EFFECTS OF SILICA FUME AND RICE HUSK ASH ON THE PROPERTIES OF CEMENT PASTE AND CONCRETE

BUN KIM NGUN

UNIVERSITI SAINS MALAYSIA

2008

EFFECTS OF SILICA FUME AND RICE HUSK ASH ON THE PROPERTIES OF CEMENT PASTE AND CONCRETE

by

BUN KIM NGUN

**Thesis submitted in fulfillment of the requirements
for the degree of
Master of Science**

May 2008

Saya isytiharkan bahawa kandungan yang dibentangkan di dalam tesis ini adalah hasil kerja saya sendiri dan telah dijalankan di Universiti Sains Malaysia kecuali dimaklumkan sebaliknya. Tesis ini juga tidak pernah disertakan untuk ijazah yang lain sebelum ini.

Disaksikan Oleh:

....

Tandatangan Calon | Tandatangan Penyelia/Dekan

Nama Calon: BUN Kim Ngun

ACKNOWLEDGEMENTS

Firstly, I would like to thank to my scholarship sponsor AUN/SEED-Net for its financial support during this master program. Meanwhile, thanks to Universiti Sains Malaysia (USM) and School of Materials and Mineral Resources Engineering (SMMRE) for their cooperation.

I would like to express my sincere appreciation to my supervisors Prof. Zainal Arifin Ahmad and Dr. Hasmaliza Mohamad (USM) for their supervisions, advices, encouragement and warm hospitality. Also, I would like to express my sincere acknowledgment to Prof. Prof. Etsuo Sakai, Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology, for his valuable comments. I would like to thank to my advisor Mr. Phat Boné, Institute of Technology of Cambodia, for his support.

Unforgettably, I would like to convey my special thanks to Dean, Deputy Dean, lecturers and all staffs of SMMRE for their kind assistants and supports. Thanks to Dean, senior lecture Dr. Megat Azmi b Megat Johari, Mr. Mohd Fadzil Arshad and all Concrete Laboratory's staffs of School of Civil Engineering for providing the facilities to conduct the research works and assistants.

Finally, I would like to express my highest gratitude to my mum, family, relatives and friends for their care and supports. I would like to dedicate my respect and appreciation to my late father whom spirit is always near me and takes care of me.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	:	American Society of Testing and Materials
BS	:	British Standard
C_3A	:	Tricalcium aluminate
C_4AF	:	Tetracalcium aluminoferrite
C_3S	:	Tricalcium silicate
C_2S	:	Dicalcium silicate
CH	:	Calcium hydroxide
CRHA	:	Cement paste or concrete which containing of RHA
CRS	:	Cement paste or concrete which containing of the combination of RHA and SF
CSF	:	Cement paste or concrete which containing of SF
C-S-H	:	Calcium Silicate Hydrate
DTA	:	Differential thermal analysis
FESEM	:	Field Emission Scanning Electron Microscopy
H	:	Water
LOI	:	Loss on ignition
MIP	:	Mercury intrusion porosimetry
OPC	:	Ordinary Portland cement
RHA	:	Rice husk ash
S	:	Silica
SF	:	Silica fume
TG	:	Thermogravimetry
XRD	:	X-Ray Diffraction
XRF	:	X-Ray Fluorescence

KESAN WASAP SILIKA DAN ABU SEKAM PADI KE ATAS SIFAT-SIFAT ADUNAN SIMEN DAN KONKRIT

ABSTRAK

Wasap silika (SF) dan abu sekam padi (RHA) merupakan bahan buangan daripada pertanian serta industri yang telah beberapa dekad digunakan sebagai bahan pozolanik ataupun bahan gantian simen dalam konkrit. Kajian ke atas pengaruh bahan-bahan ini dalam campuran sistem binari konkrit telahpun dijalankan oleh ramai penyelidik, namun kajian ini telah menekankan pada kesan gabungan kedua-dua bahan tersebut (sistem ternari) terhadap sifat-sifat konkrit. Kajian yang dijalankan adalah berkaitan dengan sifat adunan simen terkeras (hardened cement paste) dan kekuatan normal konkrit yang mengandungi SF dan RHA dalam kedua-dua sistem iaitu binari dan ternari. Tahap penggantian SF dan RHA yang digunakan dalam sistem binari ialah 10%, 15% dan 20%. Bagi sistem ternari pula, 15% telah dipilih dengan mempelbagaikan gabungan komposisi SF dan RHA. Adunan simen dicirikan dengan menentukan kandungan $Ca(OH)_2$ yang dianalisis secara terma, teknik XRD serta kajian mikrostruktur menggunakan SEM. Pencirian sifat-sifat konkrit pula dijalankan dengan menentukan kekuatan mampatan, keliangan dan penyerapan air, kebolehtelapan dan pengecutan pengeringan. Keputusan-keputusan menunjukkan pengurangan $Ca(OH)_2$ yang ketara telah berlaku pada kesemua campuran adunan simen. Penggunaan RHA dan SF dalam kedua-dua sistem binari dan ternari telah meningkatkan dengan ketara sifat-sifat konkrit berbanding campuran kawalan. Kesemua konkrit sistem ternari menunjukkan menunjukkan sifat-sifat yang lebih baik berbanding konkrit RHA serta menunjukkan sifat yang setara dengan konkrit SF. Kesimpulannya, penggantian 7.5% SF dengan RHA untuk

sistem ternari dapat memberikan sifat-sifat konkrit seperti kekuatan mampatan, keliangan, kebolehtelapan dan pengecutan pengeringan yang setara sebagaimana penggunaan 15% SF.

EFFECTS OF SILICA FUME AND RICE HUSK ASH ON THE PROPERTIES OF CEMENT PASTE AND CONCRETE

ABSTRACT

Silica fume (SF) and rice husk ash (RHA) are industrial and agricultural wastes which have been used in decades as pozzolanic materials or partial cement replacement materials in concrete. The influences of these materials in binary blended concretes had been conducted by various researchers but the effects of their combination (ternary) on the properties of concrete are yet to reveal. The investigation in this study deals with the properties of hardened cement paste and normal strength concrete containing SF and RHA in both binary and ternary systems. The replacement levels of 10%, 15% and 20% of SF and RHA are used in binary system. For ternary, 15% of the combination of both RHA and SF was selected. The cement pastes were characterized in terms of determination of $Ca(OH)_2$ content analyzed by thermal analysis and XRD techniques, and microstructure by SEM. While the concrete properties were carried out on compressive strength, porosity and water absorption, permeability and drying shrinkage. Results showed that the significant reduction of $Ca(OH)_2$ was found for all blended cement pastes. The RHA and SF used in both binary and ternary systems improved significantly the concrete properties compared to the control mix. All ternary concretes provide higher improvement of all concrete properties compared to RHA concretes and have similar properties compared to SF concretes. It could be conclude that the replacement of SF by 7.5% of RHA for the ternary concrete can get similar concrete properties such as compressive strength, porosity, permeability and drying shrinkage, as that using 15% SF.

CHAPTER 1

INTRODUCTION

1.1 General

Concrete is a predominant material used in construction. It has been traditionally considered as a composite material made with cement and possible mineral admixtures, aggregates and water. Cement is the essential binding agent in concrete which is the most widely used as construction material worldwide. However, in cement production, the carbon dioxide usually accompany with, which contributes to global warming. Agricultural waste (rice husk ash) and industrial by-product (silica fume) have been widely used as partial replacement materials or cement replacement materials in concrete works. The advantages by incorporating these supplementary cementing materials include energy consumption saving (in cement production), low cost, engineering properties improvement, and environmental conservation through reduction of waste deposit. Moreover, replacement of cement by these aforementioned materials can reduce of about 75 x 10^6 tons of CO_2 (considering a world production of about 1500 x 10^6 tons/year with emission of an average 1kg CO_2/kg cement) [Sharp, 2004]. Furthermore, these materials are used not only to reduce the quantity of cement required to achieve a given strength, but also to improve the properties and give durable concrete. Durability is linked to the physical, chemical and mineralogical properties of materials and permeability. Any improvement in these properties is likely to aid durability. Addition of a pozzolanic material to concrete mix may lead a considerable improvement in the quality of the concrete and its durability [Ali, 1987].

A pozzolanic material or pozzolan has been described as a siliceous or siliceous and aluminous material. At ordinary temperature and with the presence of moisture it chemically reacts with calcium hydroxide (lime) to form compounds possessing cementitious properties [Neville, 2002]. Rice husk ash (RHA) and silica fume (SF) are considered as rich-silica materials or pozzolanic materials used to replace a portion by mass basic of Portland cement in order to modify the physical and engineering properties of cement and concrete. When these materials blended with cement and in the presence of water, they can react with calcium hydroxide ($Ca(OH)_2$) which forms in hydrated Portland cement to produce additional calcium silicate hydrate (C-S-H). With the addition of the these pozzolanic materials, many aspects of concrete properties can be favorably influenced, some by physical effects associated with small particles which have generally a finer particle size distribution than ordinary Portland cement and others by pozzolanic and cementitious reactions resulting in certain desirable physical effects. Concrete mix proportion and rheological behavior of plastic concrete are caused by the physical effects associated with the particle size and morphology of pozzolans. Strength and permeability of hardened concrete are the main effects associated with the pozzolanic and cementitious reactions [Ali, 1987].

RHA and SF are waste materials derived from different sources. They contain similar chemical composition, usually high silica content in amorphous form, but they are differently, however, in terms of physical characteristics such particle size and particle morphology. Therefore, the influence of the two materials on the properties of hardened cement paste and concrete might be not the same even though they are used in the same range of partial replacement levels.

1.2 Problem statement

The reduction of the CO_2 emission and elimination of the lack of natural resources in cement production, the use of various waste materials as pozzolanic materials in concrete production is creating great interested to many researchers. Using these pozzolanic materials in concrete productions is not only to solve the environmental concern, but also to improve the engineering properties and durability of concrete. In concrete, the aggregate particles are held or linked together by a hardened cement paste. Therefore, the concrete and cement paste properties are interconnected to each other. To determine the features of concrete properties, it is necessary to know the features of hardened cement paste. Therefore, in order to get more understanding on the effects of pozzolanic materials in concrete, investigation on the characteristics of both hardened cement paste and concrete are necessary.

RHA and SF are agricultural and industrial wastes which have been used in decades as pozzolanic materials or partial cement replacement materials in concrete. SF is very common commercial material used in concrete production. Even though RHA has been used as cement replacement materials to improve mechanical properties of concrete such as strength and durability but very limited information of RHA on characteristics of hardened blended cement paste such as microstructure, porosity and pore size distribution, calcium hydroxide determination, and etc., and blended concrete properties compared to those of SF.

Research on the use of RHA in concrete is not new. In 1973, Mehta investigated the effect of pyro-processing on pozzolanic reactivity of RHA as reported by Nehdi (2003). Zhang (1996) found that it is possible to produce high strength concrete using fine enough RHA at an optimum replacement level. RHA and SF can be called pozzolanic or silica-rich materials which consist of high silica content and similar chemical composition but physically are different. Various works had been investigated of the individual effect (binary) and the combination of RHA and other materials (ternary) such fly ash on the engineering properties of concrete. But the ternary of blended RHA and SF is rarely seen in the literature review. Fortunately, Aminul (2007) had experimentally investigated the effect of ternary system of RHA and SF on the rheological properties of concrete. The investigation found that the combination of RHA and SF yield the most suitable rheological performance in moderating the plastic viscosity and low yield stress. Unfortunately, no investigation has been done on the effect of using ternary system of RHA and SF on the properties of hardened cement paste and concrete. Therefore, it is necessary to investigate the ternary system of RHA and SF on the hardened cement paste and concrete properties. The understanding of the effect of RHA in both binary and ternary systems on properties of cement paste and concrete could lead to an increase in the use of RHA in concrete constructions.

1.3 Objective of the study

This research is dealing about the effects of using different amounts of the pozzolanic materials such as RHA and SF as partial replacement materials in both binary and ternary systems on the properties of hardened cement paste and concrete.

The objectives of the research are:

i) To investigate on the individual effects of RHA and SF, respectively and their combination on the properties of hardened cement paste.

ii) To investigate on the individual effects of RHA and SF, respectively and their combination on the properties of fresh and hardened concrete.

iii) To find out the optimum replacement level of individual RHA and SF (binary) and optimum combination amount of each material (ternary) in terms of compressive strength of concrete.

iv) To compare of each optimum replacement level of binary concretes and ternary concrete on hardened concrete properties.

1.4 Scope of research

In this study, normal strength concrete with compressive strength of 40 N/mm^2 at 28 days under normal curing condition has been designed. The curing age of 1, 3, 7, 28, 56, and 90 days of all concrete mixes has been carried out.

The scope of this research is divided into three parts:

i) Preparation and characterization of raw materials in terms of their physical properties, chemical compositions, particle morphology, and phase identification.

ii) Characterizations of hardened cement pastes involving determination of calcium hydroxide content, porosity and pore size distribution and microstructure of both binary and ternary pastes.

iii) Characterizations of fresh concrete property such as workability (slump) and hardened concrete properties including compressive strength, porosity and water absorption, permeability, and drying shrinkage.

CHAPTER 2

LITERATURE REVIEWS

2.1 Introduction

Portland cement concretes containing pozzolanic materials which have been used as early as 1912 are now commonly used to reduce cost and improve performance of concrete [Ali, 1987]. This chapter describes about the introduction of concrete and concrete components and also highlights about what are pozzolanic materials, why these materials are used in cement and concrete, and how their effects on the properties of hardened cement paste and concrete. There are various types of pozzolanic materials but only rice husk ash and silica fume are reviewed in more detail.

2.2 Concrete

In this part, the definition, type, and components of concrete are discussed.

2.2.1 Definition

The material called “concrete” is made of the basic ingredients of hydraulic cement that is usually Portland cement, mineral aggregates and water. Moreover, the admixtures are needed to obtain the desired properties of concrete. Cement is a finely dry material that by itself is not a binder but as a result of hydration it develops the binding property. A cement is called hydraulic when the hydration products are stable in an aqueous environment and the most commonly used hydraulic cement for making concrete is Portland cement. Aggregate is the granular material which can be either fine or coarse aggregate. The term *coarse aggregate* refers to the aggregate particles larger than 4.75 mm, and the term *fine aggregate* refers to the aggregate particles smaller than 4.75 mm but larger than 75 µm. Water is a key ingredient for giving the hydration of cement. Admixtures are defined as materials other than aggregates, cement, and water, which are added to the concrete immediately before or during mixing. The admixtures can be either chemical or mineral admixture. Chemical admixtures can modify the setting and hardening characteristic of the cement paste by influencing the rate of cement hydration, whereas the mineral admixtures can modify the engineering properties and improve the durability of concrete [Mehta and Monteiro, 2006]. The detail of each concrete component will be discussed in next subsections.

Concrete is more or less plastic after mixing but subsequently hardens into a stonelike material. In concrete, the aggregate particles are held or linked together by a hardened cement paste. The definition of the word "concrete" is look very simple but the information on the internal structure and the behavior of concrete are very complex. First, the cement itself is not clearly known. It is available only an approximate picture about its composition and know much or less about what takes place in the cement and water mixture during the hydration process. But one thing has been known for certain is that the hardened cement paste is a highly complex multiphase material. Concrete has been traditionally considered as a composite material, therefore, the complex composition results in complex properties [Popovics, 1982].

2.2.2 Types of concrete

Strength grading of cements and concrete is prevalent and therefore it is useful to divide concrete into three general categories based on compressive strength [Mehta and Monteiro, 2006]:

i) Low-strength concrete: less than 20 MPa

ii) Moderate-strength concrete: 20 to 40 MPa

iii) High-strength concrete: more than 40 MPa

Moderate-strength concrete is also referred to normal-strength concrete and it is used for most structural work. High-strength concrete is, somehow, used for special application. Typical proportions of materials for producing the above three types of concrete mixtures are shown in Table 2.1. The influence of the cement paste content and water-cement ratio on the strength of concrete is obvious.

Table 2.1: Typical proportion of materials in concrete mixtures of different strength [Mehta and Monteiro, 2006]

Materials	Low-strength (kg/m^3)	Moderate-strength (kg/m^3)	High-strength (kg/m^3)
Cement	255	356	510
Water	178	178	178
Fine aggregate	801	848	890
Coarse aggregate	1169	1032	872
Cement pastes proportion			
percent by mass	18	22.1	28.1
percent by volume	26	29.3	34.3
Water/cement by mass	0.70	0.50	0.35
Strength, MPa	18	30	60

There are many different types of concrete beside the aforementioned types are not concerned in this section, are available for the concrete construction. They are such as normal-weight concrete, lightweight concrete and numerous modified concrete (e.g. fiber-reinforced concrete, expansive-cement concrete, and latex-modified concrete).

2.2.3 Concrete components

Properties of concrete depend mainly on each concrete's component property and also the other admixtures. The properties also vary, sometimes, from batch to batch without any apparent change in the composition and mostly, e.g. compressive strength, workability; vary from laboratory work and field work. This variability is due to the inherent variability of each of the ingredients entering into the mixture. The variabilities in the processes of batching, mixing, placing, compaction, and curing may contribute even more significantly to the variability in the concrete quality. Another variability in experimental results of concrete is due to sampling and testing error [Popovics, 1982].

2.2.3.1 Cement

Concrete has been traditionally considered as a composite material made with cement and possible mineral admixtures, aggregates and water. The wide range of application of concrete makes it necessary to produce Portland cements of different properties. There are several types of Portland cement (Table 2.2) were developed to ensure good durability of concrete under a variety of conditions. Usually, ordinary Portland cement is used in concrete production [Neville, 2002].

For practical purposes of selection of an appropriate Portland cement or blended cement, it is useful to consider a classification based on the relevant physical or chemical property. Furthermore for a certain type of cement, different brands different manufacturers may have different strength development characteristics due to the variations the compound composition and the fineness, which permitted by national standard specifications. In chemical compound of Portland cement, both silicates – tricalcium silicate (C_3S) and dicalcium silicate (C_2S) are the most important compounds that are responsible for the strength of hydrated cement paste. C_3S contributes to a rapid early age strength development as well as high late strength. C_2S contributes significantly to the later age strength gain. The hydration of cement compounds is also influenced by the fineness of cement. A higher specific surface results in rapid hydration kinetics but may reduce the later age strength development [Neville, 2002; Megat, 2000]

Table 2.2: Main types of Portland cement [Neville, 2002]

Traditional British description	ASTM description
Ordinary Portland	Type I
Rapid – hardening Portland	Type III
Extra rapid – hardening Portland	
Ultra high early strength Portland	Regulated set*
Low heat Portland	Type IV
Modified cement	Type II
Sulfate – resisting Portland	Type V
Portland blastfurnace	Type IS
White Portland	---
Portland – pozzolana	Type IP
Slag cement	Type S

* Not an ASTM description

Cement influences also the flow properties of concrete or mortar by virtue of the smaller particle size range it introduces into the mix; but because it is reacting chemically with the water it also introduces a time dependent stiffening. The first of these factors is responsible for the plasticity and cohesion of the mix, the second can cause problems if the mix stiffens too much between production and placing and the probability of significant stiffening occurring is increased when mixing is of too short a duration [Bye, 1997].

Ordinary Portland cement (OPC) is mostly used for general construction works. The quantity of the cement depends on how the concrete mix proportion has been designed but the cement quality must fulfill the specification either by British Standard (BS) or by ASTM. The typical specification for OPC is shown in Table 2.3.

Table 2.3: Typical specifications of OPC [BS 12: 1978]

Parameters	Specifications
Physical property	
surface area	Not less than 225 m^2/kg
Chemical composition	
SO_3	2.5 when $C_3A \leq 5\%$
	3 when $C_3A > 5\%$
LOI	Not exceed 4% (tropical climate)
Setting time	
initial	Not less than 45 min
final	Not more than 10 h
Compressive strength (concrete)	
3 days	Not less than 13 MPa
28 days	Not less than 29 MPa

Note: These specifications were abstracted from BS 12: 1978 but not all.

2.2.3.2 Aggregates

Aggregate is occupied at least three-quarters of the volume of concrete so its quality is considerable important. Aggregate with undesirable properties cannot produce strong concrete, and the aggregate properties greatly affect the durability and structural performance of concrete. The properties of the aggregate depend entirely on the properties of the parent rock, e.g. chemical and mineral composition, specific gravity, hardness, strength, and physical and chemical stability. On the other hand, there are some properties such as particle shape and size, surface texture, and absorption which possessed by the aggregate but absent on parent rock [Neville].

The particle size distribution or grading of an aggregate supply is an important characteristic because it determines the paste requirements for a workable concrete. As the aggregate grading can determine the paste requirement, it is desirable to reduce the cost of concrete by minimizing the amount of the paste but the paste should be consistent which can be handled, compacted, and finished and provide the necessary strength and durability [Mindess, 2003]. Moreover, at any given age and set of conditions, concrete strength is principally controlled by the cement content and water/cement ratio of the mix and the degree of compaction, which are interrelated factors. Aggregate grading and fine content influence the water/cement ratio and the workability, which in turn can affect compaction, so that indirectly these properties of aggregate have some influence over concrete strength [Hewlett, 1998]. The shape and texture of the fine aggregate affected only workability, but the characteristics of the coarse aggregate may also affect the mechanical properties of concrete by affecting the mechanical bond [Mindess, 2003]. It seems that the shape and surface texture of aggregate influence considerably the strength of concrete. The flexural strength is more affected than the compressive strength [Neville, 2002]. It has already been noted that aggregate particle shape influences water content and workability, which in turn will affect concrete strength [Hewlett, 1998].

The alternative to produce a good quality concrete is to use the aggregate at least two size groups – fine and coarse aggregate. The main division was made between fine aggregate (often called sand), not larger than 5 mm, and coarse aggregate, which comprises material at least 5 mm in size [Neville, 2002]

2.2.3.3 Water

Water is a key ingredient in the manufacture of concrete. Even though the quantity of water is the vital influence of concrete properties, but its quality, however, also plays a significant role. The old role of thumb stated by Nawy (1997) is "If you can drink it, you can use it in concrete". The impurities in water may affect setting of cement, strength of concrete, and may also lead to corrosion of the reinforcement. For these reasons, the suitable water should be considered for concrete mixing and curing purposes. Water should be avoided if it contains large quantities of suspended solids, excessive amounts of dissolved solids, or appreciable amounts of organic materials [Naville, 2002; Mindess, 2003]. The limits of concentration for various impurities are listed in Table 2.4. Too much impurities or very high quality of water is not suitable for mixing in concrete. Mindess (2003) had mentioned that a good quality of concrete can be made with water that would not pass normal standards for drinking water.

Table 2.4: Tolerable levels of some impurities in mixing water [Nawy, 1997]

Impurity	Maximum concentration (ppm)*	Ramarks
Suspended matter (turbidity)	2000	Silt, clay, organic matter
Algae	500 – 1000	Entrain air
Carbonates	1000	Decrease setting time
Bicarbonates	400 – 1000	400 ppm for bicarbonates of Ca or Mg
Sodium sulfate	10,000	May increase early strength, but reduce later strength
Magnesium sulfate	40,000	
Sodium chloride	20,000	Decrease setting time, increase early strength, reduce ultimate strength, and may lead to corrosion of reinforcing steel
Calcium chloride	50,000	
Magnesium chloride	40,000	
Sugar	500	Affects setting behavior

* ppm: parts per million

2.2.3.4 Chemical admixtures

In concrete production, generally, the most frequently used chemical admixtures are (1) accelerators to increase the rate of setting or the rate of hardening or both at early ages and (2) water-reducing and set-retarding admixtures to reduce the water requirement of concrete or to retard the set or both [Popovics, 1982]. Superplasticizers are commonly used as chemical admixture in concrete production.

Superplasticizers are water reducing chemical admixtures and known as high range water reducers (HRWR), superfluidifiers or super water reducers. They are more efficient than conventional plasticizer for improving workability and flow of concrete mix [Nawy, 1997]. According to Hewlett (1998), all superplasticizers consist of high molecular weight, water-soluble polymers, the majority of being synthetic chemicals and fall into four categories such as sulfonated melamine-formaldehyde condensates, sulfonated naphthalene-formaldehyde condensates, modified lignosulfonates and other such as sulfonated polystyrene, hydroxylated polymers, etc. The most widely used superplasticizers are sulfonated melamine-formaldehyde and sulfonated naphthalene-formaldehyde condensates. In addition to these, modified lignosulfates, sulfonic-acid esters, and carbohydrate esters are now being used [Omar, 2006].

Effect and application of superplasticizers

In the absence of superplasticizer, cement particles once in contact with water will tend to flocculate due to van der Waals's force of attraction, electrostatic interactions between particles of the opposite charges and surface chemical interactions between the hydrating particles. The flocculated structure of the cement paste particles could trap a certain amount of water, which then will no longer be available to lubricate the mix. With a superplasticizer, it works through deflocculation and dispersion of cement particles will occur due to adsorption and electrostatic repulsion mechanisms, which prevent the formation of entrapped water and significantly reduce the surface interaction of cement particles [Megat, 2000]. Superplasticizers have been used worldwide in concrete production especially for high strength concrete. Nawy (1997) listed the purposes of using superplasticizers in concrete mixes as follow:

i) To increase the workability.
ii) To reduce water and cement content for the purpose of reducing shrinkage and heat development.
iii) To reduce water/cement ratio for higher strengths and durability.

For increasing the workability in the concrete mix, the normal dosage of superplasticizers is between 1 and 3 liters per cubic meter of concrete. When superplasticizers are used to reduce the water content of the mix (for high-strength concrete), high dosage is needed: 5 to 20 liters per cubic meter of concrete [Neville, 2002].

2.2.3.5 Mineral admixtures

Mineral admixtures have been used for decades in concrete productions. The mineral admixtures were commonly used are silica fume, fly ash, metakaolin, blast-furnace slag, etc. They are used in order to modify the physical properties as well as mechanical properties of cement, mortar and concrete. These materials are industrials wastes and somehow pollute to the environment because of their huge deposit. The silica fumes, fly ash, etc. and as well rice husk ash, have also been known as pozzolanic materials. These materials are wildly researched and used in cement and concrete fields. The reasons why such materials are significantly used in cement and concrete production are discussed here.

2.3 Pozzolanic materials

2.3.1 Definition

A pozzolanic material or pozzolan has been is described as a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but in the presence of moisture; chemically react with calcium hydroxide ($Ca(OH)_2$) to produce cementitious products such as calcium silicate hydrate, calcium aluminum hydrate, and sulfoaluminate at ordinary temperature [ASTM C 595; Neville, 2002]. A pozzolan can be either natural or by-product material. The common pozzolanic materials have been used in cement and concrete works is given in Table 2.5.

Table 2.5: Common pozzolanic materials [Mindess, 2003]

Category	Typical materials	Active components
Natural materials	unaltered volcanic ash weathered volcanic ash (tuff, trass, etc.) pumice diatomaceous earth opaline cherts and shales	aluminosilicate glass aluminosilicate glass; zeolites aluminosilicate glass amorphous hydrated silica hydrated silica gel
By-product materials	fly ash – Class F – Class C silica fume rice husk ash calcined clays	aluminosilicate glass calcium aluminosilicate glass amorphous silica amorphous silica amorphous aluminosilicate (metakaolin)

2.3.2 Pozzolanic reaction

The amorphous or glassy silica, which is the major component of a pozzolan, reacts with calcium hydroxide to form additional calcium silicate hydrate (C-S-H). The principle reaction is given in Equation 2.1.

$$CH + S + H \longrightarrow C\text{–}S\text{–}H \qquad (2.1)$$

The extent of a pozzolanic reaction can be followed by monitoring the decrease of $Ca(OH)_2$ over time. It is known as "pozzolanic activity". The pozzolanic activity is usually tested by direct reaction of SiO_2 with $Ca(OH)_2$ and the consumption of $Ca(OH)_2$ is monitored [Mindess, 2003].

As shown in Table 2.5, there are various type of pozzolanic materials are used in concrete construction. In this review, only rice husk and silica fume are discussed in more detail.

2.3.3 Rice husk ash

Globally, approximately 600 million tonnes of rice husk is produced each year. On average 20% of the rice paddy is husk, giving an annual total production of 120 million tones [Bronzeoak Ltd, 2003]. Kartini and Mahmud (2005) stated that based on the Eighth Malaysia Plan (2001-2005) report, the production of paddy in the current country is increasing with an increase of 4% from 1995 to 2000 and an increase of up to 20% from 2000 to 2005, i.e. from 2,235 million tonnes to 2,813 million tonnes. From this figure, it is expected that the husk production could approximately be 562,600 tonnes and the ash production could be as high as 102,000 tonnes.

RHA riches in silica content which is obtained by burning rice husk to remove the volatile organic carbon such as cellulose and lignin. During burning process, rice husk will remove the volatile organic carbon such as cellulose and lignin and to produce high silica content approximately from 92 to 95 %. The ash will be produced in 18 % in weight of the total raw rice husk [Bronzeoak Ltd, 2003]. The chemical properties of ash arising from rice husks are thought to vary from region. The differences have been attributed to the conditions under which the paddy is grown, such as climate, soil, and use of fertilizers [Bronzeoak Ltd, 2003; Asavapisit, 2005]. Rice husks are residue produced in significant quantities on global basis. While they are used as fuel, they are waste product causing pollution and problem with disposal. With burning under controlled temperature, RHA is an excellent pozzolanic material and is suitable for Portland cement replacement. The chemical property of RHA is under controlled by burning condition, whereas its physical properties primarily depend on grinding media. The main consideration for beneficial use of RHA as pozzolanic material is how to obtain the silica in amorphous form. These are discussed in the next subsections.

2.3.3.1 Chemical property

Burning conditions (temperature and duration) are the major factors which determine the chemical property (silica content) in RHA. Della et al. (2002) had investigated on varying of burning temperature and duration on the chemical property of RHA. The RHA had been burnt from 400 to 700 ^{0}C for 1, 3, and 6 hours, respectively. The study revealed that 95 % of silica can be produced by burning RHA at 700 ^{0}C for 6 hours. However, this silica content may not be the same even though the rice husk has been burnt in the same condition if it was taken from different location (geographical factor).

The RHA will contain, typically, some unburnt components and the unburnt component is predominantly carbon. Typically, it is measured by reheating a sample of the ash in an oven. The difference in mass of the sample before and after heating is referred to LOI (Loss on Ignition). The LOI value is normally the same as the carbon content of the ash and this carbon content varies according to the combustion process. Bronzeoal Ltd. (2003) had reported that the LOI values of RHA ranging from 1% to 35% and a commercial RHA combustion appears to result in RHA with 5-7% maximum. The most common trace elements in RHA are sodium, potassium, calcium, magnesium, iron, copper, manganese and zinc. Differences in composition are due to geographical factors, year of harvest, sample preparation and analysis methods [Della et al., 2002].

2.3.3.2 Phase of silica in RHA

Burning out temperature and time are important factors to define whether silica remains amorphous or become crystalline in RHA. Based on the Rice Husk Ash Market Study [Bronzeoal Ltd., 2003] reported that burning rice husk at 550 °C – 800 °C, amorphous ash is formed and at temperatures greater than this, crystalline ash is formed. Furthermore, various researchers had reported the influence of burning conditions on the phase of RHA. Della et al. (2002) found that the amorphous silica of ash can be achieved with the heating temperature below 700 ^{0}C. Moreover, the highest amount of amorphous silica was obtained when the husk was burnt at 700 ^{0}C for 6 hours (compared to burning temperature of 400, 500, and 600 ^{0}C for 6 hours) and the amorphous silica in the ash begins to transform to crystalline when rice husk was burnt at temperature above 750 ^{0}C reported by Zhang et al. (1996). Nehdi (2003) highlighted that the husk can remain in the amorphous form at burning temperature up to 900 ^{0}C if the combustion time is less than 1 hour, while crystalline silica is obtained at 1000 ^{0}C with combustion time greater than 5 minutes.

2.3.3.3 Physical property

After the combustion of rice husk is completed, the ash is obtained and it was then taken to conduct the grinding process in order to get the desired physical properties such ash surface area and average particle size. These properties affected mainly by the grindability. A greater surface area is available for chemical reactions if the ash is to be used as a pozzolan. Neville (2002) reported that the surface area (measured by nitrogen adsorption) of RHA can be as high as 50,000 m^2/kg even though the particle size is large (10 to 75 µm).

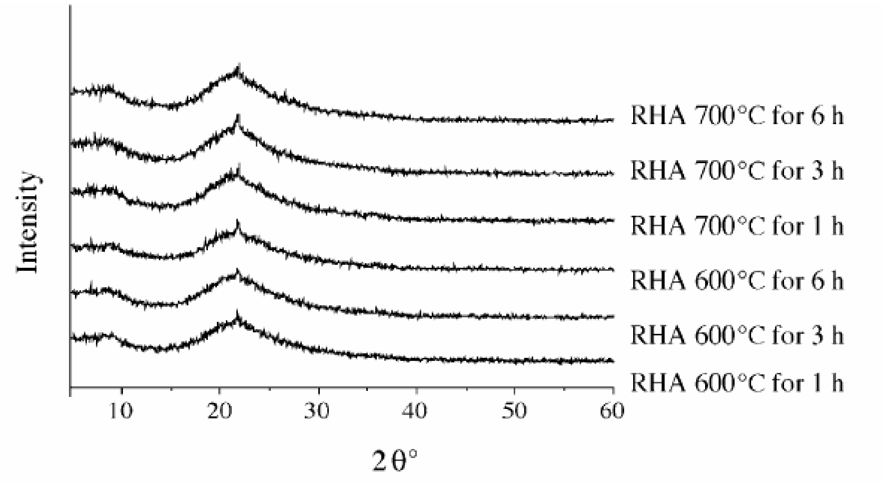

Figure 2.1: XRD patterns of amorphous silica of RHA burning in various temperatures and durations [Della et al., 2002]

The color changes of RHA are associated with the completeness of combustion process as well as with structural transformation of the silica in the ash. Generally, darker ashes exhibit higher carbon content whilst lighter ashes have achieved higher carbon burnout. Della et al. (2002) had reported that the amount of black particles decreased with increase in calcination temperature and time. At 700 ^{0}C for 6 h, the thermal treatment yielded bright white silica.

RHA has been reported that it is highly reactive pozzolanic material used to improve the properties of concrete such as compressive strength and durability. Beside these, RHA is used to reduce materials cost due to cement savings and environmental benefits related to the disposal of waste materials and reduced carbon dioxide emissions [Gemma, 2006; Saraswathy and Song, 2006].

2.3.4 Silica fume

The manufacturing processes of silicon metal and ferrosilicon alloys in an electric arc furnace occur at temperature up to 2000 ^{0}C. They generate fumes containing spherical microparticles of amorphous silicon dioxide. This is the reason why the product is called silica fume. The two major components such as the type of alloys produced and the composition of quartz and coal which used in submerged-electric arc furnace greatly influence the chemical composition of SF. The SF which is usually used in cement and concrete production is related to SF collected during the silicon alloy production containing at least 75% silicon [Hewlett, 1998; Nawy, 1997].

2.3.4.1 Chemical property

The chemical composition of SF is mainly affected by the types of alloy used. Typically, SF contains more than 80 – 85% of SiO_2 in amorphous form, is suitable to use in the cement and concrete industries. The Standard Specification for silica fume [ASTM C 1240] stated that the minimum silica content must not less than 85 % and LOI value not exceed 6 %. The trace elements are the additional materials in SF based upon the metal being produced and these elements have no impact on the performance of SF in concrete [Silica fume user's manual, 2005].

2.3.4.2 Physical property

SF particle is generally spherical shape with particle sizes are extremely fine ranging from 0.03 – 0.3 μm and the average particle size is typically below 0.1 μm. The surface area is ranging from 15,000 to 30,000 m^2/kg measured by nitrogen absorption technique (BET). For determination of surface area of SF, the BET method much be used and other methods such as sieve analysis or air-permeability testing are meaningless, reported by Silica Fume User's Manual (2005). The specific gravity of SF is generally about 2.2 but it is very slightly higher with the lower silica content. The bulk specific weight is of the order of 200 kg/m^3 and is 500kg/m^3 when compacted. SF varies in color from pale to dark grey. The carbon and iron contents seem to have preponderant influence on the color of SF [Nawy, 1997].

Base on the ACI Committee 234, SF is highly reactive pozzolanic material due to its three notable characteristics: (a) an average particle diameter of 0.1 μm (approximately 100 times smaller than average of Portland cement), (b) a high amorphous silica composition (typically more than 90% of SiO_2 content), and (c) a very high surface area of 20,000 m^2/kg (as compared to Portland cement values of 300 – 500 m^2/kg).

The amorphous structure, high SiO_2 content, and high surface area make it a very reactive pozzolan which is suitable for use in cement and concrete industries particularly in the production of high strength concrete. SF concrete was produced by modifying normal Portland cement concrete by replacing the cement with SF for a given ratio on mass basis. The inclusion of SF results in a finer pore size distribution of concrete. In addition, the ability of the fine particles of SF to act as filler improves the aggregate-cement pastes interface. Therefore, the pozzolanic reaction and the filler effects as a consequence of SF inclusion enhance the properties of concrete such as strength and impermeability [Megat, 2000]. Ali (1987) had reported that the behavior of silica fume in concrete is physiochemical. The physical phase is in the refinement of the void system of cement paste and particularly the transition zone. The chemical phase consists of the pozzolanic reaction that transforms the weak $Ca(OH)_2$ crystals into the strong calcium silicate hydrate gel. The results of these actions of SF provide significant improvements in compressive and flexural strengths along with improvement in durability. Also, Andrew et al. (2005) had reported that one of the greatest advantages of using SF in concrete results from its small size; the addition of SF widens the size distribution of the cementitious particles in concrete, allowing more efficient particle packing, densifying the interfacial transition zone and converting CH into C–S–H, thus increasing strength. However, this small particle size makes SF difficult to transport and distribute.

SF was used widely in cement and concrete production. Many researches were conducted to study the different SF replacement level on the properties of concrete. According to Neville (1995), low content of SF (less than 5% of the total mass of cementitious material) does not lead to a high strength of concrete while a large volume of SF is only marginally more beneficial than about 10%. Various researchers had stated that the use of SF in concrete results in a significant improvement in the mechanical properties of concrete, but researchers are yet to arrive at a unique conclusion regarding the optimum SF replacement percentage, and different researchers have reported different replacement levels as optimum for obtaining maximum strengths of concrete [Toutanji, 1999; Sabir, 1995, Khatri; 1995; Glodman, 1993; Bhanja, 1993].

2.4 Why pozzolanic materials used in cement and concrete production?

The manufacture of Portland cement is a process of mixture of limestone ($CaCO_3$) and clay or silt, to which small amount of iron oxide (Fe_2O_3) and sometimes quartz (SiO_2) are involved, is heated in a certain temperature. In world production of cement, the huge quantity requirement of cement is needed, the huge amount of the natural resources are also requested. Therefore, as the cement is producing, the