INFLUENCE OF STEAM CURING ON ENGINEERING AND FLUID TRANSPORT PROPERTIES OF HIGH STRENGTH GREEN CONCRETE CONTAINING PALM OIL FUEL ASH

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By

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PENGARUH PENGAWETAN STIM TERHADAP SIFAT-SIFAT KEJURUTERAAN DAN PENGANGKUTAN BENDALIR KONKRIT HIJAU BERKEKUATAN TINGGI MENGANDUNGI ABU KELAPA SAWIT

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Tesis yang diserahkan untuk

memenuhi keperluan bagi ijazah

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LIST OF ABBREVIATIONS

AASHTO	American association of state highway and transportation officials
ACV	Aggregate crushing value
ASTM	American society for testing and materials
BET	Surface area based on Brunauer-Emmett-Teller theory using nitrogen gas absorption test
BSI	British standard institution
C_2S	Dicalcium silicate
C_3A	Tricalcium aluminate
C_3S	Tricalcium silicate
C_4AF	Tetracalcium aluminoferrite
CEB-FIP	Comite Euro-international du Beton (CEB) and the federation International de la Precontrainte (FIP).
CH	Calcium hydroxide
C-S-A-H	Calcium silicate aluminates hydrates
C-S-H	Calcium silicate hydrates
DRUW	Dry-rodded unit weight
DTA	Differential thermal analysis
EDX/EDS	Energy dispersive x-ray spectroscopy
FA	Fly ash
FVCA	Fraction volume of oven dry-rodded coarse aggregate Aggregate
GGBS	Ground granulated blast furnace slag
G-POFA	Ground palm oil fuel ash
HPC	High performance concrete

HRWR	High range water reducer
HSC	High strength concrete
HSGC	High strength green concrete
ISAT	Initial surface absorption test
LOI	Loss on ignition
MK	Metakaolin
MPa	Mega Pascal
MSA	Maximum size aggregate
NCR	Normal curing regime
NSC	Normal strength concrete
O.D.	Oven-dry weight of coarse aggregate
OCCA	Optimum content of coarse aggregate
OPC	Ordinary Portland cement
POFA	Palm oil fuel ash
RCMT	Rapid chloride migration test
RCPT	Rapid chloride permeability test
RH	Relative humidity
RHA	Rice husk ash
SCR	Steam curing regime
SEM	Scanning electron microscope
SF	Silica fume
SP	Superplasticizer
TGA	Thermo-gravimetric analyses
T-GPOFA	Treated palm oil fuel ash

U-POA	Ultra-fine palm oil waste ash
VA	Volcanic ash
VP	Volcanic pumice
W-POFA	Original palm oil fuel ash
XRD	X-ray diffraction
XRF	X-ray fluorescence

LIST OF SYMBOLS

%	Percentage
µ	Viscosity of the gas (Ns/m^2)
µm	Micrometer
C_{CH}	Content of calcium hydroxide in sample (%)
C_{PR}	Chloride penetration rate (m/(v.hr))
D_{nssm}	Non-steady-state migration coefficient (m^2/s)
f	Flow (mm/m^2/s)
Fc´	Compressive strength (N/mm^2)
Frc´	Designated compressive strength (N/mm^2)
K	Coefficient of gas permeability
Kw	Coefficient of water permeability
$M_{cristobalite}$	Mass percentage of cristobalite
$M_{Crystalline:}$	Total mass percentage of crystalline phases
M_{glassy}	Total mass percentage of glassy phases
$M_{K\text{-}Al\text{-}P}$	Mass percentage of potassium aluminum phosphate
M_{quartz}	Mass percentage of quartz
Mc	The total mass of sample at 100°C
Mcc	Loss in mass at between 410 to 520°C
P_{in}	Pressure at inlet (bar)
P_{out}	Pressure at outlet (bar)
Q	Volume flow rate (m^3/s)
Te	Average value of the initial and final temperatures in the solution

U	Absolute value of the applied voltage
w/b	Water to binder ratio
w/c	Water to cement ratio
X_D	Average value of the penetration depths
ρ	Density of water

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ABSTRAK

Kajian-kajian terdahulu mengenai penggunaan abu sisa bahan bakar kelapa sawit (POFA) dalam konkrit berkekuatan tinggi jelas menunjukkan keberkesanan POFA yang terhad, di mana hanya tahap penggantian yang kecil boleh digunakan dan kekuatan awal konkrit menurun dengan ketara terutama pada kandungan POFA yang tinggi. Adalah dijangkakan bahawa kecekapan POFA boleh dipertingkatkan melalui rawatan mekanikal dan haba. Ini akan membolehkan POFA digunakan dalam kuantiti yang besar dalam konkrit berkekuatan tinggi tanpa menjejaskan sifat-sifat dan prestasi konkrit. Oleh yang demikian, objektif utama penyiasatan adalah untuk mengkaji pengaruh abu sisa bahan api kelapa sawit terawat (POFA) terhadap sifat-sifat kejuruteraan dan pengangkutan bendalir konkrit hijau berkekuatan tinggi (HSGC). Di samping itu, pengaruh pelbagai regim pengawetan stim keatas sifat-sifat kejuruteraan dan pengangkutan bendalir HSGC yang mengandungi sehingga 60% POFA terawatt juga dikaji. Kesan perawatan POFA terhadap ciri-ciri fizikal dan kimianya telah diselidiki berasaskan ujian-ujian seperti teknik XRD, analisa XRF, SEM/EDX, analisa terma dan analisa saiz zarah. POFA yang diperolehi dari kilang sawit telah dirawat menggunakan rawatan haba untuk menghapuskan lebihan kandungan karbon dan dikisar kepada saiz zarah median kurang lebih 2 µm. POFA terawatt halus (U-POFA) yang terhasil telah digunakan untuk menghasilkan HSGC dengan tahap penggantian POFA 0, 20, 40 dan 60% daripada jisim simen Portland biasa (OPC). Keputusan kajian menunjukkan bahawa rawatan yang dijalankan terhadap POFA menghasilkan pozzolan yang sangat cekap. HSGC mengandungi U-

POFA mempamerkan kebolehkerjaan dan pengekalan kebolehkerjaan yang unggul serta masa pemejalan yang terencat berbanding HSGC yang mengandungi POFA yang tidak dirawat dan juga HSC-OPC kawalan. Bagi kes kekuatan mampatan, penggunaan U-POFA mengurangkan kekuatan awal pada umur 1, 3 dan 7 hari, tetapi meningkatkan kekuatan pada 28, 90, 180 dan 360 hari untuk semua HSGC mengandungi POFA, dimana kekuatan melebihi 95 MPa dicapai untuk semua POFA-HSGC pada umur 28 hari. Manakala, sifat-sifat pengangkutan bendalir yang dinilai melalui ujian keliangan, penyerapan permukaan awal, penyerapan air, kebolehtelapan klorida pesat, penghijrahan klorida pesat, kebolehtelapan gas dan kebolehtelapan air menunjukkan peningkatan yang ketara dengan penggunaan U-POFA, di mana HSGC yang mengandungi 60% U-POFA mempamerkan peningkatan terbesar pada jangka pendek (28 hari) dan jangka panjang (360 hari). Pengaplikasian regim pengawetan stim menyumbang terhadap peningkatan kekuatan awal pada 1, 3 dan 7 hari, di mana peningkatan di dalam sifat-sifat konkrit bergantung kepada kadar penggantian U-POFA serta suhu dan juga tempoh pengawetan stim. Di samping itu, U-POFA memainkan peranan dalam mengurangkan kesan negatif yang mungkin terhasil ekoran daripada penggunaan regim pengawetan stim yang berbeza. Oleh itu, keputusan keseluruhan kajian menunjukkan U-POFA mempunyai potensi yang signifikan sebagai bahan tambah mineral pozzolan yang efisyen untuk penghasilan HSGC dengan menjanjikan sifat-sifat kejuruteraan dan pengangkutan bendalir yang unggul apabila dikenakan pengawetan biasa dan regim pengawetan stim.

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ABSTRACT

Previous studies on the utilization of palm oil fuel ash (POFA) in high strength concrete indicated clear limitation in term of the efficiency of the POFA, whereby only small replacement can be used and early strength is significantly reduced in particular at high POFA content. It is envisaged that the efficiency of the POFA could be improved via mechanical and heat treatments. This will enable the POFA to be used in greater volume in high strength concrete, without jeopardizing the properties and performance of the concrete. Thus, the main objective of this investigation is to study the influence of treated palm oil fuel ash (POFA) on the engineering and fluid transport properties of high-strength green concrete (HSGC). In addition, the influence of application of various regimes of steam curing on the engineering and fluid transport properties of the HSGC containing up to 60% of treated POFA is also studied. Effect of treated POFA on its chemical and physical properties has been studied based on tests such as XRD techniques, XRF analysis, SEM/EDX, thermal analysis and particle size analysis. POFA obtained from a palm-oil industry waste was treated via heat treatment to remove excess carbon and ground to a median particle size of about 2 μm. The ultrafine POFA (U-POFA) obtained was then utilized in the production of HSGCs with POFA replacement levels of 0, 20, 40 and 60% by mass of ordinary Portland cement (OPC). The results show that the treatment processes undertaken on the POFA result in a highly efficient pozzolan mineral admixture for HSC and will enable it to be utilized higher quantity. The HSGC containing the U-POFA exhibits superior workability and workability retention as well as extended setting times when compared with HSGC containing untreated POFA and the control OPC HSC. In the case of compressive strength, the inclusion of the U-POFA reduces early age strength of the HSGC at 1, 3 and 7 days, but enhances the strength at 28, 90, 180 and 360 days for all HSGCs containing POFA, where strength exceeding 95 MPa was achieved for all the POFA-HSGCs at the age of 28 days. Whereas the transport properties assessed via initial surface absorption, porosity, water absorption, rapid chloride permeability, rapid chloride migration, gas permeability and water permeability tests show significant improvement with the inclusion of the ultrafine POFA, with the HSGC containing 60 % U-POFA exhibiting the greatest improvement at short-term (28 days) and long-term (360 days). The application of steam curing regimes contributes towards improving the compressive strength and fluid transport properties of the HSGC at the early ages of 1, 3 and 7 days, whereby this improvement in the properties of concrete depends largely on replacement rates of cement by the U-POFA and the temperature as well as the period of steam curing. In addition, the U-POFA plays a role in lessening the negative effect that may result from the employment of the different steam curing regimes. Thus, the overall results show that the U-POFA possesses significant potential as an efficient pozzolanic mineral admixture for the production of HSGC with promisingly superior engineering and fluid transport properties when subjected to normal and steam curing regimes.

CHAPTER 1

INTRODUCTION

1.1. Introduction

Concrete is an integral part of the construction of all building structures around the world. Presently, the major thrust is on developing newer concrete in order to adhere to the latest specifications for satisfying modern construction requirements. One such new and modern type of concrete is the “high-strength green concrete” (HSGC). It is a combination of green concrete and high strength concrete. Protecting the environment is the main concern of green concrete (environmental friendly concrete). This protection is accomplished by the ability of this type of concrete to include industrial and agricultural wastes as part of the binder components. This process has three main benefits: 1) reducing the resurgence of carbon dioxide through minimization of cement usage; 2) mitigating the hazardous effects of wastes by their usage in concrete industries; this usage will completely remove wastes from being a source of environmental pollution and; 3) improving properties of high strength concrete which results in reduction of overall cost of concrete production.

High strength concrete (HSC) has undergone significant development over the past few years. The definition of HSC has been changing with the passage of time. A concrete having a compressive strength of about 34 MPa easily fitted the definition of HSC in the late 1950’s, whereby a concrete having compressive strength of more than 41 MPa was a rarity with its usage limited to only few applications. According to CEB-FIP (1990) state-of-the-art report, things changed in 1990 onwards with compressive strength of HSC defined at 60 MPa. Presently, a concrete having a compressive strength exceeding 80 MPa fits the specifications of HSC (Persson, 1996; Neville, 2012). Moreover, the applications of HSC have increased, and it has now been used in many parts of the world. HSC can be manufactured using several methods of mix design. In particular, its composition consists of strong coarse aggregates, high content of Portland cement and lower water/(cement or binder) ratio. Nowadays, high range water reducer (superplasticizer) is extensively utilized in HSC production, in addition to mineral admixtures. The production of HSC necessitates the use of low water/binder ratio (w/b), typically in the range of 0.22 to 0.35. Therefore, the use of high range water reducing admixture or superplasticiser is required to obtain this low water/binder ratio as well as to achieve adequate workability. Mineral admixtures such as silica fume are usually used in HSC mixture, to achieve compressive strength above 80 MPa at the age of 28 days. Sometimes, other pozzolanic mineral admixtures such as ground granulated blast-furnace slag and fly ash are used in order to achieve the desired HSC. However they may have limited strength especially at high replacement level and also at early ages (Neville & Aitcin, 1993; Megat Johari, 2000).

Pozzolanic materials are mostly originated from industrial or/and agricultural wastes. Therefore, the utilization of these pozzolanic waste materials to produce concrete is necessary and is beneficial from environmental point of view. Moreover, from an economic perspective, the use of these pozzolanic materials considerably decreases the quantity of Portland cement used in the production of concrete, which in turn leads to potential reduction in overall cost of producing concrete. Furthermore, these additives can contribute towards improving the engineering properties of concrete such as strength and transport properties, which consequently could lead to enhancement in durability performance. The employment of pozzolanic materials with Portland cement to manufacture high-strength concrete helps at improving the properties of HSC. The efficiency of pozzolanic materials depends on the reactions between the amorphous silica (SiO_2) and the calcium hydroxide $Ca(OH)_2$ to produce calcium silicate hydrate (C-S-H) gel. Also the fineness and shape of the pozzolanic materials make the concrete more homogeneous and denser, due to the filling and refining of the pores (Sellevold, 1987; Detwiler & Mehta, 1989; Siddique, 2011b).

Palm oil fuel ash (POFA) is a new addition to the list of pozzolanic materials. Palm oil is a popular crop in Malaysia and it constitutes one of the major agro industries in the region. Raw materials in the form of fresh fruit bunches are supplied to the palm oil industry which generates a large amount of solid waste materials in the form of empty fruit bunches, fibers and kernel shells. These solid waste materials in turn are used as fuel to heat boiler to produce steam and generate electricity required in the palm oil extraction process. After combustion, the raw materials produce around 5% POFA by weight from the overall solid wastes. Due to the limited utilization of POFA, it has to be disposed off as landfill materials, leading to a potential future environmental problem. However, many researchers (Tay, 1990; Tay & Show, 1996; Awal & Hussin, 1997) found that POFA had pozzolanic properties and could be used as a partial replacement of cement in concrete. Tables 1.1 and 1.2 present the physical and chemical properties of ordinary Portland cement (OPC) and POFA.

Table 1.1: Physical properties of OPC and POFA (Awal & Hussin, 1997)

Physical properties	**OPC**	**POFA**
Surface area (m^2/kg)	314	519
Specific gravity	3.28	2.22

Table 1.2: Chemical compositions of OPC and POFA (Awal & Hussin, 1997)

Component	**OPC** (%)	**POFA** (%)
Silicon dioxide (SiO_2)	20.2	43.6
Aluminium oxide (Al_2O_3)	5.7	11.4
Ferric oxide (Fe_2O_3)	3.0	4.7
Calcium oxide (CaO)	62.5	8.4
Magnesium oxide (MgO)	2.6	4.8
Sulphur trioxide (SO_3)	1.8	2.8
Sodium oxide (Na_2O)	0.16	0.39
Potassium oxide (K_2O)	0.87	3.5
Loss on ignition (LOI)	2.7	18.0

According to Abdul Awal & Hussin (1996), POFA fulfills the requirements of ASTM C618 (ASTM, 2005) as a good pozzolanic material and can be group in between class C and F pozzolan. Tables 1.3 and 1.4 respectively show the chemical and physical requirements of classes N, F and C of pozzolanic mineral admixtures according to ASTM C618. Based on the POFA chemical compositions in Table 1.2 and the ASTM C618 chemical requirements in Table 1.3, it is clear that the POFA does not satisfy the ASTM C618 chemical requirement with regards to LOI. The listed LOI value of 18% in Table 1.2 is much higher than the maximum allowable value of 12% for class F mineral admixture for material with acceptable performance records.

Table 1.3: Chemical requirements of classes N, F, and C based on ASTM C618 (ASTM, 2005)

Type	**Mineral admixture class**		
	N	**F**	**C**
SiO_2+Al_2O_3+Fe_2O_3, min (%)	70	70	50
SO_3, max (%)	4	5	5
Moisture content, max (%)	3	3	3
Loss on ignition, max (%)	10	6	6

Table 1.4: Physical requirements of classes N, F, and C based on ASTM C618 (ASTM, 2005)

Type	**Mineral admixture class**		
	N	**F**	**C**
Fineness; Amount retained when wet-sieved on 45 µm, max, (%)	34	34	34
Strength activity index. With Portland cement, at 7 days, min, percent of control	75	75	75
Strength activity index. With Portland cement, at 28 days, min, percent of control	75	75	75
Water requirement, max, percent of control	115	105	105
Density, max variation from average, (%)	5	5	5
Percentage retained on 45 µm, max variation, percentage points from average	5	5	5

According to Tonnayopas *et al.* (2006) pozzolanic reaction between the POFA and cement matrix can affect the development of concrete strength. In addition, it has been found that POFA had pozzolanic properties and could be used as a partial replacement of cement in concrete (Tay, 1990; Awal & Hussin, 1997; Sukantapree *et al.*, 2002). The test results on the performance of POFA revealed that it had a good potential in reducing the expansion due to alkali silica reaction (Awal & Hussin, 1997). Nonetheless, the large size of POFA particle and its porous structure make the POFA to have low pozzolanic potential. According to Abdul Awal & Hussin (1996) and Sukantapree *et al.*(2002), grinding the pozzolanic material can improve the reactivity of POFA.

The amount of gel resulting from the process of hydration of cement is important in determining the properties of concrete. Curing of concrete has a significant effect on the properties of hardened concrete. The objective of concrete curing is to keep concrete saturated to promote the hydration of cement. In general, proper curing of concrete is expected to improve its properties such as strength, abrasion resistance, durability, water tightness, volume stability, and resistance to freezing and thawing. Hydration of cement continues for several years as long as the mixture contains unhydrated cement particles, the presence of water and under a favorable temperature conditions but the rate keeps decreasing over time. Curing method, time period as well as temperature directly affects the properties of concrete. The normal curing method involves immersing concrete samples in water for specific time duration. Among the other methods is the steam curing method accomplished under atmospheric pressure conditions. This type of curing is used to improve some of the engineering properties of concrete. The steam curing is often used to accelerate the hydration process which will eventually lead to an increase in the compressive strength of concrete at early age. The steam curing method is mostly used in the production of precast concrete (Liu *et al.*, 2005; Yazici *et al.*, 2005). The advantage of using steam curing method is that the initial rate of strength development is accelerated due to the elevated temperature of steam in addition to high humidity. In faster production lines, steam curing results in achieving the desired early strength with short active curing time (Higginson, 1961; Turkel & Alabas, 2005). Most of the steam curing plants uses twenty-four hours cycle in order to speed up the production and to reduce the costs of concrete casting. Typical steam-curing cycle at the atmospheric pressure consists of four stages. The first stage is the initial delay period prior to steaming process, the second stage is a period of increase in the temperature inside the steam curing tank, in the third stage, the peak temperature for steam curing remains constant, the fourth stage is a period for decrease in the steam curing temperature.

1.2. Research Problem Statements

The recent spur in the development of activities in the field of construction and housing has resulted in increased demand for cement in Malaysia. Therefore, reducing the consumption of cement obviously helps in decreasing the construction costs. In addition, the increase in cement production to cater for the escalating demand causes greater damage to the environment due to the production of carbon dioxide during its manufacture. Hence, attempts at reducing the consumption of cement help to preserve the environment. In Malaysia, local materials such as POFA can be used as a partial substitute for cement to produce “GREEN CONCRETE” that greatly assists in reducing the environmental impact of wastes, as well as reduces the cost of construction with improvement in the performance of concrete. As a whole, extensive utilization of by-product based pozzolanic mineral admixture such as POFA could contribute towards better sustainability of the concrete industry.

Accordingly, the sufficiently amorphous POFA contains high amount of silica (SiO_2) which makes it possible to be used as a pozzolanic material in concrete. Nonetheless, previous research has shown that the maximum quantity of POFA that can be used in

HSC is about 30% from the mass of cement, when the POFA is used as partial cement replacement material. This limitation could be attributed to the coarser particle size and high unburned carbon of the POFA used. Therefore, in the present study, POFA was treated to lower the unburned carbon and to reduce the particle size and then used in the production of HSC by partially substituting ordinary Portland cement (OPC) at replacement levels of 0, 20, 40 and 60% on mass-for-mass basis. It was envisaged that the treatment process undertaken will enhance the efficiency of the POFA as pozzolanic mineral admixture for HSC and will enable it to be utilized higher quantity.

The available literature also indicates that the application of POFA as a partial substitute for cement in concrete production led to a decrease in compressive strength at early ages, with improvements in later ages. This problem somehow puts a restriction on the use of POFA in the concrete industry. This issue can probably be solved by the use of steam curing, which can raise the potential performance of concrete containing POFA at early ages. This will further enhance the POFA usage in HSC industry, especially for the precast and pre-stressed concrete. The application of POFA in concrete, especially in HSC requires further investigations. This is more pertinent when the POFA is treated for better efficiency, thus, its effects on the engineering and transport properties of HSC at early and later ages should be investigated.

1.3. Aim and Objectives

The primary aim of this study is to utilize agro-industry waste material, POFA that is locally available in Malaysia to produce HSC, which is environmentally friendly (high-strength green concrete, HSGC), as well as a concrete that has high durability to sustain the internal and external effects of aggressive environment. Thus the research intends to achieve the following specific objectives:

1) To quantify the effect of mechanical and heat treatment processes of POFA via physical and chemical characterizations.
2) To study the effect of POFA inclusion on engineering and fluid transport properties of HSGC.
3) To investigate the influence of steam curing regimes on engineering, microstructure and fluid transport properties of HSGC containing POFA.

1.4. Scope of Research

The engineering and transport properties of high-strength green concrete containing POFA are influenced by many factors. Among these factors, characteristics of the POFA used, rates of replacement of the cement with POFA, and type of curing are considered crucial.

In this research, different POFA replacement parentages namely 0, 20, 40 and 60% are examined in order to assess the influence of POFA content on the relevant properties of HSGC. In addition, the effect of different steam curing temperatures of 50^oC, 65^oC, and 80^oC with steam curing period of 16 hours is studied. Similarly, the influence steam curing periods of 6 hours, 11 hours and 16 hours are studied at steam curing temperature of 80°C. The production of HSGC requires high quality materials, optimum mix design and preparation of trial mix. Therefore, low w/b ratio is considered, and superplasticizer is added to give good fresh concrete properties. Furthermore, in order to improve the properties of POFA, it is important to optimize the properties of HSGC, which requires the treatment process (mechanical and heat treatment) the waste of palm oil fuel ash, to improve its efficiency while concomitantly conforming the requirements of relevant standards in particular ASTM C618 (ASTM, 2005).

In the fresh concrete state, the engineering properties such as setting times, workability and workability retention are evaluated. In addition, the hardened concrete state, the compressive strength and fluid transport properties are evaluated. For this study, steam curing cycle of not exceeding 24 hours is applied. The samples after being subjected to the steam curing regimes are immersed in a water tank, immediately after 24 hours until the testing ages. The concrete samples are then taken from the curing water tank to conduct tests at the ages of 1, 3, 7, 28, 90, 180 and 360 days. The influence of the POFA as partial cement replacement with steam curing regimes on engineering and transport properties of the HSGC are then evaluated. Besides compressive strength, fluid transport properties; namely initial surface absorption, porosity, water absorption, gas permeability, water permeability, rapid chloride permeability and rapid chloride migration are studied. In addition, the changes in the microstructure of the HSGC due to U-POFA inclusion and steam curing are also studied using scanning electron microscope with energy dispersive X-ray microanalysis (SEM/EDX), X-ray diffraction (XRD) and thermal analysis (TGA/DT).

1.6. Layout of Thesis

Chapter one gives the background of the study, presenting an overview of the present research. It also discusses the issues concerning the research problems, aims and objectives

Chapter two presents an introduction to the materials used for the production of HSGC. It also presents the background of the characteristics of pozzolanic materials, in addition to characteristics of the palm oil fuel ash used. It highlights the performance of the HSGC containing the pozzolanic materials, and also the effect of application of steam curing regimes on the performance of the HSGC.

Chapter three presents the materials used and methods adopted throughout the experimental work. The procedures used in the treatment of the POFA for improving its properties and increasing its efficiency are presented. In addition, the mix design and mixture proportions used for the production of HSGC, mixing, casting as well as curing procedures adopted are also described. The last part of the chapter explains the detailed experimental procedures undertaken in the research.

Chapter four presents the results and discussion on the process of treatment of the POFA and the effects on its chemical and physical characteristics. It also presents the results and discussion on the effect of using treated and untreated POFA (G-POFA and U-POFA) as partial replacement of cement by rates up to 60%, on the characteristics of fresh high-strength green concrete, namely setting times, workability, and workability retention.

Chapter five presents the results and discussion on the effect of using the G-POFA and U-POFA as partial replacement by rates up to 60% of cement mass, on the strength of the high-strength green concrete. In addition, the influence of application of steam curing regime adopted using several temperatures (50°C, 65°C and 80°C) at 16 hours and also with different periods (6 hours, 11 hours and 16 hours) at 80°C, on the properties of HSGC containing U-POFA are discussed. In addition, the results and discussion also portray the effect of using the U-POFA as partial cement replacement by rates up to 60% of cement mass, on the microstructure of the HSGC binders based on the thermogravimetric, X-ray diffraction and scanning electron microscopy analyses.

Chapter six presents the results and discussion on the effect of using the G-POFA and U-POFA as partial replacement by rates up to 60% of cement mass, on fluid transport properties of the HSGC. Moreover, the influence of application of steam curing regimes adopted on fluid transport properties of the HSGC containing U-POFA are evaluated via the initial surface absorption, porosity, water absorption, gas permeability, water permeability, rapid chloride permeability and rapid chloride migration tests.

Chapter seven presents the conclusions and recommendations for future research.

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

The rapid development in all areas of civil engineering has led to increased demand for concrete. Consequently, many researchers have focussed their attention towards developing concrete that suits the present construction requirements and are capable of withstanding the harsh surrounding environment. This has led to the development of the concept of high-strength concrete (HSC) over the years. HSC is generally employed in the construction of large structures or high-rise buildings. Their use can reduce the size of structural elements and construction weight, eventually reducing the overall cost of the building. In the context of Malaysia, where many structures are built in aggressive environment, it is very important to use a good quality HSC. Therefore, in order to minimize the damage caused by the harsh environment, mineral additives are added as part of the binder in the production of concrete. There are a large number of additives which could bring about positive impact on durability performance of concrete.

HSC could somehow induce a negative impact on the environment, because the production of HSC consumes a large amount of cement, and the process of manufacturing of cement leads to the emission of large quantity of CO_2, causing harm to the environment. It has been estimated that about a ton of carbon dioxide is generated for every ton of Portland cement produced (Mehta, 1994; Bouzoubaa *et al.*, 1998; Mehta, 2002; Turanli *et al.*, 2005). The use of cement replacement materials which partially substitutes the Portland cement in HSC helps to reduce the environmental pollution and minimize the cost of construction (Domone & Illston, 2010).

Most of the supplementary cementitious materials that are commonly used include wastes from industrial processes, thereby having significant economic advantages. Moreover, the added advantage of these additives is that they can be used to enhance the existing properties of HSC. The use of industrial and agricultural waste for the production of HSC, can therefore produce high strength green concrete (HSGC) or environment-friendly HSC. In this chapter, an introduction to the materials used for the production of HSGC is presented, and existing methods of curing concrete, which improves HSGC properties, and other properties related to this research are reviewed. Particular attention is given to the effect of the supplementary cementitious materials (pozzolanic material) and steam curing regimes, on the relevant properties of HSGC.

2.2. Materials for High Strength Green Concrete

HSC used in the construction industry usually utilizes the same materials employed for the production of normal strength concrete (NSC). However, unlike in the case of NSC, superplasticizer (sp) is an essential element of HSGC. Furthermore, for higher strength range, silica fume (SF) is normally added to concrete and other mineral admixtures such as fly ash (FA) and ground granulated blast slag (GGBS) also can be used. In addition, the use of good quality and stronger aggregate will be an added advantage to the strength of the concrete (Megat Johari, 2000; Lothenbach *et al.*, 2011). As well, pozzolanic materials in the form of waste ash originating from agriculture-based industry such as rice husk ash, palm oil fuel ash and bagasse ash can be used to partially replace the Portland cement, in order to enhance the strength and durability performance of concrete (Tangchirapat *et al.*, 2009a; Kishore *et al.*, 2011; Rukzon & Chindaprasirt, 2011).

2.2.1. Cement

Ordinary Portland cement (Type I) is normally used to produce HSC, and in situations where high early strength is required such as in precast concrete industry, rapid-hardening Portland cement (Type III) can be used. The strength development, strength potential and other properties of HSC depend on the type of cement. The strength development characteristics of HSC may not be identical. This can be due to the allowed variation in the compositions and fineness of cement, in accordance with the standard specifications, owing to variation in manufacturing practices of a certain type of cement. The major compound compositions in ordinary Portland cement (OPC) are tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF) (Neville, 2012). The silicates, C_3S and C_2S in cement are the most important component responsible for producing C-S-H gel as a result of cement hydration. Table 2.1 shows the chemical compositions, while Table 2.2 shows the compound compositions and fineness of the ordinary Portland cement.

Table 2.1: Chemical compositions of cement (Kosmatka et al., 2002)

Portland cement	**Chemical compositions (%)**						
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**Na_2O**
Min.-Max.	18.7-22	4.7-6.3	1.6-4.4	60.6-66.3	0.7-4.2	1.8-4.6	0.11-1.2
Mean	20.5	5.4	2.6	63.9	2.1	3.0	0.61

Table 2.2: Compound compositions and fineness of cement (Kosmatka *et al.*, 2002)

Portland cement	**Compound compositions (%)**				
	C_2S	**C_3S**	**C_3A**	**C_4AF**	**Blaine fineness (m^2/kg)**
Min.-Max.	40-63	9-31	6-14	5-13	300-421
Mean	54	18	10	8	369

The C_3S is responsible for early strengths at 3, 7, and 28 days and the early strength would be higher if the cement contains relatively large amounts of C_3S. On the other hand, the C_2S contributes to later age strength with slow rate of hydration at early age. Therefore, its participation increases the long-term strength, normally over the age of 28 days. Thus, cement with higher relative proportion of C_2S normally exhibits lower early strength, but higher long-term strength. Meanwhile, C_3A liberates high heat of hydration in the first few days, and it contributes significantly towards setting, with slight contribution towards the development of early strength (Taylor, 1997; Tennis & Jennings, 2000; Kosmatka *et al.*, 2002). By altering the cement compositions, its strength development characteristics can be modified. Moreover, adjusting the cement fineness facilitates easy control over rate of early strength development. Also, by making a change in the surface area of the cement from 320 to 450 m^2/kg (Blaine fineness), it is possible to increase the compressive strengths of cement mortar, between 50% to 100%, 30% to 60% and 15% to 40% at test ages of 1, 3, and 7 days, respectively (Mehta & Monteiro, 2006). A higher specific surface area will result in rapid hydration kinetics, however it may reduce the later age strength development (Megat Johari, 2000; Neville, 2012).

Production of HSC requires high content of cement; this would increase the shrinkage and creep in concrete. Therefore, it is not recommended to use big amount of cement exceeding 550 kg/m^3 to control shrinkage. The preferred content of cement in the production of HSC varies between 400 to 550 kg/m^3. Nevertheless, it is possible to use a total binder content (cement and SF) of up to 650 kg/m^3(Burg & Ost, 1992; Neville, 2012).

2.2.2. Mineral Admixture

Mineral admixture denotes minute granular materials, added to concrete and cement mortar to obtain specific engineering properties, which can be used as a partial replacement, or as an additive to cement. It is economically advantageous and promotes recycling of industrial and other waste by-products making it environmental friendly cement. Mostly, pozzolanic materials are used as mineral admixtures. Other than being pozzolanic, some of these admixtures have additional self cementitious properties. In the past, natural pozzolans from volcanic earths, tuffs, and shales were used. However, recently silica fume, fly ash, ground granulated blast furnace slag, rice husk ash and other industrial waste have become the main source of mineral admixtures (Megat Johari, 2000; Neville, 2012; Ozer & Ozkul, 2004). In ASTM C618 standard specification, pozzolan is defined as "siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties" (ASTM, 2005). The uses of mineral admixtures, pozzolanic or/and cementitious materials could affect the properties of concrete both in the fresh and hardened states. In fresh concrete, mix proportions, water requirement, setting characteristics, rheological characteristics including workability, bleeding and cohesiveness, heat evolution rate, total heat of hydration and several other properties are influenced by the use of mineral admixtures. In the case of hardened concrete, the rate of strength development and ultimate strength, permeability characteristics, sulphate and chloride resistance, alkali silica reaction, carbonation, thermal cracking and shrinkage are influenced by the use of mineral admixtures (Chandra, 1996; Neville, 2012; Sata *et al.*, 2007; Chandara *et al.*, 2010).

2.2.2. (a) Pozzolanic Materials

In general, pozzolanic materials possess different properties and react differently with $Ca(OH)_2$ in the presence of water at normal temperature to form compounds possessing cementing properties. The pozzolanic materials, having good characteristics can be used to improve the properties of concrete in terms of long-term strength and durability performance. They can be used either as partial replacement or as additive, to cement. According to ASTM C618, depending upon the compositions and particle characteristics, pozzolanic materials can be classified into three different classes; N, C and F, as shown in Table 2.3 (Toutanji *et al.*, 2004; ASTM, 2005; Elahi *et al.*, 2010; Lothenbach *et al.*, 2011).

Table 2.3: ASTM C618 requirements for fly ash and natural pozzolans for use as mineral admixtures in Portland cement concrete (ASTM, 2005)

Chemical requirements	**Mineral admixture class**		
	N	**F**	**C**
Silicon dioxide (SiO_2) plus aluminum oxide (Al_2O_3) plus iron oxide (Fe_2O_3), min, %	70.0	70.0	50.0
Sulfur trioxide (SO_3), max, %	4.0	5.0	5.0
Moisture content, max, %	3.0	3.0	3.0
Loss on ignition, max, %	10.0	6.0	6.0
Available alkalies, as equivalent, as Na_2O, max, %	1.5	1.5	1.5
Physical requirements			
Fineness: Amount retained when wet-sieved on 45 µm (No.325) sieve, max, %	34	34	34
Strength activity index: With Portland cement, at 7 and 28 days, min, percent of control	75	75	75
Pozzolanic activity index, with lime at 7 days, min. (MPa)	5.5	5.5	-
Water requirement, max, percent of control	115	105	105
Autoclave expansion or contraction, max, %	0.8	0.8	0.8
Density, max variation from average, %	5	5	5
Percent retained on 45-µm (No. 325), max variation, percentage points from average (%)	5	5	5

Note: The use of Class F pozzolan containing up to 12.0 % loss on ignition may be approved by the user if either acceptable performance records or laboratory test results are made available.

In addition, there are also some pozzolans which are non-crystalline or poorly crystalline but contain sufficient calcium to form compounds which possess cementitious properties after interaction with water. According to Malhotra & Mehta (1996), they can be classified as in Table 2.4

Table 2.4: Classification, compositions, and particle characteristics of mineral admixtures for concrete (Malhotra & Mehta, 1996)

Classification	Chemical and mineralogical compositions	Particle characteristics
Cementitious and pozzolanic Ground granulated blast-furnace slag (cementitious)	Mostly silicate glass containing mainly calcium, and silica, crystalline compounds of melilite group may be present in small quantity.	Unprocessed material is of sand size and contains 10-15% moisture. Before use it is dried and ground to particles less than 45µm (usually about 500 m^2/kg blaine). Particles have rough texture.
High–calcium fly ash (cementitious and pozzolanic)	Mostly silicate glass containing mainly calcium, and alkalis. The small quantity of crystalline matter present generally consists of quartz and C_3A; free lime and periclase may be present; CS and C_4A_3S may be present in the case of high-sulfur coals. Un-burnt carbon is usually less than 2%.	Powder corresponding to 10-15% particles larger than 45 µm (usually about 300-400 m^2/kg blaine). Most particles are solid spheres less than 20 µm in diameter. Particle surface is generally smooth but not as clean as in low calcium fly ash.
High active pozzolans Condensed silica fume	Consists essentially of pure silica in non-crystalline form.	Extremely fine powder consisting of solid spheres of 0.1 µm average diameter (about 20,000 m^2/kg surface area by nitrogen adsorption).
Rice husk ash	Consists essentially of pure silica in non-crystalline form.	Particles are generally less than 45 µm but they are highly cellular (about 60,000 m^2/kg surface area by nitrogen adsorption).
Normal pozzolans Low-calcium fly ash	Mostly silicate glass containing aluminium, iron, and alkalis. The small quantity of crystalline matter presents generally consists of quartz, mullet, sillimanite, hematite, and mangnetite.	Powder corresponding to 15-30% particles larger than 45 µm (usually about 200-300 m^2/kg blaine). Most particles are solid spheres less than 20 µm.

There are many types of mineral admixtures, in addition to new types discovered that can be classified as pozzolanic materials. Pozzolans can be classified into two types namely, natural or artificial. The natural pozzolans are formed from volcanic activity. Artificial pozzolans are produced by the combustion of traditional materials such as calcined clay, silica stone and metakaolin. Agricultural ashes such as rice husk ash, palm oil fuel ash and bagasse ash and industrial wastes such as ground granulated blast furnace slag, silica fume and many types of fly ash also fall under this category (Tay & Show, 1996; Targan *et al.*, 2003; Rukzon & Chindaprasirt, 2011).

2.2.2. (b) Pozzolanic Activity

The pozzolanic activity is the ability of pozzolanic material to react with calcium hydroxide in the availability of water to produce compounds containing cementitious properties. Interaction of active silica or non-crystalline silica glass (amorphous silica) with lime is more rapid when compared to that with crystalline silica which has lower interaction properties (Antiohos & Tsimas, 2006). New chemical compounds such as, calcium silicate hydrate (C-S-H) and calcium hydroxide ($Ca(OH)_2$) also written as (CH) are released in the hydration process of two major compounds of cement namely tricalcium silicate (C_3S) and dicalcium silicate (C_2S). Consequently the pozzolanic reaction will take place only when CH is released, such that the pozzolanic material in mortar or concrete mix, interacts to produce C-S-H along with calcium aluminate hydrate C-S-A-H, which in general terms are known as cement gels, formed from hardened cement paste (Isaia *et al.*, 2003; Lothenbach *et al.*, 2011). In general, the pozzolanic activity depends not only on the pozzolanic reaction with CH, but also on the filler effect or physical effect through distribution of the particles in the mixture. This decreases the pores of hardened paste matrix and makes it denser and more homogeneous leading to improvement in the microstructures and properties of concrete. Figures 2.1(a, b, c, d, e and f) show the different forms of particulate material in the pozzolans. Consequently, many researchers have reported that, the pozzolanic activity depends on several factors such as: 1) percentage of pozzolanic materials (SiO_2+Al_2O_3+Fe_2O_3) in mineral admixtures, 2) content of non-crystalline (amorphous) silicon dioxide (SiO_2), 3) distribution of particle size, 4) specific surface area and 5) particles shape (spherical, cuboid, plate etc. (Cordeiro *et al.*, 2011; Megat Johari *et al.*, 2011). Therefore, improving these factors will help increase the effectiveness of pozzolanic material which in turn would lead to improved properties of concrete. Equations 2.1 and 2.2 illustrate the hydration of cement and pozzolanic reaction:

$$(C_2S \text{ or } C_3S) + (H_2O) \rightarrow \text{primary C-S-H} + Ca(OH)_2 \qquad (2.1)$$

$$Ca(OH)_2 + \text{pozzolan} \rightarrow \text{secondary C-S-H} \qquad (2.2)$$

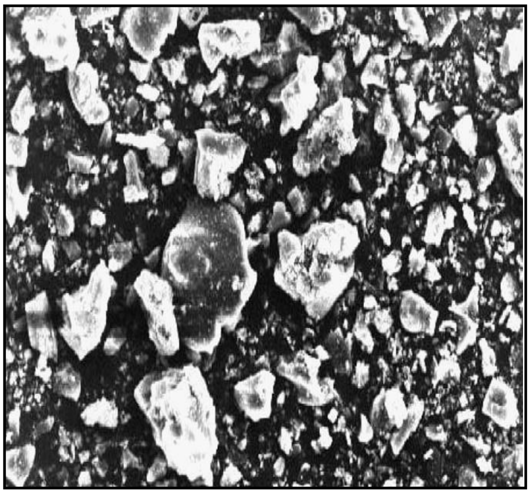

Figure 2.1 (a): Ground Rice husk–bark ash (Sata *et al.*, 2007)

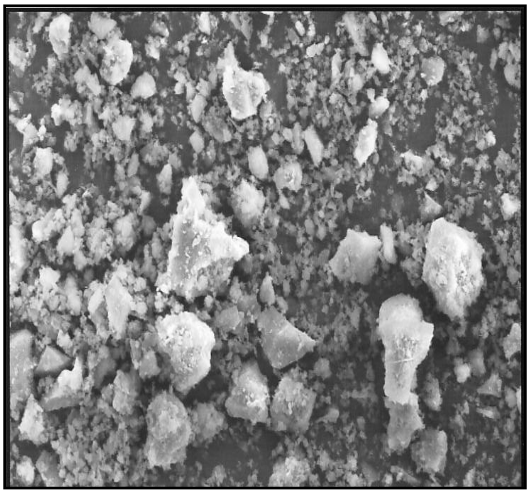

Figure 2.1 (b): Ground bagasse ash (Somna *et al.*, 2011)

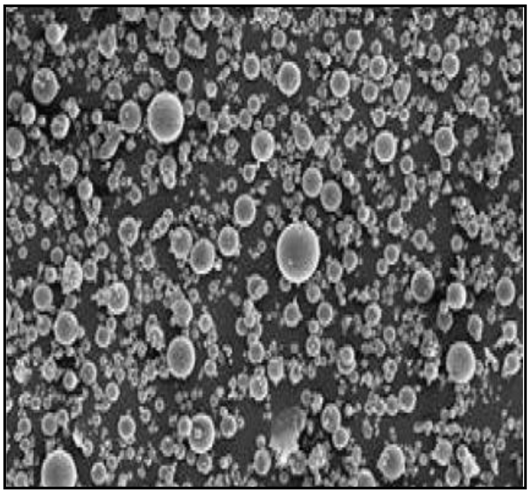

Figure 2.1 (c): Fine fly ash
(Chindaprasirt *et al.*, 2008a)

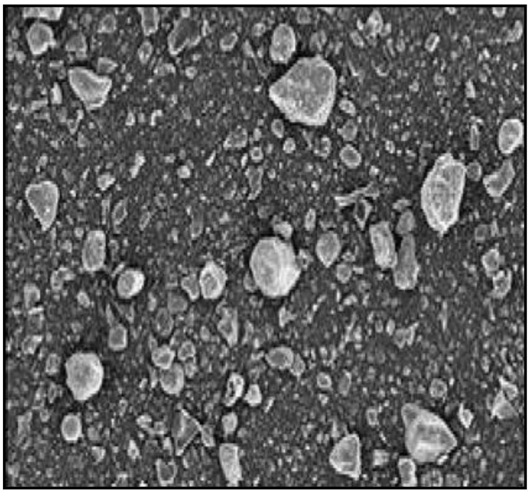

Figure 2.1 (d): Ground palm oil fuel ash
(Chindaprasirt *et al.*, 2008a)

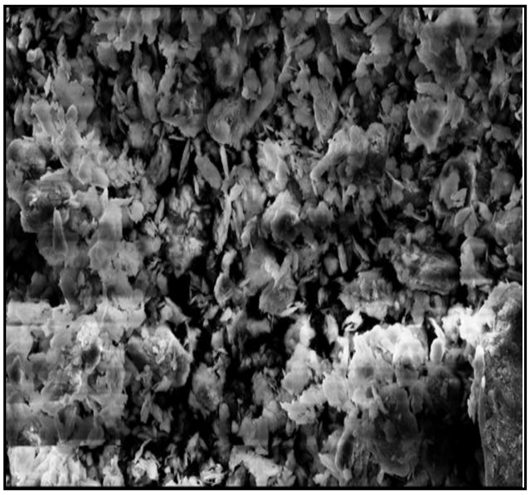

Figure 2.1 (e): Metakaolin
(Chindaprasirt *et al.*, 2008a)

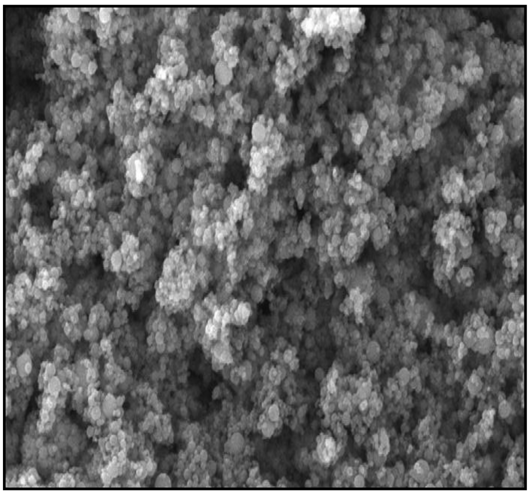

Figure 2.1 (f): Silica fume
(Chindaprasirt *et al.*, 2008a)

2.2.2. (c) Some of the Pozzolanic Materials

a) **Volcanic materials**: such as volcanic ash (VA) and volcanic pumice (VP) are found abundantly in volcanic areas around the world. These volcanic materials can be used to produce low cost construction materials that are sustainable. Volcanic materials are also classified as pozzolanic materials because they satisfy the requirements of ASTM C618 (ASTM, 2005). Moreover they react with calcium hydroxide ($Ca(OH)_2$), producing cementious materials (Hossain, 2003; Siddique, 2011a). A study by Hossain (2005) showed that VA and VP are made up of silica and have similar composition (refer Table 2.5).

Table 2.5: Chemical compositions of volcanic ash and volcanic pumice (Hossain, 2005)

Components	**VA** (%)	**VP** (%)
SiO_2	59.32	60.82
Al_2O_3	17.54	16.71
Fe_2O_3	7.06	7.04
CaO	6.1	4.44
MgO	2.55	1.94
Na_2O	3.80	5.42
K_2O	2.03	2.25
SO_3	0.71	0.14
Loss on ignition (LOI)	1.03	1.52

b) **Metakaolin** (MK) is classified as a pozzolanic material: the calcination of kaolinitic clay ($Al_2Si_2O_5(OH)_4$) at a temperature ranging between 500°C and 800°C, produces metakaolin ($Al_2Si_2O_7$). It usually contains chemical compositions in the range of 50-55% of SiO_2 and 40-45% of Al_2O_3. MK is highly reactive with calcium hydroxide and can accelerate cement hydration (Zhang & Malhotra, 1995; Shekarchi *et al.*, 2010). It contains alumina (calcium aluminate hydrates and alumosilicate hydrates) which interact with $Ca(OH)_2$ to produce alumina-containing phases C_2ASH_8, C_4AH_{13} and C_3AH_6 (Siddique & Klaus, 2009).

c) **Silica fume** (SF) is a by-product in the manufacture of silicon metal and ferro-silicon metal alloys. SF composes primarily of silicon dioxide (SiO_2) as can be seen