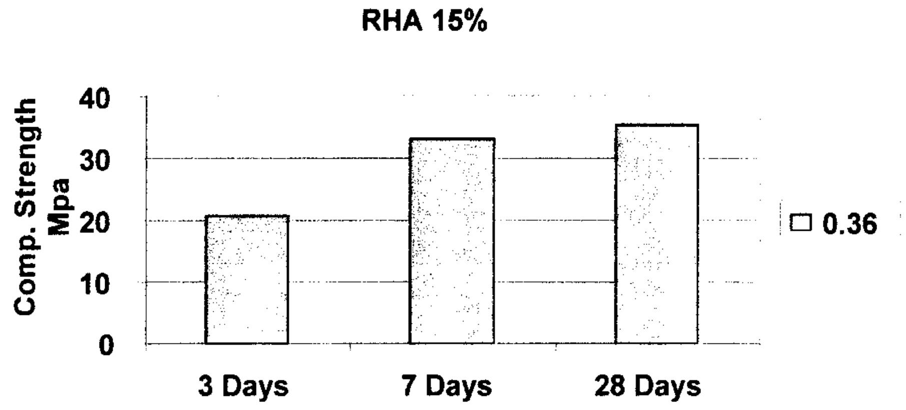


FIG 4.19: Compressive strength (RHA 15%)

For replacement ratio of 17.5 % RHA, the minimum water cement ratio was required to be 0.37. The control cement paste cubes could not be made for this w/c due to high water cement ratio. The compressive strengths of paste cubes are shown Table.4.13. Please refer FIG 4.22 for graphical illustration.

Table 4.13: Compressive strength of RHA – 17.5 % (MPa)

AGE	W/C
	0.37
1	-
3	22.41
7	30.51
28	41.21

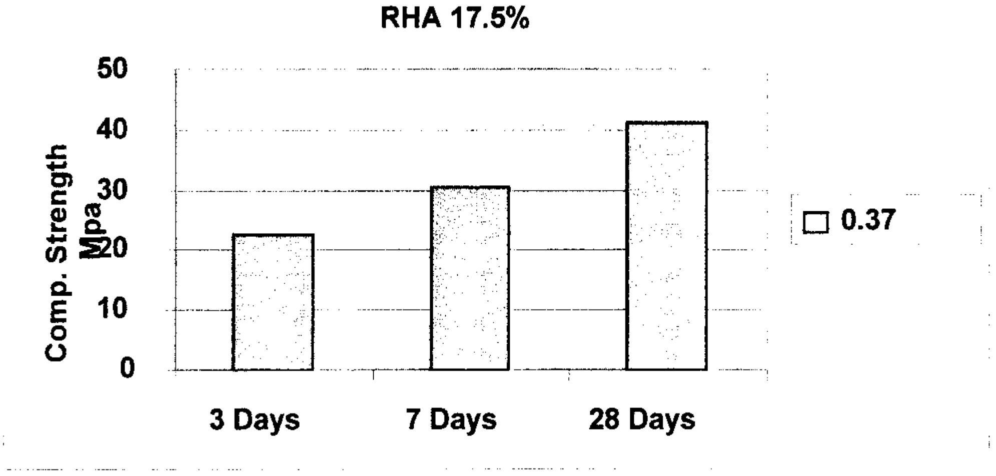


FIG 4.20: Compressive strength (RHA 17.5%)

The 28 day compressive strengths of cement paste cubes made with 20 % RHA replacement were lower than other replacement ratio and also required highest water cement ratio. Control cement paste cubes could not be made for this case also.

Table 4.14: Compressive strength of RHA – 20.0 % (MPa)

AGE	W/C
	0.39
1	-
3	17.39
7	20.84
28	32.88

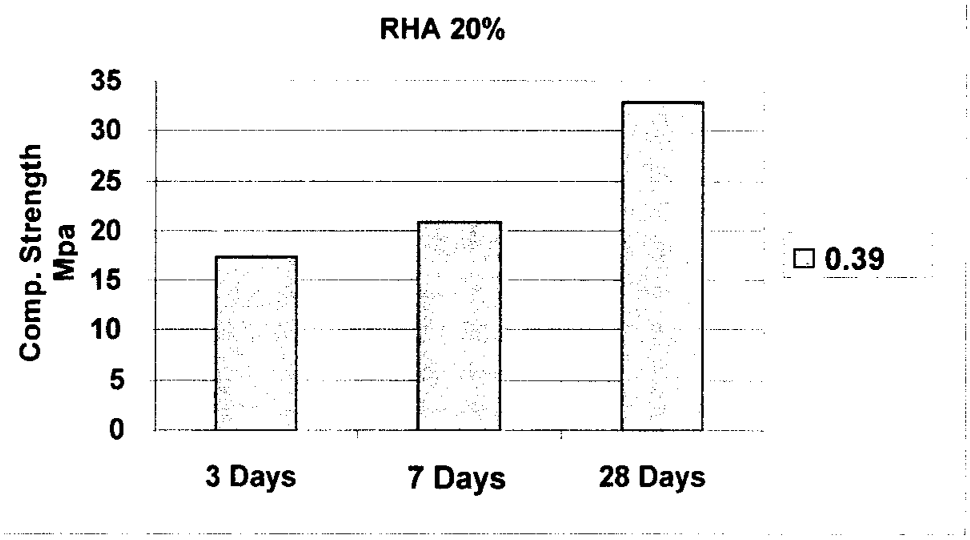


FIG 4.21: Compressive strength (RHA 20%)

Optimum water requirement of cement pastes containing various RHA replacements that give higher compressive strengths are illustrated in FIG 4.9.

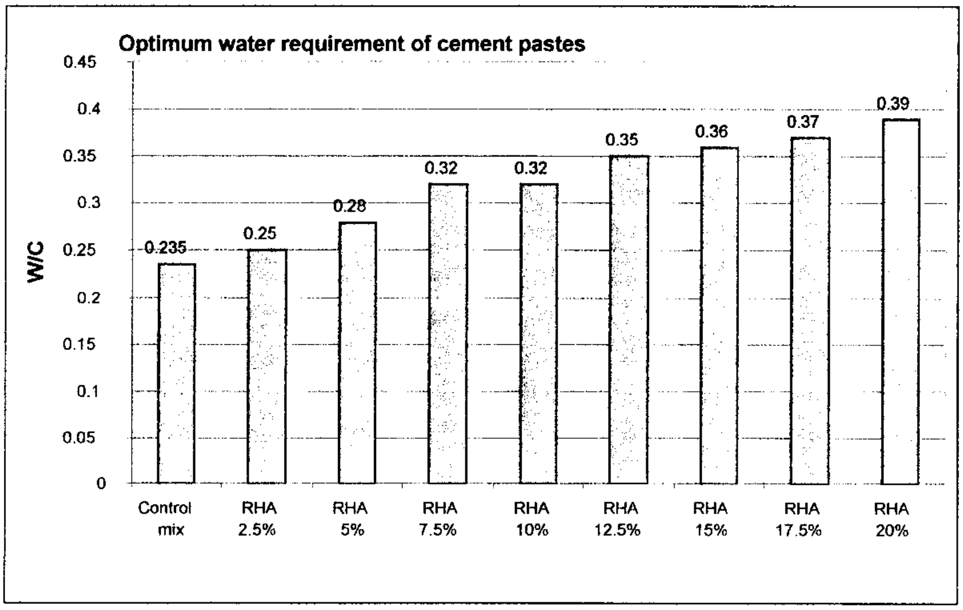


FIG 4. 22: Optimum water requirement of cement pastes containing various RHA replacements

4.9 X-Ray Diffraction (XRD)

The FIG 4.24 and FIG 4.25 show X-Ray diffractograms for the RHA sample derived from Type 1 and Type 2 burning procedure. The X –Ray diffractogram of RHA samples shows that RHA is mainly amorphous... The absence of small peaks that generally represents crystalline silica shows that RHA is mostly amorphous and peaks of equal magnitude proves that RHA samples are of uniform characteristics. It can be concluded that the type 1 and type 2 standard burning procedures yielded more reactive amorphous silica than uncontrolled combustion method. The comparison between OPC and RHA diffractograms is shown in FIG 4.26.

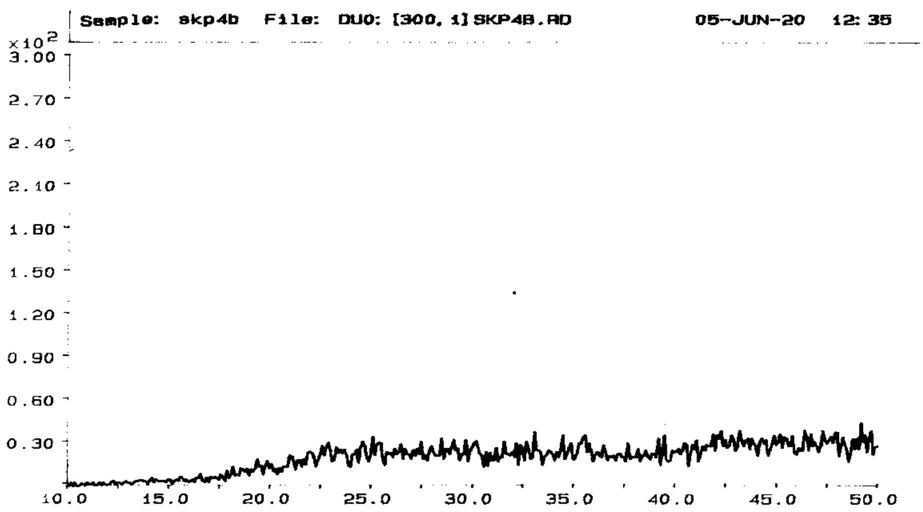


FIG 4.23: XRD pattern of RHA (Type 1)

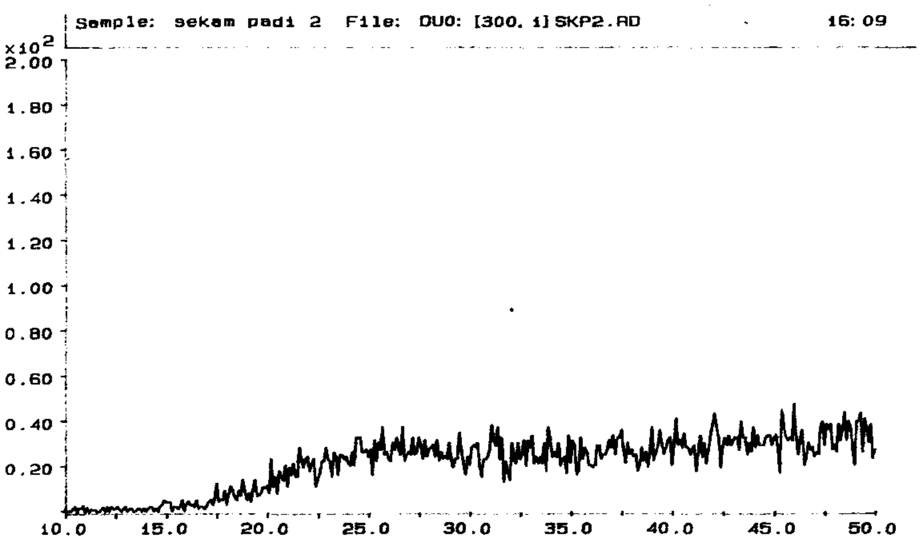


FIG 4.24: XRD pattern of RHA (Type 2)

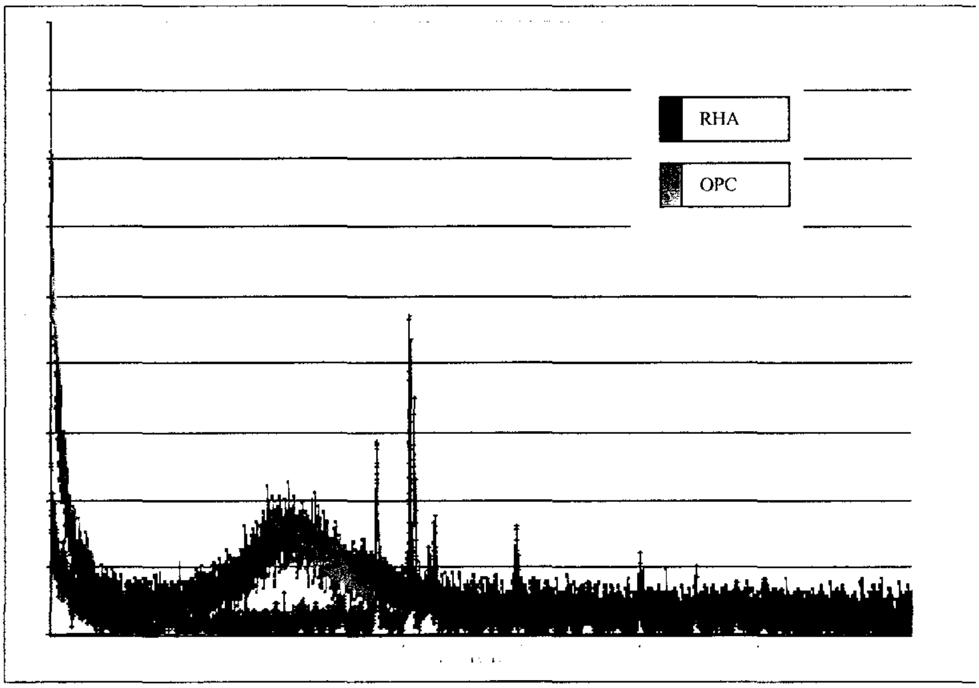


FIG 4.25: Comparison of XRD of OPC with RHA

4.10 X-Ray Fluorescence method (XRF)

The sample of Type 2 burning procedure has yielded 94.3% of SiO_2. MgO and Al_2O_3 were less than 1%. For Type 1 method, the SiO_2 content was slightly lower i.e. 93.1%.. MgO and Al_2O_3 were also less than 1%. But for second method, XRF did not detect the presence TiO_2 and ZnO. It is important to note that Cl content of Type 2 sample (0.108%) was less than Type 1 sample ((0.185%). (Refer Table 4.16). The chemical analysis of samples complies with the chemical requirements of ASTM C 1240 -97b that specify minimum SiO_2 content should be more than 85%. This in one of the standard requirements for natural pozzolans to be used as mineral admixture in concrete. But the K_2O content in these samples was found to be higher and it exceeded ASTM C 1240 – 97b recommendation of max 1.5%. The comparison of chemical and physical properties of RHA with commercially available silica fume proves that they are on par in all aspects.

Table 4.15: Chemical Element of RHA (Type 1 & 2)

	Type 1 RHA		Type 2 RHA	
Mg	12.1KCps	0.577%	11.6 Kips	0.667%
Al	0.8 KCps	0.0417%	0.9 KCps	0.0533%
Si	1265.2 KCps	84.3%	1279 KCps	88.6%
P	13.2 KCps	1.94%	12.1 KCps	1.58%
S	19.7 KCps	1.65%	7.2 KCps	0.532%
Cl	3.4 KCps	0.652%	2 KCps	0.329%
K	113.5 KCps	8.44%	108.2 KCps	6.83%
Ca	17.7 KCps	1.42%	17.4 KCps	1.14%
Ti	1.3 KCps	0.0749%		
Mn	9.6 KCps	0.199%	8.9 KCps	0.145%
Fe	14.3 KCps	0.16%	11.9 KCps	0.0796%
Cu	4.9 KCps	0.0114%		
Zn	87.4 KCps	0.425%	13.8 KCps	0.0318%
Rb	22.9 KCps	0.0421%	23.0 KCps	0.0325%

Table 4.16: Chemical Composition of RHA (Type 1 & 2)

	Type 1 RHA		Type 2 RHA	
MgO	12.1 KCps	0.682%	11.6 KCps	0.657%
Al_2O_3	0.8 KCps	0.0403%	0.9 KCps	0.0481%
SiO_2	1265.2 KCps	93.1%	1279 KCps	94.3%
P_2O_5	13.2 KCps	1.32%	12.1 KCps	1.22%
SO_3	19.7 KCps	1.19%	7.2 KCps	0.437%
Cl	3.4 KCps	0.185%	2 KCps	0.108%
K_2o	113.5 KCps	2.78%	108.2 KCps	2.63%
CaO	17.7 KCps	0.495%	17.4 KCps	0.481%
TiO_2	1.3 KCps	0.0290%		
MnO	9.6 KCps	0.0574%	8.9 KCps	0.0518%
ZnO	87.4 KCps	0.102%		
Rb_2O	22.9 KCps	0.0104%	23 KCps	0.0102%
Y_2O_3	6.5 KCps	0.000803%	5.7 KCps	0.000405%

The comparison of oxide contents of OPC with RHA was made by XRF method and results are given in Table 4.17.

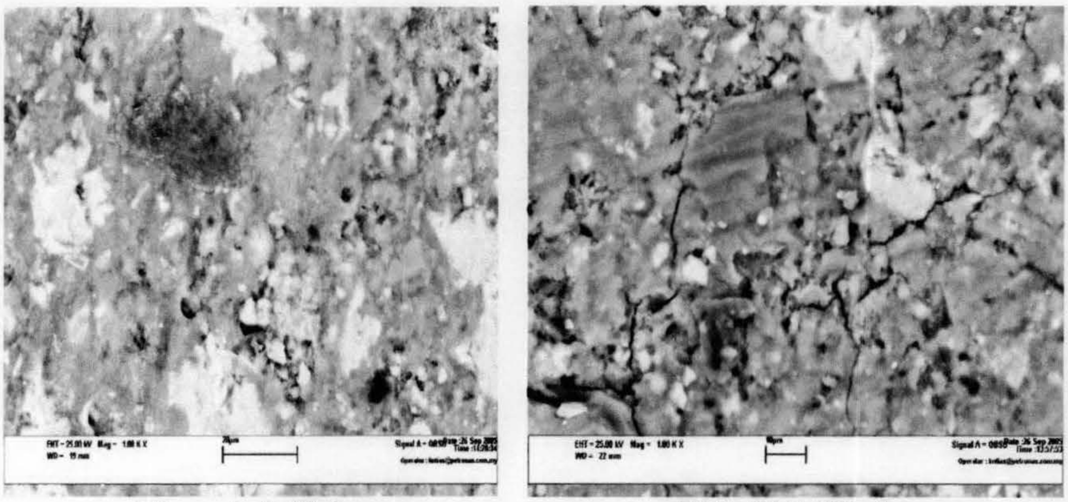
Table 4.17: Comparison of Oxide content of OPC and RHA

Cement				RHA			
Oxide content		Element		Oxide content		element	
Na2O	0.00294	Na	0.00294	MgO	0.00569	Mg	0.00617
MgO	0.0135	Mg	0.0111	Al2O3	0.000927	Al	0.00103
Al2O3	0.0807	Al	0.0588	SiO2	0.952	Si	0.905
SiO2	0.307	Si	0.205	P2O5	0.00829	P	0.0104
P2O5	0.00124	P	0.000833	SO3	0.00451	S	0.0053
SO3	0.0432	S	0.0266	Cl	0.000916	Cl	0.0027
K2O	0.0051	K	0.00691	K2O	0.0205	K	0.0513
CaO	0.511	Ca	0.637	CaO	0.00598	Ca	0.0135
TiO2	0.0029	Ti	0.00361	MnO	0.000474	Mn	0.00131
MnO	0.00143	Mn	0.00236	Fe2O3	0.000259	Fe	0.00212
Fe2O3	0.0295	Fe	0.0438	Rb2O	6.91e-05	Zn	0.000603
SrO	0.000363	Zn	0.000845			Rb	0.000211
ZrO2	0.000138	Sr	0.000662				
Sb2O3	0.000809	Zr	0.000221				
	100.00%						
		Zirconium					
		Strontium					
		Antimony oxide					

4.11 Scanning Electron Microscope:

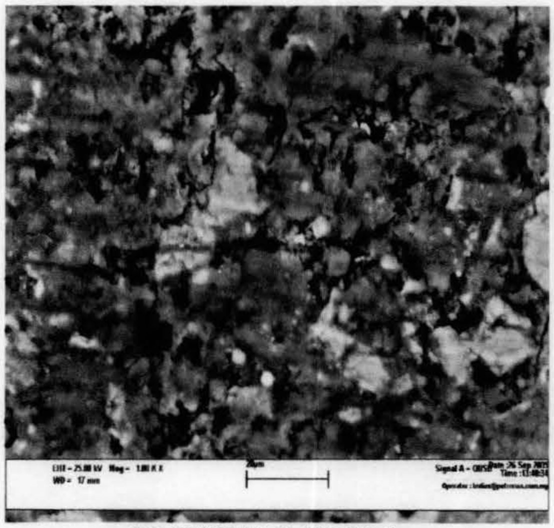
W/C 0.28% on 28 days

BSE



Mix control -28 day

R5%- RHA 5% -day



R7.5%RHA 7.5%-28 day

FIG 4.26: SEM observations of cement paste containing RHA

Scanning electron microscope observations of control mix cement paste, cement paste containing RHA 5% and cement paste containing RHA 7.5% are shown in FIG: 4.27. These cement paste cubes were scanned by SEM after 28 days of casting. The magnified images of micro space of cement paste by SEM confirmed the presence of $Ca(OH)_2$ that was produced due to hydration processes in all three types of cubes. But it was observed lesser in cubes containing 7.5% RHA due to pozzolanic reaction and higher in control mix cubes due to absence of RHA.

CHAPTER FIVE

Conclusions

The RHA samples derived from type 1 and type 2 burning procedures that were suggested in this research yielded silica contents of 93.1% and 94.3% respectively. Despite slight variation in the silica contents, the X-Ray diffraction analysis of both samples exhibited completely amorphous characteristics and no sign of quartz or other crystalline features. The mineral content of the remaining percentage of RHA samples does comply with the standard specified in ASTM C 1240 and also is similar to the mineral content in the commercially available silica fume. The Pozzolanic activity index (PAI) that indicates the chemical activeness of the mineral showed the PAI of samples to be 105. This indicated that, although two burning procedures were adopted, the resultant samples had the same chemical activeness. The higher PAI and high early strength of the samples from type 1 & 2 burnings in contrast to the RHA derived from other methods suggests that the burning method is effective in producing active silica. This reiterated the advantage of incorporating RHA to provide supplementary cementitious material in concrete. The physical properties like the average particle density 2.1 g/m^3, carbon content 2.5% and moisture content 1.5% remain to be same for both the samples. These features are almost equivalent to the commercially available silica fumes. So, this RHA has an advantage to be promoted as mineral admixtures.

The optimum w/c for cement paste cubes containing 2.5% RHA in order to get high strength was 0.25. For other replacement ratios of 5%, 7.5%, 10%, 12.5%, 15%, 17.5% & 20% RHA, the optimum w/c were 0.28, 0.32, 0.32, 0.35, 0.36, 0.37, and 0.39 respectively. For control mix, w/c of 0.25 gives high strength with low porosity. For RHA partial replacements, w/c of 0.28 provides high strength with low porosity of cement paste, but an increase of w/c to 0.33 in cement paste cubes containing RHA replacement lead to increase in strength and porosity as well.

CHAPTER SIX

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