PROPERTIES OF CONCRETE CONTAINING RICE HUSK ASH UNDER AGGRESSIVE ENVIRONMENTS SUBJECTED TO WETTING AND DRYING

by

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SIFAT-SIFAT KONKRIT YANG MENGANDUNGI ABU SEKAM PADI DI BAWAH PERSEKITARAN AGRESIF MELALUI PELEMBAPAN DAN PENGERINGAN

oleh

RAMADHANSYAH PUTRA JAYA

Tesis yang diserahkan untuk

Memenuhi keperluan bagi

Doktor Falsafah

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This thesis is dedicated to may beloved

Father (Drs. Abdullah Bin Abdul Aziz, M.Pd)

Mother (Asiyah Binti A. Rahman, A.Md.Pd)

Wife (Siti Jamaliah Binti Su'ud Mujana, S.ST)

Sister (Dewi Sri Jayanti Binti Abdullah, S.T., M.Sci)

Parents-in-law (Su'ud Mujana and Musrifah binti Sarip)

and other tsunami victims in Aceh

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LIST OF ABBREVIATIONS

ASTM	American Society of Testing and Materials
BET Apparatus	Brunauer, Emmetl, and Teller Apparatus
BS EN	British European Standards Specifications
C-H	Calcium Hydroxide
C-S-H	Calcium Silicate Hydrate
DTA	Differential Thermal Analysis
FESEM	Field Emission Scanning Electron Microscopy
LOI	Loss On Ignition
C-A-H	Calcium Aluminate Hydrate
OPC	Ordinary Portland Cement
RCPT	Rapid Chloride Permeability Test
RHA	Rice Husk Ash
RMT	Rapid Migration Test
SiO_2	Silica Oxide
TGA	Thermo-gravimetry Analysis
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

SIFAT-SIFAT KONKRIT YANG MENGANDUNGI ABU SEKAM PADI DI BAWAH PERSEKITARAN AGRESIF MELALUI PELEMBAPAN DAN PENGERINGAN

ABSTRAK

Sekam padi merupakan sisa pertanian daripada kilang beras yang dibakar pada suhu 700 °C selama 6 jam di dalam relau bagas. Abu sekam padi (RHA) dikisar menggunakan pengisar bebola makmal dengan bebola porcelain. Masa optimum pengisaran RHA telah ditentukan. Sebanyak 8 gred kehalusan RHA telah dikaji. Hasil kajian menunjukkan bahawa graviti tentu dan kehalusan RHA meningkat seiring dengan peningkatan masa pengisaran. Walaubagaimanapun, morfologi RHA akan berubah ekoran daripada pengisaran. Masa optimum pengisaran adalah kira-kira 90 minit (sehingga 9.25 μm saiz partikal) dengan peningkatan kekuatan mampatan dan indeks aktiviti kekuatan yang signifikan. Pengunaan Abu sekam padi yang dikisar selama 90 minit akan menghasilkan campuran konkrit yang kuat dan keliangan yang rendah. Selain itu, kesan pendedahan konkrit campuran abu sekam padi kepada 5% sodium klorida, 5% sodium sulfat dan air laut melalui pelembapan dan pengeringan berulang turut diujikaji. Sebanyak empat tahap penggantian RHA telah dikaji iaitu 10%, 20%, 30% dan 40% daripada berat simen. Ketahanlasakan simen campuran RHA yang didedahkan kepada persekitaran agresif telah diujikaji melalui kekuatan mampatan, *Rapid Chloride Penetrability Test* (RCPT) dan *Rapid Migration Test* (RMT). Tambahan pula, perubahan mikrostruktur yang berlaku dalam spesimen ekoran daripada kesan persekitaran agresif telah dikenalpasti melalui analisis termal, teknik XRD dan ujian SEM. Hasil kajian menunjukan abu sekam padi boleh digunakan sebagai bahan ganti di dalam simen untuk meningkatkan

ketahanlasakan konkrit. Konkrit yang menggandungi abu sekam padi sebagai bahan ganti menunjukan ketahanlasakan yang paling baik terhadap klorida, sulfat dan serangan air laut. Hasil ujikaji turut menunjukan kandungan $Ca(OH)_2$ didalam simen campuran abu sekam padi adalah lebih rendah daripada simen Portland disebabkan oleh reaksi pozallanik abu sekam padi. Gabungan ujian DTA/TGA, XRD dan analisis SEM mengesahkan kandungan *Friedels salt*, *Ettringite*, *Gypsum*, Kalsium Hidroksida, *Brucite* dan kandungan kimia yang lain di dalam spesimen.

PROPERTIES OF CONCRETE CONTAINING RICE HUSK ASH UNDER AGGRESSIVE ENVIRONMENTS SUBJECTED TO WETTING AND DRYING

ABSTRACT

Rice husk which is agro waste from a rice mill was burned at 700 °C for 6 hours in a gas furnace. The rice husk ash (RHA) was grounded using a laboratory ball mill with porcelain balls. The optimum RHA grinding time was determined. Eight different fineness grades of RHA were examined and it was found that the specific gravity and the fineness of the rice husk ash increase with an increase in grinding time. Even though, the morphology of the RHA changed with grinding. There appears to be an optimum grinding time of approximately 90 min (to 9.52 μm particle size), during which time the compressive strength and strength activity index increases significantly. The use of rice husk ash grounded for 90 min produced concrete with good strength and low porosity. On the other hand, the effect of ground RHA blended cement subjected to 5% sodium chloride solution (NaCl), 5% sodium sulfate solution (Na_2SO_4), and seawater through cyclic wetting and drying was also investigated. Four RHA replacement levels were considered in the study: 10%, 20%, 30%, and 40% by weight of cement. The durability performance of the RHA blended cement exposed to aggressive environment was evaluated through compressive strength, Rapid Chloride Penetrability Test (RCPT), and Rapid Migration Test (RMT). In addition, microstructural changes that occur in specimens due to aggressive environmental effects were identified through thermal analysis, XRD techniques, and SEM. Test results showed that RHA can be satisfactorily used as a cement replacement material in order to increases the durability of concrete.

Concrete containing 10% and 20% RHA replacements showed excellent durability to chloride, sulfate, and seawater attack. Test results also indicate that the amount of $Ca(OH)_2$ in the RHA blended cement was lower than that of Portland cement due to the pozzolanic reaction of RHA. Finally, the combination of DTA/TGA, XRD and SEM analysis leads to the positive identification of Friedels Salt, Ettringite, Gypsum, Calcium Hydroxide, Brucite, and other chemical substance formations in specimen.

CHAPTER 1

INTRODUCTION

1.1 Background

Over the years, there has been an increase in the use of industrial, agricultural, and thermoelectric plant residues in the production of concrete (Bharatkumar et al., 2005). Different materials with pozzolanic properties such as fly ash (FA), condensed silica fume, blast-furnace slag, and rice husk ash (RHA) have played an important part in concrete production (Giaccio et al., 2007). The most common pozzolan is the RHA, which is widely used in the concrete works (Rodríguez de Sensale, 2006). For instance, the utilization of RHA as a pozzolanic material facilitates the improvement of the strength and durability of cement and concrete. The addition of pozzolan decreases the formed CH by the pozzolanic reaction to produce more C-S-H gel that can improve the strength and durability of concrete (Aziz et al., 2005). A pozzolanic reaction occurs when a siliceous or aluminous material get in touch with calcium hydroxide in the presence of humidity to form compounds exhibiting cementitious properties (Papadakis and Tsimas, 2002).

In the cement hydration development, the calcium silicate hydrate (C-S-H) and calcium hydroxide ($Ca(OH)_2$, or CH) are released within the hydration of two main components of cement namely tricalcium silicate (C_3S) and dicalcium silicate (C_2S) where C, S represent CaO and SiO_2 (Omotosoa et al., 1995). According to Bishop (2001), as reported by Naji Givi et al, (2010), in the first few minutes of hydration, the aluminum and iron phases react with gypsum to form an amorphous gel at the surface of the cement grains and short rods of ettringite grow. During the period from

3 to 24 hours, about 30% of cement reacts to form calcium hydroxide and C–S–H (Villar-Cociña et al., 2003). After 10 hours hydration, C_3S has produced "outer C–S–H," which grows out from the ettringite rods rather than directly out from the surface of the C_3S particles (Kassim et al., 2004). At 18 hours of hydration, C_3A continues to react with gypsum, forming longer ettringite rods (Tamtsia et al., 2004). After 1–3 days of hydration, C_3A reacts with ettringite to form some monosulfate. "Inner C–S–H" continues to grow near the C_3S surface. Finally, after 2 weeks of hydration, the gap between the "hydrating shell" and the grain is completely filled with C–S–H (Englehardt et al., 1995). The original, "outer C–S–H" becomes more fibrous (Omotoso et al., 1998). Figure 1.1 shows the various reaction mechanisms involved in the hydration of cement. By adding pozzolanic material (i.e. RHA) to concrete mix, the pozzolanic reaction will only start when CH is released. As a result, the pozzolanic material will produce a C-S-H altogether with calcium aluminate hydrate (C-A-H) which are so called cement gels, that form the hardened cement paste (Villar-Cociña et al., 2003). The reaction between RHA and CH could also occur in blended cement containing other pozzolanic materials. The lowering effect of CH indicates that there exists the CSH gel formed in the pozzolanic reaction (Isaia et al., 2003).

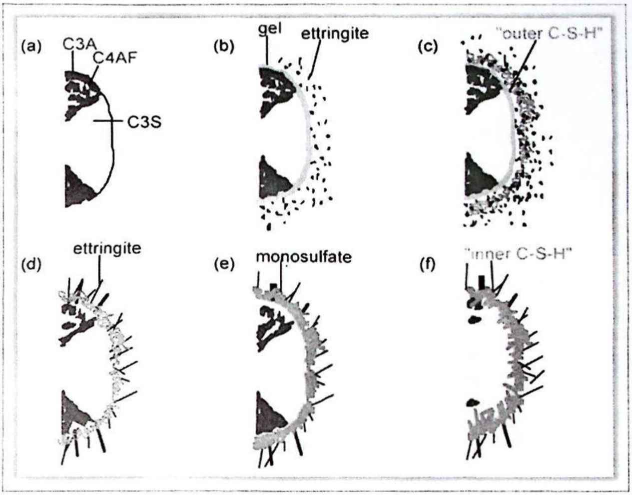

Figure 1.1: Reaction mechanism hydration of cement: (a) few minutes of hydration; (b) hydration after 10 minutes; (c) 10 hours; (d) 18 hours; (e) 1–3 days, and (f) 2 weeks (Bishop, 2001).

Previous studies have shown that the long-term performance of concrete can be improved through the incorporation of supplementary cementitious material (Saraswathy and Song, 2007). According to Roy et al. (2001), there is a slower rate of sulfate attack on concrete that contains pozzolanic materials. Chindaprasirt et al. (2008) reported that chloride-induced corrosion resistance of concrete is significantly improved with the use of RHA. It is universally accepted that concrete incorporated with pozzolanic materials and exposed to aggressive solutions, like chloride and sulfate, exhibit a substantial increase in durability due to the reduced amount of larger pores (Hussain, 1999; Dotto et al., 2004; Memon et al., 2002). When pozzolanic materials are added, calcium hydroxide $Ca(OH)_2$ is transformed into secondary calcium silicate hydrate (C-S-H) gel (Binici et al., 2008), transforming the larger pores into finer ones as a result of pozzolanic reaction of the mineral admixtures (Ahmed et al., 2009). The knowledge on the use of pozzolanic materials to increase the resistance of concrete to harmful solutions, especially chloride and sulfate solutions is beneficial to the understanding of the mechanism and the applications of these materials (Ferreira et al., 2004).

The durability of concrete under an aggressive environment has drawn the attention of engineers and scientists for over a century. According to Hekal et al. (2002) and Zacarias (2007), concrete structures exposed to severe conditions can be affected by three factors: (1) environmental conditions, such as freezing and thawing, wetting and drying, and temperature; (2) chemical attack, i.e., type of salt, concentration, and presence of more than one kind of aggressive ions; and (3) factors related to concrete properties, such as type of Portland cement (PC), water to binder ratio, etc. However, the most severe deterioration generally occurs in the wetting and drying cycle (Kaushik and Islam, 1995; Memon et al., 2002; Zuquan et al., 2007).

Cyclic wetting-drying causes continuous moisture movement through concrete pores (Sahmaran et al., 2007). This cyclic effect accelerates durability problems because it subjects the concrete to the motion and accumulation of harmful materials, such as sulfates, alkalies, acids, and chlorides. According to Hong (1998) stated that cyclic wetting and drying can increases the concentrations of ions i.e. chlorides, by evaporation of water. The drying of the concrete also helps to increase the availability of the oxygen required for steel corrosion, as oxygen has a substantially lower diffusion coefficient in saturated concrete. In fact diffusion of oxygen through air can be as high as 10,000 times the diffusion of oxygen in water (Islam et al., 2010). As the concrete dries and the pores become less saturated, oxygen will have a better chance to diffuse into the concrete and attain the level necessary to induce and sustain corrosion. For example, as illustrated in Figure 1.2, concrete structures subjected to seawater with wetting and drying exposure are most prone to deterioration, compared to concrete structures permanently submerged in seawater. In this case there is an increased availability of oxygen that also contributes to the deterioration compared to the submerged part of the structure. As well, for the concrete that is fully submerged, less chloride would enter the concrete as the dominant penetration mechanism is diffusion through the pore solution. There are several factors that can affect the degree that chlorides will enter concrete through cyclic wetting and drying. The ingress of chlorides into concrete is strongly influenced by the sequence of wetting and drying, and on the duration. Specifically, the degree of dryness is very important, and therefore the drying conditions.

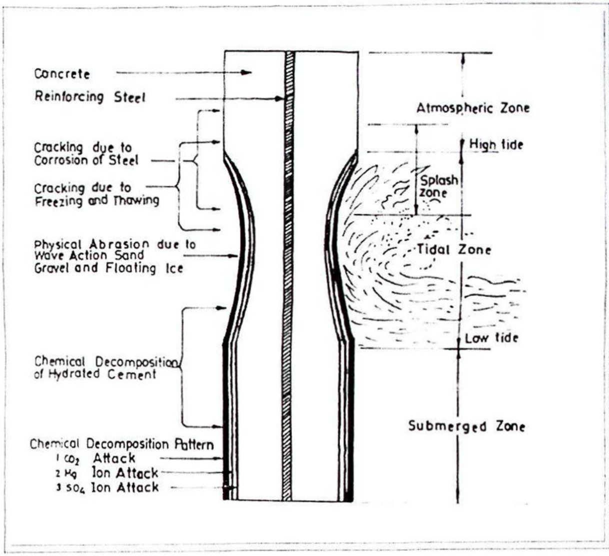

Figure 1.2: Deterioration of concrete in cyclic wetting-drying (Islam et al., 2010)

In view of all the above mentioned phenomena, it is clear that the cyclic wetting and drying is a main problem for concrete structures when exposed to an aggressive environment, such as chloride containing environment, sulfate containing environment, and seawater environment. Thus, this is the focus of the current research.

1.2 Problem statement

The durability of concrete is a major concern in the construction industry across the world. It is well known that aggressive environments are the major factor affecting the durability of concrete (Zuquan et al., 2007). The early failure of concrete may be caused by external factors or by a variety of internal causes. External factors may be due to physical or chemical in nature (cracking, strength, porosity, permeability, etc.), such as weathering, extreme variation of temperatures, wetting and drying cycles, abrasion, and also exposure to aggressive environment (Memon et al., 2002 and Hekal et al., 2002). Internal causes may be related to the choice of materials or inappropriate combination of materials (Ganjian and Pouya, 2009). However, the most aggressive chemicals that affect the durability of concrete are chlorides and sulfates with their associated cations. The chloride dissolved in water increases the rate of leaching of calcium hydroxide and thus increases the porosity and capillary absorption of concrete, and leads to loss of stiffness and strength. Calcium, sodium, magnesium, and ammonium sulfates are (in increasing order) harmful to concrete as they react with hydrated cement paste leading to expansion, cracking, spallings and loss of strength (Wee et al., 2000b). Research on the durability is still in progress. However, various parameters, i.e., cement type, cement compositions, mineral admixtures, etc., and have been thoroughly investigated in the past (Skalny et al., 2003). On the other hand, several parameters, such as chloride and sulfate concentrations, temperature, wetting and drying cycles, heating and cooling cycles, etc. need further investigation (Santhanam et al., 2001 and Sahmaran et al., 2007).

Further, in response to the demand of higher strength development in later part of the 20^{th} century, the cements produced have increased contents of C_3S, C_3A, and also higher fineness, and such cements suffer from both workability and durability problems (Aitcin and Neville 2003). Therefore, durability of concrete structures built today is compromised; consequently, the use of pozzolanic materials in modern cements makes the concrete durable. Pozzolans reduces or completely eliminates the calcium hydroxide, available from the hydration of cement by forming secondary calcium silicate hydrate gel making the concrete dense. Most of previous works (Wee et al., 2000; Al-Amoudi, 2002; Nehdi and Hayek, 2005) concentrated on concrete incorporated with supplementary cementitious materials, i.e., FA, blast-furnace slag, palm oil fuel ash (POFA), and silica fume exposed to aggressive environment. But, very limited information is available on concrete containing RHA subjected specifically to sodium chloride solution, sodium sulfate solution, and aggressive seawater as well as wetting and drying cycles. Moon et al. (2007) reported that RHA as cement replacement can enhance the strength and durability of concrete. Therefore, it is important to study the properties of concrete containing RHA under aggressive environments subjected to wetting and drying cycles. In addition, no research has been conducted to evaluate the effect of pozzolanic materials in concrete exposed to marine environment with high humidity and to the tropical climate of South East Asia, especially in Malaysia. In this regard, the main objective of this research is to study the effects of RHA waste as a supplementary cementitious material on durability performance of concrete exposed to aggressive chemicals, such as chloride solution, sulfate solution, and aggressive seawater environment. The properties investigated are compressive strength, chloride permeability and chloride penetration depths. Furthermore, thermal analysis, X-ray diffraction and microstructure of concrete were also studied.

1.3 Objectives

This research was carried out and designed based on four main objectives. The detailed objectives are outlined below:

1. To determine the optimum grinding time and to investigate the influence of grinding time on the chemical and physical properties of RHA
2. To evaluate the performance of RHA-blended cement concrete with different percentages of cement replacement and subjected to aggressive sodium chloride solution with wetting and drying cycles
3. To assess the performance of RHA-blended cement concrete exposed to sodium sulfate solution with wetting and drying cycles
4. To investigate the effect of RHA-blended cement concrete subjected to aggressive seawater with wetting and drying cycles

1.4 Scope of study

Normal strength concrete containing ordinary Portland cement (OPC) has been designed and prepared through a series of trial mixes to achieve a minimum compressive strength of 40MPa at the age of 28 days. Furthermore, the RHA replacement levels of 10%, 20%, 30%, and 40% were used to replace OPC on mass-for-mass basis. The experimental program involved studying the characteristics of raw materials in terms of their physical properties, chemical compositions, particle morphology, and phase identification. In addition, the effects of grinding time on the chemical and physical properties of RHA and the effect of fineness of RHA on the compressive strength, strength activity index, porosity, and permeability of RHA concrete, were also investigated. Laboratory testing was conducted to study the effects of sodium chloride (NaCl), sodium sulfate (Na_2SO_4), and aggressive seawater on the durability of Portland cement concrete containing RHA with repetitive wetting and drying cycles.

1.5 Layout of thesis

The thesis consists of eight chapters:

Chapter one discusses on the background of the study with a short overview of the present research and the problem statement. Several research needs are also identified. This chapter also provides the research objectives and briefly presents the scope of study.

In chapter two presents a background of the pozzolanic materials used, highlights their performance in concrete durability, and describes various aggressive chemical solutions, such as chloride solution, sulfate solution, and aggressive seawater in relation to concrete.

Chapter three provides an overview of the research program, describes the preparation and testing of aggregate, discusses the selection and testing of constituent materials, and highlights the procedures for experimental investigation, test apparatus, and mixture design.

In chapter four presents the preparation of pozzolanic materials and the grinding of RHA to different degrees of fineness. The effects of various degrees of fineness on the chemical and physical properties are also highlighted. Additionally, the chapter discusses the significance of these results and determines the optimum grinding of RHA.

Chapter five discusses the influences of different replacement levels of RHA-blended cement exposed to sodium chloride with wetting and drying cycles. The test results are highlighted.

Chapter six presents the test results and analyzes the effects of exposure of sodium sulfate on concrete containing RHA. This chapter also focuses on the wetting and drying cycles in comparison with the performances of OPC and RHA under sulfate attack.

Chapter seven presents and discusses the performance of OPC and RHA-blended cement subjected to seawater. Moreover, the chapter focuses on the wetting and drying cycles and highlights the importance of these results.

Finally, chapter eight provides a summary of the research findings, presents the contributions, and offers several recommendations for future study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Concrete is made of the basic ingredients of hydraulic cement, namely, Portland cement, mineral aggregates, and water (Mehta and Monteiro, 2006). Usually, in concrete, pozzolanic materials such as silica fume, fly ash (FA), metakaolin (MK), blast-furnace slag, RHA, etc. are used to improve the performance and durability of Portland cement concrete. This clearly indicates a positive added high value from the use of the materials (Akyuz and Pekmezci, 2002).

In the past, Giaccio et al. (2007) reported that the use of RHA as a mineral admixture for concrete is not new and considerable amount of data has been published with regard to its influence on the behavior of concrete. RHA, which is rich in silica, is obtained by burning rice husks to remove volatile carbons such as cellulose and lignin. Della et al. (2002) reported that for incineration temperatures of up to 700 °C for 6 hours, 95% silica powder, predominantly in amorphous form, could be produced. It is generally agreed upon that the use of RHA whose main chemical composition of which is silica, helps to improve the durability of concrete especially when exposed to chloride and sulfate attacks (Gastaldini et al., 2007; Saraswathy and Song, 2007).

This chapter reviews the performance of pozzolanic materials when used as partial cement replacement, and how they affect the properties of concrete. The effect of grinding on the physical and chemical properties of RHA is also reviewed. In addition, the laboratory simulation of the wetting and drying cycles that affect concrete structures are also discussed. The durability of concrete (i.e., resistance to chloride attack, sulfate attack, and aggressive seawater) made with the pozzolanic materials and other related topics from the literature are reviewed.

2.2 Pozzolanic materials used in cement and concrete

Pozzolanic materials are well known for their capability to modify the physical and mechanical properties of cement and concrete. Pozzolanic materials such as FA, silica fume, and RHA, which are mainly silicates when added to cement, react with $Ca(OH)_2$ to form additional calcium silicate hydrates in the hydrated cement matrix (Ordóñes et al., 2002). Romano et al. (2007) reported that calcium silicates (Ca_3SiO_5) are the most important components of pozzolanic materials and are responsible for most of concrete properties such as mechanical performance and durability. It was reported that the added pozzolanic materials, which are finer than cement particles, fill the pores and improve the particle packing of cement paste in the transition zone between aggregates and cement paste, leading to the reduction of permeability (Bui et al., 2005). When fine pozzolanic particles are dispersed in the paste, they generate a large number of nucleation sites for the precipitation of the hydration products. This mechanism makes the paste more homogeneous and dense as for the distribution of the fine pores (Antonovich and Goberis, 2003). On the other hand, the addition of pozzolanic materials to Portland cement increases its mechanical strength and durability when compared to the controlled specimen. Furthermore, the physical action of the pozzolanic materials provides a denser, more homogeneous and uniform paste (Morsy and Shebl, 2007).

2.3 Rice-Husk Ash (RHA)

RHA is known to be superior to other supplementary materials such as; slag, palm oil fuel ash (POFA), silica fume, and fly ash (FA). Due to its high pozzolanic activity, both strength and durability of concrete are improved (Muthadhi et al., 2007). During the past decades, extensive research has been carried out to investigate the performance of RHA in relation to the properties of concrete. Several research groups studied the effects of RHA on fresh concrete (Nehdi at al., 2003; Bui et al., 2005; Naji Givi et al., 2010). Bui et al. (2005) studied the property of fresh concrete incorporated with RHA at replacement levels from 10% to 20% and water cement ratio of 0.34. They concluded that slump value of the RHA-blended cement decreases significantly as the replacement levels of RHA increases. Other research groups focused on the behavior of RHA-blended cement in hardened concrete (Singh et al., 2002; Jaturapitakkul and Roongreung, 2003; Sakr, 2006; Gastaldini et al., 2007). Saraswathy and Song (2007) reported the compressive strength of concrete in which cement was partially replaced with RHA. Percentage replacements were 0%, 5%, 10%, 15%, 20%, 25%, and 30%. They concluded that compressive strength increases when RHA content increases. In most cases, all the RHA-replaced cement concrete exhibit higher compressive strength than the OPC concrete.

2.4 Mechanism of rice husk ash in cement concrete

The RHA mainly serves as a microfiller, pozzolan, and viscosity modifier. The addition of pozzolanic materials (i.e. RHA) decreases the formed calcium hydroxide by the pozzolanic reaction to produce more calcium silicate hydrate gel that can improve the strength and durability of concrete (Aziz et al., 2005). Yu et al. (1999) found that the amount of calcium hydroxide by 30% replacement RHA in cement paste begins to decrease after 3 days, and by 91 days it reaches nearly zero, while in the OPC paste, it is considerably enlarged with hydration time. In another study, Safiuddin (2008) reported that the RHA particles can fill the voids between the larger cement grains because of their smaller size, as shown in Figure 2.1. However, the microfilling ability of RHA is not as effective as silica fume. This is due to the RHA particles are much larger than the silica fume particles (Nehdi et al., 2003).

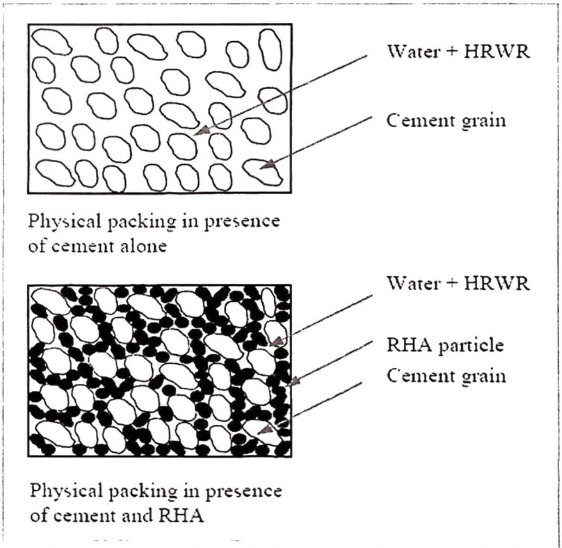

Figure 2.1: Microfilling effect of RHA (Safiuddin, 2008)

In the presence of water, the RHA actively reacts with $Ca(OH)_2$ liberated during cement hydration (pozzolanic reaction) and produces additional calcium silicate hydrate (CSH). The reaction can be formulated as follows:

Hydration reaction: C_2S or $C_3S + H_2O \rightarrow$ primary CSH + $Ca(OH)_2$ (2.1)

Pozzolanic reaction: $Ca(OH)_2$ + RHA (SiO_2) + $H_2O \rightarrow$ secondary CSH (2.2)

The pozzolanic reaction product fills the pores existing between cement grains and results in dense calcium silicate hydrate, as shown in Figure 2.2. Both microfilling and pozzolanic effects of RHA play an important role to refine the pore structure in bulk paste matrix and interfacial transition zone of concrete. The pore refinement occurring due to the secondary reaction between RHA and $Ca(OH)_2$ makes the microstructure of concrete denser and improves the interfacial bond between aggregates and binder paste. As a result, the strength, transport properties and durability of concrete are improved.

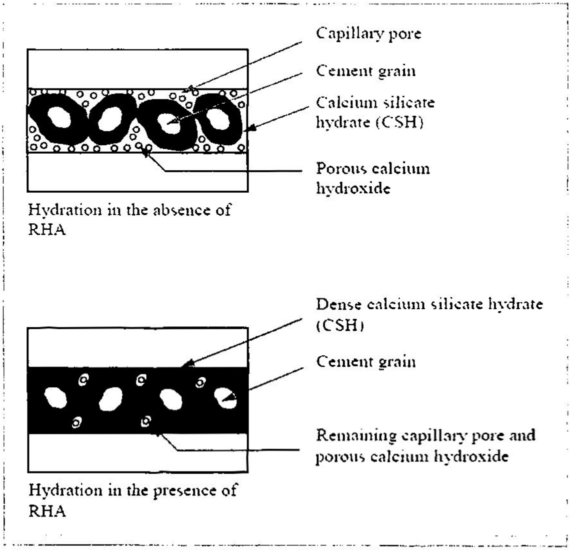

Figure 2.2: Pozzolanic effect of RHA (Zhang and Malhotra, 1996)

2.5 Grinding of rice husk ash

The burning of rice husk under controlled temperature produces a highly reactive RHA (Chindaprasirt et al., 2008). Reactivity is enhanced by increasing the fineness of the reacting materials (Asavapisit and Ruengrit, 2005). Nevertheless, the reactivity of RHA is attributed to its high content of amorphous silica and its porous nature (Prasad et al., 2001). According to Rukzon and Chindaprasirt (2008a), the properly burnt and ground RHA are also factors affecting the blended cement of concrete. In addition, Chandrasekar et al. (2003) stated that RHA, being porous in nature, has an extremely high surface area while its average size remains fairly high. Conversely, compared to silica fume with average particle size of 0.1μm, RHA has three times the surface area, with particle size of approximately 45μm (Rukzon and Chindaprasirt, 2008b). Habeeb and Mahmud (2010) also reported that grinding RHA to finer average particle size has slightly increased its specific surface area.

Previous studies showed that grinding of pozzolanic material, such as FA and RHA, into a high degree of fineness is the major factor affecting compressive strength of cement concrete (Kiattikomol et al., 2001; Jaturapitakkul et al., 2004; Paya et al., 2003). Bui et al. (2005) also reported that at a certain stage of RHA grinding, the porous structure of the particles would collapse, resulting in reduced surface area. Grinding medium and grinding time may be conveniently adopted as RHA is highly fragile and porous (Bouzoubaâ and Fournier, 2001).

Most previous studies focused on the effect of RHA or flay ash fineness on cement paste, concrete, or mortar. However, very limited information is available on the effect of grinding on the chemical and physical properties of RHA. The chemical effect is related to the fact that when produced by controlled combustion it is a highly pozzolanic material which combines quickly with calcium hydroxide forming a secondary C–S–H. The physical effect is linked to particle size, which produces a refinement on the pore structure, acts as nucleation point for hydration products, and restricts the growth of crystals generated in the hydration process. Furthermore, the performance of RHA blended cement concrete depends on various rice husk ash properties such as fineness, shape, particle size distribution, and chemical composition. This is why the present study is aimed at investigating the suitability of local agricultural (RHA) as partial replacement of cements in order to produce concrete which is not only potentially cost effective but also exhibits high performance against aggressive environmental conditions.

2.6 Cyclic Wetting and Drying

Cyclic wetting and drying process accelerate durability problem because it subjects the concrete to the movement and accumulation of harmful materials, such as sulfates, alkaline, acids, and chlorides. This cyclic action can increase the rate of corrosion in reinforced concrete structures (Hong and Hooton, 1999). Cyclic wetting and drying is a problem for reinforced concrete structures exposed to chlorides, such as: (i) marine structures, particularly in the splash and tidal zones; (ii) parking garages, in areas exposed to deicer salts; and (iii) highway structures, such as bridges and other elevated roadways. Six mechanisms govern chloride ingress into concrete (Hong and Hooton, 1999): absorption, diffusion, chloride binding, permeation, wicking, and dispersion. For structures exposed to cyclic wetting and drying, absorption and diffusion are two of the most significant mechanisms. Generally, cyclic wetting and drying allows for deeper penetration of aggressive ions, and can lead to corrosion rates 20 times higher than the rate achieved by exposure to a continuous immersion (McCarter and Watson, 1997).

2.7 Laboratory simulation of wetting and drying cycles

According to Ganjian and Pouya (2009), continuous immersion of specimens does not necessarily represent the field conditions because generally, the concentration and pH of the site generally remains constant. Conversely, simulated field exposure conditions in the laboratory with the application of wetting and drying cycles are common methods of accelerating the tests (Aköz et al., 1999; Santhanam et al., 2002; Zuquan et al., 2007).

Hekal et al. (2002) investigated the sulfate resistance of hardened blended cement pastes subjected to 10% $MgSO_4$ solution under different exposure conditions. They concluded that only the method based on drying-wetting cycles can be considered as an accelerated method. In another study, Polder and Peelen (2002) investigated the performance of concrete containing fly ash and blast furnace slag exposed to 3% NaCl solution with cyclic wetting and drying test. In their methodology, the specimen was divided into two groups. One group was continuously cured under chloride solution for up to 26 weeks while the second group was exposed to 24 hours of wetting and six days of drying. Tests for compressive strength and chloride penetration were conducted. They found that the specimens are highly affected by the wetting-drying exposure. Sahmaran et al. (2007) investigated the sulfate resistance of plain and blended cements exposed to three different conditions in laboratory simulation: (i) continuous curing in lime-saturated water; (ii) continuous exposure to 5% Na_2SO_4 solution; and (iii) subjected to 5% Na_2SO_4 solution in which the cycles consisted of wetting and drying. The blended cements used were BC (lower amount of pozzolans), BC-N (higher amount of natural pozzolan) and BC-F (higher amount of fly ash). The compressive strength tests were conducted up to 52 weeks. The results are shown in Table 2.1. The researchers found that when subjected to the cyclic sulfate exposure, all specimens display a similar behavior: compressive strength of specimens initially increases, then begins to decrease leading to eventual disintegration of the specimens in less than 17 weeks.

Table 2.1: Compressive strength of cements subjected to different curing conditions (Sahmaran et al., 2007)

Test age (weeks)	**Compressive strength (MPa)**			
	BC-N	**BC-F**	**BC**	**OPC**
Condition 1 - continuous immersion at 23 °C in lime-saturated water				
0	19.5	19.5	21.9	23.8
4	31.4	34.7	47.3	51.4
17	38.8	40.4	49.0	55.7
26	44.0	44.4	50.2	58.7
52	49.6	55.6	59.9	71.1
Condition 2 - continuous immersion at 23 °C in 5% Na_2SO_4 solution				
0	19.5	19.5	21.9	23.8
4	40.1	39.5	46.4	45.9
17	43.2	42.4	46.3	54.3
26	40.0	45.2	46.8	49.2
52	43.3	48.4	53.0	33.1
Condition 3 – 6 days immersion at 23 °C in 5% Na_2SO_4 solution and 1 day drying at 100 °C in oven				
0	19.5	19.5	21.9	23.8
1	36.7	29.8	32.0	48.0
4	39.6	37.5	39.2	63.2
8	16.2	23.9	43.5	59.4
13	*	*	29.3	49.1
17	*	*	*	39.9

**specimens disintegrated at this age*

2.8 Mechanism of chloride attack

It is well known that the ingress of chloride ions in concrete is the most severe problem affecting the durability of concrete constructions. The present of chloride in concrete may come from several different sources (Csizmadia et al., 2001), as shown in Figure 2.3. Soluble chlorides may be introduced in the fresh concrete by aggregates containing chlorides (Angst et al., 2011). Saline water is sometimes used as concrete mixing water (Zhang et al., 1999b). Calcium chloride, which contains chloride, may be used as an accelerator or a concrete admixture (Hong and Hooton, 2000). Chloride may also penetrate into concrete from the environment, such as deicing salt, seawater, etc. (Xu et al., 2009). Chloride reacts with cementitious phases to form a calcium chloroaluminate hydrate (Zuquan et al., 2007). According to Asrar et al. (1999), chlorides may either be chemically bound in compounds like Friedels salt ($Ca_3Al_2O_6 \cdot CaCl_2 \cdot 10H_2O$), which is in equilibrium with a constant chloride concentration, or be physically adsorbed on to, for instance, the amorphous calcium silicate hydrate (C-S-H) gel.

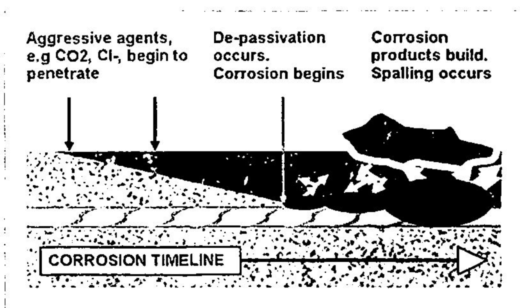

Figure 2.3: Chloride attack on concrete (Xu et al., 2009)

2.9 Effect of chloride solution in pozzolanic materials

The partial substitution with pozzolanic materials such as RHA, POFA, and FA, the main chemical composition of which is silica, helps to improve the durability of concrete especially when exposed to chloride attack (Papadakis, 2000; Isgor and Razaqpur, 2004; Chindaprasirt et al., 2007b). Chindaprasirt et al. (2008) investigated the resistance to chloride penetration of concrete made with 20% and 40% POFA, RHA, and FA as partial replacements of cement. The water cement ratio was kept constant at 0.50 and the workability was maintained at 110 mm with the aid of superplasticizer. RHA was obtained by open burning in a small heap with the maximum temperature of 650 °C. Ground POFA and ground RHA were obtained by ball mill grinding up to 45 μm. In their technique, the concrete specimens were immersed in 3% NaCl solution up to 30 days. They concluded that POFA, RHA, and FA can be used as pozzolans to replace part of Portland cement with good resistance to chloride penetration.

Sekar and Sarasvathy (2008) studied the performed and characteristic of fly ash and micro silica in the concrete structures with respect to corrosion rate. They used 0%, 20%, 25%, 30%, 35%, and 40% of fly ash as cement replacement. Water cement ratio was maintained at 0.55. In their method, 100×100×100 mm cubes were prepared and immersed in 5% H_2SO_4 and $MgCl_2$ for a period of 28 days. The compressive strength results after immersion in aggressive environment are given in Table 2.2. In their observation, there were no changes in compressive strength for the replacements up to 40% compared with OPC concrete.

Table 2.2: Compressive strength of fly ash blended concrete subjected to 5% H_2SO_4 and 5% $MgCl_2$ (Sekar and Sarasvathy, 2008)

Replacement of fly ash (%)	Compressive strength (MPa)		
	Water curing	Immersion in H_2SO_4	Immersion in $MgCl_2$
0	37.5	35.5	37.0
20	39.0	38.0	39.5
25	41.5	39.5	40.5
30	42.5	40.5	42.0
35	39.5	34.0	39.5
40	30.5	32.5	34.5

According to Prasad et al. (2006), the best qualifying parameters for testing aggressive chemical attack are based on chemical analysis, reduction in strength, and loss of weight of specimen. In this relation, Al-Amoudi et al. (1994) investigated the strength reduction in plain and blended cements exposed to chloride-sulfate environments. Pozzolanic materials namely blast furnace slag, silica fume and FA were partially replaced with OPC at 70%, 10%, and 20%, respectively. After casting, the specimens were covered with wet hessian for 24 hours prior to demoulding. Subsequently, the specimens were cured in water for a period of 14 days and then immersed in 15.7% NaCl + 2.1% Na_2SO_4 for 90, 180, and 365 days. They found that the strength reduction of concrete containing blast furnace slag, silica fume, and FA are 45%, 40%, and 16%, respectively.

There are several ways of determining chloride ion penetration in concrete specimens. However, several researchers (Wee et al. 2000a; Suryavanshi et al. 2002; Hale et al. 2002) have focused their attention on determining the permeability of concrete to chloride ions using a short-term test such as the rapid chloride permeability test (RCPT). According to ASTMC1202-10, RCPT measures the charge passed through the specimen expressed in units of Coulombs which is then related to chloride permeability of concrete. The RCPT method has been used to investigate the effect of pozzolanic materials on resistance to chloride ion penetration (Jiang et al. 2004; Mackechnie and Alexander, 2000).

Saraswathy and Song (2007) investigated the effect of RHA-blended cement concrete on chloride permeability. The cement was replaced with 5%, 10%, 15%, 20%, 25%, and 30% RHA. Test was conducted based on the ASTM C1202-94. In their technique, concrete specimens with diameter of 85 mm and thickness of 50 mm were cast and cured for 28 days. Results showed that rapid chloride permeability (charge passed) through concrete made with 0%, 5%, 10%, 15%, 20%, 25%, and 30% RHA are 1161, 1108, 653, 309, 273, 265, and 213 (in Coulombs), respectively. They concluded that replacement of RHA drastically reduces the Coulomb values. As per ASTM C1202, RHA reduces the rapid chloride penetrability of concrete from low to very low ratings and from higher to lower replacement levels. It can be said that from their study the replacement of rice husk ash refined the pores and thereby reducing the permeability.

Gastaldini et al. (2007) studied the influence of chemical activators on the chloride-ion permeability of concrete made with 20% RHA as a partial replacement of