

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Cement is the product of the silicate industry and is artificial on the major material in concrete. It is used extensively in building residential, bridges and other structures. The raw materials used in making cements are naturally occurring materials which includes gypsum, $\text{CaSO}_4 + 2\text{H}_2\text{O}$, anhydride CaSO_4 and limestone rock (Ajiwe et al., 2000).

With high cost of production and energy consumption to produce and also the major source of greenhouse gas emission, it is time to look into the use of local inexpensive raw materials or industrial waste materials in replacing cement to build the structures especially housing for the needy. The utilization of the industrial waste by- products such as silica fume, slag and fly ash as well as the agricultural residue such as rice husk ash, as cement replacement is a new trend in concrete technology in this 21st Century. Having pozzolanic properties, not only that it gives technical advantage to the resulting concrete, but it also reduces cement consumption. Thus, the resulting benefits in terms of energy saving, economy, environmental protection and conservation of resources will be substantial. The history of the utilization of rice husk ash in concrete goes back to 1946 in the United States, by work carried out by Mc Daniel (1946). It described the manufacture and behavior of blocks made from the mixtures of Portland cement, ash and rice husks. In India, the utilization of RHA has been adapted by the Central Building Research Institute in 1976 by burning the rice husk balls or cakes bonded in clay producing almost carbon-

free ash and then ground with hydrated lime to produce a cementitious material. (Mc Daniel, 1946).

Cook (1986) quoted that the utilization of the ash in concrete as up to the year 1972 is to act as a lightweight material and as insulating filler and not as a pozzolan. In 1972, Mehta applied for a Belgian patent and was issued later in 1973 on the rice husk utilization and several papers were also published (Mehta, 1983). Most of Mehta's work was on the studies of the preprocessing parameters and their influence on the ash reactivity. At the Asian Institute of Technology in Bangkok, studies on the laboratory-burnt RHA has been investigated as a pozzolana in the form of an additive in cement mortar and concrete (Columa, 1974). Study by Columa has made on RHA as a good replacement material for cement in normal concrete. Meanwhile Mehta has carried out other cement-based material since 1973 at the University of California at Berkeley, USA.

In developing countries especially in rice growing countries such as India, Pakistan and Malaysia, the concept of cement based on rice husk ash provides impetus for renewed research. This is revealed by the first workshop outlining the state-of-the-art of RHA cements conducted in Peshawar, Pakistan in 1979, and a meeting in Malaysia in 1979 (UNIDOIESCAPIRCTI, 1979). Numerous researches were carried out then and documented and published by the United Nations Industrial Development Organization (UNIDO) in 1984 and the problems associated with it were also identified. It indicated that there is a potential use of RHA cement (UNIDOIESCAPIRCTI, 1979). With the utilization of pozzolanic materials such as silica fume, slag, fly ash, metakaolin and rice husk ash as partial cement replacement, the demand on Portland cement would be reduced, and thus the cost of cement can also be reduced.

Concrete structures are generally designed for a service life of 59 years, but experience shows that in urban and coastal environments many structures begin to deteriorate in 20 to 30 years or even in less time. The lack of durable materials has serious environmental

consequences. Increasing the service life of products is long term and easy solution for preserving the earth's natural resources (Sampaio, 2000)

The world's yearly cement production of 1.6 billion tonnes accounts for about 7% of the global loading of carbon dioxide into the atmosphere. Portland cement, the principal hydraulic cement in used today, is not only one of the most energy-intensive materials of construction but also is responsible for a large amount of greenhouse gases. Producing a tonne of Portland cement requires about 4GJ energy, and Portland cement clinker manufacture releases approximately 1 tonne of carbon dioxide into the atmosphere. Ordinary concrete typically contains about 12% cement and 80% aggregate by mass (Sampaio, 2000).

During the 21st Century, the increasing demand for cement and concrete must be met by the use of mineral cement replacement materials. Substantial energy and cost savings can result when industrial by-products are used as a partial replacement for the energy/intensive Portland cement. According to Mehta, PK (1994), the cement production rate of the world is expected to grow exponentially to about 3.5 billion tonnes/year by 2015. According to his projection, most of the increase in cement demand will be met by the use of mineral cement replacement material. He also suggested that this approach is necessary to prevent the possible ecological disaster from global warming.

The presence of mineral cement replacement material in concrete is known to impart significant improvements in workability and durability. A high performance concrete with good workability and high durability can be made by a cautious choice of minerals cement replacement material and concrete mix proportions. Some of these materials can be obtained from by-products. The use of by products is an environmental-friendly method of disposal of large quantities of materials that would otherwise pollute land, water and air (Mehta, P.K, 1994). The use of the artificial pozzolans can achieve not only economical and ecological benefits but technical benefits as well. It is generally agreed that, with proper selection of admixture, mixture proportioning and curing technique, minerals additives can greatly improve the durability of concrete.

In this chapter, the definition of High Performance Concrete (HPC) and its importance to the construction industry is discussed. The principal parameters of HPC in its production, use and the problems of using HPC is also discussed and reviewed.

This chapter also briefly gives an introduction to the pozzolanic materials use and its performance in the production of HPC. As literature discussion, existing knowledge on the effect of pozzolanic materials used as replacement material to produce binary blended cement system in HPC, which are related to this study, are reviewed. Properties and performance of Ordinary Portland Cement and multiple blended binders cement containing pozzolans used to produce HPC was discussed. Finally, this chapter also discusses the role, potential and importance of using multiple blended binders as an alternative binders to OPC in producing HPC.

The concept of a PFA and cement system is not new and many patents have been published by many researchers. Chindaprasirt et al, (2007) found that the strength development of concrete containing fly ash as a cement replacement of 15%, 25%, and 35% was faster than that of the 50% cement replacement, while 25% cement replacement gave the highest compressive strength at all ages. At 15–35% content replacements, the compressive strengths were higher than that of control concrete at all ages up to 180 days. At 28 days, the compressive strength tended to increase with the curing age for all mixtures and varied from 77.3 MPa in sample of 50% fly ash to 82.5 MPa in sample of 25% fly ash. This is due to the extreme fineness of fly ash that exhibits pozzolanic properties and packing effect. These characteristics tend to improve concrete strength as well as its density (Angsuwattana et al, 1998).

In 2004, (Qingge Feng et al, 2004) found that with hydrochloric acid pretreatment of rice husks, the pozzolanic activity of rice husk ash is not only stabilized, but also the enhanced the sensitivity of the pozzolanic activity of the rice husk ash to burning conditions is reduced. The pozzolanic activity of ADR (acid-treated rice husk) is slightly affected by the change of

maintaining time, but the maintaining time has a great affect on the pozzolanic activity of RHA (no pretreatment). However, from the age of 7 days, the Ca(OH)_2 content in the cement pastes with RHA and ADR is lower than that of the control paste, though the cement content in the cement mortar with RHA and ADR at 10% replacement level is lower than that in the control. This is because of the pozzolanic reaction in the cement mortar with RHA and ADR (Qingge Feng et al, 2004)

According to Nuruddin et al, (2008), compressive strength development of MIRHA concretes were significantly higher compared to control concrete. The adequate amount of water and high pozzolanic reactivity were believed to be the main cause of this faster acceleration of MIRHA concrete. During this stage, MIRHA performed its function both as a pozzolanic material and filter (Nuruddin et al, 2008).

2.2 Cement

Cement in its general term, can be described as a material with adhesive and cohesive properties which make it capable of binding the material fragments into the compact whole. Basically, the raw materials used in the manufacture of Portland cement consist mainly of lime, silica, alumina and iron oxide. These compounds interact with one another in the kiln to form a series of more complex products and apart from a small residue of uncombined lime which has not had sufficient time to react, a state of chemical equilibrium is reached.

Neville (1997) described cement as a material with adhesive and cohesive properties that make it capable of bonding mineral fragments (stones, sand, bricks, building block) into a compact whole. The cement referred here is the hydraulic cement having the property of setting and hardening under water by virtue of a chemical reaction with it. The principal constituents of this cement are mainly of silicates and aluminates of lime. This hydraulic cement which is commonly known as 'Portland' cement is due to its resemblance of the colour and quality of the hardened cement to Portland stone, limestone quarried in Dorset,

United Kingdom. The various types and classifications of Portland cement and its properties are stipulated in accordance with ASTM C 150-2005 and BS EN 197-1:2000.

Many types of cements have been developed to ensure good durability of concrete under a variety of conditions. Table-2.1 shows a list of different types of Portland cement in the British classification together with the American classification (Neville, 1997)

Table-2.1. : Some Main Types of Portland Cement

British Classification		American Classification	
<i>Description</i>	<i>BS</i>	<i>Description</i>	<i>ASTM</i>
1.) Ordinary Portland	12:1978	Type I	C 150-84
2.) Rapid-hardening Portland	12:1978	Type III	C 150-84
3.) Low-heat Portland	1370:1979	Type IV	C 150-84
4.) Sulphate-Resisting Portland	4027:1980	Type V	C 150-84
5.) White Portland	12:1978	Type I P	C 150-84
	4627:1970		

2.2.1. Ordinary Portland Cement

In the new era of concrete industry, Ordinary Portland Cement (OPC) still remains as a major binder in hydration process to produce High Performance Concrete. It has been used as total binder in concrete mixes or as binder proportions in blended cements. The main compounds of OPC named as tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) (Handoo, Mahajan Kaila 2003).

C_3S comprises angular crystal content about 52% of OPC volume. It is responsible on initial setting and rapid strength gain especially to give an early strength (for example, 7 days). C_2S

is more rounded crystal content about 19% of OPC volume and it is responsible for long term strength. It will harden slowly, but contributes notably to strengthen at ages over a month (Ajiwe et al, 2000). While C_3A may be in rectangular or amorphous crystal forms, it is responsible for rapid setting and C_4AF , a non-crystalline composition, is responsible for grey colour with little contribution to setting or strength as placed surrounding the cement matrix content about 10% and 8% of OPC volume respectively (Taylor,G.D.

2002). The reaction of C_3A with water is very violent and leads to immediate stiffening of the paste, known as flash set. To prevent the flash setting phenomenon, gypsum will normally be added to cement clinker. The presence of C_3A with its rapid setting, high heat emission and sulphate susceptibility, is undesirable in concrete.

The actual proportions of the various compounds vary considerably from cement to cement, and indeed different types of cement are obtained by suitable proportioning of the raw materials. The major composition of OPC is lime, silica, alumina and iron oxide. With the presence of water these compounds interact with one another to produce hydrated product which is Calcium Silicate Hydrate (C-S-H) and Calcium Hydroxide ($Ca(OH)_2$).

The C-S-H takes the form of extremely small interlocking crystals which grow out slowly from cement grains to occupy previously water-filled spaces. The microcrystalline material is responsible for strength in the hardened concrete (Regourd, M.M 1992).

$Ca(OH)_2$ forms in a much larger crystal that acts as fillers in the hardened concrete but do not interlock to form strength. In the presence of moisture in the concrete matrix, $Ca(OH)_2$ will partly dissolve to form an alkaline solution that is useful to protect reinforcement in the reinforced concrete structure (Regourd, M.M 1992). The ratio of C-S-H to $Ca(OH)_2$ is approximately 7:2 by mass of concrete (Neville, 1997).

At any stage of hydration, the hardened paste consists of very poorly crystallized hydrates of the various compounds. It is referred to, collectively, as gel, crystals of $Ca(OH)_2$, with some

minor components, unhydrated cement and the residue of water-filled spaces in the fresh paste (Neville, 1997). As $Ca(OH)_2$ is crystallised in massive superimposed hexagonal plates, it has created a capillary pore in the cement paste matrix. The capillary pore has been generated either by $Ca(OH)_2$, air bubbles or micro crack that has become a factor, attributed to low engineering properties and performance of concrete (Regourd, M.M 1992).

The capillary pores represent a part of the gross volume which has not been filled by the products of hydration. Commonly, the hydration product of OPC occupy twice the volume of the original solid phase, therefore, the volume of capillary system is reduced with the progress of hydration (Neville, 1997). The hydration progress depends on water/cement ratio and on the degree of hydration. Water/cement ratios lower than 0.23 would have self-desiccation problems and a water/cement ratio higher than 0.36 used the capillary pores will occur since the volume of the gel is not sufficient to fill all the space available (Taylor,G.D. 2002).

An improvement has been obtained by several processes which reduce the porosity and the water/cement ratio. One of the process as introduced is blending OPC with pozzolanic materials named as pozzolanic cements or pozzolanic blended cement. The small particles of pozzolans will generate a large surface area for the precipitation of the hydration product, and make the cement paste become more homogeneous and dense as for the distribution of the finer pores. This is due to the pozzolanic reactions between the amorphous silica of the mineral addition and Ca(OH)_2 produced by cement hydration reactions.

Ordinary Portland Cement (Type I) is admirably suitable for use in general concrete construction when there is no exposure to sulphates in the soil or in ground water. The specification for this cement is given in BS 12:1978 (British Classification). In addition to the main compounds mentioned above, there exist minor compounds like manganese oxide, magnesium oxide, sodium oxide and potassium oxide. They usually amount to less than a few percent of the weight of cement. It should be pointed out that the terms 'minor

compound' refers primarily to their quantity and not necessarily to their importance.

2.2.2 Chemical Composition of Ordinary Portland Cement

The effect of Portland Cement on concrete strength depends on the chemical composition and fineness of the cement. There are four main types of compounds which are considered

as the major constituents of Portland Cement, and they are :

- Tricalcium silicate, $3\text{CaO}\cdot\text{SiO}_2$
- Dicalcium silicate, $2\text{CaO}\cdot\text{SiO}_2$
- Tricalcium aluminate, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$
- Tetracalcium alumineferrite, $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$

2.2.3 Hydration of Cement

This is a reaction by virtue of which Portland cement becomes a binding agent and takes place in the cement paste. In other words, the presence of water will cause the silicates and aluminates to form products of hydration which in turn produces a firm and hard mass as the hardened cement paste.

The hydration reaction for various silicates and aluminates are shown below:
(not to their exact stoichiometric equation)

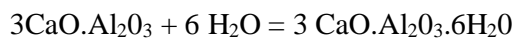
(i) For tricalcium silicates



(ii) For dicalcium silicates



(iii) For tricalcium aluminate



The hydration of tricalcium silicate and dicalcium silicate is primarily responsible for the strength of cement paste. Tricalcium silicate can be assumed to contribute most to the strength development during the first four weeks and dicalcium silicate influences the gain in strength after the next four weeks. Tricalcium aluminate contributes to the strength of cement paste at one to three days and possibly longer.

2.3 High Performance Concrete (HPC)

HPC has been widely used in construction industry nowadays. This is due to the increasing demand for more durable concrete to extend the service life and at the same time reduces maintenance cost of the concrete structure.

There have been many definitions of HPC. However, the definition has not been standardized. Nevertheless, there are several definitions of HPC proposed. ACI (2002), defines HPC as, concrete meeting special combinations of performance and uniformity requirements that cannot always be achieved routinely using manpowerl constituents and normal mixing, placing and curing practice. The ACI has also specified the compressive strength for design of 41 MPa or greater.

HPC has also been defined as concrete with water cementitious materials with ratio less than or equal to 0.35. The compressive strength characteristic is greater than 35 MPa or equal after 24 hours and after 28 days the compressive strength should be greater or equal to 70 MPa. HPC has also been defined based on special requirements and properties such as, ease to placement and compaction without segregation, enhanced long-term mechanical properties, high early-age strength, high toughness, volume stability and long life in severe environments (Hashem et al, 2002).

To achieve an ideal HPC, EG Nawy (2000) has stated five principal parameters namely i) high performance, ii) economy, iii) resistance to wear and deterioration, iv) resistance to weathering and chemicals and v) appropriate cement type. Among all parameters stated above, appropriate cement type has become the main parameter that can influence the performance of other parameters. Unappropriate type of cement used in producing a HPC might cause disintegration of the concrete in the structure.

Mailer.Y (1992) introduced two approaches in order to obtain HPC which reduces the flocculation of cement grains and widens the range of grain size.

The advantages of using cement additives in concrete are, mainly, they improve concrete properties in fresh and hardened states, and economically and ecologically beneficial. The achievement of these advantages becomes more important for HPC proportioning. However, the selection of additives needs more attention due to their different properties.

2.3.1 Cement for HPC

In achieving HPC, choosing an appropriate type of cement is important. The type of cement used depends on the type of structures, the weather and other conditions under which the structure is built and that it will exist during its life span (EG Nawy (2000).

Concrete which is exposed to the seawater sprays required a sulphate resisting cement type (Maher, A.Bader 2003). For construction that needs concrete to be quickly hardened, rapid hardening Portland cement will be essential (Taylor,G.D. 2002). EG Nawy (2000) also stated that concrete structure which is bulkier and heavier in cross-section needs less heat of hydration cement to prevent shrinkage problems and surface crack. Blended pozzolanic cement was found to be necessary in use especially to reduce temperature that rises during hydration process. At the same time, it improves the durability and engineering properties of concrete (Sabir et al, 2001).

The chemical compositions of cement have an influence to its properties and performances, but it also depends on its type and usage. The percentage variation in the chemical composition of each type gives concise reasons for the difference in reaction when in contact with water.

The size of the cement particles was also found to give an effect on the rate of reaction of cement with water (Aitcin, 2003). Larnard (1992) said that ultra fine particles of cements will react in two levels which are physical level and chemical level. In physical level the cement will react as filler between a void in hydrated cement matrix at early age. In the chemical level the cement will accelerate the hydration process. For blended cement

containing pozzolanic materials, the finer particle produces better pozzolanic reaction, but it is still depending on the quality of pozzolanic materials used. Mazloom et al, (2004) also stated that in obtaining HPC, the water/binder ratio must be reduced and binder content must be increased.

2.4 Cement Replacement

The materials for making concrete consist of cementitious binder, aggregates, water and in most cases with ready mixed concrete, one or more types in chemical admixtures. Today, the cementitious binder such as Ordinary Portland Cement or Sulphate Resisting Portland Cement is often blended with ground granulated blastfurnace slag. In general, pulverized fuel up to 30% and ground granulated blastfurnace slag up to 70% with the balance that made up of are used depending on the intended applications.

Within the past decade, silica fume has been introduced, in addition, to the other mineral admixtures to improve the performance of concrete. These mineral admixtures are chemicals that provide cementitious gel similar to those produced by the hydration of Ordinary Portland Cement. Hence they are often called supplementary cementing materials (Neville, 1997).

In recent years, the use of pozzolanic materials and slag as replacement for cement in concrete has become more and more widespread throughout the world. Particularly, in countries where such materials are produced as by-products of the industry, such usage has the added value of providing a partial solution to the problem of disposal of such materials. In the following sections, discussion on these supplementary cementing materials will be confined to, silica fume and ground granulated blastfurnace slag. They are used together with ordinary Portland cement which provides the calcium hydroxide needed for the pozzolanic reaction (Neville, 1997) .

2.5 Pozzolanic Materials

Pozzolan is a material which, when combined with calcium hydroxide, exhibits cementitious properties. Pozzolans are commonly used as an addition or as mineral replacement to Portland cement concrete mixtures to increase the long-term strength and other material properties of Portland cement concrete. Pozzolans are primarily vitreous siliceous materials which react with calcium hydroxide to form calcium silicates; other cementitious materials may also be formed depending on the constituents of the pozzolan (Agarwal, 2006).

The specific definition of pozzolan was made by ASTM C618-98 and accepted by all scientists and researchers is a "siliceous or siliceous and aluminous materials, which in itself possesses little or no cementitious property, but which is finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementing properties". Pozzolan has also been defined as any materials, regardless of its geologic origin, that possesses hydraulic properties (Ali Akhbar, 1987). Neville (1997) described pozzolans as a natural or artificial material containing amorphous silica in a reactive form. The silica can combine with calcium hydroxide of OPC in the presence of water to form stable calcium silicates which have cementitious properties.

The first known pozzolan was pozzolana, a volcanic ash, for which the category of materials was named. The most commonly-used pozzolan today is fly ash (FA), though silica fume (SF), high reactivity metakaolin (MK), ground granulated blast furnace slag (GGBS), rice husk ash (RHA) and other materials which are also used as pozzolans. In this study, it will only cover pozzolans named as silica fume (SF), fly ash (FA), metakaolin (MK) and rice husk ash (RHA). All of the pozzolans discussed was a pozzolan which is available in Malaysia. SF was already commercialised and widely used in cement and concrete industries. Other pozzolans are abundant in the country and their usages are still very few in the industries.

2.5.1 Classification of Pozzolan

ASTM C618-98 classified pozzolans into Class N, Class F and Class C. Class N is referred to as natural pozzolan such as diatomaceous earth, opaline cherts, shales, turffs, volcanic ashes and clays. The pozzolan can be calcined or not depending on its properties and compositions. Class F pozzolan is referred to as FA produced from burning bituminous coal and Class C pozzolan is an FA that is produced from subbituminous coal. Class C pozzolans contain pozzolanic properties and have some cementitious properties. In Canada, the FA is classified due to the lime content composition. FA with lime content 8%-20% will be classified as CI and classified as C when the lime content is higher than 20%.

European standard ENV 197-1:1992 recognizes two subclasses of pozzolanic cements named as Portland fly ash cement Class II/A-V and Class II/B-V. Class II/A-V contains 6 to 20% of fly ash and Class II/B- V contains 21 to 35% of fly ash.

Pozzolanic materials are also classified as natural pozzolans and artificial pozzolans. Natural pozzolans are divided into pyroclastic rocks such as zeolited materials and clastic rocks such as calcine clay. FA, SF, burnt agro residue and calcined shales are grouped under artificial pozzolans (Cook D.J, 1986).

Ali Akhbar (1987) stated in his literature on Massazza (1974) paper that the pozzolans are divided into three groups. The first group includes pyroclastic rock which is material of volcanic origin. The second group comprises altered materials with high silica content and the third group includes materials of clastic origin including clays and diatomaceous earths. Artificial pozzolans such as FA, SF and MK are included in group three pozzolans in Massazza's classifications and RHA are included in group two due to the alteration process of rice husk into ash.

Malhotra et al, (2004) classified pozzolanic materials under mineral admixtures that refer to mineral materials other than aggregates and cement that added immediately before or during concrete mixing or during manufactured of cement The mineral must have a

siliceous or siliceous and aluminous materials that may possess little or no cementitious property.

2.5.2 Standard Specification of Pozzolan

There are many standard specifications of pozzolanic materials and pozzolanic cement that have been prepared all around the world. However, for this study, only British Standard [BS6588:1991 and BS6610:1991] and American Standard [ASTM C618-98] specifications will be focused

2.5.2.1 British Standard

BS6610:1991 is a British standard specification for Pozzolanic cement. The BS has defined the pozzolanic cement as blended hydraulic binder comprising homogeneous mixture of ordinary Portland cement and pozzolana in specific proportions. The pozzolanic materials are referred as pulverized FA where the proportions of FA are not more than 50% or less than 3 5% by mass of the total quantity.

To indicate that the pozzolanic cement complies with the standard specifications requirement, 5 tests on samples of the cement named as proportion of FA by mass to the nearest 5%, the fineness, the compressive strength at 7 days and 28 days, the initial and final setting times and the soundness test are to be carried out. The requirements of standard specifications on all 5 tests are stated in Table 2.2. X is referred to as sample of pozzolanic cement test.

BS 6588:1991 is a specification standard for Portland pulverized-fuel ash cement. Portland cement and the pulverized-fuel ash have been thoroughly and intimately mixed together in a dry state to form a uniform mixture before or after grinding. The specification requirements of the cement are stated in table 2.3.

Table 2.2: BS6610: 1991 Standard Specifications Requirement of Pozzolanic Cement

Type of testing	BS6610 requirements
Proportion of FA	$35\% < x < 50\%$
Fineness	$x > 225 \text{ m}^2/\text{kg}$
Compressive Strength	At 7 days: $x > 8 \text{ N/mm}^2$ At 28 days: $x > 16 \text{ N/mm}^2$
Setting Time	Initial: $x > 45 \text{ minute}$ Final: $x < 10 \text{ hour}$
Soundness	$x < 10\text{mm}$

Table 2.3: BS6588: 1991 Standard Specifications Requirement of Portland Pulverized-fuel Ash Cement.

Type of testing	BS6610 requirements
Proportion of FA	$15\% < x < 35\%$
Fineness	$x > 225 \text{ m}^2/\text{kg}$
Compressive Strength	At 3 days: $x > 8 \text{ N/mm}^2$ At 28 days: $x > 22 \text{ N/mm}^2$
Setting Time	Initial: $x > 45 \text{ minute}$ Final: $x < 10 \text{ hour}$
Soundness	$x < 10\text{mm}$

2.5.2.2 American Standard

American Society for Testing Materials (ASTM) C615-98 is a standard specification for coal FA and raw or calcined natural Pozzolan for used as a mineral admixture in concrete where cementitious or pozzolanic action is desired. The standard requirements have been divided into two groups of requirements that are chemical requirements and physical requirements.

The standard has divided the pozzolans into 3 classes, namely Class N, Class F and Class C. The requirements of the standard for all pozzolans classes are shown in Table 2.4 and Table 2.5. All samples and test of the mineral admixture are as in accordance with the requirements of test methods ASTM C311. Although ASTM C618-98 has stated that the loss of ignition (LOI) is less than 6%, a footnote actually allows up to 12%.

ASTM C1240-04 is a standard specification for silica fume used in concrete and other systems containing hydraulic cement. Requirements stated for SF in this standard is also based on chemical requirements and physical requirements. Chemical requirements for SF are based on minimum content of SiO₂ which is 85%. The moisture content and LOI of SF has been fixed to be not more than 3% and 6% respectively.

The physical requirements of SF are based on three types of physical requirements namely maximum size of SF allowed, pozzolanic strength activity index and minimum specific area of SF used. The maximum size of SF is identified through sieve analysis by determining the percent of SF retained on 45µm sieve. It was fixed to be not more than 10%.

Pozzolanic strength activity index is determined by comparing the compressive strength of concrete containing SF with OPC concrete at 7 days. The compressive strength of SF concrete must be higher than OPC concrete at minimum 5%. Minimum specific surface area of SF is fixed to be 15m²/g using BET, nitrogen absorption method.

Table 2.4: Chemical Requirements of Pozzolanic Materials (modified from ASTM C618)

Class of Pozzolanic Materials	N	F	C
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ , min,%	70	70	50
SO ₃ , max,%	4	5	5
Moisture Content, max,%	3	3	30
Loss on ignition, max, %	10	6	6
Na ₂ O, max, %	1.5	1.5	1.5

Table 2.5: Physical Requirement of Pozzolanic Materials (modified from ASTM C618)

Class of Pozzolanic Materials	N	F	C
Fineness, amount retained on 45 µm wet sieve (%)	34	34	34
Minimum strength activity index at 7 days compared with OPC, percent of control	75	75	75
Minimum strength activity index at 28 days compared with OPC, percent of control	75	75	75
Water requirement, max, percentage of control	115	115	105
Soundness, Autoclave expansion, max, %	0.8	0.8	0.8
Density, max variation from average,%	5	5	5
Percentage retained on 45µm, max, %	5	5	5

2.6 Pozzolanic Cement

When the minerals blended with lime or with Portland cement, they are called pozzolanic cement or blended cement. The pozzolanic cement comprises a mixture of OPC with any pozzolanic materials. These materials are to be thoroughly mixed together in dry or wet state to form a uniform mixture in any proportions. BS6610: 1985 has defined pozzolanic cement as a blended hydraulic binder comprising a homogenous mixture of Ordinary Portland Cement and pozzolan in specified proportions. The composition of pozzolan in the pozzolanic cement has been proposed to be the maxima of 50%. Pozzolanic cement strength has been reported to be as low 7 and 28 days strength compared to OPC. The minimum strength on 7days is stated as not less than 8 N/rnm² and at 28 days the strength is fixed to be not less than 16N/mm² as a specification requirement of pozzolanic cement stated in BS 6610: 1985. ASTM C618-98 has allowed the strength of pozzolanic cement to be not less than 25% compared to OPC strength at 7 and 28 days as the standard specifications of pozzolanic cement to be used in the industry.

The effect of pozzolanic materials in concrete is generally divided into three effects. They are the effects of providing a bigger surface area for hydration process, the filler effect and the pozzolanic reaction effect. These three effects have been performed either during concrete at fresh stage or at the hardened stage. The effects are also reported to give effects on the engineering properties and durability properties of concrete.

During fresh stages, the use of pozzolanic materials is generally reported to reduce the workability and the bleeding of concrete due to the increments of cohesiveness value of concrete as a result of bigger surface area of the pozzolanic materials compared to OPC. The fineness of particle of the pozzolanic materials has also led to the filler effect between the transition zones in the concrete matrix. It has also provided a bigger surface area for hydration process and reduced the porosity volume that has been responsible for the early age strength of the concrete.

The pozzolanic reaction may be slower than the rest of the reactions which occur during cement hydration, and thus the short-term strength of concrete made with pozzolans may not be as high as concrete made with purely cementitious materials. However, it depends on the compositions and properties of the pozzolans. On the other hand, highly reactive pozzolans, such as silica fume and high reactivity metakaolin can produce "high early strength" concrete that increase the rate at which concrete gains strength (Sabir et al, 2001).

2.6.1 Engineering Performance

The effect of pozzolans on engineering properties of HPC containing pozzolans is referred to effects of pozzolans studied on properties of fresh concrete and hardened concrete. The properties of fresh concrete were focused on the effect on water demand, workability, bleeding and setting time. Hardened concrete properties are referred to as compressive strength, Yong's modulus of elasticity, porosity and expansion or shrinkages.

2.7 Silica Fume (SF)

SF is a by-product of the manufacturing process of silicon or various silicon alloys and silicon metal. ASTM C1240-04 has defined SF as a very fine pozzolanic material, composed mostly of amorphous silica produced by electrical arc furnace as a byproduct of the production of elemental silicon or ferro-silicon alloys. It is also known as condensed silica fume and microsilica.

The chemical composition and properties of SF depend on the composition of the principal product being made by the furnace and furnace design Malhotra et al, (2004). Usually, SF contains more than 80% to 85% of silica in non-crystalline form and has a spherical shape with average particles size of 0.1- 0.5 μm and nitrogen BET surface of 20,000 m^2/kg (Yajun et al, 2003).

The use of SF as mineral admixture or as replacement materials in concrete industry has been increasingly used in many mega projects all around the world. Many researchers reported the SF is highly reactive pozzolan that has improved the concrete properties. The effectiveness of using SF in increasing the engineering properties and concrete durability makes the SF selective materials especially to be used in obtaining high performance concrete.

SF is dry, densified and used as mineral admixture formulated to produce concrete with special performance qualities. It has been found to improve the properties of hardened concrete. These improvements are in two ways. Firstly it acts as filler between cement particles and secondly, it acts as pozzolanic materials which react chemically within the concrete to increase the amount of calcium silicate hydrate gel formed, thus improving the strength and reducing the permeability of the concrete.

Although SF could impart significant contributions to the strength and chemical resistance of concrete, it is also reported leading to increases in water demand, placing difficulties and plastic shrinkage problems in concrete (Thomas et al., 1999). Due to the high demand

for this material in the concrete industry, SF has become significantly expensive. The increase of construction costs due to the increasing price of imported silica fume compared to other admixtures that has led researchers to turn their interest toward other supplementary cementitious materials and technique to produce similar strengthening effects as silica fume.

2.7.1 Chemical Composition of SF

SF is a byproduct of the manufacturing process of silicon or various silicon alloys, having a high content of SiO_2 in amorphous form. Chemical composition of SF depends on the composition of the principal product being made by the furnace and furnace design (Mehta, 1986). A furnace which is equipped with a heat recovery system produces SF with lower value of ignition loss (LOI) or carbon content. The LOI of SF is on the range of 2.41 % to 2.75%.

Even though Table 2.5 stated that the SiO_2 content of SF is 85.49%, it may contain more than 80% of SiO_2 . The amount of SiO_2 in SF was reported to vary depending on silicon content in the alloy production. The higher the silicon content in the alloy used, the higher the silica content in the resulting silica fume (Neville, 1997). The other compositions contained in SF such as Al_2O_3 , Fe_2O_3 , CaO and alkali contents are low. Even though there is MgO content in a compound of SF, it was reported not to be deleterious to concrete.

The chemical composition of SF was not affected by time. The constancy in chemical composition is due to the relatively pure raw materials used in a production of silicon metal or ferrosilicon alloys (Mehta, 1989).

2.7.2 Physical Characteristic of SF

The particle size of SF was reported to be from 0.1 to 0.5 μm and the nitrogen BET surface is 20,000 m^2/kg (Yajun et al., 2003).

SF has a low bulk density around 2.0 to 3.0 kg/m³. The low bulk density of SF may cause difficulty in transporting and handling. In order to improve the handling and transport properties, SF was processed to increase its bulk density by densified, sluried or alletized process.

Although SF could impart significant contributions to strength and chemical resistance of concrete, it could also lead to increase in water demand, placing difficulties and plastic shrinkage problems in concrete (Thomas et al., 1999). The agglomeration particle of SF in cement paste or mortar was also reported to decrease the chemical reaction of SF during hydration process. This agglomeration of SF can reduced its effectiveness through having a larger particle diameter, a smaller surface area (SSA) and a lower pozzolanic reactivity than the unitary grains (Boddy et al, 2000).

2.7.3 Effects of SF on Fresh Concrete

The utilization of SF reported to give a significant effect to the properties of fresh concrete. The high specific surface area of SF that is bigger than OPC particles becomes the main factor of the effect. The large specific area of SF increased their capacity to absorb water that result more water being used in the mixture to maintain the workability of concrete. Malhotra et al, (2004) reported that the utilization of SF in concrete mixes would give a net effect of increased water requirement compared to OPC concrete with a same level of consistency.

Mazloom et al (2004) in their study also indicate that as the proportion of silica fume increased, the workability of concrete decreased (Megat Johari et al, 2002). They report that the effect of replacing part of cement with 5% to 10% SF is to improve the workability but as a replacement level of SF increase the workability is reduced.

The water absorption effects due to large specific surface area of SF will also control the mixes with SF to have bleeding problems. This is due to small particles of SF that will fill in the voids between the large particles of cement and absorb the entrapped water during

hardening of concrete. In the concrete mix with high cementations content and low water/binder ratio, the cohesiveness of the paste increased due to the reduction of internal bleeding in the mixture (Edward, 2001). The high cohesiveness of concrete containing SF may result the concrete to having very little bleeding or even none.

The effect of using SF to the setting time of cement paste or concrete depended on level of replacement and water/binder ratio Ali et al (2007) in his investigation reported that the addition of 5 to 10% of SF had no significant effected on setting time but in a concrete with water/cement ratio of 04 and 15% replacement level of SF the setting time was delayed. The retardation effect (initial and final setting time) will increase with higher replacement of SF to OPC and the retardation effect of SF to cement paste or concrete is due to the decreased in cement content which is responsible for early stiffening of the paste (Alshamsi et al, 1997).

The investigation of De Almeida and Goncalves (1990), as reported by Megat Azmi (2000), showed that there is no significant difference in setting times of concrete when SF introduced to non-superplasticised concrete, but for a concrete with low water/binder ratio containing superplasticize, the effect of SF was to reduce the setting time of concrete compare to control concrete with superplastized. The reduction of setting time in SF concrete is due to an interaction between SF and the superplasticized used.

2.7.4 Effects of SF on Hardened Concrete

The effect of SF on the properties of harden concrete was established by many researcher. SF was recognized as materials that can contributed significantly to the compressive strength development of concrete. The effective pozzolanic reactions and the filler effect between the transition zones were known as a reason to a better compressive strength performance. The main contribution of SF to compressive strength development at normal temperatures takes places between ages of about 3 and 28 days. The overall strength development of SF concrete are varying according to concrete proportions, composition and curing conditions Malhotra et al, (2004).

The compressive strength development of SF concrete was reported to be high during 3 to 28 days of curing period. However from 28 to 90 days the relative strength of the concrete is relatively low (Mehta, 1986). Mazloom et al., (2004) also indicated that the compressive strength of concrete mixtures containing silica fume did not increase after the age of 90 days.

The effect of SF as cement replacement materials to compressive strength of concrete reported to improve the short-term mechanical properties such as 28-day compressive strength. This effect is achieved through the combination effect of chemical and physical effects provided by SF. The chemical effect of SF that is referred to the pozzolanic reaction during cement hydration process will change the calcium hydroxide to calcium silicate hydrate faster than OPC because of high surface area and high content of amorphous silica (Peter, 1998). The fine particles of SF played a role to fill in voids contents in the concrete matrix has also been reported as a factor of a better compressive strength of the SF concrete (Roszilah et al., 2002).

The addition of silica fume to HPC seems to reduce the rate of increase of the modulus of elasticity with age. The reason for this is due to the high rate of hydration of concrete containing silica fume. At an early age, silica fume concrete has higher strength gained but gradually decreases to ordinary concrete. Hence, the elastic modulus at an early age is higher, with a gradual decrease over time. Hani et al., (2005) have their investigation results show that adding silica fume resulted in an increase in strength and modulus at early age. However, there has been no change in the modulus at 28 and 56 days.

The reduced of bleeding in SF concrete can lead to plastic shrinkage cracking under drying condition. Results indicated that the plastic and drying shrinkage of concrete with silica fume cement concrete specimens were more than those in the plain cement concrete specimens (Neville, 1997). Therefore, proper curing technique was proposed to prevent the problem from occurring when SF is used. The shrinkage strains in SF cement concrete specimens cured by continuous water-pending were reported to be less than that in similar concrete specimens cured by covering them with wet burlap (Al- Amoudi et al., 2007).

The percentages of SF replacement did not give a significant influence on total shrinkage; however, the autogenous shrinkage of concrete increased as the amount of SF increased. The results have also indicated that the increase of the proportion of SF lowers the amount of expansion. (Mazloom et al., 2004)

2.8 Fly Ash (FA)

FA is a finely divided residue that is a by-product of the combustion of ground or powdered coal exhaust fumes of coal-fired power stations. In certain places, FA is also known as

pulverized fuel ash (PFA) and it was found to possess pozzolanic properties due to contents of SiO_2 and Al_2O_3 (Xinghua et al., 2002). This material represents a substantial reserve of pozzolanic materials if it can be fully recovered. It is generally finer than cement and consists mainly of glassy-spherical particles.

2.8.1 Chemical Composition of FA

Combustion of ground or powdered coal will produce a residue named fly ash (FA). The chemical composition of FA may vary from one batch to another. This, however depends on the minerals associated with the coal and the burning condition during the combustion of FA. In general, FA contains SiO_2 , Al_2O_3 and Fe_2O_3 and the amount of these three compositions has been stated as the main requirement of ASTM C 618-94 in determining the classification of FA. Ravindra, (1986) stated that the classification of FA through the amount of SiO_2 , Al_2O_3 and Fe_2O_3 is confusing, since it was found that many class C FA meet class F requirements. It is also found that FA relatively contains more alumina and less silica as compared to other pozzolans (McCarthy et al., 2005).

CaO is also contained in FA but its composition depends on the type of coal used. The composition of CaO was found to be low, as less than 10% in bituminous coal and more than 10% in sub bituminous coal (Neville, 1997). The CaO composition will establish either the FA having a cementitious property or not. FA with high level of CaO will have cementitious properties as an additional to pozzolanic properties while FA with low level of CaO only has a pozzolanic properties (Ravindra, 1986). The amount composition of CaO is also used to identify the classifications of FA. FA with low CaO has been classified as class F and high CaO content classified as Class C.

Other than the four composition discussed before others, composition such as MgO, Fe₂O₃ alkalis and carbon have been also determined. The carbon content is assumed to be equal to the LOI. Even the amount of MgO of FA is the highest amount the pozzolans but the MgO is not harmful because it exists in a non-reactive form (Neville, 1997).

2.8.3 Physical Properties of FA

FA consists of glassy spherical particles with some crystalline matter and carbon in the form of un-burnt coal which varies from plant to plant (Ali Akhbar, 1987). The particle diameter of FA is between less than 1 μm and 1000 μm with an average size of 20 μm, and the specific surface measure of FA is usually between 250 and 600 m²/kg and the overall value of specific gravity is 2.35 (Neville, 1997).

Mineralogy analysis of FA typically contains about 50%-90% of glass. The reactivity of glass in FA depends on the chemical composition especially the CaO content. The typical crystalline minerals of low calcium FA are quartz, mullite, sillimanite, hematite and magnetite. These minerals do not possess any pozzolanic activity. High calcium FA contains minerals that may react with water which is tricalcium aluminate, calcium aluminosulfate, anhydrite, free CaO, and alkali sulfates. High calcium FA also contains quartz and periclase but these two minerals do not give any effects to the reactions (Malhotra et al, 2004).

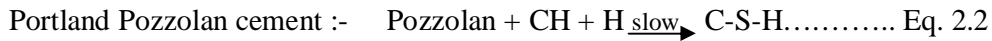
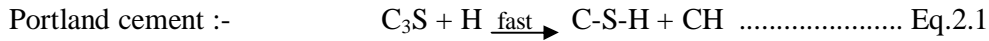
2.9 Rice Husk Ash as Pozzolanic Material

Rice husk ash is a general term used to describe the type of ash produced from burning rice husk. Rice husks are the shells produced during the de-husking operation of paddy rice, which is the by-product of rice paddy milling industries. Studies conducted by Ankra (1976) at the University of California, Berkeley as reported by Ismail and Waliuddin (1996), have indicated that the silica of soil migrates in the plant in the shape of monosilicic acid by evaporation, and under electron microscope studies, it showed the dispersion of silica throughout the cellular structure of the husk. Study by Hwang and Chandra (1997) shows that the un-burnt rice husks contain about 50% cellulose ($C_5H_{10}O_5$), 25-30% lignin ($C_7H_{10}O_3$) and 15-20% of silica (SiO_2). Burning Of rice husk will remove the cellulose and lignin, thus leaving behind silica ash.

Pozzolanic materials primarily consist of SiO_2 , Al_2O_3 and Fe_2O_3 , the total of these specified to be a minimum of 70% for mineral admixture Class F or N and 50% for mineral admixture Class C for use in concrete (ASTM 618, 2003). When these are mixed with Portland cement and water, the oxides which are in an amorphous structure will react chemically at ordinary temperature with the calcium hydroxide (produced by the hydration of calcium compounds in Portland cement) to form calcium silicate hydrate (C-S-H) compound, thus possessing cementing properties. The reaction is secondary to the hydration of the clinker compounds and occurs at a slower rate than the main chemical reaction. Therefore, it is expected that as the cement replacement increases, the initial strength of the cement - pozzolana material decreases, but at later ages it will increase more rapidly than Portland cement as cementitious material has replaced the calcium hydroxide (Cook et al., 1976).

ACI Committee 232 (2002) defines pozzolan as "a siliceous or siliceous and aluminous material, which itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties."

With respect to the main C-S-H forming reaction, a comparison between Portland cement and Portland pozzolan cement blended can be made and given as follows as described by Mehta and Monteiro (1993) :-



Where, the symbols used are. C = CaO H = H₂O S=SiO₂

James and Subba (1986) quoted that the above reactions sequence will explain the setting process that leads to either development of strength or its enhancement. They also stated that the long terms decrease in strength of RHA-cement might be due to changes in morphology or crystalline of C-S-H and unreacted silica.

RHA is a general term describing all types of ash produced from burning rice husk which is a waste product of rice industry. It has been reported to have very high silica content as high as that of silica fume after burning process at certain temperature (Kartini et al., 2005). The silica ash produced varies from gray to black depending on the inorganic impurities and unburned carbon amounts (Della et al., 2002). The silica in the ash undergoes structural transformations depending on the temperature regime it undergoes during combustion. At 550°C - 800°C, amorphous silica is formed and at greater temperatures, crystalline silica is formed, the type of RHA suitable for pozzolanic activity is amorphous rather than crystalline (Metha, 1994). The specific surface area of RHA can be as high as 50 000m²/kg, even though the particle size is larger which is 10 to 75 μm. This may be due to the particle complex shapes of RHA as reflecting their original plant origins (Neville, 1997).

RHA has many applications due to the variation in its properties. It is an active pozzolan and has several applications in cement and concrete industry. It is also highly absorbent,

and it is used to absorb oil on hard surfaces and potentially to filter arsenic from water (Metha., 1994). It has been reported to be produced in Malaysia as almost 526,000 tonnes per year of rice husk from 2.813 million tonnes of Malaysian paddy industry, and this may contribute to a total of 102,000 tonnes of RHA per year (Kartini et al., 2005).

The utilization of RHA as cement replacement materials has been accepted as an alternative to transform rice industrial residue into useful raw materials and at the same time avoiding damage to the environment.

2.9.1 Production of Rice Husk Ash

2.9.1.1 Burning Temperature

The objective of burning rice husk is to remove by controlled oxidation the cellulose and lignin present, while maintaining and preserving the original cellular structure of the rice husk (Mehta, 1992). It has been established that the silica in the ash undergoes structural transformation under varied temperature conditions, thus influencing both the pozzolanic activity of the ash and its grinding ability.

When rice husks were first heated, weight loss due to evaporation of absorbed water occurs at temperature up to 100°C and at 350°C. Further weight loss has occurred and the husks then commence to burn. From 400°C to 500°C, the residual carbon oxidizes and the silica in the ash is still in an amorphous form. Majority of weight loss occurred at this period. As the temperature increased, the conversion to other crystalline forms of silica progresses and further prolonged in incinerator at temperatures beyond 800°C produces crystalline silica that is normally whitish in colour. It was suggested that the best burning temperature for keeping the silica in amorphous state which is grey in colour and highly cellular form was at 500°C to 600°C (Cook, 1986).

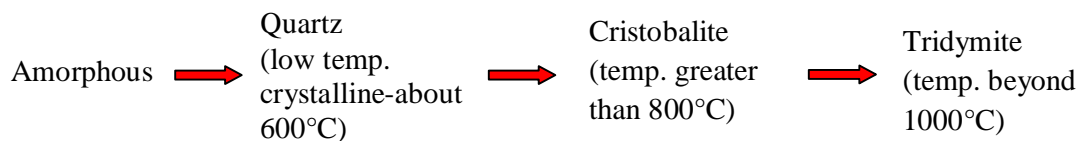
Mazlum and Uyan (1992) reported that burning the husk at 400°C and 500°C for one and half (1½) hour produced amorphous silica. Cook et al. (1976) reported that the combustion

of rice husks at 450°C for four hours produces a material that conforms to the ASTM C618-2003 Class N pozzolan.

Mehta (1992) and Hwang and Wu (1989) stated that in order to produce an ash of high pozzolanic activity, the burning temperature must be such that the silica should be in a non-crystalline state and in a highly micro-porous structure. They also concluded that the best contribution of RHA on strength of concrete was obtained when the RHA was in amorphous

form obtained by low burning of rice husks and with the holding time less than one (<1) minute. Feasibility study conducted by Rego et al. (2004) on composing Portland cement with the incorporation of amorphous and crystalline RHA revealed that amorphous RHA yielded significant increased in compressive strength as compared to crystalline RHA.

Patel (1988) reported that the temperature of carbonization is preferably below 700°C to avoid any transformation of amorphous to crystalline form. Cook et al. (1976, 1986), Chopra et al. (1981) and Ibrahim and Helmy (1981) stated that when there has been over burning of RHA, the transformation of crystallization scheme of the amorphous silica (SiO₂) will change into cristobalite, quartz and tridymite as shown below:-



However, when it is burnt at low temperatures much un-burnt carbon will remain and normally the ash is blackish in colour. The influence of carbon content as investigated by Cook and Sumanvitaya (1981) up to 20% by weight of the ash did not significantly influence the strength development and beyond 30% the strength decreased.

Boateng and Skeete (1990) reported that the incineration of rice husks obtained from Guyana at temperature ranges of 550°C to 700°C generally produced amorphous silica, while a temperature in excess of 900°C produced unwanted crystalline form and for a temperature of about 800°C maintained for 12 hours gave a small proportion of crystalline silica.

Above all, the quality of RHA depends on the method of ash incineration, the degree of grinding and on the preservation of cellular structure and the extent of amorphous materials within the structure. Figure 2.1 shows the diffusion process for obtaining a reactive cellular rice husk based on the data obtained from Ankra (1976), Mehta and Pitt (1976) and Hwang and Chandra (1997).

From the figure, it shows that the optimum incineration condition is important to obtain reactive RHA with microporous and cellular structure. In order to produce an ash with high pozzolanic activity, the silica should be held in a non-crystalline state and in a highly microporous structure, as only the active amorphous silica contributes to the development of cementitious properties. Therefore, many researchers (Hwang and Chandra, 1997; Mazlum and Uyan, 1992; Mehta, 1992; Sugita et al., 1992; Hwang and Wu, 1989; Patel, 1988; Chopra et al., 1981) have put their effort to produce amorphous silica by controlling the burning temperature.

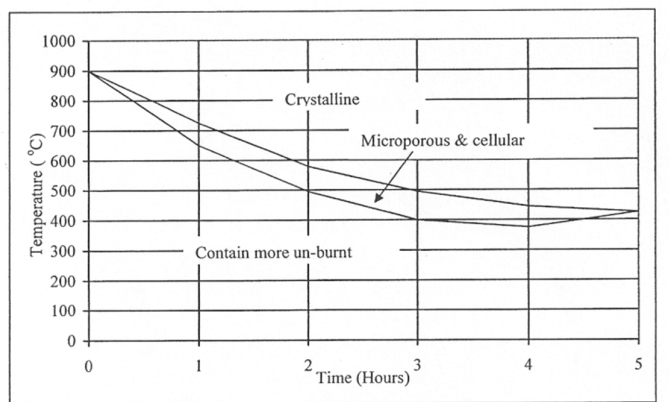


Figure 2.1: The optimum incineration condition curve for obtaining reactive cellular RHA
Adapted from Ankra (1976), Mehta and Pitt (1976) and Hwang and Chandra (1997)

2.9.2 Physical Properties of Rice Husk Ash

The physical properties of ash need to be determined, as it is an early indication of the quality of ash to be used in the concrete. The physical properties commonly determined for the ash are fineness, setting time and soundness. The physical requirements for pozzolans can be obtained from ASTM C618-2003 and BS 3892: Part 1: 1997.

The physical properties of RHA are influenced by the condition of pyroprocessing. Cook (1986) quoted that the compacted unit mass of the RHA ranges from 200 to 400 kg/m³ and the bulk density ranges from 2000 to 2300 kg/m³. It is also known that the specific gravity of RHA is much less than that of OPC; therefore weight-to-weight replacement would therefore cause an increase in the volume of cementitious material. This would require additional water for lubrication that would tend to lower the strength.

The physical characteristic of RHA can be altered depending on the production of RHA technique. RHA has complex particle shapes in amorphous stage with a porous structure that reflects its plants origins (Neville, 1997). In order to obtain a high specific surface area the milling process was proposed (Della et al., 2002).

Generally, the particle mean size of RHA is around 33µm, but after the milling process, the particle mean size of RHA may decrease to 0.681µm-1µm. The high surface area of RHA prepares a bigger surface area for chemical reaction, during the hydration process of cement. The bigger surface area may also give effects on increasing the water requirement and water absorption of the cement paste (Singh et al., 2002).

2.9.2.1 Fineness

RHA of essentially pure silica in non-crystalline form are highly cellular (with fineness about 600000 cm²/g using nitrogen absorption method) and are very fine particle with higher specific surface as compared to the OPC (about 3020-3350 cm²/g).

The influence of fineness as reported by Shimizu and Jorillo (1990) and Chopra et al. (1981) on the compressive strength showed that the increase in fineness resulted in the increase of compressive strength. The relationship between specific surface, w/c ratio and compressive strength based on Chopra et al. report is shown in Table 2.6. The findings agreed with Lao et al. (1984) that stated that the strength of RHA concrete is higher than the control mix with the same w/c ratio if the fineness of RHA is higher than 85% passing No. 325 sieve. They further concluded that because of higher water requirements in making RHA concrete, therefore, its strength is lower than the normal mix with similar workability.

However, Mehta (1992) stated that the RHA particles should not be very fine in order to develop pozzolanic activities in the presence of Portland cement. The reason was the source of high surface area in RHA is in the microporous structure of individual particles and with RHA particles in the range 10-75 μm , it exhibits satisfactory pozzolanic reaction.

Cook (1986) reported that the reactivity of the ash is related to its surface area and the amount of amorphous silica. Ash reactivity has to be balanced against the water demands, as the high specific surface area of RHA will significantly increase the amount of water required to produce a workable concrete.

Al-Khalaf and Yousif (1984) described the effect of burning and grinding parameters on the properties of RHA concrete, in which rice husks when burnt at temperature ranged between 450⁰C to 850⁰C for periods ranging from 0.5 to 5 hours will produce Blaine surface area of 5000 - 21000 cm^2/g .

Table 2.6: Relationship between Specific Surface, Water/Binder Ratio and Compressive Strength of OPC - RHA Blended Cement

Mixture designation	Specific surface (cm^2/g)	$\frac{w}{c + \text{RHA}}$	Compressive Strength (N/mm^2)		
			3 days	7 days	28 days
Control	3780	0.42	24.7	30.7	43.9
LA - 1	5500	0.43	17.8	26.7	42.6
LA - 2	7000	0.45	25.5	37.9	51.7
LA - 3	8500	0.47	27.5	48.1	59.6

Adapted from Chopra et al. (1981)

2.9.2.2 Setting Time

Neville (1997) defined the term setting as '*the stiffening of the cement paste from a fluid to a rigid state and the terms initial set and final set are used to describe the arbitrarily chosen stages of setting*'. It is a transformation in the cement paste, in the mortar or concrete, from fluid material to one that is solid and rigid. The setting process is accompanied by the temperature changes in the cement paste. The initial setting is the start of solidification which indicates the point at which the paste is no longer workable, while the time required to fully solidify the mortar indicates the moment when setting ends.

The study on the rate of hydration of paste with RHA is important in predicting its strength development. Study conducted by Hwang and Wu (1989), revealed that the heat evolution curve of cement paste with RHA is similar in shape to that without RHA. They also revealed that addition of RHA in cement performs as a kind of accelerator that shortens the setting time through the absorption of the surrounding water, that is, increasing the amount of RHA and w/b ratio in the mix resulted in shortening of setting time. When comparing with the OPC control, the setting time for OPC-RHA paste is shorter and as the percentage of replacement increases from 5% to 20%, the setting time reduces. The reason is due to the water adsorption ability of the cellular form of RHA, hence reducing the surrounding w/c ratio.

Neville (1997) quoted that the reaction between cement and water was exothermic and because of its higher cement content, the plain cement paste would evolve greater amount of heat.

The result of Ikpong (1993) agreed with the findings of Stroeven et al. (1999) and Cook et al. (1976) who reported increased setting times of OPC-RHA pastes over those of plain cement paste, well above the level indicated in ASTM C595-2003. The studies also indicated that up to 20% cement replacement could be achieved without any significant adverse effect on concrete properties.

Cook and Suwanvitaya (1981) also reported that the carbon content in the ash influences the setting time as tabulated in Table 2.7. From the table, it can be seen that an increase in the carbon content decreases both the initial and final setting time. They also reported that the presence of up to 20% carbon (by weight) in the ash does not significantly influence compressive strength. The strength reduction only becomes noticeable at carbon contents of 30% and higher; this is mainly due to a corresponding reduction in silica content.

Table 2.7: Influence of Setting Time with Percentage of RHA in OPC Paste

References	Binder Mix (%)		Ash carbon content (%)	$\frac{w}{c + RHA}$	Setting times	
	Portland	RHA			Initial (min)	Final (min)
Cook and Suwanvitaya (1981)	100	0	-	-	40	80
	80	20	42	-	50	170
	80	20	14	-	120	190
	60	40	42	-	35	50
	60	40	14	-	70	110
Hwang and Wu (1989)	100	0	-		240	600
	95	5	-		180	540
	90	10	-	0.35	150	480
	85	15	-		120	390
	80	20	-		90	330
	100	0	-		180	480
	95	5	-		180	450
Mahyuddin (1993)	90	10	-	0.47	150	480
	85	15	-		120	390
	80	20	-		30	330
	95	5	-	0.33	214	259
	90	10	-	0.35	222	282
	85	15	-	0.45	273	314
	80	20	-	0.47	280	325
Ikpong (1993)	70	30	-	0.54	295	365
	60	40	-	0.61	310	420
	100	0	-	-	125	243
	70	30	-	-	208	272
Singh et al. (2002)	60	40	-	-	245	339
	50	50	-	-	281	392
	90	10	-	0.42	225	320

Study by Mahyuddin (1993) as indicated in Table 2.9 revealed that the reactivity of RHA cement depends upon the specific surface area, hence, RHA cement with finer particles exhibit superior setting behaviour and compressive strength. He suggested that the increase in percentages of ash in OPC would result in an increase of w/c ratio, thereby increases the initial and final setting time of cement paste.

His finding is agreeable with Ikpong (1993) who suggested that higher water to cement ratio tends to increase the setting time because of less contact between the open matrix and the silica cellular structure, thus causes a reduction in early strength development. Study conducted by Singh et al. (2002) on effect of replacing 5, 10, 15, 20, 25 and 30% by weight of OPC with RHA on setting times has shown that at 10% replacement with RHA and with w/b ratio of 0.42, the initial and final setting times are at maximum (that is 225 min and 320 min), and it is considered to be an optimum limit of RHA concentration.

2.9.2.3 Soundness

Soundness is the ability of a cement paste, mortar or concrete to withstand internal stresses generated during cement hydration, without cracking (Neville, 1997). This expansion may take place due to delay or slow hydration of some compounds present in the hardened cement, namely free lime, magnesia, and calcium sulfate. Soundness of cement can be determined from the test devised by Le Chatelier as prescribed by BS EN 196-3: 1995. The values of expansion for RHA by various researchers are given in Table 2.1. The BS EN 197-1:2000 states that the expansion of pozzolanic cement should not exceed 10 mm.

Literature on soundness with regards to RHA blended mortar can be hardly found. No test was carried on the use of RHA blended cement. However, fly ash blended with OPC has found to be advantageous in reducing expansion phenomena probably to the fact that the concrete contains a lower amount of Portland cement than concrete without fly ash.

2.9.3 Chemical Composition of Rice Husk Ash

Chemical composition of RHA depends on the type of rice husk used and the combustion process of the rice husk in producing RHA. Generally, RHA consists 80% to 90% of silica. The ash produced by controlled burning of the rice husk between 550°C and 700°C incinerating temperature for 1 hour transforms the silica content of the ash into amorphous phase (Boateng, and Skeete, 1990). The rice husk ash produced by burning temperature lower than 500°C was reported to contain unburnt carbon around 30% that adversely affects the pozzolanic activity of RHA (Cook., 1986). The burning of RHA in air was reported to lead the formation of silica ash but it depends on the inorganic impurities and unburnt carbon amounts (Della et al., 2002). Della, 2002 in his work also reported that the RHA with 95% of silica powder could be produced after the RHA calcined at 700°C for 6 hours.

The loss on ignition value for RHA may vary and it depends on the combustion process. The resulting RHA is whitish gray in colour. Colour changes are associated with the completeness of the combustion process as well as structural transformation of the silica in the ash. Thus, whitish gray colour of the resulting ash is an indication of complete oxidation of the carbon in the ash.

RHA has been reported to contain alkalise of high pH that may give an effect on the expansion of cement (Neville, 1997). Singh et al., (2002) stated that the presence of high pH alkalise in RHA may help breaking the glass structure to dissolve faster and enhances its reactivity with calcium hydroxide. It also reacts with calcium hydroxide resulting into complete elimination of Ca(OH).

The chemical composition of the rice husk varies depending on the type of paddy species, and upon burning most of the evaporable components that is. cellulose and lignin will be removed, leaving behind the silica ash (Mehta, 1992; Hwang and Wu, 1989). Therefore, the characteristics of the ash obtained depend on the components of the rice husk, temperature and time of burning. Table 2.10 shows the chemical compositions of RHA

produced due to different burning temperature as reported by Hwang and Wu (1989). From the table, it shows that the higher the burning temperature, the greater the silica (Si) content in the ash and the K, S, Ca, Mg as well as several other compounds are revealed to be volatile, thus, affecting the quality of the ash produced.

Table 2.8: Chemical Composition of RHA (Taiwan) under Different Burning Temperatures

Component		Temperature (^o C)				
		<300	400	600	700	1000
Element (%)	Si	81.90	80.43	81.25	86.71	92.7
	K	9.58	11.86	11.80	7.56	2.57
	Ca	4.08	3.19	2.75	2.62	1.97
	Na	0.96	0.92	1.33	1.21	0.91
	Mg	1.25	1.20	0.88	0.57	0.66
	S	1.81	1.32	1.30	1.34	0.16
	Ti	0.00	0.00	0.00	0.00	0.45
	Fe	0.43	1.81	0.68	0.00	0.68
Oxide (%)	SiO ₂	88.01	88.05	88.67	92.15	95.4
	MgO	1.17	1.13	0.84	0.51	0.59
	SO ₃	1.12	0.83	0.81	0.79	0.09
	CaO	2.56	2.02	1.73	1.60	1.16
	K ₂ O	5.26	6.48	6.41	3.94	1.28
	Na ₂ O	0.79	0.76	1.09	0.99	0.73
	Fe ₂ O ₃	0.29	0.74	0.46	0.00	0.43

Adapted from Hwang and Wu (1989)

Chemically, RHA is a heterogeneous mixture of crystalline and amorphous compounds of SiO₂, Al₂O₃, etc. with varying proportion of CaO and other minor components as shown in Table 2.8. From the table, it is clearly shown that the SiO₂ in the RHA presents as primary constituent. The range of SiO₂ content in RHA obtained from various researches is between 80% and 97%. The wide difference in the percentage of SiO₂, is due to the type of paddy species, the temperature and time of burning as suggested by Hwang and Wu (1989).

The reaction of the Ca(OH)_2 with silica rich RHA in blended concrete will form extra C-S-H and less portlandite which contributes to improvement in the strength of the concrete and its resistance to acid attack, carbonation and penetration. A study by Qiyun et al. (1999) shows that the presence of RHA as pozzolan accelerates the early hydration of C_3S and C_3A due to depression of Ca^{2+} ionic concentration in the liquid phase. RHA will stimulate the dissolution of C_3S by the absorption of Ca^{2+} ion on the surface of RHA particles and provide increasing site for the precipitation of C-S-H.

A study conducted by Yu et al. (1999) on the reaction between RHA and Ca(OH)_2 solution at 40°C temperature found that after adding RHA to the Ca(OH)_2 solution, the concentration of Ca^{2+} and OH^- were reduced with time due to the interaction between Ca(OH)_2 and RHA. This was due to the pH value that was directly related to the amount of free OH^- anions in the solution. It is also shown that the electrical conductivity was mainly dependent on the effective concentration of Ca^{2+} and OH^- ions in the solution.

Investigations had been conducted in many countries incorporating RHA in concrete as cement replacement, and it is found that it could improve numerous properties in concrete. This is due to the presence of SiO_2 in RHA and Ca(OH)_2 in cement paste, which react to produce C-S-H that will contribute to the improvement in the strength and durability of concrete.

2.10 Characteristics of Fresh Concrete with Rice Husk Ash

2.10.1 Effects on Fresh Concrete

The addition of RHA as partially cement replacement materials to OPC has been reported to increase the water requirement of cement paste to become consistent. Since RHA take some time in participating in the hydration process, they simply adsorb water because of higher

surface area and hence, the water consistency of the composite becomes higher as compared to that of OPC alone. The water required for standard consistency linearly increases with an increase in RHA content. As the specific surface area of RHA is much higher than cement, it needs more water (Singh et al, 2002). Cook (1986) also reported the result on water demand increment of RHA concrete. The increment of water demand of RHA may be due to the carbon content that may also influence its setting times.

One of the effects of RHA on the properties of fresh concrete is reported to reduce the workability of concrete. The use of RHA also required more superplasticizer and more air-entraining admixture compared with the control OPC concrete in order to obtain the same slump and air content (Malhotra et al., 2004). The air entraining agent for RHA concrete mixtures was also found to be higher than that of SF concrete mixtures and this can likely be due to its higher carbon content compared to SF (Nehdi et al., 2003)

The addition of RHA as cement replacement materials in cement paste was found to increase the initial and final setting times. During this period RHA does not contribute in the setting process and simply acts as fillers and causes a dilution effect, because of that, setting times of the mixes are enhanced. Ganesan et al ; (2007) in his study found that up to 15%, increasing the RHA level increases the initial setting time. At 20%, 25%, 30% and 35%, there is a decrease in initial setting time

The initial setting time measured for RHA blended cements up to 35% is higher than that of control OPC. On the other hand, the final setting time continues to decrease with the increase in RHA up to 35%. The similar conclusion also made by Cook,(1986) that noticed the carbon content in RHA below 20% (by weight) does not significantly influence the setting time but the increase of setting time was noticeable when the carbon content in RHA is 30% and higher,

2.10.2 Effect on the Workability

Workability as defined in ASTM C 125 (2003) is "property determining the effort required to manipulate a freshly mixed quantity of concrete with minimum loss of homogeneity". Whereas, the ACI definition of workability, given in ACI 116R-90 (ACI, 1994) is "that property of freshly mixed concrete or mortar which determines the ease and homogeneity with which it can be mixed, placed, consolidated, and finished",

Concrete behaviour in terms of its consistency is normally dominated by the relative proportions of aggregate, cement and water. In order to measure this behaviour, slump test as in accordance to BS EN 12350-2: 2000 need to be carried out.

The characteristics of fresh concrete with RHA at early age depend on the w/b ratio, the percentage proportion of RHA, the amount and fineness of cement, aggregate type and grading admixtures and mixture proportion of concrete. As quoted by Mehta (1983), at a given w/c ratio, small addition of RHA which is less than 2% to 3% by weight of cement will improve the stability and workability of concrete by reducing the tendency towards bleeding and segregation. The reason for this is due to the large surface area of RHA that is in the range of 500000 cm²/g to 600000 cm²/g measured by nitrogen absorption (Mehta, 1992).

However, due to the adsorptive character of cellular RHA particles, concrete containing RHA requires more water for a given consistency. Thus, large additions would produce dry or unworkable mixtures (Hwang and Wu, 1989; Shafiq et al., 1988). Study conducted by Shafiq et al. (1988) showed a decrease of 60% in the flow value when the percentage content of RHA was 40% as compared to the control mortar. Beside the cellular structure, the reason for this is that the RHA is much finer than that of ordinary Portland cement. Mehta (1978) reported a reduction in slump from 95 to 12.5mm when 30% of Portland cement in a concrete mix was replaced with RHA.

A study conducted by Shimizu and Jorillo (1990) showed that increase in the water requirement for a constant consistency of RHA concrete mix resulted in decrease in strength. They also revealed that as the percentage of replacement of RHA increased, the mixture possessed harsh characteristics. It was due to the overall decrease in the amount of the binding medium, change in overall fineness of cement and change in the water requirement. Sumadi and Abu (1989) showed that increase in w/b ratio resulted in better compaction as a result of improved workability, thus this resulted in increase in strength of the mortar. Table 2.9 showed some of the results obtained from their studies.

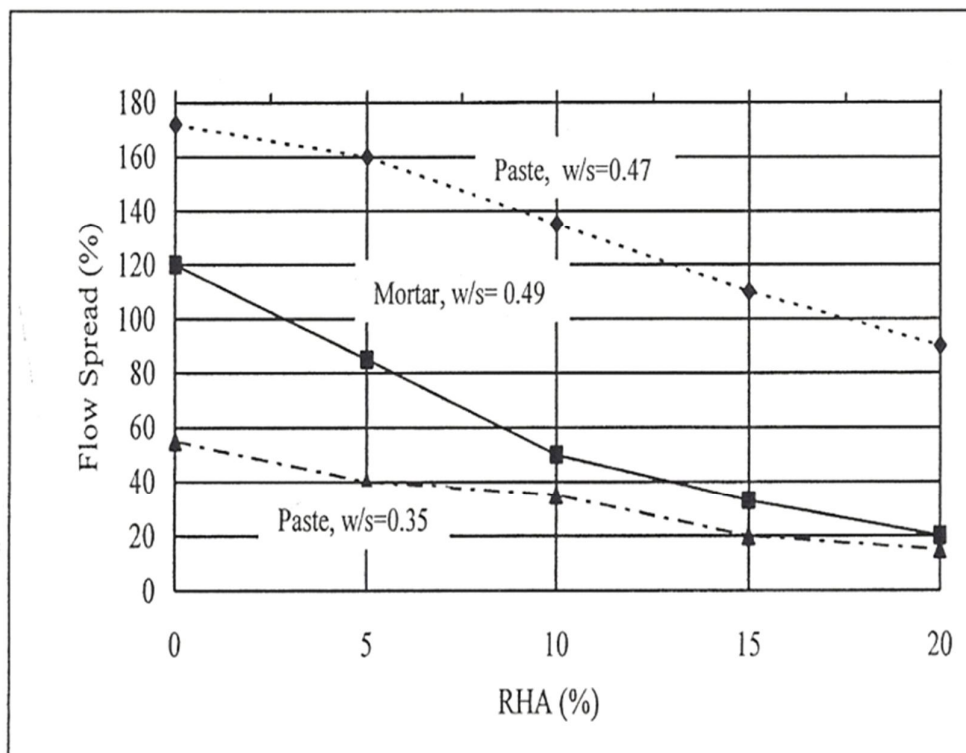


Figure 2.2: Workability of cement paste and mortar with RHA
Adapted from Hwang and Wu (1989)

Table 2.9: Water/binder ratio and compressive strength of RHA cement mortar cube

Mixture Designation	$\frac{w}{c + RHA}$	Compressive Strength at
		28 days (N/mm ²)
OPC		10.89
RHA20	0.40	4.35
RHA35		1.18
OPC		14.44
RHA20	0.50	16.32
RHA35		15.03
OPC		10.17
RHA20	0.60	26.63
RHA35		29.24
OPC		13.05
RHA20	0.65	25.00
RHA35		26.40
OPC		13.50
RHA20	0.70	20.50
RHA35		23.00

Adapted from Sumadi and Abu (1989)

2.10.3 Effect of Superplasticizer on the Workability

Superplasticizing (Sp) admixture is a functional extension of normal plasticizing admixture in that it disperses cement agglomerates efficiently. Sp is anionic surfactant that is negatively charged. It will chemically adsorb onto the cement agglomerates, and the resulting repulsion will cause dispersion of the cement flocks. This dispersion allows high workability concrete to be obtained without increasing water content, thus giving flowing concrete.

Neville (1997) quoted that Sp does not alter fundamentally the structure of the hydrated cement paste, and the main effect being a better distribution of cement particles and consequently better hydration. There are two main types of Sp, namely, the sulphonated melamine-formaldehyde condense (SMF) and the sulphonated naphthalene-formaldehyde condense (SNF).

Singh et al. (2002) stated that the effect of adding 1% of Sp on the consistency of 10% OPC-RHA blended resulted in reduction in w/b ratio. Wada et al. (2000) also reported that due to large specific surface area of the RHA, the Sp content of the mortar and concrete mixtures increased with increasing RHA content to achieve a given consistency.

Shafiq et al. (1988) in their investigation revealed that by adding 2% of Sp in the 40% RHA mortar mixes the flow increased by 40%, whereas with 30% RHA the flow increased by about 50%. However, for the control mortar with the addition of Sp, the mortar became fluid in which its flow value could not be determined. Brookes et al. (1979) revealed that inclusion of Sp did not influence shrinkage, creep and modulus of elasticity of concrete.

2.11 Characteristics of Hardened Concrete and Cement Paste with Rice Husk Ash

The characteristics of hardened concrete with RHA emphasize more on the strength of the concrete itself. The effect of RHA on the strength properties in terms of its compressive strength, modulus of rupture, tensile splitting strength, static and dynamic modulus of elasticity, Poisson's ratio, ultrasonic pulse velocity value, rebound number, drying shrinkage, expansion and durability criteria will be discussed in various sub-headings.

The effect of curing on the characteristic strength of hardened concrete will also be discussed. The term curing is defined by Garnbhir (2006) is "a process of creation of an environment (that is. the desirable condition such as suitable temperature, provision of ample moisture or prevention of loss of moisture, and the avoidance of premature stressing or disturbance) during a relatively short period immediately after placing and compaction of the concrete, favourable to the setting and hardening of concrete". Curing is essential in obtaining satisfactory long-term durability performance, particularly in hot and dry climates (McCarter and Ben-Saleh, 2001).

A study by Patel et al. (1988) showed that hydration is greatly reduced when the relative humidity within the capillary pores drops below 80% and suggested that hydration at a maximum rate can proceed only under condition of saturation. The prevention of loss of

water from the concrete is of importance not only because the loss adversely affects the development of strength, but also because it leads to plastic shrinkage, increased permeability and reduced resistance to abrasion.

2.11.1 Compressive Strength

A study conducted by Cook et al. (1976) in terms of the compressive strength of cement paste with RHA revealed that increase in the replacement level of more than 20% resulted in decreasing compressive strength at 28 days as compared to 100% of OPC cement. In their study, it was also highlighted that the increase in strength was greater for all the replacement level tested (10%, 20%, 30% and 40%) from 28 to 90 days compared to the 100% OPC concrete mix. This is expected because the pozzolanic activity which is related to the ability of silica to combine with $\text{Ca}(\text{OH})_2$ to produce cementitious C-S-H occurred at a slower rate. As the cement replacement increased, the initial strength of the cement replacement material decreased.

Table 2.10: Compressive Strength of Cement-RHA Blended Concrete

Mix Description Cement + RHA : Sand: Gravel (1 : 1.68 : 2.53)	$\frac{w}{c + \text{RHA}}$	Compressive Strength (N/mm^2)	
		28 days	90 days
C100:0-1	0.45	35.85	38.72
C100:0-2	0.55	35.16	37.80
C100:0-3	0.65	26.89	29.17
C90:10-1	0.49	40.67	45.55
C90:10-2	0.55	33.09	36.73
C90:10-3	0.65	27.58	31.03
C80:20-1	0.53	33.78	37.00
C80:20-2	0.62	33.44	36.28
C80:20-3	0.69	26.20	29.89
C70:30-1	0.75	18.61	21.03
C70:30-2	0.93	14.48	16.22

Adapted from Cook et al. (1976)

Table 2.12 shows the result of their study on the compressive strength of blended cement RHA concrete. In 1981, Cook and Suwanvitaya reported that for OPC replacement of more than 40% with RHA, the compressive strength is significantly reduced at 365 days. They also concluded that as $w/(c + \text{RHA})$ ratio increased, the strength decreased, and this finding is in accordance with the conventional w/c ratio concept of strength.

Sugita et al. (1997) also reported that the addition of RHA resulted in increased in compressive strength and at the RHA blending ratio of 20%, the concrete attained the maximum increment in strength. They also suggested that the 28 days compressive strength of concrete with different w/c ratios increased with the addition of RHA. Their results are tabulated in Table 2.11.

Their reasons for these were included that; the ground RHA is a porous material and with large number of mesopores, resulting in RHA having high water absorption characteristic. Therefore, the practical w/c ratio in RHA blended mortar is less than the used because a portion of free water has been absorbed in the mesopores in RHA. Besides, the RHA used in their study have high content of SiO_2 , that is about 91.9%, and is very active. Thus, it can quickly react with the Ca^{2+} and OH^- ions in the liquid phase of hydrating cement. Therefore, in comparison with the normal concrete, there will be more C-S-H and less portlandite in the RHA blended, thus these contributed to an increase in the strength of concrete.

Giaccio et al. (2007) also reported that the incorporation of 10% RHA at lower w/b ratio (0.4 - 0.5) resulted in higher compressive strength compared to control OPC concrete, with relative compressive strength of RHA concrete increase to near 9% and 7% at 28 days and 90 days respectively. Study by Mehta and Pritz (1978), showed that in a high strength concrete mixture containing 30% of RHA, by weight of total cementing material, gives about 8% higher strength at the age of 28 days compared with those of control Portland cement concrete. Moreover, the adiabatic temperature rise is lower for the RHA concrete.

Table 2.11: Compressive Strength of Cement-RHA Concrete Cured in Water for 28 days

Cement (kg/m ³)	RHA		$\frac{w}{c + RHA}$	Compressive Strength, N/mm ² (interpolate from graph)
	(kg/m ³)	(%)		
283.8	0	0	0.65	22.0
255.4	28.4	10		23.0
198.6	85.2	30		27.0
245.9	0	0	0.75	16.0
221.3	24.6	10		22.5
196.7	49.2	20		24.5
172.2	73.8	30		21.0
123.0	123.0	50		16.5
233.1	0	0	0.80	13.0
209.8	23.3	10		19.5
186.5	46.6	20		22.0
163.2	69.9	30		21.5
116.6	116.6	50		17.0

Adapted from Sugita et al. (1997)

Adding the correct amount of RHA is important to achieve high strength. A study conducted by Hwang and Wu (1989) showed that large amount of RHA have an adverse effect and reduce strength. Highly active RHA are effective in amounts as low as 10% and tend to increase rather than decrease the strength at early ages. In fact, the early strength of concrete is a function of w/b ratio. The early strength of concrete will be similar as long as the w/b ratio is kept constant, but the ultimate strength will be enhanced due to pozzolanic reaction. However, Hwang and Chandra (1997) showed that at high w/b ratio, the addition of RHA to cement paste will not only reveal a significant effect on strength at early ages, but the strength at later ages also tend to be higher than those with lower w/b ratios. Shimizu and Jorillo (1990) in their study reported that as the percentage of RHA increases, the amount of water needed to maintain a constant consistency of 100 mm slump increases and this undoubtedly resulted in decrease in strength. The results of their study are best translated as in Table 2.12 .

Table 2.12: Compressive Strength at 28 Days of Cement-RHA Blended Concrete

Mix Code	Cement (kg)	RHA (kg)	$\frac{w}{c + RHA}$	Compressive Strength at 28 days	
				kg/cm ²	N/m ²
MG - 0 (Control)	313	-	0.58	283	27.8
MG - 80:20	250	39.49	0.68	214	21.0
MG -70:30	219	59.23	0.83	156	15.3
MG -60:40	187	78.97	0.93	116	11.4
HG - 0 (Control)	356	-	0.50	352	34.5
HG - 80:20	285	44.98	0.59	259	25.4
HG -70:30	249	64.45	0.74	169	16.6
HG -60:40	214	89.96	0.81	144	14.1
HG -50:50	178	112.45	0.87	106	10.4

Note: HG represents high grade
 MG represents medium grade
 Adapted from Shimizu and Jorillo (1990)

A research conducted by Coutinho (2003) on the compressive strength of RHA concrete on 10%, 15% and 20% replacement of cement with RHA taken at 80 days showed strengths of 41.5, 41.7 and 43.0 N/mm² respectively as compared to control mix which showed a strength of 35.1 N/mm². All the mixes have a constant percentage of Sp and w/b ratios of 1.2% and 0.43% respectively. This showed that the replacement of cement with RHA has an influence on its strength and the higher the replacement; the higher will be the strength at later ages (that is. based up to 20% replacement). Zhang et al. (1996a) reported that the higher compressive strength of RHA concrete is due to the reduced porosity, reduced Ca(OH)₂, and reduced width of the interfacial zone between the paste and the aggregate.

Chindaprasirt et al. (2005) in their report on the compressive strength of concrete with 40% and 60% replacement of RHA from total cementitious content of 333 kg/m² plus Sp showed that at higher replacement level, lower compressive strength resulted. Both RHA concrete exhibited lower strength compared to the OPC concrete. Their reason was owing to the low amount of Portland cement and hence, low calcium hydroxide such that both

the initial and the subsequence reactions were lower. The SiO₂ of OPC and RHA used in their study were 20.90% and 88.33% respectively.

A study conducted by Ikpong (1993), on various grades of concrete from 15 N/mm² to 40 N/mm² with varying levels of cement substitution by volume, taken up to age of 90 days, reveals that each of the compressive strength increased with age but decreased with RHA content. Proportion by volume was adapted because of the remarkable difference in specific gravities of the RHA and cement (2.12 for RHA and 3.15 for cement). The SiO₂ of RHA used in his study was 82.12% with L.O.I of 8.60. The variation of compressive strength with age and levels of replacement are presented in Table 2.13.

Table 2.13: Variation with Age of Compressive Strength of RHA Concrete

Design Strength (N/mm ²)	% RHA content	Cement Content (kg)	RHA (kg)	Water (kg)	Compressive Strength			
					7 days	14 days	28 days	90 days
15	0				13.1	17.8	25.8	28.3
	30	N/A	N/A	N/A	12.1	16.0	25.0	27.6
	40				8.9	11.8	19.9	24.7
	50				5.7	10.3	13.7	17.8
20	0	270	-	185	17.5	23.9	33.1	37.1
	30	189	81	197	15.8	18.2	29.1	35.2
	40	162	108	204	13.4	15.2	27.2	33.9
	50	135	135	211	10.6	12.7	23.0	28.7
30	0	321	-	192	28.4	37.6	43.5	46.3
	30	224.7	96.3	196	22.6	32.0	38.3	43.2
	40	192.6	128.4	203	16.7	27.5	31.8	37.1
	50	160.5	160.5	216	9.1	16.2	19.6	22.1
40	0				32.4	38.8	44.2	47.6
	30	N/A	N/A	N/A	24.0	33.5	39.4	44.9
	40				18.5	29.3	34.6	38.9
	50				10.0	18.1	22.5	22.9

Adapted from Ikpong (1993)

Mazlum and Uyan (1992) in their study showed that the compressive strength of mortar with cement replacement of 10%, 20% and 30% with RHA was greater than that of the control mortar until the 56 days and remains constant beyond that time. As shown in, Table 2.14, the compressive strength increased remarkably in the course of time proportional to the increase in the amount of RHA, with 20% replacement showed the most effective RHA percentage replacement.

However, Mahyuddin (1993) in his study reported that the strength of cement mortar blended with RHA replacement up to 25% gave good compressive strength; but beyond that level of replacement, the strength of cement mortar blended with RHA is lower compared to mortar without RHA. He also stated that the effectiveness of the grinding and the temperature of burning have significant effect on the surface reactivity.

Table 2.14: Compressive Strength of Mortars

Cement (kg)	RHA (kg)	$\frac{w}{c + RHA}$	Sp (%)	Compressive Strength, N/mm ²			
				28 days	56 days	84 days	112 days
450	0			34.3	35.5	41.5	38.5
405	45			36.7	37.4	42.9	42.0
360	90	0.55	2	36.8	39.7	42.4	42.9
315	135			34.2	38.4	41.3	40.9

Adapted from Mazlum and Uyan (1992)

Wada et al. (2000) in their research on the RHA concrete subjected to different curing conditions that is moist-cured at 20°C and 85% relative humidity for 1 day and water-cured at 20°C until the age of 28 days showed that irrespective of the curing condition, the compressive strength of the RHA concrete is higher than that of the control concrete. The reason was probably due to the higher pozzolanic reactivity of RHA concrete. Saricimen et al. (2000) in their study have shown that exposure to water curing of plain and pozzolanic cement concrete resulted in an increase in the compressive strength.

RHA was also known as a pozzolanic material that can improve the engineering properties of concrete especially at hardened state of concrete. The high silica content at amorphous stage of the RHA was reported to be the contributory factor of the improvement. The effectiveness of using RHA as cement replacement materials or as additive in the concrete mixes depends on factors named as type of rice husk used, incineration degree of RHA, fineness of RHA and replacement level of RHA to OPC.

The increase in compressive strength of concrete with RHA produced by controlled incineration is mainly due to the pozzolanic effect. Gemma, (2006), study on the effect of incineration degree of RHA to the concrete engineering properties concluded that, RHA that produced by open burning provides a positive effect on the compressive strength and had a comparable effect as the controlled incineration RHA at early ages, but in the long term, the behaviours of the concretes with RHA produced by controlled incineration was more significant.

The rate of hydration in concrete made with part replacement of cement by RHA is slow as compared to concrete with OPC only. This fact is very dominant during the initial three days of age of concrete. This rate of slow hydration also affects the 150 day strength of concrete made by part replacement of cement by RHA in the mix (Muhammad et al, 1996).

The RHA concrete was found had higher compressive strength at 91 days in comparison with that of the concrete without RHA, although at 7 and 28 days a different behaviour was observed between the control concretes with the RHA concrete. The increase in compressive strength of concretes with residual RHA is better justified by the filler effect (physical) at early age than by the pozzolanic effect (chemical/physical) at late age (Bui et al, 2005).

The results indicate that optimum replacement of cement by RHA will be around 10% to 20% with finely ground RHA. It simply indicates that in the presence of RHA, some alkalis are liberated in the solution that further breaks the glassy network and enhances its reactivity with calcium hydroxide. RHA also reacts with calcium hydroxide resulting into complete elimination of Ca(OH) (Singh et al, 2002).

The strength development in cement is mainly due to the formation of calcium silicate hydrate. The increase in strength in the presence of RHA is due to the formation of additional amount of calcium silicate hydrate as a result of pozzolanic reaction (Singh et al, 2002).

The cement paste incorporating RHA did not show any increase in the compressive strength compared with that of the control portland cement paste. The higher compressive strength of the RHA concrete compared with that of the control concrete is due probably to its reduced

porosity, reduced Ca(OH)₂ content, and the reduced width of the interfacial zone between the paste and the aggregate (Zhang et al, 1996).

Zhang et al (1996) as illustrated in Figure 2.3 also stated that the use of RHA as cement replacement materials had comparable effects to SF at 10% replacement level on the compressive strength at 90 and 180 days but lower than SF before 28 days.

The reduction of concrete durability due to the reaction of sulphate is to leach the Ca⁺ ion from the concrete matrix and replace with Mg⁺⁺ ion, increased the volume of concrete with sulphate crystal and increased the internal strain of concrete matrix that will generate more micro crack (Neville, 1997). Magnesium sulphate chemically reacts with calcium hydroxide in the presence of water to gypsum and magnesium hydroxide. The latter salt is relatively insoluble and poorly alkaline (pH < 10.4). At this low pH, the stability of calcium silicate hydrate (C-S-H) is reduced. The decomposition of C-S-H may proceed to completion and all the calcium content of the binder may be replaced by magnesium, thereby leading to disintegration of concrete.

2.11.2 Modulus of Rupture

Flexural strength is also expressed in terms of the modulus of rupture (MOR). In 1990, Shimizu and Jorillo reported that the modulus of rupture for RHA concrete is lower

compared to OPC concrete. The result of their study on the modulus of rupture of cement-RHA blended concrete is presented in Table 2.15.

Table 2.17: Modulus of Rupture of Cement-RHA Blended Concrete

Mix Code Cement : RHA	Cement (kg)	RHA (kg)	$\frac{w}{c + RHA}$	Modulus of Rupture at 28 days	
				kg/cm ²	N/m ²
MG - 0 (Control)	313	-	0.58	28.5	2.79
MG - 80:20	250	39.49	0.68	22.1	2.17
MG -70:30	219	59.23	0.83	23.3	2.29
MG -60:40	187	78.97	0.93	15.5	1.52
HG - 0 (Control)	356	-	0.50	35.1	3.44
HG - 80:20	285	44.98	0.59	27.4	2.69
HG -70:30	249	64.45	0.74	25.9	2.54
HG -60:40	214	89.96	0.81	21.9	2.15
HG -50:50	178	112.45	0.87	19.4	1.90

Note: HG represents high grade MG represents medium grade
Adapted from Shimizu and Jorillo (1990)

The ash was obtained from the open burning in the field of variety of rice husk in the Philippines. The ash used in Shimizu and Jorillo's study was at its natural fineness with 47.67% and 25.29% passing No. 100 and No. 200 sieve respectively. From the table, it can be seen that irrespective of the grade, the MOR for RHA concrete is smaller compared to the control concrete, and it reduces as the amount of replacement with RHA increases.

Not many work were obtained on the MOR of cement-RHA blended concrete. However, there are few research work carried out on MOR of cement-RHA blended mortar. Investigation conducted by Mazlum and Uyan (1992) showed that the modulus of rupture of mortar with RHA has generally increased with the increase in the amount of RHA and that mortar with 30% RHA has the greatest modulus of rupture. This can be seen in Table 2.18.

Table 2.16: Flexural Strength of Cement-RHA Blended Mortar

<i>Cement</i> (kg)	<i>RHA</i> (kg)	$\frac{w}{c + RHA}$	<i>Sp</i> (%)	Flexural Strength, N/mm ²			
				28 days	56 days	84 days	112 days
450	0			5.6	6.2	6.4	3.6
405	45			6.4	7.4	7.4	7.5
360	90	0.55	2	6.4	7.4	7.9	7.8
315	135			7.0	8.0	8.4	7.9

Note * Relative values calculated in relation to control mortar at 28 days

Adapted from Mazlum and Uyan (1992)

A study conducted by Kilinckale (1997) on mortar containing the 20% RHA showed that the 28 days and 56 days modulus of rupture were higher than the control mortar. However, a study conducted by Mahyuddin (1993) on basic mix composition of mortar of 1:2.5 (1 part of cement to 2.5 part of sand by weight) with 0.5 w/c ratio and replacing cement with RHA by 5, 10, 15, 20, and 30% has indicated that the modulus of rupture of these cement-RHA blended mortar have lower strength than the control (that is, 5 N/mm²) and 30% RHA replacement showed the lowest strength achieved.

The values of the flexural strength for these cement-RHA blended mortars were 4.8, 4.0, 3.7, 3.5 and 2.8 N/mm² respectively. It was reported that the reasons for the discrepancy were due to the difference in fineness of RHA used and different burning temperature adapted in producing the ashes.

2.11.3 Tensile Splitting Strength

The common tests used to estimate the tensile strength of concrete is the splitting tension test. Compared to direct tension, the splitting tensile strength is known to overestimate the tensile strength of concrete by 10 - 15% as reported by Mehta and Monteiro (1993). Table 2.17 shows the results obtained from the study conducted by Shimizu and Jorillo (1990) on the

RHA concrete subjected to tensile splitting test. From the table, it can be derived that irrespective of the grade, the tensile splitting strengths of cement-RHA blended were lower than the control concrete. It also shows that as the amount of replacement with RHA increases, the tensile splitting strength decreases, and agrees with Cook's finding.

Table 2.17: Tensile Splitting of Cement-RHA Blended Concrete

Mix Code Cement : RHA	Cement (kg)	RHA (kg)	$\frac{w}{c + RHA}$	Modulus of Rupture at 28 days	
				kg/cm ²	N/m ²
MG - 0 (Control)	313	-	0.58	30.1	2.95
MG - 80:20	250	39.49	0.68	23.8	2.33
MG -70:30	219	59.23	0.83	19.2	1.88
MG -60:40	187	78.97	0.93	16.8	1.65
HG - 0 (Control)	356	-	0.50	36.5	3.61
HG - 80:20	285	44.98	0.59	29.7	2.91
HG -70:30	249	64.45	0.74	22.6	2.22
HG -60:40	214	89.96	0.81	20.1	1.97
HG -50:50	178	112.45	0.87	15.5	1.52

Note: HG represents high grade
 MG represents medium grade
 Adapted from Shimizu and Jorillo (1990)

Cook et al. (1976) in their research on cement replacement with RHA of between 10% and 40% showed that increase in replacement level results in decrease in the splitting tension when tested at 28 days. For the 30% and 40% replacement level, the 28 days tensile splitting strength was considerably lower than the plain cement concrete. The result of their work is presented in Table 2.18. Karasudhi and Nimityongskul (1979) also reveal that addition of RHA with decreasing amount of cement in the mix decreases the concrete splitting tensile strength.

Table 2.18: Tensile Splitting Strength of Cement-RHA Blended Concrete

Mix Description Cement + RHA : Sand: Gravel (1 : 1.68 : 2.53)	$\frac{w}{c + \text{RHA}}$	Splitting Strength (N/mm ²) 28 days
C100:0-1	0.45	2.93
C100:0-2	0.55	2.75
C100:0-3	0.65	2.17
C90:10-1	0.49	3.45
C90:10-2	0.55	3.15
C90:10-3	0.65	2.69
C80:20-1	0.53	2.69
C80:20-2	0.62	2.79
C80:20-3	0.69	2.28
C70:30-1	0.75	1.74
C70:30-2	0.93	1.52
C60:40-1	0.85	1.17
C60:40-2	1.09	0.96

Adapted from Cook et al. (1976)

2.11.4 Non-Destructive Test on Rice Husk Ash Concrete

The term "non-destructive testing" is taken in its broad sense to include methods that cause localized surface damage, but are non-destructive in relation to the body of the concrete under examination. Non-destructive testing may be applied to both new and existing structures. For new structures, the principal applications are for quality control, monitoring of strength development or resolution of doubts about the quality of materials or construction. For existing structures, normally it will be related to an assessment of structural integrity or adequacy, and material deterioration.

2.11.4.1 Ultrasonic Pulse Velocity

The pulse velocity method has been used successfully both in laboratory as well as field to evaluate the quality of concrete. It involves the use of sonic waves to detect internal structure changes in concrete, to obtain the dynamic modulus of elasticity, Poisson's ratio and to estimate the strength of concrete test specimens resulting in no damage to the concrete element being tested. Neville (1997) defined the pulse velocity through concrete as the outcome of the time taken by the pulse to travel through the hardened cement paste and through aggregate.

Naik and Malhotra (1991) reported that there are many factors that affect the pulse velocity; it can either be the factors affecting the concrete properties or factors affecting the pulse velocity measurement regardless of the properties of concrete. The pulse velocity for ordinary concrete is typically in the order of 3660 m/sec, and it is not dependent upon the size and the shape of a specimen.

Sturup et al. (1984) revealed that there is no unique relation between ultrasonic pulse velocity and compressive strength exist. However, the rate of hydration is different for different cements and as the degree of hydration increase the strength will increase and the pulse velocity will also increase (Facaoaru, 1970).

Neville (1997) concluded that for a given aggregate and a given richness of the mix, the ultrasonic pulse velocity of the concrete is affected by changes in the hardened cement paste, such as a change of w/c ratio, that is as the w/c ratio increases, the density, compressive and the modulus of rupture and the corresponding pulse velocity decreases. Naik and Malhotra (1991) and Bungey (1989) stated that the effect of curing conditions on the pulse velocity through saturated concrete was higher (can be up to 5%) than the same concrete in a dry condition.

A study conducted by Ikpong (1993) revealed that increased in the gel-space ratio of concrete at advanced age was markedly different from that of the same concrete at an early

age. The former consists of a compact network of aggregates strongly held together by cement gel that accounted for the increased strength of such concrete, whilst the latter consists of a near discrete pack of aggregates, stiffened cement paste, capillary water and a relatively small proportion of cement gel. His research on RHA concrete showed that the initial gel-space ratio is invariably much less than that of a corresponding conventional concrete.

However, the gel-space ratio at advanced age was very close to that of the early age. The results of his study on the compressive strength and the pulse velocity are shown in Table 2.19.

Table 2.19: Variation with Age of Compressive Strength and Pulse Velocity of Concrete
Designed Strength of 30 N/mm²

% RHA content	Cement Content (kg)	RHA (kg)	Water (kg)	Compressive Strength, f_c (N/mm ²)		
				7 days	28 days	90 days
0	321	-	192	28.4	43.5	46.3
30	224.7	96.3	196	22.6	38.3	43.2
40	192.6	128.4	203	16.7	31.8	37.1
50	160.5	160.5	216	9.1	19.6	22.1

% RHA content	Cement Content (kg)	RHA (kg)	Water (kg)	Pulse Velocity, V (km/sec)		
				7 days	28 days	90 days
0	321	-	192	4.38	4.70	4.74
30	224.7	96.3	196	4.23	4.63	4.68
40	192.6	128.4	203	4.00	4.44	4.60
50	160.5	160.5	216	3.15	3.61	3.81

Note:- For the mixes containing RHA, the combination of cement and RHA was proportioned by volume, because of the remarkable difference in the specific gravity of the RHA and cement, that is. 2.12 and 3.15 respectively.

Adapted from Ikpong (1993)

From the table, it can be seen that the compressive strength and pulse velocity of RHA concrete decreased with increased in RHA content. These were due to the slower hydration of cement and the secondary pozzolanic reaction involving the silica and alumina present in the ash. In addition, increase in RHA required increase in water content for equal workability (Singh et al., 2002; Wada et al., 2000; Shimizu and Jorillo, 1990; Hwang and Wu, 1989). Thus, this has resulted in more capillaries being left in RHA concrete as hydration progresses. Therefore, this increases the time of travel of the pulse and hence, decreases the calculated velocity.

The above statement agreed with Neville (1997) who stated that the speed of pulse propagation is much less through voids, than through solid matter and in fact, the pulse cannot travel directly through the voids but is deflected round it so that the pulse can be transmitted through the solid concrete matter. He also stated that pulse travels faster through a water-filled void than through an air-filled. Table 2.20 shows the pulse velocity classification established for concrete as suggested by Neville (1997).

Table 2.20: Classification of the Quality of Concrete on the Basis of Pulse Velocity

Pulse velocity, V (km/sec)	Quality of concrete
≥ 4.5	Excellent
3.5 - 4.5	Good
3.0 - 3.5	Doubtful
2.0 - 3.0	Poor
< 2.0	Very poor

Adapted from Neville (1997)

2.11.4.2 Rebound Hammer

The rebound hammer test or also known as the Schmidt rebound hammer test is based on the principle that the rebound of an elastic mass depends on the hardness of the surface against which the mass impinges. It is useful in the assessment of uniformity of concrete within a structure, and can also be used to establish whether the rebound number has

reached a value known to correspond to the desired strength (Neville, 1997; Malhotra, 1991). The rebound number is an arbitrary measure because it depends on the energy stored in the given spring and on the size of the mass. The rebound number will be governed by the energy absorbed by the concrete which is both related to its strength and stiffness. However, the results are very difficult to predict because it is affected by the smoothness of the test surface, size, shape and rigidity of the specimens, the age of the specimen, surface and internal moisture conditions of the concrete, type of coarse aggregate and cement and type of mould and carbonation of the concrete surface, to name a few.

There was a wide degree of disagreement on the correlation between compressive strength of concrete and the hammer rebound number among various researchers. However, Malhotra (1991) reported that by consensus, the accuracy of the estimation of compressive strength of test specimens cast, cured and tested under laboratory conditions by a properly calibrated hammer lies between $\pm 15\%$ and $\pm 20\%$ and probable accuracy of estimation of concrete strength in a structure is $\pm 25\%$.

Extensive researches have been conducted on the normal strength concrete incorporating OPC in terms of its rebound numbers. However, no research has been conducted and reported for concrete incorporating MIRHA.

2.12 Durability of Concrete with Rice Husk Ash

Durability as defined by ACI Committee 201(1991) is its ability to resist weathering action, chemical attack, abrasion, or any other process of deterioration; that is, durable concrete will retain its original form, quality and serviceability when exposed to its environment.

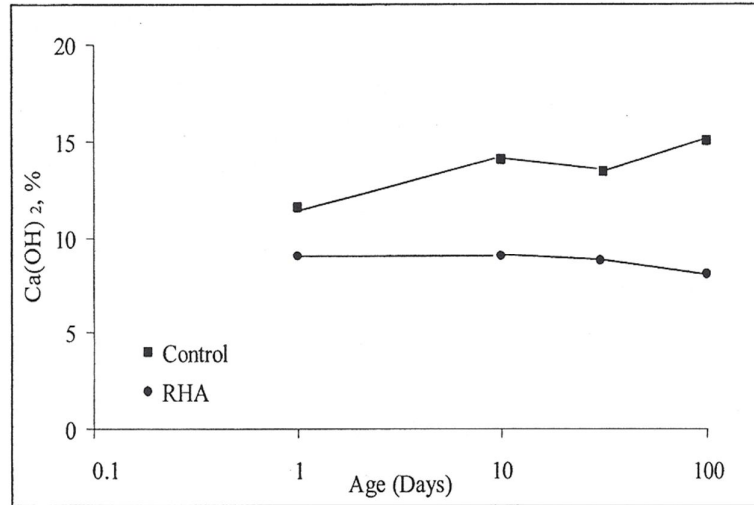
Water is the primary agent of most durability problems in concrete. In porous solids, water is known to be the cause of many types of physical and chemical processes of degradation. The physical-chemical phenomena associated with water movements in porous solid are

controlled by the permeability of the solid (Mehta and Monteiro, 1993). The rate of chemical deterioration of concrete would depend on whether the chemical attack is confined to the surface of concrete or inside the material itself, or by the type of concentration of ions in water and by the chemical composition of the solid. Mehta (1977) in his report stated that OPC contains approximately 60% to 65% of CaO, about 25% is released upon hydration as free Ca(OH)_2 and it is this product which makes Portland cement prone to deterioration in acidic environment.

The physical effects of the chemical reaction between Portland-RHA cement will produce pore-size refinement and grain-size refinement (Hwang and Chandra, 1997; Mehta, 1992). The pore-size refinement is referred to the process of transformation of the secondary hydration products. These are mainly C-S-H around the pozzolan particles which contain large capillary voids into a microporous product containing numerous fine pores. Meanwhile, grain-size refinement is referred to as the process of transformation of a system containing large grains of a component into a product containing smaller grains. Both the pore-size refinement and grain-size refinement processes strengthen the transition zone, thus reducing the microcracking and increasing impermeability of the concrete.

Speare et al. (1999) also studied the durability of mortars containing RHA. They noted an increase in compressive strength, an improvement in absorption characteristics and a reduction in oxygen permeability for RHA mortars.

Cook (1986) suggested that the improved overall durability of Portland cement-RHA is related to the physical structure of the hydrated cements as well as the reduction in the amount of Ca(OH)_2 with regards to structure. A study conducted by Zhang et al. (1996a) on Ca(OH)_2 content as shown in Figure 2.3 shows that RHA paste has a lower Ca(OH)_2 than the control cement paste. These lower Ca(OH)_2 and lower unhydrated cement content for RHA clearly indicate the pozzolanic reactivity of the RHA.



x-axis Age	y-axis Control	y-axis RHA
1	11	9
10	14	8.8
55	13	8
100	15	7

Adapted from Zhang et al. (1996a)

Figure 2.3: Calcium Hydroxide Content in OPC and RHA paste

Zhang et al. (1996a) through their research demonstrated that incorporation of RHA in cement paste and concrete will reduce its porosity. The Ca(OH)_2 amount, as a result of hydration in the interfacial zone and the width of the interfacial zone between the aggregate and the paste, also reduced, compared with that of the control Portland cement composite.

Their study on the porosity of the paste as a function of the distance from the aggregate surface on test specimens cured for 28 days is shown in Table 2.21. From the table, it indicates that the incorporation of RHA reduced the porosity in the interfacial zone compared with that of the control Portland cement composite.

Table 2.21: Porosity of OPC and RHA paste as a function of the distance from aggregate surface on the test specimen

Paste	Distance from the aggregate surface (micron)		
	20	33	43
	Porosity (%)		
OPC	25	17	11
RHA	18	9	5

Adapted from Zhang et al (1996a)

Sugita et al. (1997) and Gambhir (2006), in their study, found out that the amount of $\text{Ca}(\text{OH})_2$ in the hardened cement paste and concrete added with RHA, was greatly reduced compared with the paste and concrete without RHA addition. This is due to the paste or concrete blended with RHA that reacts quickly with the Ca^{2+} and OH^- ions released from the hydration of cement and as a result, more C-S-H gel formed. With higher formation of C- S-H gel and lower content of portlandite in the RHA blended concrete, resulted in superior to normal concrete in terms of resistance to acid attack, carbonation and penetration of chloride ion. However, the above results could be achieved provided proper control of temperature to produce the amorphous silica in the ash is made.

Many studies have shown that RHA improves the durability of concrete by modifying the micro and macro structure of cement paste (Speare et al. (1999); Sugita et al. (1997); Zhang et al. (1996a); Hwang and Chandra (1997); Gambhir (2006); Mehta (1992); Manmohan and Mehta, (1981)).

Hwang and Chandra (1997) reported that addition of pozzolanic materials could affect both the strength and permeability by strengthening the aggregate-cement paste interface and by blocking the large voids in the hydrated cement paste through pozzolanic reaction. Pozzolanic reaction occupies the empty space in the pore structure, thus making the paste or concrete dense. They also reported that above 54 kg/m^3 RHA addition, there is no influence on the strength; however, it decreases the permeability of concrete. Mehta (1992) in his study

on cement paste with RHA additions shows that there is a significant reduction in the porosity of the cement paste and also refinement in the pore structure.

The fine and cellular RHA particles will have direct beneficial effect in reducing bleeding and segregation characteristic of concrete mixtures due to its large water absorption ability, high internal surface area as well as microporous and amorphous particles.

Reduction in bleeding on the other hand would result in a stronger transition zone between solid matters and cement paste and thus, leads to a more impermeable and durable concrete.

2.12.1 Permeability

Permeability as defined by Mehta and Monteiro (1993) is the property that governs the rate of flow of a fluid into a porous solid. Permeability that is dictated by the microstructure of concrete controls the ingress of moisture or gases into the concrete, thus prevents chemical degradation. Chemical degradation as a result of reaction between an external agent and the ingredients of concrete decreases as the permeability of concrete reduces. Therefore, it is generally observed that the less permeable the concrete, the greater will be its resistance to aggressive solutions or pure water.

In concrete technology, permeability normally refers to a pressure induced flow, as in D'Arcy's permeability. In the determination of concrete durability in aggressive environments, permeability of concrete is one of the important properties. The study of permeability of concrete is important because the penetration by materials in solution may adversely affect the durability of concrete. As the concrete permeability is lowered, the resistance to the penetration by these aggressive agents increases. Therefore, the more permeable the concrete, the lower will be its resistance to deterioration.

The parameter that has the largest influence on durability is w/c or w/b ratio. Permeability of concrete does not only depend on porosity, but also on the size, distribution, shape and continuity of the pores (Mehta and Monteiro, 1993). When the w/c or w/b ratio decreases, the porosity of the paste decreases and hence, the concrete decreases its permeability. Low cement content, inadequate curing and poor consolidation also cause permeable concrete. The permeability of cement paste decreases with age because gel gradually fills the original water filled space. Permeability also varies with the degree of hydration. For pastes hydrated to the same degree of hydration, the permeability is lower with lower w/c ratio or higher cement content. For the same w/c ratio, the permeability of paste with coarser cement particles is higher than that with the finer cement.

Neville (1997) quoted that the existence of the pores in concrete is of different kinds. Therefore, it is important to distinguish between porosity and permeability. Porosity as defined by Neville (1997) is a measure of the proportion of the total volume of concrete occupied by pores, and is usually expressed in per cent. If the porosity is high and the pores are interconnected, they contribute to the transport of fluids through concrete, therefore, its permeability is also high. However, if the pores are discontinuous or otherwise ineffective with respect to the transport, then the permeability of the concrete is low, even if its porosity is high.

Water permeability property as indicated by saturated water absorption of RHA blended concrete specimens after 28 and 90 days of curing shows that at 28 days curing, the percentage of water absorption increases with RHA content up to 35%. This is due to the fact that RHA is finer than OPC and also it is hygroscopic in nature. When the curing time was increased to 90 days the percentage of water absorption values decreased considerably with increase in RHA content up to 25%. Even at 30% RHA, the value was lower compared to that of control. Obviously, with prolonged curing, addition of RHA leads to a reduction of permeable voids (Ganesan et al., 2007).

Ganesan et al., (2007) also found that the chloride diffusion coefficients of RHA blended concrete specimens are continuously decreased with the increase in RHA content up to 25% of RHA. At 30% and 35% RHA, there is an increase in diffusion coefficient and

these values are also lower compared to that of control. This observation is true for both 28 and 90 days cured specimens. Thus, chloride diffusion is also considerably reduced by partial replacement of OPC with RHA. There is a 28% reduction in chloride diffusion coefficient for 30% RHA blended concrete compared to control concrete. The transport of chloride ions through RHA blended concretes depends on the pore structure of the concrete while the electrical conduction depends on both pore structure characteristics and electrical conductivity of the pore solution.

Cook (1986) has also reported that highly reactive pozzolana, such as RHA is able to reduce the size of voids in hydrated cement pastes, thus, making them almost impermeable even at early age (7-28 days). Zhang et al. (1996), who also studied the incorporation of the RHA in concrete stated that the used of RHA as cement replacement materials successfully reduced the porosity and the Ca(OH) content. The amount in the interfacial zone and the width of the interfacial zone between the aggregate and the cement paste compared with the control portland cement composite was also reduced. However, the porosity of the rice-husk ash composite in the interfacial zone was higher than that of the silica fume composite.

2.12.1.1 Gas Permeability

Manmohan and Mehta (1981) in their investigation confirmed that in cement pastes containing 10% to 30% of RHA, after 28 days of hydration the concrete was almost impermeable. This is due to pore refinement attributed to RHA fineness or a transformation of large permeable pores to small impermeable pores. This statement agreed with the study conducted and reported by Mehta (1992), RHA being a pozzolanic material is capable of pore refinement especially the paste in the immediate vicinity of the zone surrounding coarse aggregate particles in concrete, thus, reducing the permeability of concrete with increasing RHA.

Mehta (1992) also stated that each percent of RHA can improve at least 0.6 times of permeability at year one and the permeability of the cement paste with RHA is in the

range of 1×10^{-11} cm/sec. Therefore, there is a potential usefulness of RHA as a cement or concrete additive for applications, where the corrosion of reinforcing steel is a major concern, especially in those areas that need water resistance and good durability such as that in the marine environment.

Another study conducted by Mehta (1989) showed that the addition of pozzolanic admixtures (finely divided siliceous materials) to a concrete mixture improved the properties of concrete mainly by modification of the transition zone structure. There is a reduction in permeability of fresh concrete, causing a corresponding reduction in internal bleeding which helps to decrease the porosity of the transition zone.

However, a study corroborated by Cook (1984) showed that the total porosity of mixture containing RHA is greater although the permeability has considerably reduced.

The addition of microporous RHA absorbs large amount of water surrounding the solid matter, thus , producing a low w/c ratio and refining the pore structure. Thus, the pozzolanic reaction between cement and RHA modifies the pore structure; that is, it occupies the empty space in the pore structure that reduces the water permeability of concrete.

This statement agreed with Sugita et al. (1997) in which they stated that the more the added RHA, the less the coefficient of air permeability and water permeability. They also stated that the higher the w/c ratio (65% or 75%), the coefficient of air permeability and coefficient of water permeability of RHA blended concrete are much smaller than those of concrete without RHA addition. They quoted three reasons that attributed to such a condition: the practical w/c ratio of concrete is decreased due to the addition of RHA; more C-S-H gel and less portlandite are formed in concrete; and the average pore size of concrete is reduced.

Speare et al. (1999) in their determination in terms of oxygen permeability found that with higher content of cement (400 kg/m^3), the coefficient of permeability is lower and with the

presence of RHA, the effect of using high cement content was found to be not significant as compared to control mix. Table 2.22 shows the average results of coefficient of permeability for RHA concrete cured in water for 28 days and stored at $20 \pm 2^\circ\text{C}$ and $65 \pm 5\%$ RHA at the age of 37 days.

Table 2.22: Oxygen Permeability Coefficient of Cement-RHA Blended Concrete

Mixture Designation	$\frac{w}{c + \text{RHA}}$	Coefficient, K (m²)
OPC	0.32	4.62×10^{-17}
5% RHA	0.34	4.10×10^{-17}
10% RHA	0.37	4.36×10^{-17}

Adapted from Speare et al., (1999)

2.13 Microwave Incinerated Rice Husk Ash (MIRHA) as Pozzolanic Material

This is a study on the usefulness of using an agro-waste, known as microwave incinerated rice husk ash (MIRHA) as part replacement of cement with locally available ingredients. The performance will be compared with that specimen using silica fume which is widely used in producing high strength concrete (HSC) (Salmia Beddu et al., (2009).

In this study, an effort was made to evaluate the usefulness of using MIRHA as part replacement of cement with locally available ingredients. According to Nuruddin et al (2008), compressive strength development of MIRHA concretes has been significantly higher compared to control concrete. The adequate amount of water and high pozzolanic reactivity were believed to be the main cause of this faster acceleration of MIRHA concrete. During thus stage, MIRHA performed its function both as a pozzolanic material and filler (Nuruddin et al (2008).

Table 2.23 Percentage Increment in Strength between MIRHA and SF Concrete

Mix	w/b	% increment in strength	
		3 to 7 days	7 to 28 days
MIRHA500a	0.3	14	5
SF500a	0.27	22	26
MIRHA500b	0.3	21	15
SF500b	0.27	39	39
MIRHA550a	0.3	19	16
SF550a	0.27	10	7
MIRHA550b	0.3	62	1
SF550b	0.27	53	19

Adapted from S.Beddu et al. (2009)

A study by (Salmia Beddu et al., (2009) as indicated in Table 2.23, MIRHA gave higher early age strength compared to silica fume. The highest increment of compressive strength of MIRHA and silica fume from 3 to 7 days is 62% and 53% respectively. The highest increment between 7 and 28 days for MIRHA and SF concrete is 16% and 39% respectively. The finer particles size enables MIRHA to act as filler that seeps into the tiny spaces between cement particles and as well as spaces between cement particles and aggregate. A greater surface area providing space for nucleation of C-S-H and calcium hydroxide Ca(OH)_2 . This will accelerate the reactions and form smaller calcium hydroxide crystals.

The amount of alkalis in MIRHA used, referred to K_2O is 3.77%. The presence of alkalis (high pH) will break the glassy structure of Ca(OH) and that become easier and the dissolution will become fast. Singh et al. (2002) indicates that in the presence of RHA, some alkalis are liberated in the solution which further breaks the glassy network of GGBS and enhances its reactivity with calcium hydroxide. RHA also reacts with calcium hydroxide resulting into complete elimination of Ca(OH) . The effect of alkalis has also been found to increase early strength development and decrease the long term strength (Neville, 1997).

2.13.1 Production of Microwave Incinerated Rice Husk Ash (MIRHA)

By burning method, the ash produced contains about 95% pure silica and if properly prepared, it is in an active form which behaves very much like cement (United Nations Industrial Development Organization, 1984). Green Concrete as the name suggests is eco friendly and saves the environment by using waste products generated by industries in various forms like rice husk ash, micro silica to name a few, to make resource-saving concrete structures. The use of green concrete helps in saving energy, emissions and waste water. Green concrete is often also cheap to produce as it uses waste products directly as a partial substitute for cement, thus saving energy consumption in production of per unit of cement. Over and above all green concrete have greater strength and durability than the normal concrete.

Microwaves are part of the electromagnetic spectrum and are located between 300 MHz and 300 GHz. Microwave heating is defined as the heating of a substance by electromagnetic energy operating in that frequency range. There is a fundamental difference in the nature of microwave heating when compared to conventional methods of heating material. Conventional heating relies on one or more of the heat transfer mechanisms of convection, conduction, or radiation to transfer thermal energy into the material. In all three cases, the energy is deposited at the surface of the material and the resulting temperature gradient established in the material causes the transfer of heat into the core of the object. Thus, the temperature gradient is always into the material with the highest temperatures being at the surface. In microwave heating, the microwave energy not only interacts with the surface material but also penetrates the surface and interacts with the core of the material as well. Energy is transferred from the electromagnetic field into thermal energy throughout the entire volume of the material that is penetrated by the radiation.

Microwave heating does not rely on conduction from the surface to bring heat into the core region. Since the heating rate is not limited by conduction through the surface layer, the material can be heated quicker. Another important aspect of microwave heating is that it results in a temperature gradient in the reverse direction compared to conventional

heating. That is to say, the highest temperature occurs at the centre of the object and heat is conducted to the outer layer of the material..

Advantages of microwave firing can be summarised as: Short cycle and uniform heating of even the special shaped products can be realised thanks to internal heat generation of products by microwave and high energy efficiency can be realised as the heating of kiln body is not required and finally, The environment-friendly heat treatment can be realised with less noise and exhaust gas.

Due to the husk that is hard to handle, people normally burn it and bury under paddy fields as organic manure. By controlling the burning temperature, RHA can be a green material and re-utilized in construction materials. Therefore, burning procedure to obtain RHA that is highly reactive that needs to be established, so that it can be used as cement replacement. Hence, the optimum replacement percentage of OPC by RHA that improves the quality of concrete need to be identified.

Burning the RHA with higher temperature increases the SiO_2 content. However, it is not suggested to burn rice husk above 800°C longer than one hour, because it tends to cause a sintering effect (coalescing of fine particles) and is indicated by a dramatic reduction in the specific surface (Hwang and Chandra, 1997). In order to produce MIRHA with high reactive silica content, controlled combustion of rice husk the equipment used for this experiment was specially designed and developed at the Universiti Teknologi Petronas.

The UTP Microwave Incinerator (UTPMI) used in the research adapted the Air Cooled Magnetron system with an overall dimension of 2.3m(H) x 4m(W) x 4m(L) with a chamber capacity of 1m^3 . Ceramic filter is used in the emission and ash control system with PLC mode of operation. Flue Gas Filter equipped with the microwave incinerator provides significant positive effect to the environment. It distils all the dust and ashes that are resulted from rice husk incineration, hence the air pollution from burning process can be reduced (Hwang and Chandra, 1997). The temperature ranges to 1600°C with operating temperature of 800°C .

The effect of burning temperature and percentage inclusion of MIRHA on normal strength concrete to obtain quality rice husk ash that can significantly improve the concrete compressive strength. The utilization of Microwave Incinerated Rice Husk Ash (MIRHA) into the concrete mix proportions has given various effects to the concrete properties. The improvement of compressive strength results of MIRHA concrete samples was influenced by the quality of MIRHA and mix proportion used.

Based on the study done by Kamal et al, (2008), the effect of microwave incinerated rice husk ash (MIRHA), burnt at different burning temperatures on the compressive strength of concrete. The performance of concrete mixes was determined by the compressive strength test at ages 3, 7 and 28 days.

The test results showed that 5% replacement of MIRHA with 800°C burning temperature provided good acceleration in compressive strength development in concrete. It was also shown that the inclusion of 10% replacement of MIRHA with 700°C burning temperature improved the strength of concrete. MIRHA with burning temperature 600°C also revealed that the optimum replacement of MIRHA was 5%. The results were compared to the normal concrete without MIRHA.

2.13.2 MIRHA high strength concrete

(Salmia Beddu et al., (2009) in their investigation confirmed that the highest increment of compressive strength of MIRHA and silica fume from 3 to 7 days is 62% and 53% respectively. The highest increment between 7 and 28 days for MIRHA and SF concrete is 16% and 26% respectively. The finer particles size enables MIRHA to act as filler that seeped into the tiny spaces between cement particles and as well as spaces between cement

particles and aggregate. A greater surface area providing space for nucleation of C-S-H and calcium hydroxide Ca(OH)_2 . This will accelerate the reactions and form smaller

calcium hydroxide crystals. It is possible to get strength above 70 MPa using MIRHA. The performance of MIRHA is almost similar to silica fume even though MIRHA need higher water demands. At early age the performance of MIRHA concrete is better than silica fume concrete which is the maximum increment of 62% compared to 39% respectively.

2.13.3 MIRHA foamed concrete

Nuruddin and Bayuaji, (2009) in their study found that the excess non- evaporable water (NEW) in MIRHA foamed concrete demonstrated that the hydration of MIRHA foamed concrete, which produced calcium silicate hydrates, was more than the normal plain foamed concrete. This in turn would enhance the strength and durability of the foamed concrete. Nevertheless, this was only true for 5% inclusion which was the optimum level. For 10% and 15% samples, the capability to react with Ca(OH)_2 available from the cement hydration process was quite limited since the amount of Ca(OH)_2 present in the paste was sufficient for 5% inclusion.

It can be said that for foamed concrete modified with 5% level of MIRHA provided some favorable effects. From the raw data, the 5% MIRHA foamed concrete has on average across the board, 13% higher compressive strength compared to plain foamed concrete. Definitely, this is a way forward for MIRHA foamed concrete to be further developed and to be used as structural members in the concrete construction industry. (Nuruddin and Bayuaji, 2009).

A study by Nuruddin and Bayuaji, (2009) reported that the investigation carried out is to better understand the effect of the MIRHA, water binder ratio, and sand cement ratio on the foamed concrete. The experimental work (using the Taguchi method) is designed to give the optimum working conditions of the parameter that affects the physical properties of concrete

mixtures. One of the advantages of Taguchi method over the conventional design, in addition to keeping the experiment cost at the minimum level, is that it minimizes the variability around the investigated parameters when bringing the performance value to

target value. Its other advantage is that the optimum working conditions determined by the laboratory work can also be reproduced in the real production environment.

A new method is established using taguchi method for determination of the optimum composition of material proportion and the effect of MIRHA properties and durability of foamed concrete. Lightweight Foamed Concrete (LWFC) consists of many components; it is critical to use a systematic approach to identify optimal mixes and investigate the most effective factors under a set of constraints (Fadhil and Ridho, 2009).

2.13.4 Effect of Used Engine Oil on MIRHA Concrete

Nuruddin, Shafiq, and Beddu, (2009) reported that the strength increment of MIRHA concrete is due to the high amorphous silica and fineness of MIRHA used. The effective burning method of UTP microwave incinerator adapted to produce amorphous silica in the rice husk ashes is instrumental in creating good quality MIRHA concrete. The addition of MIRHA causes an increment in the compressive strength. This is due to the capacity of pozzolan, consuming the calcium hydroxide generated during reactions of hydrated cement paste. The end product of the pozzolan reacts to the formation of C-S-H gel.

Compressive strength of concrete containing 0.15%-0.5% used engine oil that gives almost similar result and starts to decrease at 0.8% of usage. It was believed that the decrease of compressive strength due to the heavy metal content can delay the setting and lower the strength. Used engine oil can act as chemical plasticizer the same as superplasticizer to improve workability, air content and strength of MIRHA concrete. It was found that 0.5% inclusion of used engine oil demonstrated better concrete with respect to slump value, air content and compressive strength compared to MIRHA control mix.