INFLUENCE OF MULTIPLE BLENDED BINDERS ON ENGINEERING PROPERTIES AND DURABILITY OF CONCRETE

by

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PENGARUH PEREKAT CAMPURAN BERBILANG KE ATAS SIFAT-SIFAT KEJURUTERAAN DAN KETAHANLASAKAN KONKRIT

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**Tesis yang diserahkan untuk
Memenuhi keperluan bagi
Ijazah doktor falsafah**

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LIST OF ABBREVIATION

HSC	High Strength Concrete
HPC	High Performance Concrete
OPC	Ordinary Portland Cement
BBC	Binary Blended Cement
TBC	Ternary Blended Cement
SF	Silica Fume
FA	Fly Ash
MK	Metakaolin
RHA	Rice Husk Ash
ACI	American Concrete Institute
MPa	Mega Pascal
C_3S	Tricalcium Silicate
C_2S	Dicalcium Silicate
C_3A	Tricalcium Aluminate
C_4AF	Tetracalcium Aluminoferrite
C-S-H	Calcium silicate Hydrate
$Ca(OH)_2$	Calcium Hydroxide
ASTM	American Society for Testing and Materials
BET Apparatus	Brunauer, Emmetl, and Teller Apparatus
SiO_2	Silica Oxide
Al_2O_3	Alumina Oxide
Fe_2O_3	Ferum Oxide
CaO	Calcium Oxide
MgO	Magnesium Oxide
LOI	Loss of Ignition
BS	British Standard

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INFLUENCE OF MULTIPLE BLENDED BINDERS ON ENGINEERING PROPERTIES AND DURABILITY OF CONCRETE

Abstract

The influence of multiple blended binders in the forms of binary blended cement (BBC) and ternary blended cement (TBC) on the properties and performance of concrete is investigated. The mineral admixtures used are silica fume(SF), fly ash (FA), metakaolin (MK) and rice husk ash (RHA). They are used to partly replace the cement by direct replacement method on mass-to-mass basis. The mix proportions of the concretes are kept nominally the same with constant water/binder ratio and the same superplasticizer content for all concrete mixes, so as to isolate the effect of each binder type. Most of the mineral admixtures used are abundantly available in the country and analyses performed indicate their compliance with standard specification requirements as pozzolan. They are used to replace ordinary Portland cement (OPC) at replacement level of 0 (control mix) to 40% (TBC mix). Analyses on the binders also exhibit their compliance with standard specification requirements which are comparable to OPC. The engineering properties of the TBC concretes are generally comparable with those of OPC and better than OPC:FA BBC concrete when cured continuously in water. The durability performance of the TBC concrete exposed to air is found to be comparable to that OPC concrete. Nonetheless when exposed to sulphate and chloride environments the durability performance seems to be more effected in comparison to the OPC concrete. This could be due to the very early exposure to the aggressive environments

PENGARUH PEREKAT CAMPURAN BERBILANG KE ATAS SIFAT-SIFAT KEJURUTERAAN DAN KETAHANLASAKAN KONKRIT

Abstrak

Kajian telah dijalankan berhubung pengaruh penggunaan perekat campuran berbilang dalam bentuk simen campuran binari (BBC) dan simen campuran ternari (TBC) terhadap ciri-ciri dan prestasi konkrit. Bahan tambah mineral yang digunakan ialah abu silika (SF), abu ringan (FA), metakaolin (MK) dan abu sekam padi (RHA). Bahan mineral tersebut telah digunakan sebagai bahan gantian separa kepada simen secara gantian terus berdasarkan nisbah berat simen. Bahan campuran konkrit yang sama digunakan untuk semua bancuhan dengan nisbah air/perekat yang tetap dan kandungan bahan super pemplastikkan dikekalkan bagi mengenalpasti kesan bahan mineral ke atas sifat-sifat konkrit. Bahan mineral yang digunakan merupakan bahan mineral yang banyak terdapat di dalam Negara telah dianalisis dan didapati memenuhi keperluan spesifikasi piawai untuk bahan tambah mineral dalam konkrit. Bahan mineral digunakan untuk mengantikan simen OPC dari 0 (bagi bancuhan kawalan) hingga 40%(bagi bancuhan TBC). Analisa ke atas bahan perekat yang dihasilkan adalah didapati simen campuran yang dihasilkan memenuhi spesifikasi piawai yang dirujukan bahkan ianya juga didapati setanding dengan simen OPC. Ciri-ciri kejuruteraan yang terdapat pada konkrit TBC secara amnya didapati setanding dengan konkrit OPC dan ianya juga didapati lebih baik berbanding dengan konkrit BBC dengan perekat OPC:FA. Keputusan yang diperolehi mendapati bahan mineral yang digunakan berpotensi dalam penghasilan simen campuran. Prestasi ketahanlasakkan konkrit dengan bahan perekat TBC dalam pendedahan udara didapati standing dengan konkrit OPC, walaubagaimanapun ianya didapati lebih rendah berbanding dengan konkrit kawalan apabila ia didedahkan secara terus kepada persekitaran yang mengandungi garam sulfat dan klorida.

CHAPTER 1 INTRODUCTION

1.1 BACKGROUND OF STUDY

In comparison to other construction materials such as timber and steel, concrete is the most widely used construction material because of its global availability, relatively cheap, flexible and versatile in term of its application, can be tailored to achieve various strength level and durability. The grade of concrete is normally based on 28 days compressive strength of the concrete. Since the application of concrete is versatile, the production of wide range of grade from the lowest (i.e 20MPa to 200 MPa) is possible. The different application would require concrete with different strength, workability and durability. Higher grade of concrete is usually utilized for high end application such as precast work, high strength concrete and etc. [Nawy, 2001]. The blended or multi-blended cements are essential for higher grade of concrete rather than the normal grade of concrete. The disadvantage of high strength concrete is that it requires a lot of cementitious materials which is the most expensive ingredients in the concrete. Therefore, research on the production and application of blended or multi-blended cement for producing concrete is much needed.

In general, ordinary Portland cement (OPC), coarse aggregates, fine aggregates and water are the basic ingredients used in the production of normal concrete. However, the production of High Strength Concrete (HSC) or sometimes also known as High Performance Concrete (HPC) requires a proper selection of materials especially the binders that contribute to the superior performance. In addition, the production of HSC normally requires a higher content of Portland cement or binder, stronger aggregates with smaller maximum size and lower water/binder ratio (Bharatkumar et al., 2001). Furthermore, chemical and mineral admixtures such as high range water reducer and silica fume are normally included in the production of HSC. Due to the higher consumption of OPC in the production of HSC, the search for alternative binders or cement replacement materials has thus become a challenge. The importance of using Binary Blended Cement (BBC) in HSC/HPC has been revised. To note that using BBC, other aspects especially in terms of gaining early strength, reduction of workability and high heat liberation cannot be addressed, hence the use of the multiple blended binders would be one way to address all aspects in HPC.

From the perspectives of economy, technology and ecology, cement replacement materials have an undisputed role to play in the construction industry. Small amounts of inert fillers have always been acceptable as cement additives, but if the fillers have pozzolanic properties, they impart not only technical advantages to the resulting concrete but also enables larger quantities of cement replacement to be achieved. Many of these mineral admixtures are industrial by products, and correctly considered as waste, so that the resulting benefits in terms of energy savings, economy, environmental protection and conservation of resources are substantial [Malhotra and Mehta,(2004)].

It has been generally accepted that the roles of pozzolanic materials in concrete industry are not only to increase the strength of concrete but also at the same time to enhance the durability performance of concrete. Due to the enhancement of concrete durability, HSC has also been called as High Performance Concrete (HPC). Either the materials are used as minerals admixtures or as partial cement replacement materials in concrete mixes, they normally give positive effect on the engineering, physical and mechanical properties of concrete [Aitcin, (2003), Baalbaki et al., (1992), Ramezanianpour, (1987)].

1.2 PROBLEM STATEMENT

Service life of concrete has become short due to premature deterioration problems especially to the structure in severe and extreme environmental exposure conditions. Due to these problems HPC should be proposed to reduce the deterioration of concrete structure and having longer period of service life. Neville (2002) stated that the HPC concrete normally used higher content of cement (450 to 550 kg/m^3) to achieve its specific target strength. Taylor (2002) reported that a concrete with high content of cement may face high heat of hydration problems that may increase the formation of micro crack and porosity that could significantly reduce the durability of concrete. In addition, the production of cement has also been reported to contribute to environmental problems caused by the extraction of raw material and CO_2 emission during cement manufacture (Sabir et al., 2001). In addressing these concerns and other environmental problems related to the disposal of waste industrial by products and also because of economic advantages, mixtures of Portland cement (OPC) and pozzolans known as binary blended cement (BBC) has been introduced.

The use of Binary Blended Cement (BBC) system based on industrial by products or natural pozzolan has been known to improve long-term strength and to enhance durability performance of concrete [Sabir et al.,(2001), Uzal and Turanli, (2003), Omar,(2002)]. Most of these mineral admixtures are industrial by products, and could be correctly considered as waste, so that the resulting benefits in terms of energy savings, economy, environmental protection and conservation of resources are substantial [Swamy, 1986]. With the intention of reducing environmental problems, producing low cost binder, reducing the consumption of cement by using higher replacement level of OPC, as well as achieving higher strength and durability performance, the Ternary Blended Cement (TBC) is introduced in this study. Due to the importance of providing a new type of cement to support the concrete construction industry's demand, this research is believed to be significant. The information about TBC are still limited and this study is significant in providing more information and creating a better understanding of TBC for high strength concrete application.

Pozzolan is recognised as materials that can give positive effects on concrete properties but there is still considerable reluctance to use these materials as widely as they deserve. Malaysia has a lot of pozzolan resources. However, only a little amount of these materials are used, especially in the concrete industry. This phenomenon may be due to the lack of research done on these materials especially in the Malaysian concrete industry.

1.3 AIM AND OBJECTIVES

The aim of this research was carried out and designed based on four main objectives. The objectives are:-

a) To identify and assess the properties of the pozzolanic materials used in the investigation so as to determine their suitability to be used as partial cement replacement materials in the production of TBC and BBC cementitious systems.

b) To formulate and produce TBC containing pozzolanic materials available in Malaysia, to be used in the production of high strength concrete (grade C60).

c) To investigate the engineering properties of fresh and hardened concrete containing TBC.

d) To study the durability related properties of the TBC concrete under different curing conditions, and compare with those of OPC and BBC concretes.

1.4 SCOPE OF RESEARCH

The TBC system was formulated based on optimum 28 days compressive strength performance of concrete containing BBC at various replacement levels of the selected pozzolanic materials. A control HPC mix containing OPC was designed and prepared through series of trial mixes to have minimum compressive strength of 60 MPa at 28 days of age.

The pozzolanic materials used in this investigation were silica fume (SF), fly ash (FA), metakaolin (MK) and rice husk ash (RHA). All of the pozzolanic materials used were obtained locally. Some of them are already established in the concrete industry and available in the market (SF), but some of them were produced in the laboratory to control the quality of the pozzolanic materials.

The experimental program involved studying the properties of materials used, effect of TBC system on the cementitious properties, as well as influence of TBC systems on properties of fresh concrete, engineering properties of hardened concrete and properties related to durability performance under different curing conditions. Four curing conditions were utilized namely; normal water curing, air curing, water containing sulphate and water containing chloride. The properties and performance of the HPC containing TBC system were compared with those of HPC containing BBC and OPC.

1.5 DEFINITION OF TERMS

1.5.1 Pozzolanic materials

Pozzolanic materials or pozzolans are siliceous or siliceous and aluminous materials, which in themselves possess little or no cementitious value but in the presence of moisture, can react with lime to produce cementitious products such as calcium silicate hydrates and calcium aluminium, furnished by the hydration of the anhydrous calcium silicates present in the Portland cement [BS 6610 (1985)].

1.5.2 Ternary Blended cement (TBC)

TBC is a multi component cementitious system produced by combining two types of pozzolanic materials with OPC at specified replacement level. It was prepared during the mixing process.

1.5.3 Binary blended cement (BBC)

BBC is a blended cementitious system produced by combining one type of pozzolanic material with OPC at a specified replacement level. It was prepared during the mixing process.

1.5.4 High performance concrete (HPC)

Hashem. et al., (2002) stated that the definition of HPC is not standardized, nevertheless several different definitions of HPC have been proposed and from all the definitions HPC can be summarized as concrete with superior properties that is not only high in strength but also have great durability performance in extreme environmental exposure.

1.5.5 Multi Blended Cement (MBC)

MBC refers to blended cement either in binary system or in ternary blended system used in this investigation.

1.6 LAYOUT OF THESIS

The thesis consists of seven chapters. They are introduction, literature review, material properties and mix proportions, binder properties, engineering properties, durability performance, and finally, conclusions and recommendations.

Chapter one is an introduction to the research which comprises of overview of works, problem statement, objective, scope of research and definition of terms that have been used in this investigation.

In chapter two, an introduction to the pozzolanic materials used and their performance in the production of HSC are presented. Existing knowledge on the effect of pozzolanic materials used as mineral admixture or replacement material to produce binary blended cement system in HSC, which are related to this study, are reviewed.

Chapter three outlines the pozzolanic sample preparations and productions that were used in the investigations. Details of pozzolanic materials properties used in the investigations are also described in this chapter. Subsequently, the mixing, casting, curing procedures and experimental design and program are also presented.

In chapter four, the properties of pozzolanic materials used throughout the experimental program are evaluated. The influence of different replacement levels of the pozzolanic materials on properties of binder of the ternary blended cementitious system is compared with those of BBC and OPC cementitious systems. Evaluations are based on the tests specified by British Standard Specification for Ordinary Portland Cement, BS 12:1996.

Chapter five presents the influence of TBC system in HSC on the engineering properties compared to HSC containing BBC and OPC cementitious system. The engineering properties considered include workability, compressive strength, surface hardness and concrete uniformity.

Chapter six presents the results and discussion on the effects of pozzolanic materials used as minerals replacement in TBC compared to BBC and OPC on the durability performance of HSC. The prepared specimens were cured under different curing condition and the durability performance was assessed through the engineering properties named as porosity, permeability, expansion and shrinkage, water absorption, carbonation, sulphate and chloride concentration level. The performances of HSC under different curing conditions are compared and discussed with those of specimens cured under standard curing condition.

Finally, conclusions of the research works and recommendations for future studies are presented in chapter seven.

CHAPTER 2 LITERATURE REVIEW

2.1 INTRODUCTION

Concrete structures are generally designed for a service life of 60 years, but experience shows that in urban and costal environments, many structures begin to deteriorate in 20 to 30 years or even less time after being constructed [Nawy, 2001]. This premature deterioration arising from lack of durability of concrete could have serious environmental and economic consequences. Increasing the service life of concrete in long-term is one of the solutions for preserving the earth's natural resources [Sampaio et al., 2000].

The world's yearly cement production of 1.6 billion tons 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 construction materials but it is also responsible for a large amount of greenhouse gasses [Aitcin, 2003]. Production of a tonne of Portland cement requires about 4 GJ of energy, and Portland cement clinker manufacture releases approximately 1 ton of carbon dioxide into the atmosphere. Ordinary concrete typically contains about 12% cement and 80% aggregate by mass [Sampaioet et al., 2000]. Hence, any effort on reducing the consumption of cement could somehow contribute to reduction in potential environmental problems, reduction in cost, as well as preservation of natural resources, which as a whole could contribute to sustainable development.

In the current and future construction scenario, the increasing demand for cement and concrete must be supplemented by the use of supplementary cementitious materials such as fly ash and rice husk ash. The use of such materials as partial replacement for the more energy-intensive Portland cement could result in substantial energy and cost savings. According to Mehta (1994), the cement production rate of the world is expected to grow exponentially to about 3.5 billion tons/year by 2015. He presumed that most of the increase in cement demand could be supplemented by the use of mineral cement replacement materials. He also suggested that this approach is necessary to prevent the possible ecological disaster due to global warming.

The presence of mineral cement replacement materials in concrete is known to impart significant improvements towards concrete durability. In addition, some of the mineral admixtures such as fly ash and ground granulated blast-furnace slag could enhance the workability of concrete. A high performance concrete with adequate workability and superior durability can be produced by a proper selection of mineral cement replacement materials and concrete mix proportions. Some of these materials can be obtained from industrial and agricultural by-products. The use of by products is an environmental-friendly method of disposing large quantities of materials that would otherwise pollute the land, water bodies and air [Mehta, 1994]. The use of these artificial pozzolans could bring about not only economical and ecological benefits but technical benefits as well. It is generally agreed that with proper selection of materials, mixture proportioning and curing technique, minerals additives can greatly improve the durability performance of concrete.

In this chapter, the definition of High Performance Concrete (HPC) and its importance to the construction industry are discussed. The principal requirements of HPC in term of its production, applications and problems associated with the use of HPC are also discussed and reviewed.

This chapter also introduces the common pozzolanic materials being used in the production of HPC. As literature discussion, existing knowledge on the effect of pozzolanic materials used as mineral additives or partial cement replacement materials to produce binary blended cementitious system in HPC, which are related to this study, are reviewed. Properties and performance of Ordinary Portland cement and binary blended cementitious system containing pozzolans used to produce HPC are discussed. Finally, this chapter also discusses the role, potential and importance of using ternary blended cement (TBC) as an alternative binders to OPC in producing HPC.

2.2 HIGH PERFORMANCE CONCRETE (HPC)

HPC has been widely used in the construction industry for the past few decades. This is due to the increasing demand for more durable concrete to extend the service life and at the same time to reduce maintenance cost of concrete structures.

There are several definitions of HPC. ACI 363R(1992) defined HPC as concrete meeting special combinations of performance and uniformity requirements that cannot always be achieved routinely using conversional constituents and normal mixing, placing and curing practices. In addition, ACI 363R(1992) also specified that compressive strength for design should be at least 41 MPa or greater.

HPC was also defined as a concrete with water/binder ratio of less than or equal to 0.35 and shall have a characteristic compressive strength of at least 35 MPa or greater after 24 hours and at least 70 MPa or greater after 28 days [Roszilah et al., 2002]. Furthermore, the concrete should meet special requirements such as, ease of placement and compaction, resistant to segregation, enhanced long-term mechanical properties (high early-age strength, toughness and volume stability) and superior long-term durability performance in severe environments [Hashem et al., 2002].

To achieve an ideal HPC, Nawy (2001) stated down five principal parameters as the following:

High performance

Economy

Resistance to wear and deterioration

Resistance to weathering and chemicals

Appropriate cement type.

Amongst the parameters stated above, an appropriate cement type has been recognised as the major factor that can influence performance of concrete with regards to the other parameters. The use of inappropriate type of cement in producing HPC might cause disintegration of the concrete in the structure when exposed to certain aggressive environmental exposure. Malier (1992) introduced two approaches as means of obtaining HPC, which are, reducing the flocculation of cement grains and widening the range of grain size of the binder. These could be realized by using combination of both chemical admixture such as high range water reducer and mineral admixture such as silica fume. Here, the high range water reducer will mainly disperse the binder particles through the adsorption and electrostatic repulsion mechanisms, while the much finer silica fume will act as filler, filling the interstitial spaces between the coarser cement particles. The net effect will be a denser cement paste matrix, which will contribute to enhanced mechanical properties as well as durability performance.

The major advantages of using mineral additives in concrete are mainly, the improved concrete properties in the fresh and hardened states, as well as the potential economical and ecological benefits. Since HPC requires relatively higher binder content than normal concrete, the utilization of mineral additives could offer greater potential benefits. However, the selection of the mineral additives may require more attention due to their varying properties and effects.

2.3 CEMENT FOR HPC

In order to produce HPC, selecting an appropriate type of cement is important. In choosing the appropriate type of cement, parameters such as the type of structure, the weather and other conditions under which the structure is to be built and the probable exposure condition of the structure during its life span should be given due consideration [Nawy, 2001].

Concrete structures exposed to marine environment and seawater sprays may require the use of sulphate resisting cement type [Maher and Bader, 2003]. For construction that needs a concrete to harden and develop early strength quickly, rapid hardening Portland cement will be essential [Taylor, 2002]. According to Nawy (2001), concrete structure with bulkier and heavier in cross section needs cement with low heat evolution characteristic to prevent excessive temperature gradient and probable thermal cracking which are normally associated with mass concrete. For this case, blended pozzolanic cement was found to be necessary to reduce the temperature rise during hydration process and at the same time to improve the durability performance of concrete [Sabir et al, 2001].

The chemical compositions of cement could have significant influence on its properties and performances. The variation in the chemical compositions of any type of cement in particular the aluminate is one of the factors that determine the rate of reaction of cement when in contact with water [Fabien and Kimberly, 2007]. In addition, the size of the cement particles or it fineness, which is normally indicated by its specific surface area also plays an important role in determining the reactivity of cement [Aitcin, 2003]. According to De Larrnard (1992), ultra fine particles of cement would react in two levels which are physical and chemical levels. In physical level, the cement will react as filler between the voids in hydrated cement matrix at early age, and on the chemical level, the cement will accelerate the hydration process. For blended cement containing pozzolanic materials, the finer particles produce a better pozzolanic reaction but it is still depending on the quality of pozzolanic materials used. Mazloom et al., (2004) stated that besides utilizing appropriate binder, water/binder ratio must be reduced and binder content should be increased in order to produce HPC.

2.4 ORDINARY PORTLAND CEMENT (OPC)

In the new era of concrete industry, Ordinary Portland Cement (OPC) still remains as a major binder used to produce HPC. OPC is either used as the sole binder in concrete mixes or as a major proportion of binder in blended cements. OPC consists of four major compound compositions, namely the tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) [Neville, 2002].

C_3S comprises of angular crystals which constitutes about 52% of OPC volume. It is responsible for initial setting and early strength gain of cement, especially to give an early strength (e.g. 7 days). C_2S are more rounded crystals that represent about 19% of OPC volume and it is responsible for long-term strength development. It will harden slowly but contributes notably to strength at ages over a month [Ajiwe et al., 2000]. In the case of C_3A which is normally in rectangular amorphous crystals, it mainly influences the setting characteristics of cement, whereas the non-crystalline C_4AF is responsible for the grey colour of cement with little contribution to setting as well as strength. The C_3A and C_4AF constitute about 10 and 8% of OPC volume, respectively [Taylor, 2002]. It is worth mentioning that the reaction of C_3A with water is very violent and leads to immediate stiffening of the cement paste, known as flash set. To prevent the flash setting phenomenon, gypsum is normally added to cement clinker. The present of excessive C_3A with its rapid setting, high heat evolution and sulphate susceptibility, is undesirable in concrete.

The actual proportions of the different major compounds could vary considerably from cement to cement, and indeed different types of cement are obtained by suitable proportioning of the raw materials. The major compositions of OPC are 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 the previously water-filled spaces. The microcrystalline material is responsible for the strength of the hardened concrete [Regourd, 1992].

$Ca(OH)_2$ forms a much larger crystals which act 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 the steel reinforcement within the reinforced concrete structure [Taylor, 2002]. The ratio of C-S-H to $Ca(OH)_2$ is approximately 7:2 by mass of concrete [Neville, 2002].

At any stage of hydration, the hardened cement paste consists of very poorly crystallized hydrates of the various compounds, referred to collectively as gel, crystals of $Ca(OH)_2$, some minor components, unhydrated cement and the residue of water-filled spaces from the fresh paste [Neville, 2002]. The formation of $Ca(OH)_2$ crystals creates a bridging effect between crystallized C-S-H and because of $Ca(OH)_2$ is crystallised in massive superimposed hexagonal plates, it creates capillary pores in the cement paste matrix (Figure 2.1). The capillary pores, either induced by $Ca(OH)_2$, air bubbles or micro crack have become a factor that contributes to an inferior engineering properties and durability performance of concrete [Regourd, 1992].

The capillary pores represent part of the gross volume of hardened cement paste which has not been filled by the products of hydration. Commonly, the hydration products 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, 2002]. The progress of hydration is governed by the water/cement ratio and the degree of hydration. Water/cement ratios of lower than 0.23 would promote self-desiccation problems and a water/cement ratio higher than 0.36 will induce the formation of the capillary pores since the volume of gel is not sufficient to fill all the space available [Taylor, 2002].

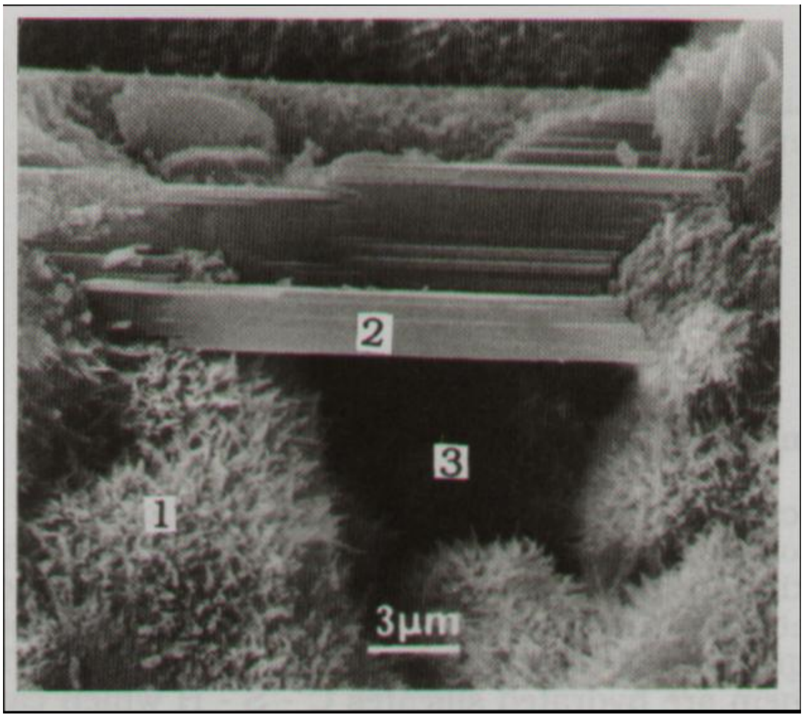

Figure 2.1: Hydrated OPC cement paste, w/c = 0.5, (1) Fibrous C-S-H, (2) $Ca(OH)_2$, (3) capillary pore [Regourd,1992].

An improvement of capillary pore formations has been obtained by several processes, which reduce the porosity and the water/cement ratio problems. One of the processes introduced is by blending the OPC with pozzolanic materials either by using pre-blended pozzolanic cements or by mixer blending of cement with pozzolanic mineral admixtures. The small particles of pozzolans will act as fillers, filling the spaces between the coarser cement particles. In addition, the pozzolanic reactions between the amorphous silica of the mineral additive and $Ca(OH)_2$ produced by cement hydration reactions will occupy the pores which are not occupied by OPC hydration products. Hence, the hardened cement paste will be much more homogenous and denser, with finer pore size distribution.

2.5 POZZOLANIC MATERIALS

Pozzolan is a material which, when combined with calcium hydroxide, exhibits cementitious properties. Pozzolans are commonly used as additives or as mineral replacements to Portland cement concrete mixtures to increase the long-term strength and other 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 pozzolans [Agarwal, 2006].

The specific definition of pozzolan according to ASTM C618-98 and accepted by almost by all scientists and researchers dealing with cementitious materials and concrete is a "siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious property but which will in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementing properties". Other description for pozzolan includes any material, regardless of its geologic origin, which possesses hydraulic properties [Ramezanianpour, (1987)]. In addition, Neville (2002) 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 material was named. The most commonly-used pozzolan today is fly ash (FA), though silica fume (SF), high reactivity metakalolin (MK), ground granulated blast furnace slag (GGBS), rice husk ash (RHA) and other materials are also used as pozzolans. In Malaysia a waste from palm oil industry named as Palm Oil Fuel Ash or POFA has been found to possess pozzolanic properties and has shown a promising potential to be used in concrete, however a careful design with an adequate amount of ash should be chosen to establish the potential benefit [Abdul and Warid.,1997]. Weerachart et al., (2007) recommended that the optimum replacement levels of OPC with POFA is between 20 to 30% while Chea et al., (2010) reported that POFA has a unburned carbon content and this unburned carbon reduced the workability of concrete and need more superplasticizer to be added in the concrete mix to maintain the fluidity level of concrete. However, the current study only focuses on silica fume (SF), fly ash (FA), metakaolin (MK) and rice husk ash (RHA). These pozzolans are generally available in Malaysia. SF is commercially available, even though it originates from overseas. Sources of other pozzolans are rather abundant, nonetheless the utilization of these materials in the local concrete industry is very limited.

2.5.1 Silica fume (SF)

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

The chemical compositions and properties of SF are influenced by the composition of the principal product being made by the furnace and furnace design [Malhotra and Mehta, 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 area of 20,000 m^2/kg [Yajun and Jong., 2003].

The use of SF as a mineral admixture or as partial cement replacement material in concrete industry was increasing in many mega projects all around the world. Many researchers reported and agreed that SF is a highly reactive pozzolan that could improve the properties and durability performance of concrete. Hence, SF has been highly regarded in the concrete industry especially in the production high strength and high performance concrete.

SF is normally used in dry and densified form as mineral admixture, proportioned to produce concrete with special performance qualities. It could generally improve the properties of hardened concrete through the filler effect and pozzolanic reaction with lime 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 strength and chemical resistance of concrete, it could also lead 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 mineral admixtures has led researchers to turn their interest toward others supplementary cementitious materials and technique to obtain similar technical benefits as in the case of SF.

2.5.1.1 *Chemical composition of SF*

SF as a by-product of the manufacturing process of silicon or various silicon alloys has a high content of SiO_2 in amorphous form. The chemical compositions of SF depend 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 loss on ignition (LOI) or carbon content. The LOI of SF is on the range of 2.41 to 2.75%.

According to Neville (2002), the SiO_2 content of SF could range from as low as 80 % to greater than 90 %. This variation is influenced by the 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. Others compositions such as Al_2O_3, Fe_2O_3, CaO and alkali contents are normally low. Even though MgO is usually found as part of SF composition, but it was reported not be deleterious to concrete.

The chemical compositions of SF have been reported to be consistent, i.e. not affected by time. This is due to the relatively high purity of the raw materials used in the production of silicon metal or ferrosilicon alloys [Mehta, 1986].

2.5.1.2 *Physical characteristic of SF*

In term of mineralogy, SF consists essentially of an amorphous silica structure with a wide scattering peak. The amorphous silica structure and the fine particle are the main reasons for the excellent pozzolanic activity of SF [Sanchez et al., 1999]. The particle size of SF was reported to range from 0.1 to 0.5 μm and the nitrogen BET specific surface area is 20,000 m^2/kg [Yajun et al., 2003].

SF has a low bulk density of around 2.0 to 3.0 kg/m^3. The low bulk density of SF may cause difficulty in transporting and handling. In order to improve the handling and transport properties, SF is usually processed to increase its bulk density by densified, sluried or palletized process [Yajun and Jong., 2003].

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

2.5.2 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 place FA is also known as pulverized fuel ash (PFA) and it was found to possess pozzolanic properties due to the 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.

Two major classes of fly ash are specified in ASTM C 618 on the basis of their chemical compositions resulting from the type of coal burned; the two classes are designated as Class F and Class C. Class F fly ash is normally produced from burning anthracite or bituminous coal, and Class C is normally produced from the burning of sub-bituminous coal and lignite (Halstead, 1986. Class C fly ash usually has cementitious properties in addition to pozzolanic properties due to free lime, whereas Class F is rarely cementitious when mixed with water alone (Halstead, 1986). Some Class C FA may contain lime content of higher than 10% and low sulphur content.

Even though the use of FA in concrete has increased in the last 20 years, less than 20% of the FA collected has been used in the cement and concrete industries (Helmuth, 1987).

2.5.2.1 *Chemical compositions of FA*

Combustion of ground or powdered coal will produce a residue known as fly ash (FA). The chemical compositions of the FA may vary from one batch to another depending on the minerals associated with the coal and the burning condition during the combustion of the coal. In general, FA contains SiO_2, Al_2O_3 and Fe_2O_3 and the amount of these three compositions constitutes as the main requirement of ASTM C 618-94 in determining the classification of FA. Swamy (1986) stated that the classification of FA through the amount of SiO_2, Al_2O_3 and Fe_2O_3 is confusing, since many class C FA was observed to comply with class F requirements. In addition, FA was also reported to contain more alumina and less silica in comparison with other pozzolans [(McCarthy et al., 2005].

CaO is another oxide that normally presents in FA but its composition is governed by the type of coal used. The composition of CaO is usually lower than 10% for bituminous coal and greater than 10% for sub-bituminous coal [Neville, 2002]. The CaO composition will establish either the FA possesses a cementitious property or not. FA with high level of CaO will have cementitious properties as an additional to the pozzolanic property, while FA with low level of CaO only has a pozzolanic property [Ravindra,1986]. The amount of CaO is also used to identify the classifications of FA. FA with low CaO is classified as class F and that with high CaO content is classified as class C. ASTM C618 stated that, FA with CaO content of less than 10 % is classified as Class F while FA with CaO content greater than 10% is classified as class C [Ravindra, 1986].

Other than the four oxide compositions discuss earlier, other compositions such as MgO, Fe_2O_3, alkalise and carbon are also present and normally determined. The carbon content is assumed to be equal to the LOI. Even though the amount of MgO of FA is in many cases higher than that observed in other pozzolans, but the MgO is not harmful because it exists in a non-reactive form [Neville, 2002].

2.5.2.2 *Physical properties of FA*

FA consists of glassy spherical particles with some crystalline matter and carbon in the form of unburnt coal, which varies from plant to plant [Ramezanianpour, 1987]. The particle diameter of FA ranges between less than 1μm to 100μm with an average particle size of 20μm, while the specific surface area of FA is usually between 250 and 600 m^2/kg and the overall value of specific gravity is 2.35 [Neville, 2002].

Mineralogy analysis of FA typically contains about 50 - 90% of glass. The reactivity of glass in FA is depending on the chemical compositions especially the CaO content. The typical crystalline minerals of low calcium FA are quarzt, mullite, sillimanite, hematite and magnetite. These minerals do not posses any pozzolanic activity. High calcium FA contains minerals that may react with water, which are tricalcium aluminate, calcium aluminosulfate, anhydrite, free CaO, and alkali sulphates. High calcium FA also contains quartz and periclase but these two minerals do not give any effect on the reactions [Malhotra and Mehta, 2004].