# EFFECT OF CURING CONDITION ON THE CHARACTERISTICS OF MORTAR CONTAINING HIGH VOLUME SUPPLEMENTARY CEMENTITIOUS MATERIALS

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# EFFECT OF CURING CONDITION ON THE CHARACTERISTICS OF MORTAR CONTAINING HIGH VOLUME SUPPLEMENTARY CEMENTITIOUS MATERIALS

## ABSTRACT

The purposes of this research were to studies the physical and chemical properties of materials, compressive strength, flexural strength, water absorption and porosity of multi-blended cements under different curing methods. Due to an enormous amount of different types of waste materials as by-product from different sectors like industrial and agricultural produced globally but not deposited safely. One solution to this crisis lies in recycling waste into useful products. Fly ash (FA), palm oil fuel ash (POFA), ground granulated Blast furnace slag (GGBFS) and rice husk ash (RHA) were used to replace with 50% to 75% ordinary Portland cement (OPC) by mass. Specimens were cured in water (WC), air under room temperature (AC), the combination of hot-water at 60ºC for 24 h followed by curing in water (HWC), and air (HAC). The results showed that HAC could be an effective curing method with higher compressive and flexural strengths, lower water absorption and porosity for blended cement mortars. Mortars containing GGBFS in binder had higher enhancement on compressive strength under early hot water curing. While, at 24 h hot water curing mortar containing OPC-RHA-FA binder showed better quality in properties compared to the other binders.

**Keywords**: Mortar, Supplementary Cementitious Materials (SCM), Curing, Temperature, Waste Materials.

# KESAN KEADAAN PENGAWETAN ATAS KARAKTERISTIK MORTAR YANG MENGANDUNG BAHAN PENGIKAT TAMBAHAN BERSIMEN TINGKAT TINGGI

## ABSTRAK

Tujuan kajian ini dijalankan adalah untuk mengkaji sifat-sifat fizik dan kimia bahan-bahan, seperti kekuatan mampatan, kekuatan lenturan, sifat penyerapan air dan lembapan oleh simen campuran dengan menggunakan kaedah pengawetan yang berbeza. Secara globalisasi, terdapat banyak jenis bahan-bahan buangan dari sector pertanian dan perindustrian yang tidak dibuang secara selamat. Salah satu cara penyelesaian untuk mengatasi krisis ini adalah dengan mengitar semula bahan buangan untuk dijadikan produk yang boleh digunakan semula. Abu terbang (FA), abu buangan kelapa sawit (POFA), ground granulated blast furnace slag (GGBFS) dan abu sekam padi (RHA) telah digunakan untuk menggantikan daripada 50% kepada 75% simen Portland (OPC). Specimen telah diawet ke dalam air (WC), dibawah udara suhu bilik (AC), dengan gabungan air panas pada suhu 60oC selama 24 jam diikuti oleh pengawetan di dalam air (HWC), dan pada suhu bilik (HAC). Hasil kajian menunjukkan bahawa HAC boleh menjadi satu kaedah pengawetan yang berkesan dengan kekuatan mampatan dan lenturan yang lebih tinggi, keliangan dan penyerapan air yang lebih rendah untuk campuran simen mortar. Mortar yang mengandungi pengikat GGBFS mempunyai kekuatan mampatan yang lebih tinggi dibawah pengawetan air panas pada peringkat awal. Manakala, pengawetan air panas mortar selama 24 jam yang mengandungi OPC campur RHA dan FA menunjukkan hasil kualiti yang terbaik berbanding pengikat yang lainnya.

**Kata Kunci**: Mortar, Bahan Pengikat Tambahan (SCM), Pengawetan, Suhu, Bahan Sisa

# ACKNOWLEDGEMENTS / DEDICATION

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## 1.1    Background

High priority has been given to protect and preserve the environment from abundant non-renewable waste materials, which are hazardous if not disposed of safely. The total wastes accumulated are not valuable and will cause pollution when disposed of for a long time. Another priority is to reduce the use of a huge amount of cement as a binder in the construction industry.

Malhotra (2000) stated that the rate of the world's population will increase explosively from 1.5 billion to 9 billion by 2050. This will result in an increased demand for energy, housing, food and particularly the demand for concrete. The total concrete production is forecasted to grow up to about 18 billion tons annually by 2050 (Malhotra, 2000). Unfortunately, the huge amount of concrete produced detrimental to the environment. The rising demand for concrete will lead to the need for cement as the main binder in concrete production. As shown in Figure 1.1, the world cement production has been increasing from year to year. In 2014, the total cement production reached 310 billion tons in Asia. This upward trend started near the end of the 20th century (Bohari et al, 2015). The main consumer of cement is the construction industry, which uses it to produce common materials, such as mortar and concrete.
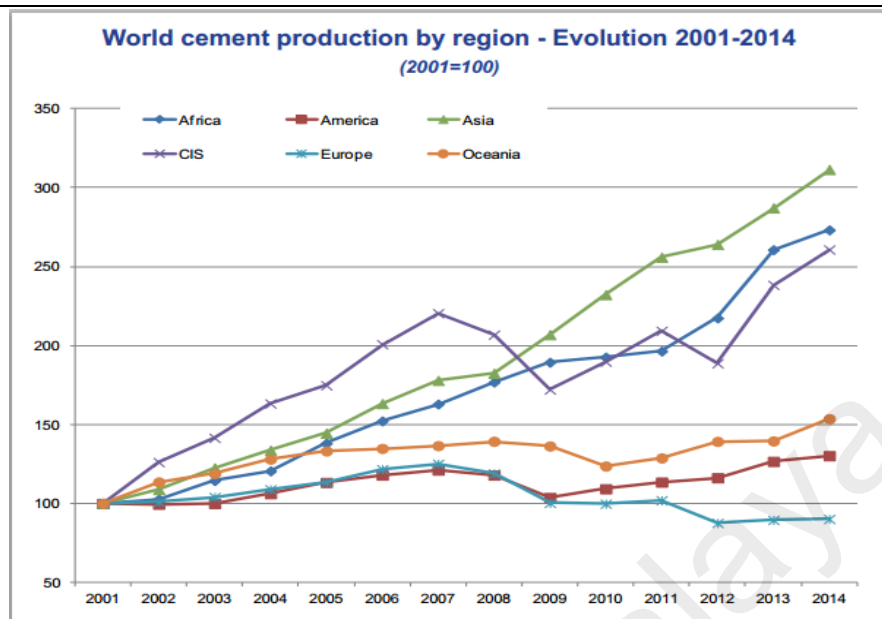
**Figure 1.1: Global production of cement (CEMBUREAU, 2015)**

Mortars are recognized as a significant part of construction (Lucas et al., 2009). As a constituent of concrete, mortar is defined as a workable paste used to bind building blocks such as concrete. It is an engineered material that can meet almost any desired specification, as well as being adaptable, incombustible, affordable and easily obtained. Ranjbar et al., (2001) noted that the need towards sustainability and sustainable environment has made the use of pozzolanic materials in mortar being popular. Various pozzolanic materials used will determine the durability of mortar and also affect the strength performance of mortar and concrete. The effectiveness and efficiency of mortar should be judged at 28 days to obtain the desired compressive strength. However, it is sometimes necessary to find alternative solutions to speed up the merging process of the particles contained in the mortar, thereby allowing the desired strength to be achieved earlier, while retaining the principle of a friendly-environment mortar.

There have been studies conducted to change old materials and methods for curing mortar to recycle materials and performance-based acceleration process for curing mortars. The understanding of the type of recycle materials which can be used in the production of mortar is important. In order to achieve a good performance of mortar, methods of mixing materials and curing that support compressive strength have been developed by several researchers (Zain & Radin, 2000; Aly et al., 2011; Ezziane et al., 2007; Sajedi, 2012; Barnett et al., 2006; Almabrok et al., 2015).

The revival of green construction in the past 30 years has developed many researches on the properties and performance of mortar (Craig & Wood, 1970; Ezziane et al., 2007; Sajedi, 2012; Bohari et al., 2015). Most of the researches are focused on the best practice of using cementitious materials, cementitious mortar, and normal mortar but none of them using high volume cementitious materials as binder with different curing conditions. In many circumstances, most conservators prefer to use Portland cement as binder in mortar and plaster because it has ability to set and harden in wet condition as well as develop reliable mechanical strength.

This thesis is concerned with utilization of cementitious materials for the production of mortar and the sustainability of environment. The investigation work involves activities which give new values to the waste materials. Besides, they help make the structure more durable, more friendly-environment and more strength compared to ordinary mortar containing 100% Portland cement. The factors to be taken into account include the environmental problem such as landfill, air and land pollutions, due to the use of Portland cement excessively, flooding, radiation, the combination of cementitious materials,

composition of the mortars, the workability of fresh mortar, and the curing conditions of mortars containing cementitious materials. The main factors that can affect the workability of fresh mortar are combination inside the binder and w/c ratio. The optimization of workability of the binder simplifies the mix design of mortar. In addition, the advantage in investigating cementitious mortars can contribute to sustainability by modifying hazardous material to be valuable, creating new production method for binder and mortar, and producing an effective curing method for construction industry.

## 1.2    Problem Statement

About 2.5% of the total emissions across the globe is the result from Portland cement manufacturing which causes a great concern to the environmental sectors (Noorvand et al., 2013). At the same time, the type and amount of waste products increases with the growth in population. These wastes remain in the environment for a longer duration since they are unused. If those waste materials are not deposited safely, they may be hazardous. The solution to this environmental crisis lies in the recycling of waste materials to be partial replacement of Portland cement in the construction industry. To minimize the exploitation of Portland cement, the use of waste and by-product materials in high volume as cement replacement is being focused in this study.

Local waste materials such as rice husk ash (RHA) and fly ash are a latent hydraulic binder (Neville, 1995). It must be activated to react and provide the desirable mechanical properties using several methods. Attempts (Chithra & Dhinakaran, 2014; Barnett et al., 2006; Muhmood et al., 2009; Sajedi & Razak, 2011; Wongkeo et al., 2012; Jaturapitakkul et al., 2007; Jaturapitakkul et al., 2011; Khan et al., 2012; Hasanah et al., 2015) have been

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made to overcome the problem of slow strength development in cementitious mortars and concretes using temperature and suitable curing regimes. Temperature is a key variable affecting the curing of cement-based materials, because it influences both the early hydration kinetics and the mechanical properties of the hardened cement paste, mortar or concrete. Hasanah et al., (2015) said that the hydration temperature has a significant impact on the hydration of cement paste and concrete. Consideration of the effects of high curing temperatures or heat treatment accelerate the hydration process of cementitious materials but they are limited to a specific time and generally cured at temperature in the range of $40^{\circ}$C to $100^{\circ}$C (Barnett et al., 2006; Muhmood et al., 2009; Sajedi & Razak, 2011; Wongkeo et al., 2012; Khan et al., 2012). Therefore, the effectiveness use of initial thermal method on different curing conditions of mortar containing high volume cementitious material are being the focus of study. In addition, the thermal process will be a break-through solution for construction industry in many ways such as reducing the number of Portland cement production as well as contributes to the landfill and air pollution, reduce cost of construction, the specimens can cured anywhere according to the needs and it does not need a large place or space to cured the specimens.

The main problem observed from previous experimental works is low early strength of SCM mortar. Therefore, the use of SCMs should not be done randomly due to the characteristics of latent hydraulic binder. To overcome that problem, supplementary cementitious materials must be activated to react and provide the desirable mechanical properties using several methods. One of these activation methods is the thermal method. At the same time, the sensitivity of cementitious materials should get attention before

combined them with Portland cement. Unfortunately, several researchers ignored this factor. To fill in the gap, this thesis will discuss the increase of strengths at early ages by using ten types of mixes in different curing conditions. The type of mixes derived from combination of one and two SCMs with certain volume.

## 1.3 Aim and Objectives

This research aimed to produce a mortar containing high volume cementitious materials. The outputs of research desire to fulfill the objectives of sustainable development. The main objective of this study is to manufacture mortar using high volume cementitious materials and cured at different curing conditions. Various analysis consisting of physical, chemical and mechanical properties, are used to evaluate the properties of cementitious materials and cementitious mortar.

The specific research objectives are:

1) To investigate the properties of local waste materials from industry and agriculture that will be used as supplementary cementitious materials and an invention towards an environmentally friendly mortars..

2) To find the proper combination of cementitious materials as partial cement replacement in order to produce high strength mortar containing high volume cementitious materials.

3) To investigate the effect of initial heating process as accelerated curing method on mechanical and physical properties of mortar containing high volume cementitious materials.

4) To characterize the mixture proportion of mortar by identifying few parameters and examine the influence of different curing condition on the characteristic of mortar.

## 1.4    Scope of The Study

A normal mortar with only using ordinary Portland cement (OPC) is needed to be deeply observed particularly on the presence of SCMs as partial cement replacement. Normal mortar with 100% OPC as binder is used as the control. The entire specimens will be cured in water curing (WC) as a standard curing, air curing (AC), hot-water curing (HWC) and hot-air curing (HAC). It should be noted that the specimens will be divided in two groups based on the thermal curing method with or without heating process. Furthermore, both of the groups are separated based on ambient curing condition, in water or under room temperature (air). Then, the specimens will be tested at 1 day, 3 days, 7 days, 14 days, 28 days, 56 days and 90 days for compressive strength and all the test result will be compared with the control mortar at the same ages and conditions.

The scope of study is shown below:

a) Cement used is ordinary Portland cement (OPC) type I MS EN 197-1-CEM I 42.5 N. The properties explained more detail in Chapter II.

b) Supplementary cementitious materials (SCMs) used are fly ash (FA), ground granulated blast-furnace slag (GGBFS), palm oil fuel ash (POFA) and rice husk ash (RHA). The properties explained more detail in Chapter II.

c) Cube mould used was 50 mm x 50 mm x 50 mm.

d) Prism mould used was 150 mm x 40 mm x 40 mm.

e) For thermal method, the constant temperature of heating process was $60^{\circ}C$ for 24 hours.

f) Ambient temperature in water is about $23^{\circ}C$ (100% humidity) and under room temperature of $27\pm3^{\circ}C$ (about 85% humidity).

g) Observe the compressive strength of hardened mortars (with and without SCMs) in normal stage (1-day after demolding) and the initial short time heating (for 2.5 h and 5 h). Each stage has 3 specimens for this test. The results are based on average.

h) Compare the compressive strength of control mortar and SCMs mortar in four curing conditions at early ages (1 day, 3 days, 7 days and 14 days). Each curing condition has 3 specimens for this test. The results are based on average.

i) Compare the compressive strength of control mortar and SCMs mortar in four curing conditions at later ages (28 days, 56 days and 90 days). Each curing condition has 3 specimens for this test. The results are based on average.

j) Compare the flexural strength of control mortar and SCMs mortar in two curing conditions using thermal method (HWC and HAC) at 7 days and 28 days. Each curing condition has 3 specimens for this test. The results are based on average.

k) Compare the water absorption of control mortar and SCMs mortar in four curing conditions at 56 days. Each curing condition has 3 specimens for this test. The results are based on average.

l) Compare the porosity of control mortar and SCMs mortar in four curing conditions at 56 days. Each curing condition has 3 specimens for this test. The results are based on average.

**1.5 Thesis Outline of The Research Study**

The thesis is composed of five chapters including introduction and conclusions. The thesis is divided into two parts. The first part is introduction to the research study followed by the literature review. The second one covers the experimental procedures and corresponds to the research objectives. The outlines of the thesis are as follows:

CHAPTER I - INTRODUCTION

This Chapter contains background of research (problem statement), hypothesis, the scope of study and the objectives of research

CHAPTER II – LITERATURE REVIEW

The detailed explanation of mortar and supplementary cementitious materials are mentioned. This Chapter reports the previous studies of mortar in several conditions. References of the materials used in this research are also stated.

CHAPTER III – EXPERIMENTAL PROCEDURES

This Chapter summarizes the methodology and several tests applied in the experimental work.

CHAPTER IV – RESULTS AND DISCUSSION

Results obtained were put in this chapter and discussed further as explanation of research achievement. This Chapter will also highlight the main point of the research methodology.

CHAPTER V – CONCLUSIONS AND RECOMMENDATIONS

This Chapter delineates the summary of the results obtained. The conclusions are the answers of research objectives which have mentioned in CHAPTER I. Besides conclusions, the future work is also provided in the recommendations for further research studies.

# CHAPTER 2: LITERATURE REVIEW

## 2.1 Introduction

With the increasing public concern about sustainable development, the concept of green mortar is growing faster. In general, green mortar can be defined as a mortar with less cement consumption due to the cement's energy-intensive production process together with the large amount of carbon emissions it accounts for. It is widely accepted that producing one ton of cement releases approximately one ton of carbon dioxide, and the yearly cement production would be responsible for about 7-8% of the global loading of carbon dioxide released to the atmosphere (Malhotra, 2000; Mehta & Monteiro, 2006). Using supplementary cementitious material (SCM) to replace cement in the production of mortars would be of great benefit and help to mitigate this problem.

This chapter presents the literature review on mortar containing cementitious materials. The discussion begins with a brief history of Portland cement. The review then focuses on the hydration of Portland cement and ettringite formation. Furthermore, the environmental problems caused by the use of Portland cement are also discussed. The research study also focuses on classifying supplementary cementitious material (SCM), raw materials and the process involved in manufacturing cement based materials. This knowledge is vital because the cementitious materials produced have different properties based on their origin. This information is important in order to understand the properties of SCM and cementitious mortar. This chapter also reviews the performance of fresh and hardened cementitious mortar and the availability of indigenous source for producing SCM in Malaysia. Furthermore, the effect of different types of blended cements and curing conditions are also reviewed.

### 2.2 Portland Cement

### 2.2.1   History of Portland Cement

The use of Portland cement had a prior history before develops extensively. People are required to set up a masonry structures by using an array of large flat stones which are placed on top over each other and applied small stones as a filling into the gap between the large stone structures. As time passes, the ancient people proposed materials that can be used to attach the stones. First binder had been produced by early Greeks and Romans from volcanic ash mixed with slaked lime (Blezard, 1998). Furthermore, natural cement rock found in 1818, followed by discover of Portland cement in 1800's. Portland cement was developed in England by bricklayer Joseph Aspdin in early 1824. It called *Portland* because concrete made with it resembled the natural stone from the Isle of Portland.

### 2.2.2   Hydration of Portland cement

Hydration is the process in which ions are surrounded by water molecules arranged in certain circumstances (Odler, 1998; Kurtis, 2000). Water is essential in cement chemistry and acts as a constituent in the reaction products. When water is mixed with Portland cement, a complicated set of reactions is initiated that is called hydration of Portland cement. The main characteristics of a hydrated Portland cement are related to stability of volume, heat of hydration, resistance to the chemical aggression and high mechanical strengths. The flow diagram of hydration process is shown in Figure 2.1.

```
┌─────────────────────────┐        ┌─────────────────────────┐
│  RAW MATERIAL           │        │  LIME STONE, CLAY/LOAM, │
│  (FOR CEMENT            │        │  SHALE/FLAKES           │
│  MANUFACTURING)         │        └───────────┬─────────────┘
└─────────────────────────┘                    │
┌─────────────────────────┐        ┌───────────▼─────────────┐
│  RAW MATERIALSPARTICLE  │        │     O₂Si CaAlFe         │
│  ELEMENTS               │        └─────────────────────────┘
└─────────────────────────┘
┌─────────────────────────┐        ┌─────────────────────────┐
│ OXIDES CONTAIN IN RAW   │        │ CaO, SiO₂, Al₂O₃, Fe₂O₃ │
│ MATERIAL FOR CEMENT     │        └─────────────────────────┘
│ MANUFACTURING           │
└─────────────────────────┘
        ( ON INCINERATION - CLINKER
          CREATED → GYPSUM )
┌─────────────────────────┐
│  C₃S - C₂S - C₃A - C₄AF │
│  (COMPOUND STRUCTURES)  │
└─────────────────────────┘
┌─────────────────────────┐
│ MILLING PROCESS OF THE  │
│ CLINKER →PORTLAND       │
│ CEMENT FORMED           │
└─────────────────────────┘
┌─────────────────────────┐       ┌──────────────────────────┐
│ HYDRATION PROCESS→      │ ◄──── │ C – S – H gel + Ca(OH)₂  │
│ PRODUCTS DEVELOPED      │       └──────────────────────────┘
└─────────────────────────┘
```

**Figure 2.1: Schematic presentation of cement hydration (Bye, 1983)**

Figure 2.1 describes the organizing hydration process of Portland cement. The main

product of the hydration of Portland cement is the calcium silicate hydrate or C-S-H gel.

The hydration process result indicates that chemical composition such as $SiO_2$ and $CaO$ (in

the vicinity of the interface) is one of the major factors for the increase in bond strength. This product highly contributes to the mechanical strength of mortars and concretes (Aly et al., 2011; Shafiq & Nuruddin, 2010; Bohari et al., 2015). The important factors influencing to the characteristics of concrete production are the formation level of the hydration products, the stability of the structure, quality and quantity of the product, as well as the continuity for the future. As can be seen from Figure 2.1, Portland cement is made finely pulverizing the clinker produced by burning a definite mixture. Portland cement contains four main compounds are:

a. $C_3S$ (tricalcium silicate) –Alite $= 3CaO.SiO_2$, this phase reacts rapidly with water producing relatively large amounts of heat to form calcium silicate hydrate. It is the main contributor to the early strength of cement hydrate.

b. $C_2S$ (dicalcium silicate) –Belite $= 2CaO.SiO_2$, this phase reacts slowly with water to form the same product as $C_3S$. It increasingly contributes to strength at later ages.

c. $C_3A$ (tricalcium aluminate) – Aluminate $= 3CaO.Al_2O_3$, this compound reacts very rapidly with water producing relatively large amount of heat and a very rapid set.

d. $C_4AF$ (tetracalciumaluminoferrite) – Ferrite $= 4CaO.Al_2O_3.Fe_2O_3$, this compound reacts rapidly with water but produce not much heat and strength. In general, the initial reaction rate is fast but as the hardening process, the reaction rate is intermediate between alite and belite.

According to Sharmin et al (2017), the basic chemical components of Portland cement are Ca (calcium), Si (silicon), Al (aluminium) and Fe (iron). Compounds hydrate when water is mixed with anhydrous cement compounds and react one another. Thus, hydrogen bonding and dissolving of ions in water are most likely to be of great importance for the hydration process (Sajedi, 2012; Hasanah et al., 2015). Therefore, water and cement require a proper ratio to obtain high strength in mortar and concrete production. According to Neville (1995), it is generated as a consequence of the hydration of the silicate phases according to the following reactions:

$$C_3S + H_2O = C\text{-}S\text{-}H + Ca(OH)_2 \qquad (eq.1)$$

$$C_2S + H_2O = C\text{-}S\text{-}H + Ca(OH)_2 \qquad (eq.2)$$
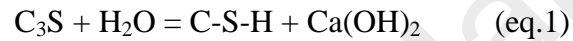
When alite, $C_3S$, hydrates it forms calcium hydroxide CH and a solid calcium silicate hydrate that consists of a varying composition of C, S and H which is denoted as C-S-H gel. The hydration products of belite, $C_2S$, are similar to those of alite. The most important product from the hydration process of Portland cement is C-S-H gel, due to the adhesive and acts as a glue in cementitious materials. Belite is much slower in reacting compared to alite. It also has less CH formed (Sharara et al., 2004). Calcium hydroxide found inside cement volume around 50 percent and cause deterioration of concrete.

### 2.2.3 Ettringite formation

According to Odler and Subauste (1999), ettringite (Aft phase, abbreviated as $C_3A \cdot 3C\overline{S} \cdot 32H$) is formed in the hydration of a variety of inorganic binders. More than that, ettringite is formed as a consequence of the chemical reaction between the sulphates and aluminates usually present in the hydration products of Portland cement.

The ettringite denotation in chemical reaction is $3CaO.Al_2O_3.CaSO_4.32H_2O$ (calcium sulfoaluminate). Sulphate and aluminate are normally found in Portland cement (Erlin, 2009). It also presents in supplementary cementitious materials and admixtures. Most of the sulphate in Portland cement normally reacts to form ettringite at early ages and called *primary ettringite*. This takes places during the first stages of hydration before the hardening stages. Figure 2.2 shows the ettringite formation from chemical reactions to microscopic detail.

It can be seen that the process to form ettringite involves a high increment of volume. Initial stage of the hydration system occurs in the plastic state (Leonard, 2012). It means that the surface beyond compounds is able to absorb incremental volume so that the expansive phenomenon will not lead to mortar disintegration. Disintegration occurs after hardening whereby the space will not be enough to accommodate the increase in volume thereby leading to cracking and loss of mass. Mydin et al (2014) assumed that when concrete or mortar or cement paste is exposed to water for long periods of time, the ettringite can slowly dissolve and will reform to be any available voids or micro-cracks. Under microscopic results (scanning electron microscopy), needle like crystals of ettringite are often observed lining air voids or cracks. The ettringite crystals in air voids and cracks are typically 2 to 4 µm in cross section and 20 to 30 µm long (Hyde, 2000). Primary ettringite is formed during the plastic stage and secondary ettringite is formed after hardening and will lead to cracking and disintegration.

where V1 and V2 are the incremental volume of alumina and sulphate

**Figure 2.2: Ettringite formations ((1) Hyde, 2010; (2) Erlin, 2009; (3) Leonard, 2012)**
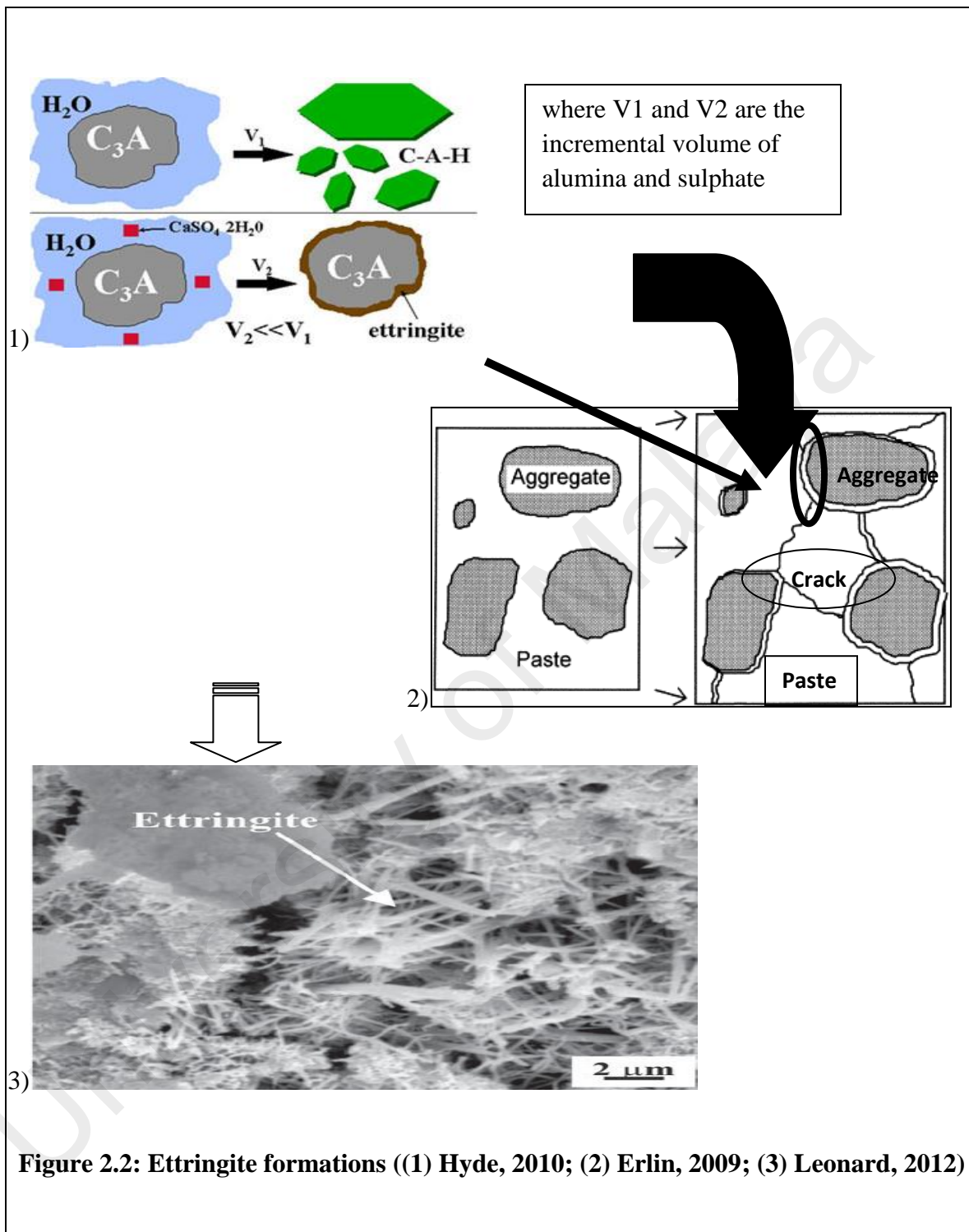
### 2.2.4   Environmental issues of Portland Cement

Portland cement is heavily used as a construction material in modern society. With the growth in urbanization and industrialization, the demand for concrete is increasing day by-days. Therefore, raw materials and natural resources are required in large quantities for concrete production worldwide. Unfortunately, a considerable quantity of concrete is being produced, the effect of which is contrary to its benefits. One of disadvantages effect is arising temperature around the concrete place (urban heat island). Other than that, in the last 100 years, the concrete industry has had an enormous effect on the environmental appearances (Awal & Shehu, 2013; Aprianti et al., 2016)

In addition, $CO_2$ emissions are produced during the manufacturing process with a large volume of raw materials required to produce the billions of tons of concrete worldwide each year (Sajedi & Razak, 2011). The cement industry alone is estimated to be responsible for about 7% of all the $CO_2$ generated worldwide (Malhotra, 2000). It has been found that every ton of Portland cement produced releases approximately one ton of $CO_2$ into the atmosphere.

Furthermore, during the production of cement and concrete, issues like carbon dioxide emissions, along with the use of energy and aggregate consumption in great amounts, the demolition waste of concrete and filler requirements, contribute to the common environmental impact that concrete has making it a non-friendly that is unsuitable for sustainable development. Boakye (2012) mentioned that cement production is, however, harmful on the environment due to carbon dioxide emission. Reducing cement production

while maintaining sustainable development has been an important issue in the development of construction materials. Researchers have agreed and suggested that the use of Portland cement should be minimized and exposed in control (Bagel, 1998; Boubitsas, 2001; Khan et al., 2012; Aldahdooh et al., 2013; Alengaram et al., 2013; Yusuf et al., 2014). Most of them suggested to reduce cement production while maintaining sustainable development has been an important factor in the development of construction materials. Replacing Portland cement with other recycled materials has been a good alternative. The relationship between cement production and total of $CO_2$ emission released are shown in Figure 2.3.



**Figure 2.3: The relationship between cement production and CO2 emitted globally (Peters, 2014)**
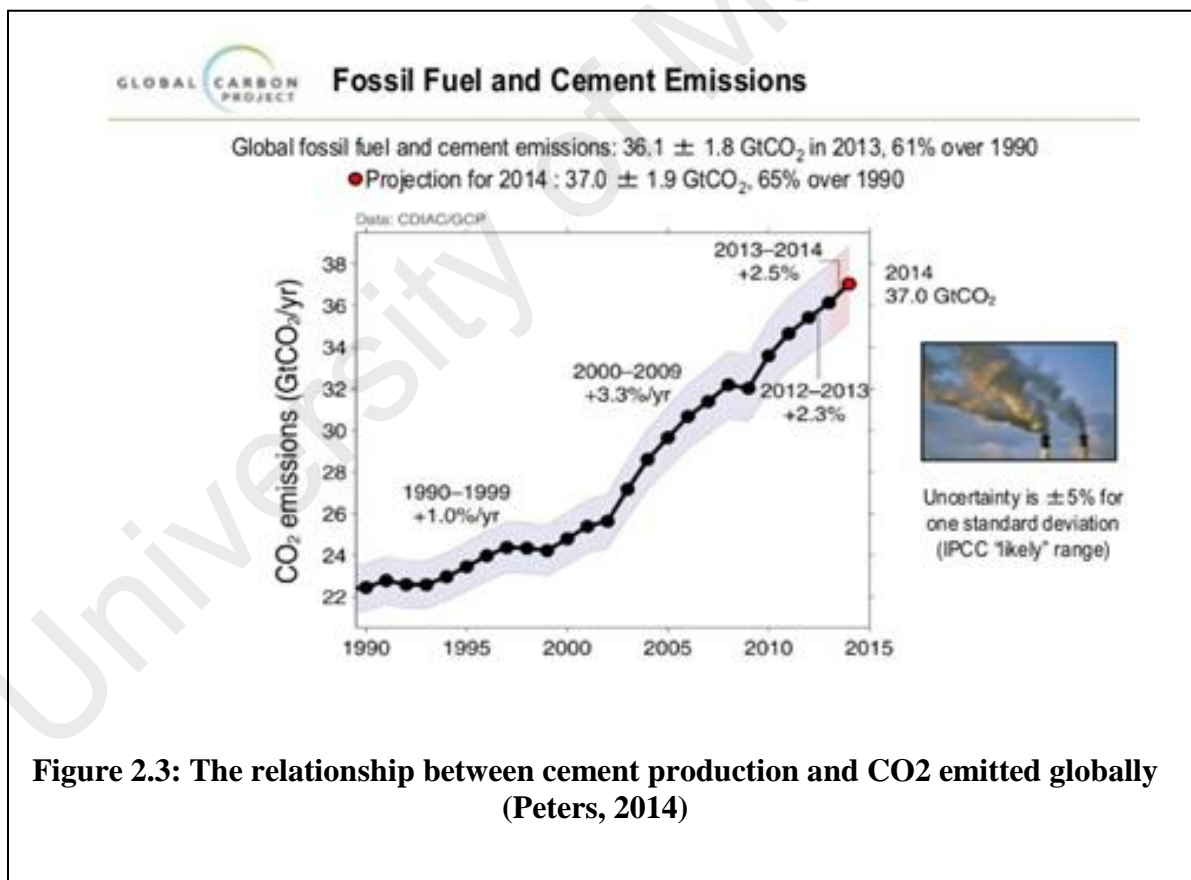
In 1990, total of $CO_2$ emissions is 22.5 GtCO$_2$/yr. The total emissions between 1990 and 1999 are increase for about +1,0 %/yr. Furthermore, from 2000 to 2009, the total emissions

also increase is around +3.3%/yr. This trend as can be seen from 2012 to 2014 which is increase about 2.4%/yr. It means the incremental volume of cement production release global arise number of $CO_2$ emissions annually.

In summary, the presence of the cement manufacturing process can be one of the serious ecological disasters. It can be seen from the use of stones as raw materials, production process, until air pollution. It should be highlighted that the ecological disasters always occur due to the delays in realizing and recognizing that fault. Hence, to minimize and reduce the negative impact of the concrete industry through the excessive usage of raw materials, the use of supplementary cementitious materials, the source of which is both reliable and suitable for alternative preventive solutions promotes the environmental sustainability of the industry.

## 2.3 Supplementary Cementitious Materials

Supplementary cementitious material (SCM) is a material that, when used in conjunction with Portland cement, contributes to the properties of the hardened concrete through hydraulic or pozzolanic activity, or both (Nurdeen et al., 2012; Hesami et al., 2014). Encouragements of SCM are described to three sectors: economical, environmental and technical. From economical view, in most markets SCM is less expensive than cement (except silica fume). Islam et al., (2014) explained that the use of recycled materials (by-products) will reduce landfill and cement use which decrease $CO_2$ emissions at the same time. Besides, the use of SCM will improve the performance of mortar and concrete (with appropriate use).

Several wastes materials which have been used as supplementary cementitious materials are described in Figure 2.4.



**Figure 2.4: Microscopic features of fly Ash, slag and silica fume and natural pozzolan**

**(Agarwal, 2006)**
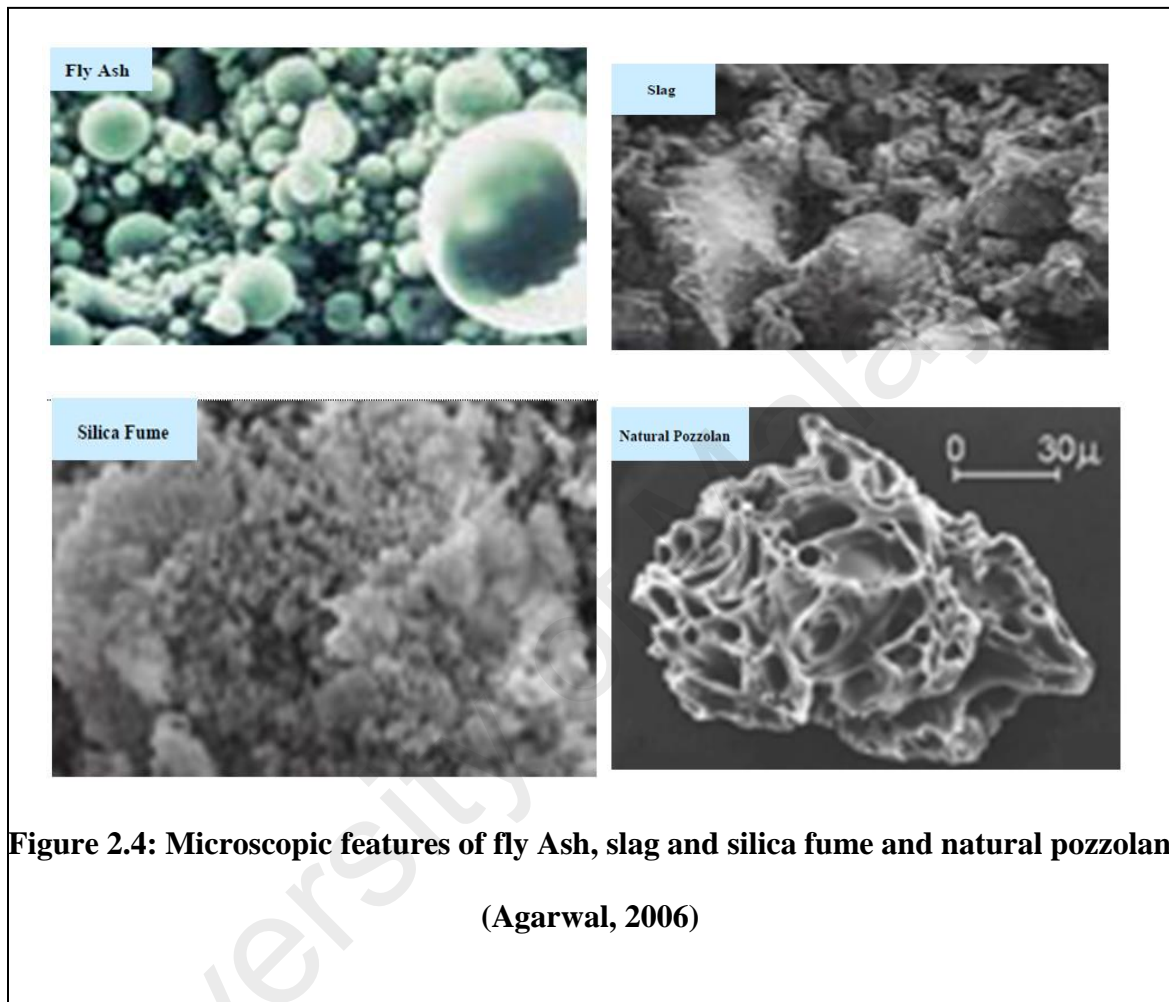
The microstructures of those waste materials tested by scanning electron microscopy (SEM). Fly Ash, as described in Figure 2.4, is in a spherule form. The particles of fly ash are glassy, and spherical in shape. Otherwise, slag is in a prism (Bagel, 1998).

The appropriate use of SCM can influence several things, such as increase the strength of concrete (Sata et al., 2007), reduce permeability to water (Sajedi & Razak, 2011), suppress deleterious expansion due to alkali silica reaction (ASR) (Yusuf et al., 2014) and so on.

However, the performance of SCM-mortar is influenced by the type of SCM (physical &chemical properties), the level of replacement used, the origin of the Portland cement and curing conditions (Xu & Sarker, 1994; Ramezanianpour et al., 2009; Zain et al., 2011; Varga et al., 2012; Sajedi et al., 2012)

Several studies have been focusing on finding an alternative which can be used as supplementary cementitious materials (Aldahdooh et al., 2013; Bamaga et al., 2013; Ramezanianpour et al., 2009; Zain et al., 2011; Varga et al., 2012; Sajedi et al., 2012). Wastes from industry and agriculture which are disposed off and less valuable, provide an opportunity to realize these potential benefits to reduce the exploitation of cement production in construction industry. Hence, researchers have been investigating for effectiveness, efficiency and easily available of waste materials to be cement replacement which are pozzolanic in nature. The required materials should be by-product or rich in silicon (Si) and aluminum (Al) from its origin (Sajedi & Razak, 2011).

### 2.3.1   Pozzolanic Materials

Pozzolanic materials are natural substances or industrial by-products having an amorphous or partially crystalline structure formed by silica, silico-aluminium compounds or a combination of both (Papadakis et al., 2002). According to ASTM C 618 (2012), a pozzolan is defined as ''a 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 to form compounds possessing cementitious properties (pozzolanic activity).'' It can be explained that pozzolanic materials are the things when combined with Portland cement will react to form

cementitious properties, whereas by themselves do not have any cementitious properties. Therefore, a cementitious material can exhibit a self-cementitious (hydraulic) activity and it contains quantities of CaO while a pozzolanic materials requires $Ca(OH)_2$ in order to form strength. It is generally accepted that the CaO content of the last material is sufficient to react with all the pozzolanic compounds and shows pozzolanic activity (pozzolanic and cementitious materials). Consequently, all these materials are often used in mixture with Portland cement which contains the essential for their activation, $Ca(OH)_2$ from its hydration.

The possible chemical reaction between silica and $Ca(OH)_2$ in the presence of water is as follows:

$$n.SiO_2 + n.Ca(OH)_2 + H_2O \rightarrow n.Cax. SiOx. n.H_2O \quad (eq. 3) \qquad (Sata\ et\ al., 2007)$$

It can be found that the secondary C-S-H gel is formed from reaction between silica ($SiO_2$) with $Ca(OH)_2$ as stipulated in the chemical equilibrium above (eq.3). The classification of pozzolans can be divided into natural or artificial types. The volcanic activity created the product naturally which is called natural pozzolan. Whereas, the artificial types are formed by the firing or burning process of raw materials such as calcined clay and shale, silica-stone, fly ash and agricultural ashes in the furnace for a certain temperature.

### 2.3.2   Waste Products as Supplementary Cementitious Materials

Waste materials, such as fly ash, silica fume, ground granulated blast slag, rice husk ash, and palm oil fuel ash, have been successfully used in concrete for decades (Chusilp, 2009;

Tangchirapat, 2009; Nurdeen et al., 2012; Khan et al., 2012). These were once problematic, land filled waste materials are now considered valuable commodities for use in enhancing certain properties of concrete and mortar. Successful usage as partial or whole replacement of Portland cement, contributes to solve landfill problem, reduction in the cost of building materials, gives a satisfactory solution to the environmental issues and problems associated with waste management, save energy, and helps environmental protection from pollution. Agricultural wastes, such as rice husk ash, wheat straw ash, and sugarcane bagasse ash, hazel nutshell ashes, are involved as pozzolanic materials and used as cement replacement.

The concept of utilizing waste material for building applications has a long and successful history, which includes fly ash, slag, and silica fume (Montakarntiwong et al., 2013). They explained that the economic benefits of using alternative materials are best realized in situations where the cost of the alternative material is less than that of cement powder while providing comparable performance. This cost must consider the source of the alternative material, its transportation, processing, and should consider savings through diversion, such as tipping fees and landfill management costs. It will also lead to a more environmentally sustainable construction industry (Jaturapitakkul et al., 2011; Montakarntiwong et al., 2013; Hasanah et al., 2015). It also can result in sustainable points in the atmosphere and energy category of Leadership in Energy and Environmental Design (LEED) rating system (Shafigh et al., 2014).

### 2.3.2.1 Rice Husk Ash (RHA)

Rice husk is natural sheaths which are formed on rice grains during their growth, denote as an agricultural solid waste material and enormously available in rice-producing countries

(Husni et al., 2017). Jauberthie et al., (2000) stated that rice husk ash (RHA) is a carbon neutral green product gained from raw rice husk that was changed to ash using the combustion process. It is a good pozzolan but they have no commercial interest when removed during the refining process. The rice milling industry is one of the most important fields in certain countries, such as China, India, Indonesia, Malaysia and Bangladesh. By the end of 2013, rice husk harvest about 742 million metric tons product of rice paddy annually in the world (Rice Market Monitor, 2009) with more than 20% being husk. India produces around 160 million tons of rice husks (widely available waste) which during milling process, about 78% of weight as rice, broken rice and bran, rest 22% of weight of paddy as husk. Malaysia alone produces approximately 3 million tons of rice paddies, each year.

Table 2.1 shows the top 10 highest countries of rice paddy production in 2013. Asia is still expected to sustain growth in the world rice production in 2013. The advantage of rice produces high volumes of rice husk, which is a low-density residue of the process (Zain et al., 2011). The rice producing countries are distressed with the landfill problem from mitigating waste from rice husk burning process, and have been attempted to utilize it economically. When dumped, this waste takes a large area, where it can be self-incinerated, spreading the ashes and causes a great problem to the environment. Owing to the increasing of environmental problem, the biodegradable process of rice husk takes 3 to 5 years depending on its intrinsic properties (Zhao et al., 2008). It takes long time to be valuable materials.

**Table 2.1: World production of Rice Paddy, Potential husk, and ash production in**

**2013 (Rice market monitor, 2014)**

| Country | Rice Paddy Production in 2013 (Mt) | Husk Produced (20% of total) (Mt) | Potential Ash Production (18% of husk) (Mt) |
|---|---|---|---|
| China | 200 | 40 | 7.20 |
| India | 160 | 32 | 5.76 |
| Indonesia | 90 | 18 | 3.24 |
| Bangladesh | 45 | 9 | 1.62 |
| Vietnam | 30 | 6 | 1.08 |
| West Africa | 13.40 | 2.68 | 0.07 |
| Brazil | 12.30 | 2.46 | 0.44 |
| Pakistan | 9 | 1.80 | 0.32 |
| Egypt | 6.10 | 0.32 | 0.06 |
| Malaysia | 3 | 0.60 | 0.11 |
| Europe | 2.90 | 0.58 | 0.10 |
| Australia | 1.20 | 0.24 | 0.04 |
| Others | 168.50 | 33.70 | 6.07 |
| Area (ha) | | | 164 million hectares |
| Total (world) | | | 741.4 Million tones |

Therefore, researchers (Khan et al., 2012; Goncalves & Breggman, 2007; Sensale, 2010) try to find out the ways on utilizing waste from rice husk. Figure 2.5 shows the process of biodegradation of rice husk. Without utilization, this large quantity of rice husks goes waste and becomes a major challenge to the environment thereby leading to destruction the land and its surrounding dumped areas. A huge amount of RHA produced globally estimated to be implying a growth more than 7.5 million ton or approximately 1.1 % each year (Rice Market Monitor, 2014).

**Figure 2.5: The biodegradation process of rice husk (Zhao et al., 2008)**



**Figure 2.6: (a) Raw rice husk (b) Rice husk ash (RHA) (Zain et al., 2011)**

Rice husk, as displayed in Figure 2.6 (a), is a raw form after milling process. It was then fired in a furnace gas with rate of $10^{\circ}$C per minute up to $700^{\circ}$C, maintained at this temperature for 6 hours. Then, let them to cool down in a room temperature as show in Figure 2.6(b). The various chemical composition of rice husk ash is due to the type of paddy, differences in the type of land, harvest year, combustion temperature, cooling method and geographical conditions.

The colour of rice husk ash (RHA) ranges from white grey to black, depending on sources of raw materials, method of incineration, time and burning temperature (Raman et al., 2011). Many ways were thinking to throw them by using commercial method of RHA. Rice husk was burnt in a furnace/incinerator with a controlled atmosphere at $600^{\circ}$C to $800^{\circ}$C at laboratory (Goncalves & Bergmann, 2007). After firing process, the ash produced was cooled, either in rapid terms nor slowly. Rapid cooling method was done by distributing the ash in trays uniformly at the laboratory ambient temperatures of $21 \pm 1^{\circ}$C after reaching the required temperature of $800^{\circ}$C. Otherwise, leaving the ash in the incinerator involved as slow cooling. It can be used a big way to make special supplementary in concrete mixes. This RHA in turn contains around 85% - 90% amorphous silica (Goncalves &Bergmann, 2007; Nagrale, 2012). One example of the result from burning process of rice husk is shown in Figure 2.7.

**Figure 2.7: (a) Raw rice husk from Selangor, Malaysia (b) RHA before grinding (c) RHA after grinding (Raman et al., 2011)**

Figure 2.7a shows photos of the rice husk in raw conditions that was obtained from a rice mill located in Kuala Selangor, Malaysia. The RHA conditions before and after the grinding process are displayed in Figures 2.7b and 2.7c, respectively.

The physical and chemical properties are mentioned in Table 2.2. RHA should meet the requirements for chemical composition of pozzolan to be used in cement and concrete as stated per ASTM C618 (2012). The amount content of silicon dioxide ($SiO_2$), iron oxide ($Fe_2O_3$) and aluminium oxide ($Al_2O_3$) in the ash should not be less than 70%, and loss of ignition (LOI) must be up to 12% as mentioned in ASTM requirement. RHA is a very fine material. The average particle size of rice-husk ash ranges from 5 to10 μm (Gonzalves & Bergmann, 2007).

**Table 2.2: The properties range of Portland cement (OPC) and rice husk ash (RHA) (Gonzalves & Bergmann, 2007; Raman et al., 2011; Nagrale, 2012; Zain et al., 2011)**

| *Chemical Composition (%)* | OPC | RHA | CCA |
|---|---|---|---|
| $SiO_2$ | 20.40 – 21.98 | 80.7 - 95.87 | 65.39 – 67.33 |
| $Al_2O_3$ | 3.68 – 5.27 | 0.36 – 0.41 | 5.97 – 9.14 |
| $Fe_2O_3$ | 2.27 – 4.19 | 0.13 – 2.86 | 3.74 – 5.61 |
| CaO | 61.50 – 65.4 | 1.12 – 1.5 | 10.29 – 12.89 |
| MgO | 1.20 – 4.80 | 0.30 – 0.82 | 1.82 – 2.33 |
| $SO_3$ | 2.19 – 2.95 | 0.67 – 1.17 | 1.01 – 1.11 |
| $Na_2O$ | 0.11 – 0.20 | 0.85 - 1.15 | 0.36 – 0.48 |
| $K_2O$ | 0.30 – 1.04 | 0.77 – 2.11 | 4.20 – 5.64 |
| LOI | 0.36 – 2.30 | 2.81 – 6.55 | 0.99 – 1.47 |
| *Physical Properties* | | | |
| Median particle size (µm) | - | 5 - 10 | 29 - 45 |
| Specific gravity | 3.05 - 3.28 | 2.02 - 2.21 | 2.51 – 3.55 |
| Blaine Fineness ($m^2$/kg) | 336.5 - 399 | 350 – 376.8 | 272 - 385 |



**Figure 2.8: SEM of RHA particles ground for (a) 15 min (b) 60 min (c) 120 min (d) after sieving analysis (Raman et al., 2011)**
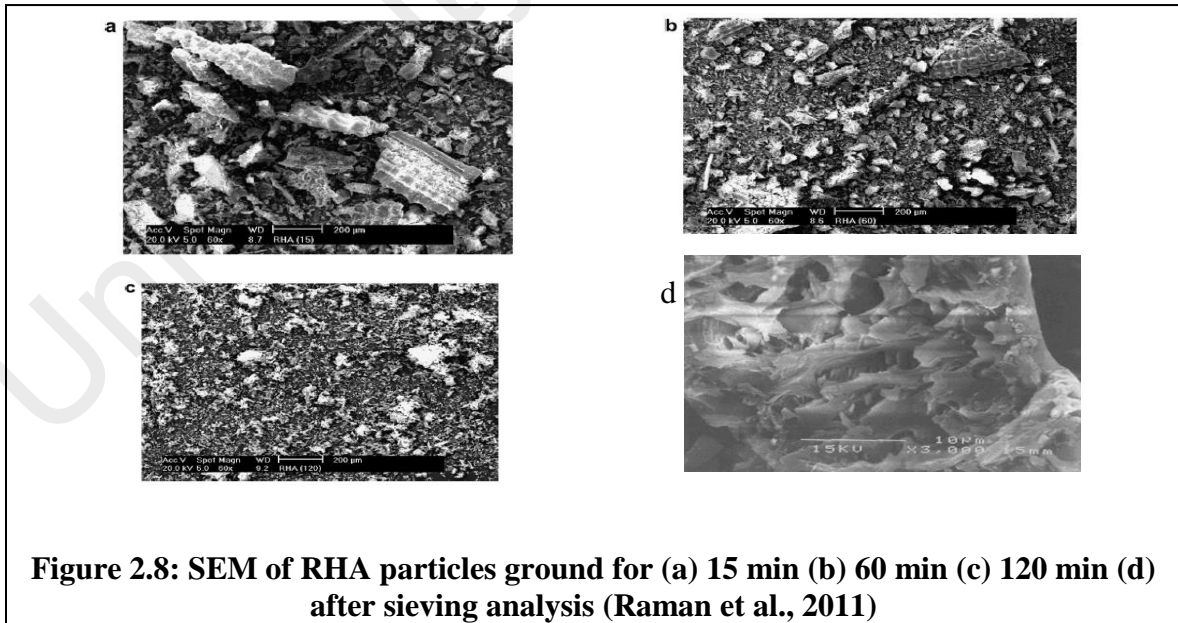
Figure 2.8 shows that the cellular shape of rice husk ash getting broken due to the longer period of grinding process (Raman et al., 2011). After milling process for 15, 60 and 120 min, the average diameter of rice husk ash particle was 49.0 μm (Figure 2.8 a), 41.0 μm (Figure 2.8 b) and 16.6 μm (Figure 2.8 c), respectively. As describe in Figure 2.5 a, the cellular shape of RHA could be clearly seen. The transformation occurs for 120 min (Figure 2.8 c), the cellular particles become smaller and disappeared. This observation examines that the RHA sample is composed of irregular shaped particles with micro pores. It could affect significantly to the properties of the final products. Figure 2.8 d clearly shows the smooth surface of ashes from rice-husk with particle size around 10 μm. Researchers (Sata et al., 2004; Chusilp et al., 2009; Tangchirapat et al., 2009; Hesami et al., 2014; Gastaldini et al., 2014) agree that finer pozzolanic ash is better. Fineness of rice husk ash is important because it influences the rate of reaction and the rate of gain in concrete strength. Other than influencing the rate of reaction, fineness also influences water–cement ratio, creep, shrinkage, and workability of concrete. Raman et al., (2007) reported that finer rice husk ash particle yields larger surface area and increases strength of concrete. Chemically reactive very fine substance would fill empty columns in concrete in an optimum manner.
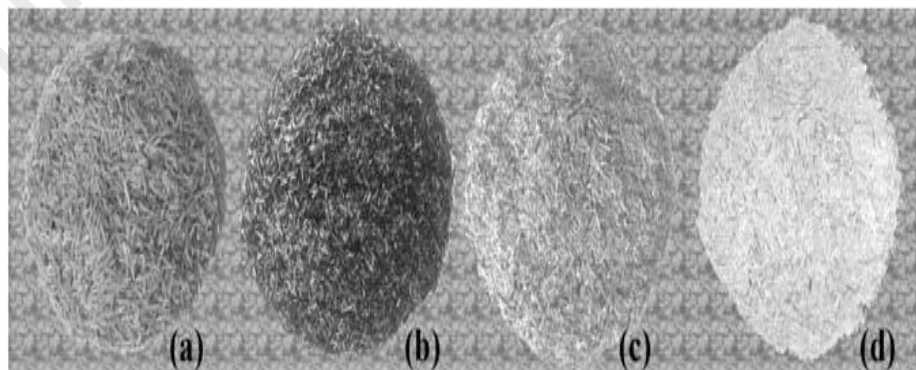
**Figure 2.9: (a) rice husk (b) high carbon RHA (c) Optimum RHA (d) RHA with crystalline silica (Goncalves& Bergmann, 2007)**

Figure 2.9 shows a photo of rice husk in raw conditions (2.8a), RHA after combustion process with high carbon (2.9b) as well as the optimum and crystalline silica condition (2.9c and 2.9d).

According to Sugita et al., (1997), the possibilities of C-S-H gel formation in RHA – mortar caused by the reaction between $SiO_2$ presence in RHA and the $Ca(OH)_2$ in hydrating cement. In combustion process, the matrix of cellulose–lignin from raw rice husk burning up and remains only a porous silica skeleton. RHA is considered as a good super-pozzolanic material in the production of concrete due to its high silica content. Thus, RHA contains a large volume of silica (Goncalves & Bergmann, 2007; Khan et al., 2012) and constitutes a highly reactive pozzolanic. The optimized and highly reactive rice husk ash is found when it is incinerated under controlled temperature. The optimized of RHA properties, could be used as a pozzolanic material in concrete. The duration and temperature of furnace are important parameters, influencing the reactivity of RHA pozzolans. Silica in the rice husk initially exists in the amorphous form, but may become crystalline when rice husk is burnt at higher temperature. In addition, silica in rice husk ash will not remain porous and amorphous when combusted for a long time at a low temperature ($< 500^{o}C$) or a very high temperature in a short time (only few minutes). In the other words, the produced rice husk ashes containing up to 90 percent amorphous silica entirely satisfy other requirements of ASTM standard C618 (2012).

The use of RHA as a supplementary cementitious material for producing high strength concrete was explored as early as 1942 (Raman et al., 2011). In most studies, it has been indicated that the standard compressive strength of concrete combined with or without cementitious materials (SCMs), is within the range for conventional concrete (15 – 45 MPa) with a density of about 2400 kg/m$^3$ (Sugita et al., 1997; Hesami et al., 2014; Gastaldini et al., 2014). Yet, recent cases have reported the possibility of producing high strength concrete up to 55 MPa and 72 MPa for 7 and 28 days of curing (Gastaldini et al., 2014) respectively. Promoting the compressive strength of concrete and the ability to produce high strength concrete with SCMs, such as RHA, is very important because the compressive strength of concrete plays a fundamental role in the design and construction of concrete structures (Shafigh et al., 2014). The methods and procedures for producing high strength RHA concrete have been examined in various published papers (Goncalves & Bergmann, 2007; Sensale, 2014). Table 2.3 shows some selected mix proportions of concrete containing RHA in several combinations of designs.

**Table 2.3: Selected mix proportion of rice husk ash (RHA) concrete according to the compressive strength**

| Mix No. | RHA (%) | Cement | Aggregate | | Water | Superplast icizer (SP) % | 28-Day Cube Compressive Strength (Mpa) | Reference |
|---|---|---|---|---|---|---|---|---|
| | | | Fine | Coarse | | | | |
| 1 | 15 | 420 | 815 | 995 | 189 | 1 | 46.9 | Ramezanianpour et al. (2009) |
| 2 | 15 | 550 | 710 | 180 | 162 | 1.1 | 53 | Raman et al (2011) |
| 3 | 10 | 481 | 690 | 1050 | 162 | 0.9 | 47.8 | Hesami et al. (2014) |
| 4 | 15 | 628 | 1997 | 4283 | 628 | 1 | 50 | Nagrale et al. 2012) |
| 5 | 10 | 393 | 723 | 1018 | 165 | 0.5 | 40 | Sensale (2010) |
| 6 | 0 | 540 | 230 | 1320 | 205 | 0.5 | 48.5 | Rahman et al. (2014) |
| 7 | 25 | 400 | 150 | 1400 | 250 | 0.9 | 42.9 | |
| 8 | 20 | 300 | 94 | 1456 | 250 | 0.9 | 33.5 | |
| 9 | 5 | 376 | 844 | 951 | 210 | 1 | 35.4 | Madandoust et al. (2011) |
| 10 | 30 | 277 | 844 | 951 | 210 | 1.1 | 26.6 | |

*Unit = kg/m$^3$

In general, the RHA concrete had higher compressive strengths at various ages up to 90 days when compared with the normal concrete without RHA or SCMs. Improvements in mechanical and durability properties of the concretes containing RHA can be explained by the chemical and physical effects of RHA. The chemical effect is mainly due to the pozzolanic reactions between the amorphous silica of RHA and calcium hydroxide (C-H) produced by the cement hydration to form C-S-H gel (calcium-silicate-hydrates). RHA reduces the number of the large pores and increases the probability of transforming the continuous pores into discontinuous ones. Hence, all these mechanisms make the microstructure of the paste more homogeneous and denser. The performance of concrete with RHA as supplementary cementitious material (partial cement replacement) is outstanding considering resistance to water (Hesami et al., 2014; Khan et al., 2012) and chloride ion penetrations (Gastaldini et al., 2014), which are in many cases the most important characteristics concerning durability and corrosion prevention. Highlighted properties that the result of air permeability and chloride ion penetration will show different behaviors depending on the *w/c* ratio used in mixtures. Moreover, the incorporation of RHA in concrete materials resolves the current problems associated with RHA disposal. The use of RHA has been associated with advantages namely, increased compressive and flexural strengths, reduced permeability, increased resistance to chemical attack, increased durability, reduced effects of alkali-silica reactivity (ASR), reduced shrinkage due to particle packing, making concrete denser, enhanced workability of concrete, reduced heat gain through the walls of buildings, reduced amount of superplasticizer, reduced potential for efflorescence due to the decrease of calcium hydracids (Sata et al., 2007).

### 2.3.2.2 Palm Oil Fuel Ash (POFA)

The oil palm is a tropical palm tree, which is easily cultivated in tropical countries, such as Malaysia, Indonesia, Thailand, Africa, and Latin America, 90% of the palm oil production is generated by three of the ASEAN countries (Hansen, 2007; Shafigh et al., 2014). Palm oil can be grown in many parts of the tropical world, but is mainly productive within the equator line, which include Indonesia, Malaysia, and several parts of Thailand. The high productivity of oil palm is concentrated in the tropical zone; located $10^o$ to the North or South of the equator.
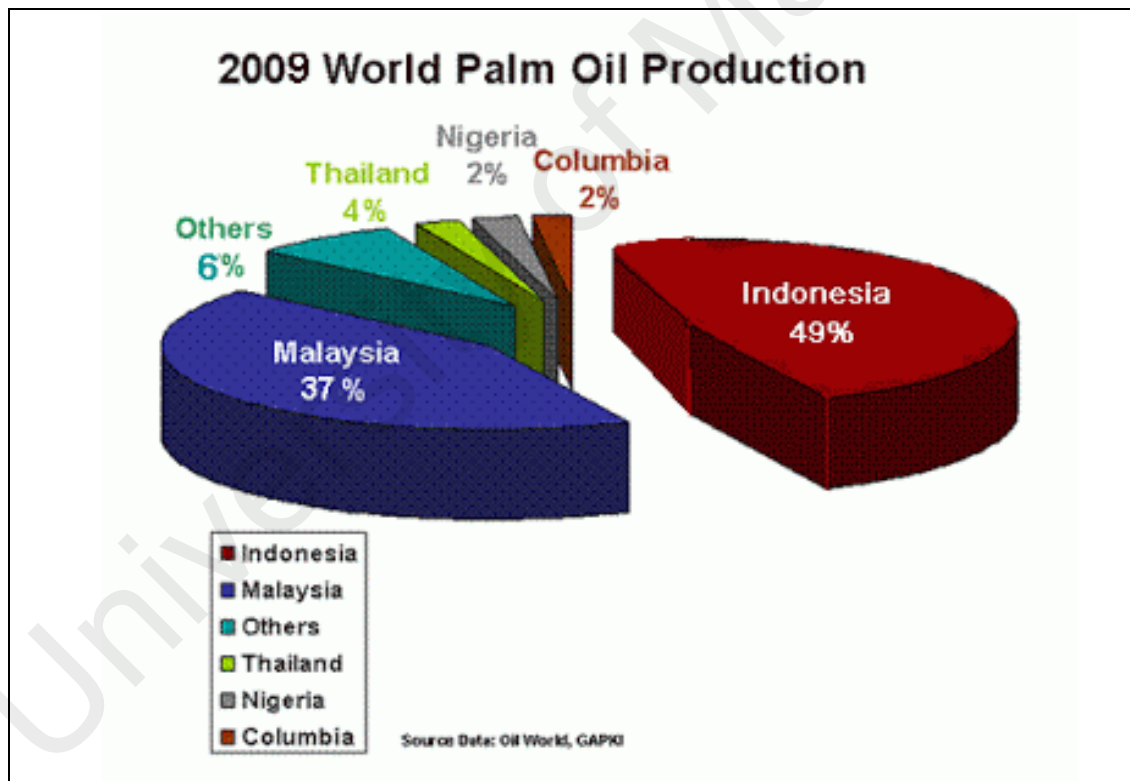


**Figure 2.10: World Palm Oil Production in 2009 (Oil Palm Market Monitor, 2014)**

Figure 2.10 shows the worldwide production of palm oil in 2009 (Oil Palm Market Monitor, 2014). Malaysia produces 7 million tons of crude palm oil each year (Shafigh et

35

al., 2014), and Thailand produces 100,000 tons of POFA annually (Jaturapitakkul et al., 2007), which is likely to increase due to the development of palm tree plantations. The ongoing expansion of oil palm plantations in the humid tropics, particularly in Southeast Asia is generating considerable concern. The responses of utilizing the wastes from oil palm are also expanded (Hussin & Ishida, 1999; Hussin & Awal, 2007). The common method used is biodegradation process or well known mostly as composting material. Naturally composting will take place within a few weeks to 2 years to really mature compost. The length of time depends on the characteristics of the composting material which is composted, composting method used, and with or without the addition of compost activator.
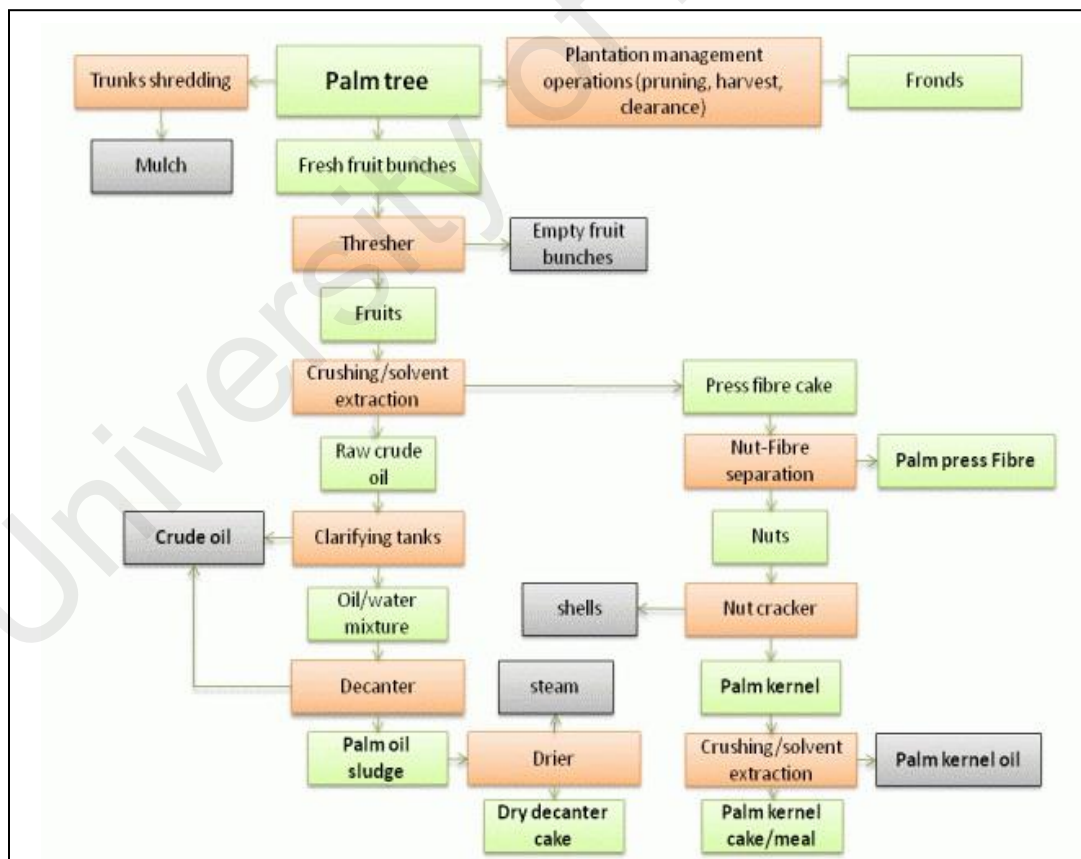


**Figure 2.11: the biodegradation process of oil palm (Hussin & Awal, 2007)**

Palm trees are generally used in commercial agriculture. Figure 2.11 shows the biodegradation process of the oil palm waste products. They do not produce branches and are spread by sowing the seeds. It comprises an oily, fleshy outer layer, with a single seed (kernel), which is rich in oil (Alengaram et al., 2013). Tangchirapat et al. (2009) defined POFA as an agro-waste ash from which palm oil residue, such as palm fibre and shells. It is burnt at temperatures of $800 - 1000^{o}C$ to produce steam for the generation of electricity in biomass thermal power plants. The typical oil palm residue constitutes 15% shell and 85% fiber. To produce energy, the empty fruit bunches are burned in a boiler. Generally, it also produces about 5% ash by weight of solid waste. The solid waste and ash material produced are rarely used, thus, posing a serious ecological problem through the concomitant pollution of the environment. Thus, it should present a feasible solution to both the problem of land-filling as well as the high cost of building materials and pollution of the planet. Basically, waste disposal is always considered as a "negative value" due to the costly practices. In addition, the manageable maximized use of POFA will produce "positive value" products as well as reducing the environmental problems. Compared to other types of palm-oil by-product, both the 20th and 21st centuries, POFA has represented an environmental disruption pollutant that ends-up in the atmosphere without being utilized.
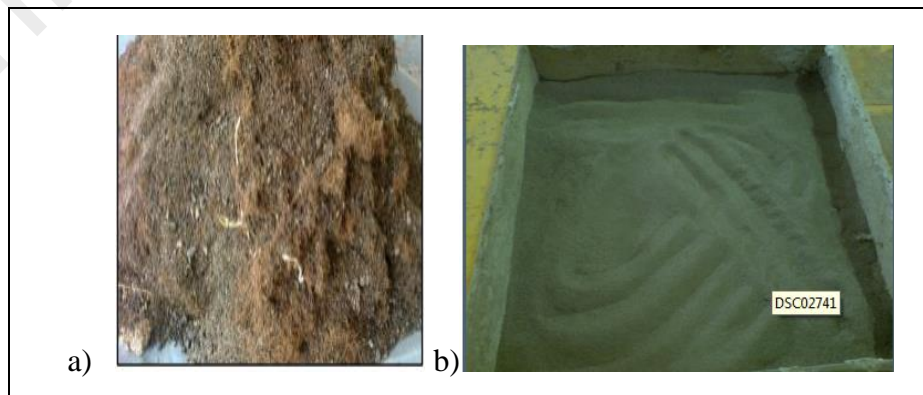


**Figure 2.12: a) Palm oil residue b) Palm oil fuel ash (Sata et al., 2004)**

Figure 2.12a shows the residue from the palm oil industry, and, after analysis using a 300 µm sieve, becomes ash, as presented in Figure 2.12b. The manufactured process of POFA varies from the initial preparation to the incineration process. Noorvand et al. (2013) examined the initial preparation of POFA after the combustion process by dried samples in an oven at $105 \pm 5^{o}C$ for 24 h. Tangchirapart et al. (2009) prepared the ash using the combustion process at a temperature of about 700 to $1000^{o}C$ and sieve No. 16 (1.18 mm opening) to remove foreign materials during the incineration process. They found three different types of POFA based on specific gravity original size (OP), medium size (MP) and small size (SP). The specific gravity was 1.89, 2.36, and 2.43 for OP, MP, and SP, respectively. It can be concluded that the grinding process not only improves the fineness of POFA, but also the specific gravity.

Another preparation method was conducted by Abdul Awal and Shehu in 2013, in which the ash was obtained from the foot of the flue tower in Johor, the southern state of Malaysia. Thereafter, it was sieved through a 150 µm filter and ground in a modified Los Angeles abrasion test machine with 10 stainless steel bars (12 mm diameter and 800 mm long) instead of steel balls inside in order to increase the fineness. The ash produced sometimes varied in colour, from whitish grey to a darker shade, based on its carbon content (Tangchirapat et al., 2009; Jaturapitakkul et al., 2007; Sata et al., 2004). At the end, it was noted that the raw materials for POFA could come from the fuel industry, self-combustion in a furnace or other milling industries. All the fine ash was trapped while escaping from the burning chambers of the boiler then sieved through a 150 µm to 300 µm filter to remove the bigger sized ash particles as well as any materials that had not been considered. In other words, the physical characteristics of POFA are very much influenced

by the operating system in the palm oil factory. The ash was ground in a Los Angeles abrasion test machine that contains within it 10 to 20 stainless steel bars instead of steel balls.

Madurwar et al., 2013 stated that in bulk condition, POFA is greyish in colour and becomes darker as the proportions of unburned carbon increases. The properties of POFA are described in Table 2.4.

**Table 2.4: The properties range of Portland cement (OPC), palm oil fuel ash (POFA) (Madurwar, 2013; Awal&Shehu, 2013; Bamaga et al., 2013; Rahman et al., 2014)**

| *Chemical Composition (%)* | OPC | POFA |
|---|---|---|
| $SiO_2$ | 21.9 | $59.62 - 66.91$ |
| $Al_2O_3$ | 4.86 | $2.5 - 6.44$ |
| $Fe_2O_3$ | 3.30 | $1.9 - 5.72$ |
| CaO | 62.30 | $4.92 - 6.4$ |
| MgO | 2.3 | $3.00 - 4.52$ |
| $SO_3$ | 2.10 | $0.30 - 1.28$ |
| $Na_2O$ | 1.15 | $0.19 - 0.76$ |
| $K_2O$ | 0.32 | $4.97 - 7.52$ |
| LOI | 1.11 | $6.57 - 10.02$ |
| *Physical Properties* | | |
| Median particle size (μm) | - | 10.45 |
| Specific gravity | 2.90 - 3.14 | 2.42 |
| Blaine Fineness ($m^2$/kg) | 305 | 493 |

The main oxide of POFA is silicon dioxide or $SiO_2$ (Yusoff, 2006; Sumathi et al., 2008). It has been explained that POFA is moderately rich in silica content (59.6 % - 66.9 %) compared to that of OPC. In addition, the amount of iron content (1.9 % - 5.7%) is similar to that of CaO, which is very low, i.e. about 5%. However, it is much finer than OPC and its specific gravity is around 1.90 to 2.45 as mentioned in Table 2.4. Furthermore, the combustion process influences the amount of carbon present in the ash. For instance, the loss on ignition (LOI) detected was 8.25%, which is somewhat higher than the maximum value of 6.0% stipulated in ASTM C618 (2012). The difference in the amount of the chemical components in POFA is due to the material source, and burning process and efficiency (time and temperature).

The formation of calcium-silicate-hydrate (C-S-H) is gained from the reaction between $SiO_2$ and $Al_2O_3$ in a pozzolanic material with $Ca(OH)_2$ in a cement paste. The $Ca(OH)_2$ is used as an indicator in pozzolanic reaction. Chindaprasirt et al. (2007) reported that the increasing portion of the pozzolanic replacement and fineness will cause a reduction in the $Ca(OH)_2$ content, while improving the sulphate resistance in concrete. They found that high fineness POFA has a faster pozzolanic reaction than coarse POFA (without sieving). Hence, POFA can improve the compressive strength of concrete due to its high fineness which is denser and more homogeneous. In addition, the use of POFA as a binder satisfies the chemical requirement in ASTM C618 as a pozzolanic material by having a loss on ignition (LOI) of less than 10%. Hence, it could be beneficial in the manufacture of concrete. Many researchers (Shafigh et al., 2014; Tangchirapat et al., 2009; Jaturapitakkul et al., 2007; Madurwar et al., 2013) have found solutions for making use of this by-product to be a valuable waste. In 2011, Jaturapitakkul et al. investigated the compressive strength

of mortar due to the pozzolanic reaction of POFA for 10% - 40% of cement replacement by weight of binder. The compressive strength of mortar due to the pozzolanic reaction of POFA varied from 0.1 MPa to 4.5 MPa at 7 days and 2.5 MPa to 22.5 MPa at 90 days. This result confirms that the pozzolanic reaction of POFA is small at an early age and increases in significance at a later age. It also shows that the pozzolanic reaction of POFA increases with arising particle fineness, cement replacement rate and age of concrete. Furthermore, POFA (median particle size of approximately 10 µm) has been utilized in the production of HPC, in which the highest compressive strength was found to be in the range 60 – 86 MPa, which was obtained at the POFA replacement level 20% at 28 days with a total binder content of $550 - 560$ kg/m$^3$(Sata et al., 2004; Sata et al., 2007; Madurwar et al., 2013). According to Jaturapitakkul et al. (2007), the increased fineness of POFA will reduce the expansion and loss in the compressive strength of concrete due to the pozzolanic reaction. They suggested that POFA could be used as a pozzolanic material as well as to improve the sulphate resistance of concrete. Meanwhile, Sata et al. (2007) studied the ability of POFA as a pozzolan to improve the strength of concrete. All researchers attributed the improvements in the behavior of the POFA concrete to the pozzolanic reaction through which the hydration products were released. The development of the compressive strength for selected mixtures is presented in Table 2.5.

**Table 2.5: The selected mix proportion of high strength concrete**

| No | Mix Proportion (kg/m3) | | | | | | | w/c | Slump (mm) | Compressive Strength (MPa) | | References |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cement | POFA | | Sand | Coarse Agg. | Water | SP (l) | | | | | |
| | | Kg/m3 | % | | | | | | | 28 days | 90 days | |
| 1 | 495.0 | 55.0 | 10 | 753 | 959 | 176 | 6.8 | 0.32 | 250 | 60 | 68 | (Tangchirapat et al., 2009) |
| 2 | 440.0 | 110.0 | 20 | 745 | 950 | 176 | 8.6 | 0.32 | 240 | 61 | 70 | |
| 3 | 385.0 | 165.0 | 30 | 738 | 940 | 176 | 11.6 | 0.32 | 250 | 59 | 66 | |
| 4 | 400.0 | 100.0 | 20 | 711 | 1067 | 145 | 11.5 | 0.28 | - | 37 | 52 | (Bamaga et al., 2013) |
| 5 | 400.0 | 100.0 | 20 | 711 | 1067 | 145 | 11.5 | 0.28 | - | 49 | 53 | |
| 6 | 540.4 | 145.3 | 25 | 1057 | 1340 | 168 | 50.4 | 0.23 | 169 | 175 | 182 | (Aldahdooh et al., 2013) |
| 7 | 214.0 | 213.0 | 50 | 787 | 961 | 205 | - | 0.29 | 115 | 41 | - | (Awal&Shehu, 2013) |
| 8 | 171.0 | 256.0 | 60 | 787 | 961 | 205 | - | 0.29 | 90 | 36 | - | |
| 9 | 128.0 | 299.0 | 70 | 787 | 961 | 205 | - | 0.29 | 80 | 28 | - | |
| 10 | 504.0 | 56.0 | 10 | 757 | 971 | 153 | 8.5 | 0.28 | 200 | 89 | 91 | (Sata et al., 2007) |
| 11 | 448.0 | 112.0 | 20 | 749 | 962 | 151 | 11.8 | 0.28 | 185 | 94 | 93 | |
| 12 | 392.0 | 168.0 | 30 | 742 | 952 | 148 | 16.9 | 0.28 | 185 | 87 | 91 | |
| 13 | 270.0 | 30.0 | 10 | 804 | 1024 | 216 | - | 0.72 | 80 | 39 | 40 | (Tangchirapat&Jaturapitakkul, 2010) |
| 14 | 240.0 | 60.0 | 20 | 801 | 1021 | 210 | - | 0.70 | 60 | 32 | 39 | |

For concrete mixtures containing various proportions of POFA, the results show that the compressive strength is more than 55 MPa at 28 days. Concrete samples with 20% and 30% POFA show values of 59 and 61 MPa, respectively. After 28-days, the compressive strengths of all concretes containing POFA were higher than the normal concrete, as mentioned in Table 2.5. The use of 20% POFA resulted in a compressive strength of as high as 70 MPa at 90-days. Two different POFA (CAPOFA and ALPOFA) were collected from diverse palm oil industries. The different mixtures shown in sample G(I) indicate that using additional fibre (steel) as a binder aggregate to produce a significant compressive strength of 175 MPa at 28-days compared with no fibre. Meanwhile, at the same POFA proportions of 10%, 20%, and 30%, but combined with 10% SF, it produced an extraordinary strength of up to 93 MPa. Furthermore, POFA can be used as a cement replacement up to 30% in producing high-strength concrete, and the compressive strength obtained is higher than concrete made from Portland cement. The inclusion of the ultrafine POFA tends to reduce the water demand of the high-strength concrete (Aldahdooh et al., 2013). Overall, the results described and presented show that POFA possesses great potential pozzolanic cementing materials with possibly superior engineering properties in proper mixing and curing systems. It could also lead to the greater utilization of waste material from the agricultural side. Subsequently, by minimizing the volume of waste, which is disposed of landfill, will protect the environment as well as reduce the emission of GAGs (greenhouse gases $CO_2$). Furthermore, the use of POFA contributes to a sustainable industry and may contribute to a reduction in the construction cost.

**2.3.2.3 Fly Ash (FA)**

Fly ash is a product formed from burning coal process in a power station (Babu and Rao, 1993; Kosmatka and Panarese, 2002). Fly ash which is produced during the coal combustion process has negative impacts on the environment, mainly as air and soil pollution. Hence, fly ash must be utilized to an environmentally friendly purpose. Using fly ash as an admixture and additives for construction purposes is one of the bright solutions to the environment (Ahmaruzzaman, 2010).The amount and type of waste generated increases with growth in population. The sample of fly ash can be seen in Figure 2.12.
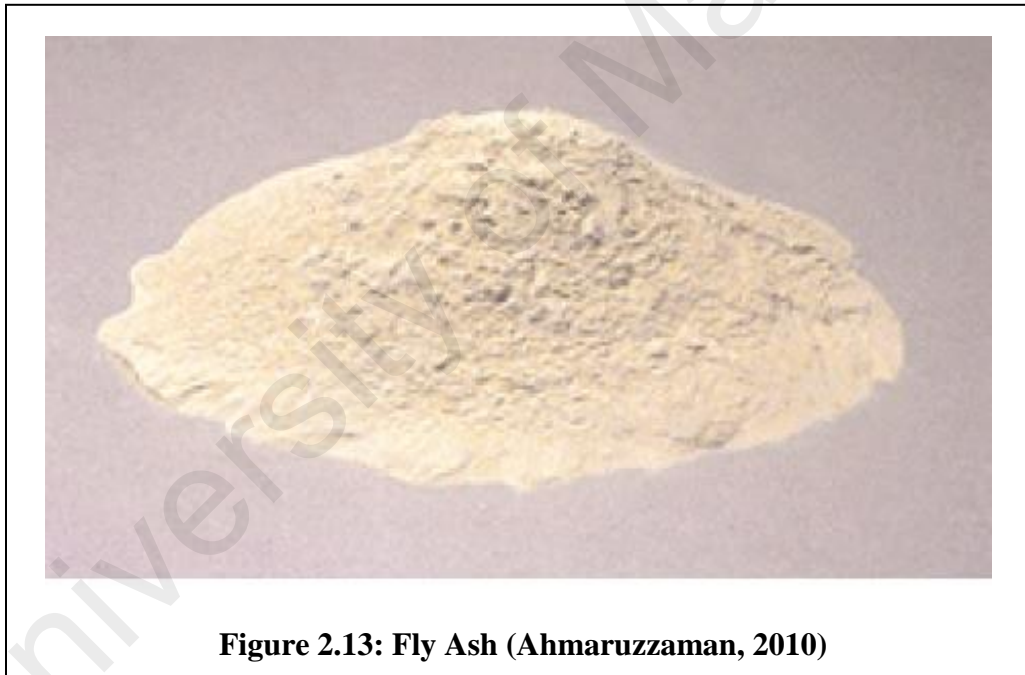


**Figure 2.13: Fly Ash (Ahmaruzzaman, 2010)**

Waste materials, such as fly ash, has been successfully used in construction industry for decades (Malhotra, 2000; Lian & Zhuge, 2010; Arnesto & Merino, 1999; Lilkov et al., 2014).Fly ash has been widely used in many research purposes; one of them is using it as a cement replacement material in concrete (Malhotra, 2000). Fly ash has similar characteristics to pozzolanic materials, where it has high content of $SiO_2$ (silica) and $Al_2O_3$

(alumina) (Park & Tia, 2004). According to ASTM C 618, a pozzolan is defined as ''a 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 to form compounds possessing cementitious properties (pozzolanic activity).''A cementitious material which is formed from pozzolanic activity generally contains of CaO and can exhibit a self-cementitious (hydraulic) activity, whereas in order to form strength products, the fraction of $SiO_2$, which is active for pozzolanic reactions, requires $Ca(OH)_2$ from cement hydration. Usually, the CaO content of the latter material is insufficient to react with all the pozzolanic compounds. Thus, it also exhibits pozzolanic activity (Chindaprasirt et al., 2007). Fly ash production in different countries annually is shown in Table 2.6.

**Table 2.6: Annually production of fly ash in different countries (Park, 2009)**

| Country | Fly Ash Production Annually (tons) |
|---|---|
| India | 117 million |
| US & EU | 115 million |
| China | 100 million |
| Germany | 40 million |
| Australia | 10 million |
| Canada | 6 million |
| Korea | 4.8 million |
| Thailand | 3.5 million |
| France | 3 million |
| Denmark, Italy & Netherlands | 2 million |
| Indonesia | 6.1 thousand |

Fly ash of pulverized coal is generally generated from the combustion in thermal power plants. One ton of pulverized coal can produce fly ash of around 30%-40% by using circulation fluidized bed combustion technology (Huangling et al., 2006). Large quantities of fly ash are usually discharged directly to waste dumps or stockpiled landfills, which is leading to substantial land occupation and environment pollution (Chindaprasirt et al., 2007). In some countries, this waste is found in abundant amount and it requires extra attention with respect to handling. As can be seen from Table 2.6, it is estimated that more than 3.5 million tons of fly ash has been produced annually in Thailand since 2001, however, only half has been utilized (Chindaprasirt et al., 2007). In Korea, approximately 4.8 million tons fly ash has been generated annually (Okamoto & Masui, 2000). Meanwhile, approximately 50 million tons of fly ash are generated annually in China (Hu & Li, 2015), which poses a challenge for fly ash and firing residues disposal.

Several investigations were reported about properties and mechanism of fly ash itself. Lian and Zhuge (2010) have studied the cementitious properties and hydration mechanism of blended cement. A lower pore size in the matrix of cement paste is making the increment on the strength of blended cement. Chindraprasirt et al., (2007) has reported the effect of fly ash fineness on microstructure of blended cement paste. According to the authors, the blended cement paste containing fly ash generally exhibited a lower pore size than that of Portland cement type I paste. At 28 days, the peak of capillary pores of fly ashes paste was located at 50.4 nm with the incremental pore volume of 0.0266 ml/g. However, the effect may be significantly dependent on the properties of fly ash derived from combustion method and coal types. Hence, an understanding on characteristics of fly ash is urgently

needed. Particle size distributions and particle shapes of PC, OFA, and CFA by SEM are shown in Figures 2.14 and 2.1.
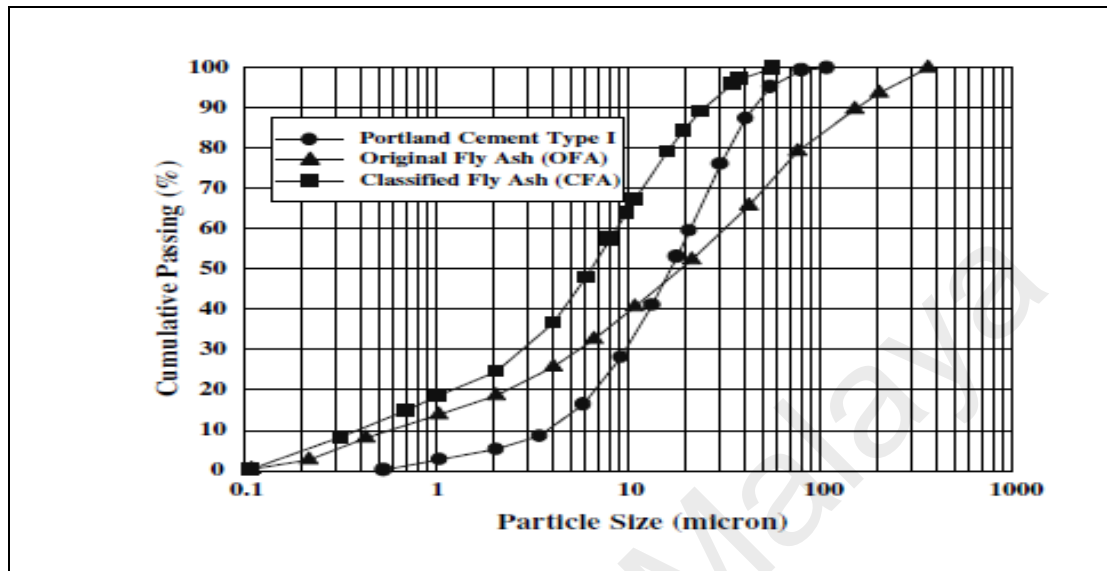


**Figure 2.14: Particle size distribution of OPC, OFA and CFA (Huangling et al., 2006)**
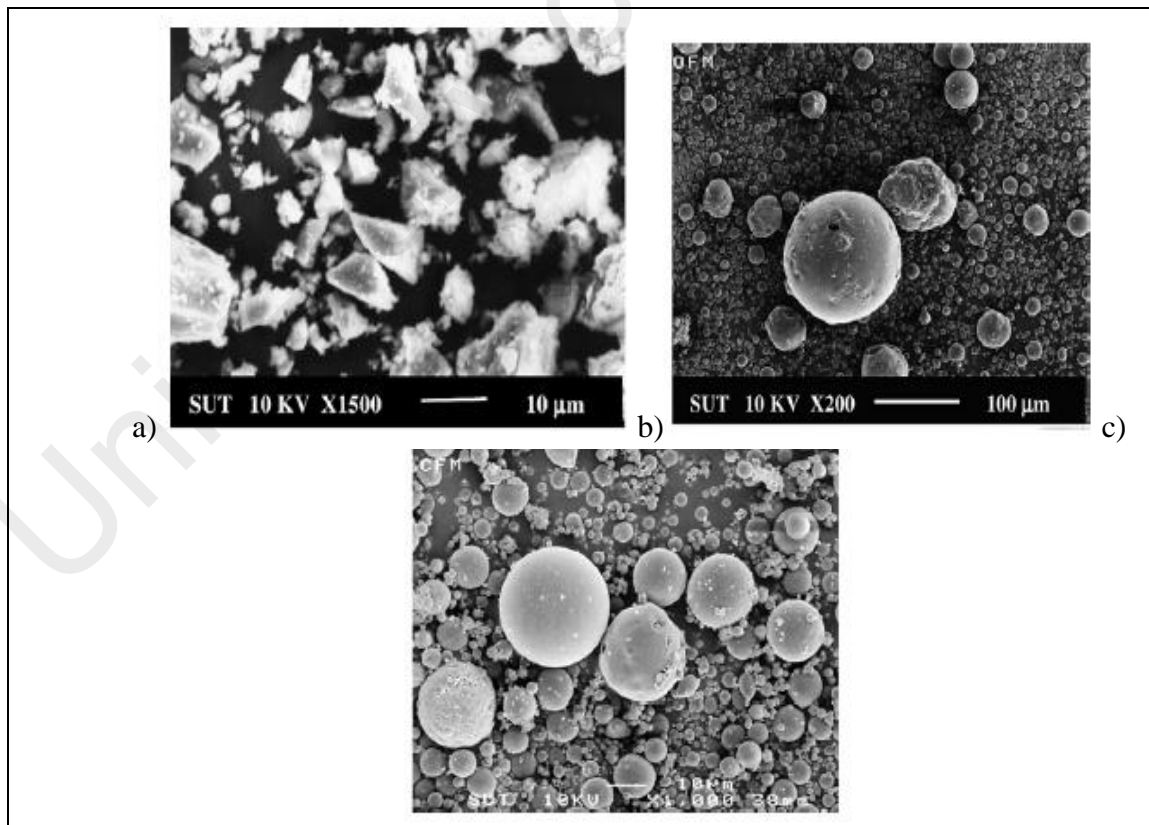


**Figure 2.15: SEM of PC type I and fly ashes (a) PC type I (b) Original fly and (c) Classified fly ash (Chindaprasirt et al., 2007)**

Figure 2.14 shows that the particle sizes in fly ash vary from less than 1 μm (micrometer) to more than 100 μm with the typical particle size measuring under 20 μm. Only 10% to 30% of the particles by mass are larger than 45 μm (Huangling et al., 2006). Most of the fly ash particles are solid spheres and some are hollow chemosphere. Also present are plerospheres, which are spheres containing smaller spheres. Ground materials, such as Portland cement, have solid angular particles, as shown in Figure 2.15.

Utilization of fly ash is deemed environmentally friendly because it can bring benefits to the environment like mitigating the negative impact on the environment. Otherwise, the other important thing should be pay attention is the physical and chemical properties of fly ash. The properties of fly ash will influence the hydration system when FA is combined with Portland cement. The physical and chemical properties of fly ash are given in Table 2.7.

**Table 2.7: Physical properties of fly ash (Huangling et al., 2006; Chindaprasirt et al., 2007)**

| Physical Properties | | | |
|---|---|---|---|
| | OPC I | OFA (Class C) | CFA |
| Density (g/cm$^3$) | 2.10 | 2.43 | 2.67 |
| Blaine's (m$^2$/kg) | 360 | 300 | 510 |
| Particle size (μm) | 14.1 | 19.1 | 6.4 |
| Specific gravity | 3.15 | 2.33 | 2.54 |
| Chemical Composition (%) | | | |
| SiO$_2$ | 20.90 | 45.69 | 44.72 |
| Al$_2$O$_3$ | 4.76 | 24.59 | 23.69 |
| Fe$_2$O$_3$ | 3.41 | 11.26 | 11.03 |
| CaO | 65.41 | 12.15 | 12.67 |
| MgO | 1.25 | 2.87 | 2.63 |
| SO$_3$ | 2.71 | 1.57 | 1.28 |
| Na$_2$O | 0.24 | 0.07 | 0.07 |
| K$_2$O | 0.35 | 2.66 | 2.87 |
| LOI* | 0.96 | 1.23 | 1.42 |

*LOI = Loss on Ignition (%)

Since part of cement is substituted with fly ash in a mixture of concrete, the reaction between oxides will start after one or more weeks after mixing process. Khayat (2000) has stated that Fly ash doesn't start showing its pozzolanic properties until one or more weeks after the mix is made. The hydration process will start with the reaction of with $SiO_2$ as oxide component present in the fly ash to form C-S-H (Calcium hydroxide) gel. The C-S-H gel is the substantial compounds which bring benefit to increase the strength of concrete (Babu and Rao, 1993). Since fly ash is rich in calcium oxide, it can be directly used for strengthen purposes when used as partial replacement of cement. The limitations used of fly ash are the quality of the fly ash should be good, because poor quality fly ash concrete make concrete less attractive (Babu and Rao, 1993).

The successful use of such waste material, as whole or partial replacement of conventional Portland cement, contributes to solving the disposal problem of the wastes, energy saving, conservation of natural resources, a reduction in the cost of construction materials, and helps environmental protection from pollution. The use of SCMs such as fly ash from coal combustion represents a viable solution to partially substitute ordinary Portland cement. The use of such materials, where no additional clinkering process is involved, leads to a significant reduction in $CO_2$ emissions per ton of cementitious materials (grinding, mixing and transport of concrete use very little energy compared to the clinkering process) and is also a means to utilize by-products of industrial manufacturing processes.

**2.3.2.4 Ground Granulated Blast Furnace Slag (GGBFS)**

In general definition, Ground Granulated Blast Furnace Slag (GGBFS) is iron dust also called metal cinder from refining process which is a valuable by-product (Saridemir et al.,

2009). GGBFS was first developed in 1853 in Germany (Malhotra and Povindar, 1996). GGBFS is prepared by heating silicates and alumino-silicates with iron in a blast furnace inside a molten condition. The molten slag is then cooled rapidly from $2730^{o}F$ to freezing point to form a granulated material. This material is ground to less than 45 microns. The formed material has a glassy surface. It consists of silicates and alumino-silicates (Malhotra and Povindar, 1996). GGBFS is known to have hydraulic properties (Ahmaruzzaman, 2010). A sample of GGBFS is shown in the Figure 2.16.



**Figure 2.16: Ground Granulated Blast Furnace Slag (GGBFS) (Ahmaruzzaman, 2010)**

In recent years, the usage of GGBFS in construction has increased. Records indicate that blast furnace cement was used for the mortar during the construction of the Empire State Building in the 1930s (Garcia et al., 2009). The chemical and physical properties of GGBFS influence hydration process. Cementitious properties have been built-in it, but these have to be activated. The normal means of achieving this is to combine the material with Portland cement (Muhmood et al., 2009). The chemical compositions of slag are shown in the Table 2.8.

**Table 2.8: Chemical Composition of Slag (Garcia et al., 2009; Ahmaruzzaman, 2010; Sajedi et al., 2012)**

| Mineral | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $Na_2O$ | $K_2O$ | LOI |
|---|---|---|---|---|---|---|---|---|---|
| wt% | 30-39 | 8-14 | < 1 | 36-42 | 3-12 | 2-3 | 0.1-0.4 | 0.3-0.5 | 0.3-0.7 |

Besides, earlier usage of slag cement in Europe and elsewhere demonstrate the long-term performance of slag concrete in many ways. It has been observed that GGBFS can be effectively used to reduce the pore sizes and cumulative pore volume considerably leading to more durable and impermeable concrete (Sajedi et al., 2012; Muhmood et al., 2009; Garcia et al., 2009). Concrete combine with GGBFS has many advantages, they are; enhanced durability, restrained heat of hydration, easier finish-ability, higher compressive strength, lower permeability, environmentally friendly and economical value (Barnett et al., 2006; Sajedi et al., 2012; Muhmood et al., 2009). GGBFS is used as additional or combination mix proportion with ordinary Portland cement in both of mortar and concrete for many applications as shown in Figure 2.17.
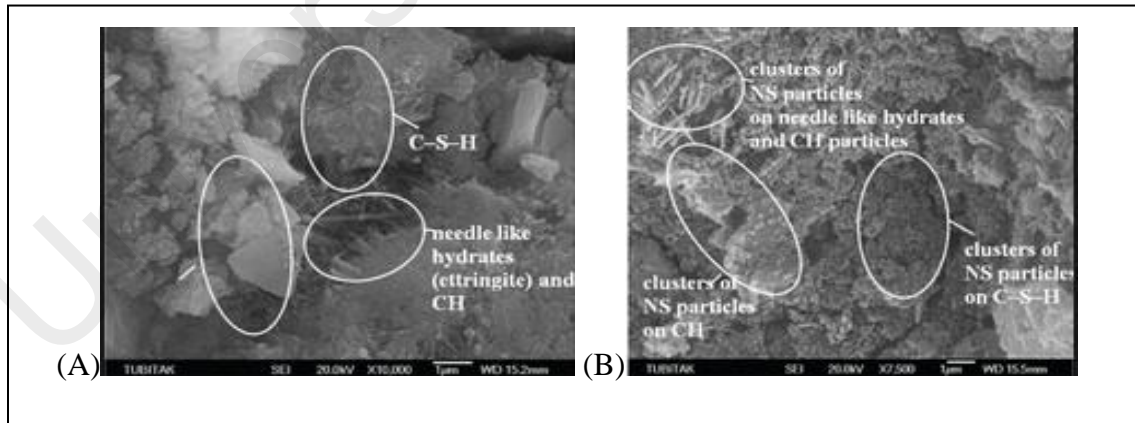


**Figure 2.17: SEM display of the mortar contains GGBFS in the early age (7 days), (A) OPC mortar magnification x10000, (B) OPC with GGBFS mortar magnification x7500 (Garcia et al., 2009).**

Figure 2.17 explained the hydration process of mortar containing GGBFS and OPC. GGBFS has ability to fill the spaces between OPC less than OPC mortar due to the fineness and granules of GGBFS (Garcia et al., 2009). Fineness and granules absorb water to reduce the water content in mortar mixes. It should be stressed that the hydration process of GGBFS at later ages will produce the same strength with mortar containing OPC, due to the crystalline phase sets faster in a high temperature. Whenever mortars containing GGBFS and were cured under high temperature for certain time, the crystalline phase inside the GGBFS properties will react and set faster and produce tighten bonding between the aggregate. It caused the incremental strength of mortar.

### 2.3.2.5   Other Waste Materials

Other than fly ash (FA), GGBFS, rice husk ash (RHA) and palm oil fuel ash (POFA), there are several waste materials that origin from agriculture can be used as supplementary cementitious materials. The other types of agricultural waste are bagasse ash (Singh et al., 2000; Ganesan et al, 2007; Cordeiro et al., 2008; Chusilp et al., 2009), wood waste ash (Ban & Ramli, 2011; Siddique, 2012; Ramos et al., 2013), bamboo leaf ash (Dwivedia et al., 2006; Cocina et al., 2011; Frias et al., 2012), saw dust ash (Udoeyo & Dashibil, 2000; Kupka et al., 2008), corn cob ash (Adesanya& Raheem, 2009, Raheem et al., 2010), etc. Otherwise, this waste material is relatively new in the construction industry. Only few studies have been carried out to use them in mortar and concrete mixture.

### 2.4      Blended Cements

Blended cements are obtained by mixing OPC with mineral admixtures or cementitious materials. Research highlights were triggered by interest in eco-friendly environment and

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sustainability development. Kejin (2003) stated that blended cements are being considered superior as compared to conventional OPC category of binder. A gap in knowledge is about the variation or proper combination of blended cements containing cementitious materials in the production of high performance of mortar. Potential benefits of blended cements are improved workability and durability, lower risk of thermal cracking and reduced overall production cost (Kejin, 2003; Aitcin 2000). Blended cements combinations are divided in two types, they are binary blended cements and ternary blended cements.

### 2.4.1 Binary Blended Cements

Binary blended cements are mixtures containing Portland cement and one SCM. Aitcin (2000) stated that modernization in construction industry is more than simply a mixture of cement, water and aggregate but contains more mineral components, admixtures and etc. Cost and environmental savings are the main reasons to develop such of binary blended cements.

Several researchers have conducted an experiment of binary blended cements. Zhang et al., (1996) found that the strength of binary blended cement containing 10% RHA in concrete exhibited higher strength compared to OPC concrete at all ages but had similar strength at one day strengths. Zahairi (1990) found that the POFA mortar up to 35% replacement is possible to produce mix having equivalent strength compared to the OPC mortar mix. It is also reported that the higher the POFA content is the lower will be the strength than OPC mortar at lower water to cement ratio of 0.40.

Paya et al., (2001) conducted an experiment with combined RHA and OPC in a mixture. They want to prove the effect of amorphous silica in RHA. It was found that the binary blended cement containing RHA showed a better performance than a blended containing

PFA material. RHA contains large amounts of silicon dioxide and highly reactive pozzolanic materials so it is beneficial to the construction industry in terms of strengthening the structure and protect the environment. Furthermore, Yusuf et al. (2014) investigated the effect of GGBFS on binary blended cement compared to OPC mortar. It was found that combination of GGBFS and OPC exhibited higher strength compared to OPC mortar at early ages subjected to hot air curing condition. It was cleared that under water curing condition, OPC mortar gave lower strength than OPC with GGBFS mortar. It is related to the presence of crystalline structure from GGBFS which can improve strengths at later ages. It is noted that GGBFS blended cements have less strength than that of OPC at early curing period, particularly at high dosage of slag.

Elinwa and Awari (2001) successfully investigated the potentials of ground nut husk ash concrete by partially replacing Ordinary Portland Cement with ground-nut husk ash. Adewuyi and Ola (2005) applied water works sludge as partial replacement for cement in concrete production. Ezeh and Ibearugbulem (2009) found good prospect in partially replacing cement with periwinkle shell ash in river stone aggregate concrete. Many other researchers have confirmed rice husk ash a pozzolanic material that can be used to partially replace OPC in making cement composites (Cordeiro et al., 2009; Habeeb & Fayyadh, 2009; Rukzon et al., 2009).

Papadakis (2000) concluded that in the case where ordinary Portland cement is replaced by FH (high calcium fly ash), the final strength will exceed that of the control only if the content of active silica in the fly ash is higher than that in the cement. Whilst, in the case of tested fly ash, similar strengths are observed due to almost equal active silica content.

Sensale (2010) studied the effects of partial replacement of Portland cement by RHA on the durability of conventional and high performance cementitious materials. Different percentages of RHA replacement levels were investigated. Two RHAs and several water cementitious materials ratio are also studied. The results were compared with OPC mixture and it is concluded from the results that the incorporation of two types in concretes show different behaviors for air permeability and chloride penetration depending on w/c ratio used. Otherwise, in mortar it reduces the mass loss of specimens exposed to hydrochloric acid solution and decreases the expansion due to sulfate attack and the ASR reaction. In general, it can indicate that an enhanced performance, proving the feasibility of its rational utilization as a SCM.

Bagel (1998) and Boubitsas (2001) supported the previous statement by conducting a study about the effect of binary and ternary blended cements on mortar. For instance, the high level portions of slag and silica fume used in the binding system cause the mortars reached relatively satisfactory level of compressive strength and contributed to the significantly denser pore structure (Sajedi & Razak, 2011). In 2001, Boubitsas evaluated the effect of binary blended cement mortar containing 45% (by mass) GGBFS and 55% OPC with presence of 1% superplasticizer. The results obtained possess the highest improvement of mechanical properties, hydration kinetics and microstructure of hardened mortar.

In conclusion, the power of binary blended cements in the production of high performance of concrete and mortar depends on the chemical and physical properties of SCM used. It is highlighted that the combination between OPC and one SCM should be adjusted properly. Due to the hydration effect of SCM in blended cements influenced the workability and durability of concrete and mortar.

### 2.4.2   Ternary Blended Cements

Ternary blended cements is the combination of Portland cement and two types of SCMs. Not much different from binary blended cements, combination of two SCMs also emphasizes the high performance of concrete and mortar as well as reduction of the production cost. The knowledge related to the multiple blended cement systems and their currently practical application is rather finite. However according to Jones *et al.* (1997), the combination of multiple materials as a blended binder is now an alternative which can be take a seriously for the concrete structure.

Khan *et al.* (2000) inspected the performance development of mortar containing OPC, PFA and SF using binary and ternary blended systems. Substitution of 8-12% SF as partial cement replacement showed the optimum performance, producing the highest compressive strength and the lowest percentage of porosity. Sumadi and Loon (2008) concluded that ternary blended cement mortars exhibit better resistance than the control mortar. The results found were higher in durability than control mortar when subjected to chemical attack. The strength of ternary blended cement mortar exhibited 24% higher than control mortar in seawater curing condition. Moreover, they found that due to the balancing effect in reactivity and water demand of SF and PFA, the strength increases at early ages.

Sobolev and Yeginobali (2005) investigated the use of slag as partial replacement in binary blended cement. They also studied to improve repairing material purposes of slag cement binder in the chemical industry at high thermal or acid resistance is needed. It was found that the binary system containing slag is inappropriate. The enhancement of slag cement binders could be achieved with the addition of SF and superplasticizer. According to Isaia

*et al.* (2003), when less reactive pozzolan is employed in ternary mixtures together with another more reactive such as SF or RHA, there is a synergy between these pozzolans, thus the obtained results are higher than those verified in the respective binary mixture.

Antiohos et al., (2007) investigated the effects of ternary blended cement mortar containing two types of fly ashes, with high and low calcium content. The synergy between the different types of fly ash was considered the main reason for the excellent performance of the ternary mixtures. The results obtained that the blends with equal contributions from each fly ash (50:50 ratio) were found to be the most effective for moderate cement substitution. Whilst at advance cement replacements the apodosis of the intermixtures, particularly after the first week of hydration, is highly depended on their active silica content. Since no significant alterations in the nature of hydration products were detected, the superior performance of the ternary blends was mainly attributed to synergistic effects between the utilized ashes. Results evidenced a combined synergic action between the different ashes possibly initiated by physical and chemical (pozzolanic) mechanisms. The effectiveness of blending different ashes resulted in improvements of the mechanical properties of the respective binary systems almost throughout the curing period. Finally, the principal idea lying beneath the effort presented herein is that beneficial assets of the one type of ash could compensate for the shortcomings of the other.

It can be concluded that the strength of ternary blended cement increased with an increase of silica content that could potentially hinder the next reactions of negative compounds. The strength of ternary blended cement after curing is significantly increased with better endurance and durability to the chloride environment. It is also possible to use ternary

blended cement in chloride or corrosive environment, which perform better than the ordinary Portland cement in terms of compressive strength retention. The ternary blended cement system was also showed greatly lower percentage of the total porosity and water absorption than binary blended cement and OPC mixtures. It is due to the interlocking effect between particles of SCMs. Finally, it can be summarized that the strength and durability properties of ternary blended cement mixtures are much better when it is provided with a sufficient curing systems. The ternary blended cement mixture performs better resistance than OPC mixture, after specific time of exposure to chemical attack. When the multiple combinations used in a blended binder system, they will exhibit manifold benefits such as decreasing the cost of construction and also reduce the adverse effect of waste disposal. The utilization of agricultural and industrial wastes to be constructive and valuable materials has not just been environmental benefits, but may also conserve and preserve the natural resources (Sumadi & Loon, 2008; Khan et al., 2000; Awal & Shehu, 2013; Aprianti et al., 2016).

## 2.5    Curing

Curing is the process by which hydraulic cement matures and develops hardened properties over time as a result of the continued hydration of the cement in the presence of sufficient water and heat (Mehta & Monteiro, 2006). ASTM C 125 examined that curing is also used to describe the action taken to maintain moisture and temperature conditions in a freshly placed cementitious mixture to allow hydraulic cement hydration and pozzolanic reactions to occur so that the potential properties of the mixture may develop. Neville (1995) stated that curing is the process used for promoting the hydration of cement with the aim of keeping the specimens saturated or as nearly saturated as possible until the originally water-

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filled space in the fresh cement paste has been filled to the desired extent by the products of cement hydration. Proper curing allows the cementitious material within the mixture to properly hydrate. Alamri (1988) explained that a proper curing reduces the rate of moisture loss and provides a continuous source of moisture required for hydration. Therefore, good curing reduces the porosity and provides a fine pore size distribution in concrete.

## 2.5.1 Effect of Different Curing Conditions on Compressive Strength

The effect of different curing conditions will affect the hydration process and the strength of concrete and mortar. Extensive research studies have been carried out to study the influence of different curing conditions on the properties of concrete and mortar.

### 2.5.1.1 Water Curing Condition

Water curing is where the specimens of mortar were cured in water under normal temperature ($20^{o}C \pm 5$ and 100% RH). Boakye et al., (2014) investigated the effects of different curing conditions on the compressive strength development of concrete made with pulverized copper slag (the fineness of particles are similar with granulated furnace slag) as partial replacement of ordinary Portland cement. Curing conditions are divided by three, namely water curing, solar chamber curing and ambient air curing up to 90 days. The experimental results indicate as the copper slag (fineness pulverized slag) content increases the compressive strength decreases for all curing methods. For OPC concrete, the compressive strength decreased for 3 days curing in water curing condition about 31% and 28% of the solar chamber and ambient air curing conditions, respectively. Beyond 28 up to 90 days of curing, the specimens were cured in water yielded a higher compressive strength of about 40% and 20% more than the ambient air and solar chamber curing conditions, respectively. For the water cured samples, the compressive strength reduction of the copper

slag concrete samples were more pronounced at early curing ages. The early strength reduction could be due to the slower rate of hydration, which is a typical characteristic of metallurgical slag influences on concrete. However, beyond 28 to 90 days, the strength gain of the copper slag concrete was slightly higher than that for control samples for about 43% on average. This observation could be attributed to the increased in pozzolanic and hydraulic activities. The higher late strength development for concrete samples cured in water was attributed to water providing adequate moisture for further hydration as compared to the solar chamber and ambient air. The pozzolanic reaction takes place after the production of sufficient $Ca(OH)_2$.

Ozer and Ozkul, (2004) conducted a research study on the development of OPC concrete and pozzolanic cement concrete using initial water curing condition. The results obtained that the OPC concretes, except 14-day or continuously water-cured ones, show strength losses between 90 and 180 days. On the other hand, the pozzolanic cement concretes continue increasing strength beyond 90 days, which can be attributed to the suppressing effect of the pozzolanic activity over the shrinkage cracking. This shows that pozzolanic cement concretes are more sensitive to the inadequate curing than OPC concretes. It can be concluded that poor curing conditions are more adversely effective on the strength of concretes made by pozzolanic cements than that of OPC, and it is necessary to apply water curing to the former concretes at least for the initial 7 days to expose the pozzolanic activity. However, when the pozzolanic cement concretes have sufficient initial curing, they can reach the strength of OPC concretes in reasonable periods of time.

Termkhajornkit et al., (2006) explained the effect of water curing condition on compressive strengths of fly ash - cement paste by quantitative data of hydration degree. The result shows that the hydration degree of belite is affected by water curing conditions, more so than that of fly ash and alite. Fly ash still continues to hydrate even without an extra, external supply of water. The strong influence of curing conditions on fly ash–cement concrete is not due to changes in the hydration degree of fly ash, but rather is due to the effect of curing conditions on the hydration degree of cement, especially belite.

When the water to binder ratio is low enough, the hydration of cement plus small hydration of fly ash are considered to be enough for adequate compressive strength at the beginning. Then, compressive strength of fly ash–cement paste becomes less sensitive to the water curing period.

Jo et al., (2007) studied experimentally the properties of cement mortars with nano $SiO_2$. After being demoulded at the age of one day, all specimens were cured in water at $20 \pm 1^{o}C$ for 7 and 28 days. The experimental results show that the compressive strengths of mortars with nano-$SiO_2$particles were all higher than those of mortar containing silica fume at 7 and 28 days cured in water. It is demonstrated that the nano-particles are more valuable in enhancing strength than silica fume. The results of these examinations indicate that nano-scale $SiO_2$ behaves not only as a filler to improve microstructure, but also as an activator to promote pozzolanic reaction and suitable to cured in water with 100% RH. The nano-silica is more effective than silica fume due to its fineness. These increases in the strengths of the mortars with nano-silica are attributable to the nano sized particles and extensive surface area which is filled the interfacial zone between aggregates.

Rukzon and Chindaprasirt (2012) presented the use of bagasse ash (BA) as a pozzolanic material for producing high-strength concrete. The test results indicate that the incorporation of BA up to 30% replacement level in water curing condition increases the resistance to chloride penetration. Besides, the use of 10% of BA produced concretes with good strength and low porosity. Reasonably, the substitution of 30% BA is acceptable for producing high-strength concrete.

Tangchirapat et al. (2006) conducted research on the use of cementitious material in concrete production. The result show that, by using water curing condition and the small size of POFA at rates up to 30% (SP-retained on a sieve No. 325 of 1.0%) to replace Portland Type I cement, has sulfate resistance as good as that of Portland Type V cement and also produces the compressive strength of concrete at 90 days as high as the control concrete made from Portland cement Type I. Reversely, the suitability of water curing condition and the specimens containing POFA caused delay in both initial and final setting times. Therefore, it can be highlighted that the development strength for concrete or mortar in water curing conditions depends on the fineness and the volume of replacement of cementitious materials.

Many researchers conducted studies on the effect of water curing conditions on the properties of concrete and mortar (Wild et al., 1996; Erdogdu & Turker, 1998; Hekal et al., 2002; Chindaprasirt et al., 2004; Sajedi & Razak, 2011; Pangdaeng et al., 2014). Wild et al., (1996) concluded that the development on the strength with water curing is discussed as filler effect. The optimum replacement proportion for OPC to be used as binder in mortar is 20% by weight and that contributed to the maximum strength which is restricted beyond 14 days. In addition, Pangdaeng et al., (2004) assumed that water curing conditions

significantly affected the properties of mortar. The use of water curing method increased the strength due to the formation of additional C-S-H gel from particles of water ($H_2O$). Otherwise, Sajedi and Razak, (2011) contrary reported that the use of water curing conditions only suitable for certain proportion of cementitious volume except the specimens which explored 100% of Portland cement inside. This phenomenon caused by the silica content in SCMs and the type of blended cements applied for.

**2.5.1.2 Air Curing Condition**

Air curing condition is the process to cure specimens under room temperature of $\pm 37^{o}$C with 70% RH. Sajedi and Razak (2011) also investigated the effect of different curing conditions on mortar containing slag. They stated that the highest and lowest compressive strengths are attributed to the specimens of OPC mortar water cured using grounded OPC for duration of 6 h (OM–G6–WC)and OPC mortar air cured under room temperature with oven heated after demoulding of the specimens at $60^{o}$C for duration of 20 h (OM–OH–AC), respectively. The maximum levels obtained of compressive strengths at 7, 28, and 90 days are 57.5, 70.3, and 76.0 MPa, respectively. Comparison of OPC mortars heated in bath water or oven shows that water heated has the higher results than those of oven heated and it also is more practical and feasible. They also observed that the specimens have higher strengths in air under room temperature compared to water cured after heating in water at $60^{o}$C for duration of 20 h.

Prasad et al., (2006) stated that for full hydration of binder and strength development in the concrete, the continuous, longer and moist curing is required. Initial curing condition affects the sulphate resistance of concrete or mortar. This statement is also supported from previous statement by Mangat and Khatib (1995) as well as Osborne (1999). They reported

a beneficial effect of short initial air curing, as opposed to continuous moist curing, on long-term Sulphate resistance of plain and blended concrete. The possible reasons for such behavior could be initial dry curing reduces the calcium hydroxide concentration in surface zone and reduce the availability of calcium hydroxide for sulphate attack.

Furthermore Ghrici et al., (2006) also studied the effect of air curing condition on the development of compressive strength of mortar. This study was conducted to assess the effect of incorporating natural pozzolana with ordinary Portland cement on the properties of cement, mortar and concrete. The air temperature is almost similar to that of water curing.

However, the relative humidity is lower and this causes a higher rate of water evaporation from the mortar surface and a more rapid cessation of hydration especially on the skin of the specimens. The compressive strength at 28 days in laboratory air curing was about 72% of that of water curing for both OPC and NP specimens at 10−20% replacement level. For higher replacement level, the relative strength was lower (48−62%) showing the sensitivity of blended cement specimens to the lack of moist curing. Only a slight relative gain in strength after 7 days was observed for all specimens indicating a cessation of the hydration by lack of humidity. No strength loss was observed with natural pozzolana cement specimens after immersion in sulphate solutions for up to 180 days. This is due to the fact that drying at high temperature leads to higher water evaporation from the surface leading to micro-cracks and restricted hydration, therefore higher porosity and permeability and lower strength are expected.

Subsequently, the experimental results showed that the physical characteristics of the cement containing natural pozzolana are in conformity with the standards requirements

and that the strength of pozzolanic cement is lower than the plain Portland cement at early age, but can reach the same order of strength at longer term ages. It seems that the period of initial moist curing has a significant effect and a minimum period of initial moist curing of 7 days is necessary.

Nahata et al., (2014) evaluated the effectiveness of curing the cement mortars under room temperature. Air curing method has lowest compressive strength at 28 days for different w/c ratios compared to conventional water curing method. The air curing method should be avoided in construction due to the fact that the desired strength cannot be achieved using this method. Contrary, Ramli and Tabassi (2012) approved that the air curing method is effective and brings benefits to the strength improvement of mortars. In addition, Yang et al., (2011) examined that the mortar containing slag is not suitable to cure under room temperature, because the C-S-H gel product is much higher in water curing method than in air curing method. This trend was contributed to the strength development and permeability results of cement-slag mortars.

### 2.5.1.3 Other Curing Conditions

Other than the 3 conditions that were mentioned before, there are also another type of curing conditions. Alamri (1988) conducted research on the influence of curing with the properties of concretes and mortars. Three environments were chosen as follows, $20^{o}C$ with 70% relative humidity (RH), $35^{o}C$ with 70% RH and $45^{o}C$ with 30% RH. The results found that the durability properties of plain OPC samples were adversely affected by the two hot environments when compared to $20^{o}C+70\%$ RH for all curing durations.

On the other hand, while OPC/PFA and OPC/GGBFS samples cured for one day or more at $35^{o}C+70\%$ RH showed similar or worse durability results compared with those cured at $20^{o}C+70\%$ RH, better results were obtained at $45^{o}C+30\%$ RH than in either of the other two environments. As to the effects on strength, for any given curing period, environments hotter than $20^{o}C+70\%$ RH adversely affected the OPC and OPC/GGBFS samples but not those containing PFA. As conclusion, the hot curing conditions will influence the properties of fresh concrete in several ways including an increase in the rate of evaporation of water from the concrete and mortar mixes. Acceleration in the rate of setting and an increased water demand for constant workability are also affected.

Aminur et al. (2010) also investigated the effect of different curing conditions on the properties of concrete. Five different curing conditions, namely water curing (WC), self-curing(SC), air dry curing (ADC), one-day delay curing (1-DC) and three-days delay curing (3-DC) were employed. Two types of concrete namely, concrete C1 (brick chips as coarse aggregate) and C2 (pebbles gravel as coarse aggregate) were prepared. It was found that, the concrete C1 and the normal water curing appeared to be better than concrete C2 and other types of curing condition.

Aldea et al. (2000) compared autoclaving ($175^{o}C$) and steam ($80^{o}C$) curing conditions to normal curing ($20^{o}C$ and 100% relative humidity) in order to obtain the better performance of slag cement concrete. Under autoclaving conditions, concretes with 50% slag has no effect on strength, whereas 75% slag replacement reduces the compressive strength no matter what curing type is used. Results obtained with autoclave curing are comparable to those obtained with normal curing for no slag and 50% slag replacement. Steam curing

induces the greatest decrease in compressive strength for most of the materials tested. This is probably due to a less uniform distribution of the hydration products in the pastes because of the rapid initial hydration, which is reflected in changes in the large capillary pore distribution (Mindess & Young, 1981). Meanwhile, when 25% slag used in replacement of OPC produced an optimum strength for both normal and steam curing conditions. Normal curing provides higher compressive strength compared to fast curing up to 50% slag replacement. This can be attributed to the increased volume of large mesopores (Young, 1988).

The properties of concrete exposed to elevated temperature are of great importance in terms of structural stability and assessment of serviceability state of the structure. Concrete samples were made where ordinary Portland cement was replaced by 50%, 60% and 70% palm oil fuel ash. The samples were thermally treated to elevated temperatures of $200^{\circ}C$, $400^{\circ}C$, $600^{\circ}C$ and $800^{\circ}C$ in an electric furnace for a period of 1 h after attaining the peak temperature. Specimens exposed to elevated temperature were cured in air and were tested for visual observation, change in weight, ultrasonic pulse velocity and residual compressive strength. It has been observed that the higher the temperature, higher was the residual weight loss of concrete samples. Along with the loss of residual compressive strength, the ultrasonic pulse velocity of concrete was also reduced at elevated temperature. Data generated in this study was used to develop simple relationship for expressing residual compressive strength as a function of ultrasonic pulse velocity (Awal & Shehu, 2014).

Several researchers also conducted an experimental work on autoclave and steam curing conditions (Aldea et al., 2000; Yazici et al., 2008). For autoclave curing, the samples with the molds were put into the autoclave 6 h after casting, and the curing temperature was raised from room temperature (T= $20^{\circ}C$) to $175^{\circ}C$ and P = 0.5 MPa (75 psi) after 2 h. The

temperature was maintained constant at 1758$^{o}$C for 15 h, and then cooled to room temperature in 2 h. Steam-cured samples were cast in molds for 6 h, and then pre-steamed in a water bath at room temperature (T =20$^{o}$C) for another 6 h. Then, the temperature was raised from room temperature to 80$^{o}$C over 2 h, maintained constant at 80$^{o}$C for 15 h, and then cooled to room temperature in 2 h. For improved durability, room temperature curing is the best, but steam curing is preferable to autoclave curing, if rapid strength development is required.

The reason for the loss of strength can be due to internal or external factors. The internal factors are those linked to the chemical composition of the reacted products. The external factors are due to the variability of specimens, testing procedures, and other factors. One other factor that has an important effect is the temperature. The initial curing temperature has an important effect and can reduce or increase strength at long curing times, i.e. advanced age (Sajedi & Razak, 2011).

Finally, it can be concluded that the curing conditions will affect the compressive strength of mortar depending on the type of blended cements prepared and the environment point of view. Duration of curing influenced the compressive strength development.

## 2.5.2 Effect of Different Types of Fine Aggregates on Compressive Strength of Mortar

Aggregates have a significant influence on mechanical properties of mortars and concrete. The parameters, such as specific gravity, particle size distribution, shape and surface texture, influence actually the properties of mortars and concrete in the fresh state. Neville (1995) has explained that the mineralogical composition, toughness, elastic modulus and

degree of alteration of aggregates are generally found to affect the properties of mortars and concrete in the hardened state.

Wills (1967) investigated the effect of particle shape of both fine and coarse aggregates on water demand on concrete. He found that the shape of the fine aggregate has a more significant impact on water demand than the shape of the coarse aggregate. Hewlett (2003) found that the particle size distribution of the fine aggregate was found to have a greater influence in the properties of concrete than that of the coarse aggregate within the permitted standard limits.

Goncalves et al. (2007) investigated the performance of cement mortars using manufactured fine aggregates produced by cone crushing or impact crushing has been compared to that of mortars prepared from a natural sand control sample. The results indicate that the characteristics of the mortars such as compressive strength and absorptivity – which can be considered secondary or dependent properties are governed by the packing density of the mixture independently of grading and particle shape of the sand used.

Various scholars have conducted experimental studies on cement mortars and reported that the shaped particles and surface texture of fine aggregate is important. Sand has less amount of clay, but it contains a high fineness. Sand with high angularity possesses less workability because it produced a large surface area. The effects of particle shape and texture of fine aggregates are primarily important than the effects of particle of coarse aggregates in concrete production. By using angular shape of fine aggregates, the better interlocking of particles can be achieved. It will lead to the strength improvement of

concrete (Donza et al., 2002). The gap gradation between particles of fine aggregate influenced the performance of mortar mixture (Ara et al., 2010). Otherwise, the dosage of fine aggregate does not much affect the performance of mortar, as if they failed to attain the flowability or air content observed in mortar (Cabrera et al., 2011). Porosity of fine aggregate also effect on the strength improvement of mortar (Zhao et al., 2014). The use of high surface fine aggregates affected the long-term performance of mortars exposed to chemical solutions (Bederina et al., 2013; Vijayaraghavan & Wayal., 2013). Whilst, bond strength of high surface area of fine aggregate is more and hence leading to economy savings in construction (Sureshbabu & Thomas, 2013).

As a conclusion, the choice of the appropriate type of fine aggregate for a given application is of primary importance as far as properties of mortars and concrete are concerned.

### 2.5.3   Effect of Different Initial Curing Duration on Compressive Strength

The fact is that the hydration of cement can take place only in capillaries containing water. From this fact, the needs of curing arise in order to gain high quality of mortar. Cakir and Akoz (2008) affirmed that the placing of an appropriate mix must be followed by curing in a suitable environment during the early stages of hardening and a loss of water by evaporation must be prevented. Therefore, if the high quality of mortar related to the strength and durability is to be realized, it is extremely important that the mortar should be cured adequately.

Researchers have mentioned the importance of curing particularly if containing supplementary cementitious materials such as fly ash and GGBFS are used. Other parameters, which have to pay attention with regards to the early curing conditions is subjected to dry and hot environments immediately after casting (Ramezanianpour & Malhotra, 1995). The study of Ozer and Ozkul (2004) shows that initial limited water curing does not only improve compressive strength of concrete compared to air curing, but that as initial limited period gets longer the compressive strength gets higher. Moreover, research conducted by Sajedi and Razak (2011) shows that, the effect of the first week water curing of OPC 50 mm mortar cubes after casting is equal or even more than that of 12 weeks of water curing after the first week of casting. Furthermore, Abalaka and Okoli (2013) strengthened the findings from previous researchers that limited initial water curing is very important in improving mechanical properties of concrete production. Their findings divided by two stages. Stage 1 shows that water-cured specimens had higher compressive strength at 90 days compared to air-cured specimens. It is due to the growth of C-S-H gels promoted by continuous cement hydration in the water cured specimens resulted in the strength increases recorded. On stage 2 conducted at 28 days of curing, the results show that cubes exposed to longer initial curing duration tend to have higher compressive strength compared to cubes that were cured for only one day. Other than that, at 90 days of curing, cubes that were only cured for 4 days recorded the maximum compressive strength whereas the maximum compressive strength of cube specimens was recorded after only 4 days of initial water curing and test ages of 28 and 90 days, more solid hydration products were formed at longer initial wet curing durations as seen from the results of durability properties measured.

As conclusion from the experimental work conducted by Abalaka and Okoli (2013), it shows significant beneficial effects of early initial water curing for a few days over air curing. It also shows that the initial 4 days of curing was sufficient to develop compressive strength higher than the compressive strengths at 28 and 90 days of continuous water curing.

Satish et al. (2011) investigated the effect of elevated temperature curing on compressive strength of plain concrete and concrete with partial replacement of cement by industrial wastes. The method of initial curing used in this study is elevated temperature. Elevated temperature, in this study means that after 24 hour of casting all demoulded concrete specimens were exposed to hot water curing at $40^{o}$C, $50^{o}$C and $60^{o}$C for 1 day, 3 days, and 6 days. Then, they were transferred to curing tank with water at room temperature and left there until they reached their test age. The results show that under elevated temperature it is clear that the temperature have a positive influence upon the strength development, but not at the same rate in time period. The influence of temperature upon the rate of compressive strength decreases proportionally with time. Hence, the temperature activates hydration process as the same manner like chemical reaction. Under elevated temperature, the faster formed hydrate causes a great porosity and a loss of ultimate strength.

Previous investigations (Razak & Sajedi, 2011; Barnett et al., 2006; Muhmood et al, 2009) showed that hot water curing method improves strength at the early ages. However, at a later age, a loss of ultimate strength may occur in specimens. This is due to the important numbers of formed hydrates have no time to arrange suitably and this causes a loss of ultimate strength. This behaviour has been called the crossover effect. For ordinary Portland cement (OPC), it appears that the ultimate strength decreases with curing temperature linearly.

Adam and Horianto (2014) studied the optimum temperature and duration of curing to achieve higher strength on geopolymer mortar. The specimens were prepared by varying the initial curing temperature of 80, 100 and 120°C, for the duration of 4, 6 and 20 hours. The results show that the highest compressive strength was obtained at the temperature and duration of curing of 120°C and 20 hours.

Magzoub (2003) explained that the specimens after demoulding must be kept saturated for a better hydration and to minimize shrinkage cracking. More detailed, the surface is particularly susceptible to insufficient hydration because it dries first. If temperatures are favorable, hydration is relatively rapid during the first few days after concrete is placed. However, it is important for water to be retained in the concrete during this period, that is, for evaporation to be prevented or substantially reduced.

Finally, from the previous researches conducted by several scholars, it can be demonstrated that an elevation of the initial curing temperature reduces the long term compressive strength of the mortar. Reversely, an increase of the curing temperature seems to have no detrimental effect on the long term compressive strength of mortar. However, the successful initial curing method depends on the type of SCMs used in mortar.

## 2.5.4 Effect of Different Blended Cement Types Under Various Curing Temperature on Compressive Strength of Mortar

Supplementary cementitious materials (SCMs), both artificial and natural pozzolans, are commonly used as a partial replacement of Portland cement in concrete. Kosmatka and

Wilson (2011) stated that the practice of using SCMs is increasing, with the world average percent clinker in cement having decreased from 85% in 2003 to 77% in 2010, and it is projected to further decrease to 71% in the future.

The reductions of cement production surely bring good news for the sparkle future of building development and the environment all over the world. In the U.S., SCMs are usually added to concrete rather than blended with clinker, and currently more than 60% of ready-mixed concrete uses SCMs (CEMBUREAU, 2011). It shows that the utilization of waste material to be valuable due to the actual concern of green-house gas emissions. Many literatures also reported that concrete containing SCM often perform better in terms of workability, robustness, strength and durability (Khatri et al., 1995; Kwan and Ng, 2010; Lothenbach et al., 2011).

One thing that should be a concern when using SCMs as a partial replacement of Portland cement is the process of unification of particles or blending through hydration process. It should be noted that the different type of blended cements will produce different behavior of its hydration. Each type of SCM has different properties. Therefore, to understand more clearly the effect of SCM in blended cement as a binder, it should be brought closer to the mortar. As the concrete strengths depend on several factors and mainly mortar strength, so it is preferred working with mortar.

Researchers have conducted experimental works about the effect of SCM combined with Portland cement as a binder in concrete and mortar. Ezziane et al., (2007) investigated the effect of natural pozzolan on the compressive strength of mortar under various curing

temperatures. A first set of mortar specimens was made with 0%, 10%, 20%, 30% and 40% of natural pozzolan replacement and cured under constant curing temperature of 20, 40 and 60$^{o}$C with saturated humidity. The second set incorporating only 20% of natural pozzolan was exposed to elevated temperatures for 1, 3 and 7 days and then cured in saturated environment under a temperature of 20$^{o}$C. The result noticed that the pozzolan cement is characterized by a weak strength at early age followed by an increase exceeding especially that of the OPC after 28 days. The ultimate strength depends on the curing temperature and the curing period of time. They concluded that when natural pozzolan is used as partial substitute of OPC, the optimal replacement rate is about 15% for a normal curing temperature and up to 20% for curing under an elevated temperature.

Many scholars also explained the technical details for low and moderate level replacement of cement (Agarwal, 2006; Escalante-Garcia et al., 2009; Haider et al., 2012; Wonkeo et al., 2014). The percentage of low and moderate for cement replacement levels are 5% to 40% by mass, respectively (Escalante-Garcia et al., 2009; Wonkeo et al., 2014). In addition, Agarwal (2006) has reported that 10% by mass replacement of pozzolan mortar, the compressive strength obtained was 18 MPa in 7 days and 25 MPa in 28 days. Ezziane et al., (2007) investigated a set of mortar specimen which was made with 40% of natural pozzolan as cement replacement. The compressive strength result for 90 days reach up to 39 MPa under constant 40$^{o}$C temperature for 6 h hot water curing.

On the other hand, high volume replacement levels of cementitious material have been an interesting topic for research and also industry. Varga et al., (2012)evaluated properties of mortar containing high volume of type C fly ash under standard curing. Test results

indicated that the use of 40% by mass of type C fly ash in mortar increased at the early age day compressive, but reduced the modulus of elasticity. However, all these strength properties and abrasion resistance showed continuous and significant improvement at the ages of 190 and 365 days, which was most probably due to the pozzolanic reaction of FA at later ages. It was concluded that Class C fly ash can be suitably used up to 50% level of cement replacement in mortar for use in precast elements and reinforced concrete construction.

Herera et al., (2011) studied concrete were produced with mass substitution of cement by fly ash up to 75%. They concluded that using this level of fly ash was not effective to gain the strength of concrete. Then, Sajedi & Razak (2011) made an experiment using high volume replacement levels up to 60% of slag, with constant w/c ratio of 0.33 and under water and air curing conditions. They used chemical activation and found that the maximum strength could be achieved was about 63 MPa at 56 age days for 50% replacement level. Based on many investigations (Stephen, 2004; Kim et al., 2002; Varga et al., 2012; Wongkeo et al. 2012) on the effect of using cementitious materials in mortar, it was found that the effect of curing method and the volume level of cement replacement significantly influence the strength and durability. As information that generally, slag replacement is often 60 to 75% by cement weight.

Hasanah et al., (2015) investigated the effect of high volume nano palm oil fuel ash (POFA) in the mortar. They concluded that to get a better performance in terms of strength development, the ash used has gone through heat treatment and was ground up to less than 1 μm. The incorporation of more than 80% nano size POFA as cement replacement has produced a mortar having a compressive strength more than OPC mortar at a later age. The

overall results have revealed that the inclusion of high volume nano POFA can produce a mortar mix with high strength, good quality and most importantly that ismore sustainable. It shows that the fineness particle of POFA affected the strength.

Li and Kwan (2014) studied the effect of ternary blended cement containing CSF (condensed silica fume) and FAM (fly ash microsphere) to improve the performance of mortar. CSF has a large surface area filled into the voids between cement grains which would release the water entrapped. By adding FAM that is finer than cement but not as fine as CSF, the water entrapped in the voids couldbe released without excessively increasing the surface area. This may produce a better flowability than adding CSF alone. The result was found that the blending of OPC with fine SCM can effectively improve the packing density of solid particles in mortar. They considering both the strength and flowability, ternary blending with 20% FAM and 10% CSF seem to be the optimum. Recently, in 2011, Aitcin (2011) pointed out that with SCMs finer than cement (hereafter referred to as superfine SCMs) added to fill into the voids of the particle system, the concrete will bleed less, shrink less and attain higher strength.

Siddique (2003) conclude that fly ash could reduce the compressive strength, flexural strength and modulus of elasticity of concrete at 28 days, but there was a continuous and significant improvement of strength properties beyond 28 days.

Barnett et al., (2005) investigated the strength development of mortars containing ground granulated blast furnace slag (GGBFS) and OPC. From the experimental works, it was found that all mortars gain strength more rapidly at higher temperatures. At the early age,

strength is much more sensitive to temperature for higher levels of GGBFS due to the crystallinity of particles bring the acceleration and effectiveness in obtaining the strength.

Wongkwo et al. (2011) studies the physical properties, compressive strength and drying shrinkage of multi-blended cement under different curing methods. Fly ash, ground bottom ash and undensified silica fume were used to replace part of cement up to 50% by weight. Specimens were cured in air at ambient temperature, water at $25^{o}$C, $40^{o}$C and $60^{o}$C, sealed with plastic sheeting for 28 days. The results show that absorption and volume of permeable pore space (voids) of blended cement mortars at 28 day under all curing methods tend to increase with increasing silica fume replacement. The compressive strength of blended cement with fly ash and bottom ash was lower than that of Portland cement control at all curing condition while blended cement with silica fume shows higher compressive strength. In addition, the compressive strength of specimens cured with water increased with increasing curing temperature. The drying shrinkage of all blended cement mortar cured in air was lower than that of Portland cement control while shrinkage of blended cement mortar containing silica fume, cured with plastic sealed and water at $25^{o}$C was higher than Portland cement control due to pore refinement and high autogenous shrinkage. However, the drying shrinkage of blended cement mortar containing SF cured with water at $60^{o}$C was lower than that of Portland cement control due to lower autogenous shrinkage and the reduced micro-porosity of C–S–H.

Turk (2012) studied the effects of using supplementary cementitious materials in binary and ternary blends on the fresh and hardened properties of self-compacting mortars. Moreover, compressive and flexural tensile strengths of the hardened mortars were measured at 28 and

91 days whilst dry unit weight and the dynamic modulus of elasticity tests were performed at 28 days. Test results have revealed that at high shear rates, the fluidity of mortars increased regardless of the dosage and type of mineral admixtures. Also, ternary mixtures generally predominate the respective binary mixtures in terms of viscosity. The compressive strength of the control mortar performed better than binary blends of FA and all ternary mortars whilst the flexural tensile strength of the control mortar was in general higher than all binary and ternary mortars for all curing ages. The ternary use of PC, SF and FA improved the deficiencies of SCMs with binary blends of FA. Moreover, increases in SF and FA contents caused a decrease in 28-day dynamic modulus of elasticity of the mortars with binary and ternary blends. Furthermore, Turk (2012) also highlighted two points of his studies, they are 1) to provide greater sustainability in construction, use of mineral admixtures is inevitable and 2) Use of ternary blends improved the deficiencies of mortar with binary blends of fly ash.

### 2.5.5   Effect of other parameters on mechanical properties of mortar

Other parameters that influenced the mechanical properties of mortar containing cementitious material (SCM) include loss on ignition (LOI), fineness of SCM, specific gravity, type of Portland cement, water used for curing, mixing method, placing of fresh mortar, voids, percentage of additives used, acid attack, water cement ratio (Dean, 1974; Maher, 1998; Alonzo et al., 2000; Mukherjee & Pathak, 2003; Cyr et al., 2006).

Loss-on-ignition is a common and widely used method to estimate sediment properties (i.e., water content, organic matter, inorganic carbon and minerogenic residue), because it is the quickest and cheapest among all the methods employed for determining some of those

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parameters (Dean, 1974; Maher, 1998). On the other hand, total carbon determined automatically is the fundamental parameter for describing the abundance of organic and inorganic carbon in sediments. Carbonate carbon determination by means of loss-on-ignition is strongly influenced by the distribution of the fine fraction. A rise in clay content is closely followed by a rise in extra weight-loss. Care must be taken in the interpretation of carbonate content via loss-on-ignition as a paleo-environmental indicator.

Alonzo et al., (2000) explained that mainly smoothed bars were used, but also some ribbed bars were tested. Chloride thresholds in the range of 1.24–3.08% and 0.39–1.16%, by weight of cement, for total and free chlorides, respectively, and in the range of 1.17–3.98 for $Cl^-/OH^-$ ratio were found for chlorides admixed in the mixing water. Active corrosion is considered when, in a small exposed area, the corrosion rate of the rebar is higher than 0.1 $\mu A/cm^2$. The threshold in the case of $Cl^-/OH^-$ results a bit higher than that found in a previous work for synthetic pore solution, although the two types of data can be fitted together finding a good correlation.

Lawrence et al., (2005) and Cyr et al., (2006) stated that for short hydration times (1 to 2 days), the nature of mineral admixture is not a significant parameter, as mortars containing the same amount of different kinds of admixtures having equivalent fineness present similar strengths. For long hydration times (up to 6 months), the excess strength due to fly ash pozzolanic activity is quantified by the difference between the strengths of mortars containing the same proportions of inert and pozzolanic admixtures with the same fineness.

Furthermore, Lawrence et al., (2005) explained that in the case of inert mineral admixtures and water to cement ratio, the increase in strength with the fineness of mineral admixtures cannot be explained by the filler effect, but can be attributed to the physical effect of

heterogeneous nucleation. These results will be used for the elaboration of an empirical model leading to the quantification of both physical and chemical effects. This model presents strong similarities with the previous model based on calorimetric results.

Mukherjee and Pathak, (2003) stated that the rate of hydration depends on the fineness of cement particles, and for a rapid development of strength a high fineness is necessary. Hydration products are responsible for attained strength, while pores have a negative effect on strength. The strength of cement and concrete materials is perhaps the most important overall measure of quality, although other properties may also be critical.

Varga et al., (2012) evaluated properties of mortar containing high volume of type C fly ash under standard curing. Test results indicated that the use of 40% (by mass) type C fly ash in mortar increased at the early age day compressive, but reduced the modulus of elasticity. However, all these strength properties and abrasion resistance showed continuous and significant improvement at the ages of 190 and 365 days, which was most probably due to the pozzolanic reaction of FA at later ages. It was concluded that class C fly ash can be suitably used up to 50% level of cement replacement in mortar for use in precast elements and reinforced concrete construction. The concrete were produced with mass substitution of cement by fly ash up to 75%. They concluded that using this level of fly ash was not effective to gain the strength of concrete. Then, it shows an experiment using high volume replacement levels up to 60% of slag, with constant w/c ratio of 0.33 and under water and air curing conditions. They used chemical activation and found that the maximum strength could be achieved about 63 MPa at 56 age days for 50% replacement level. Based on many investigations on the effect of using cementitious materials in mortar, it was found that the effect of curing method and the volume level of cement replacement significantly influence the strength and durability.

It can be concluded that the ability of mortar containing cementitious materials in order to obtain the required strength depends on the curing method, chemical and physical properties of SCMs, volume level of replacement, and duration of curing.

# CHAPTER 3

## EXPERIMENTAL PROCEDURES

### 3.1 INTRODUCTION

Mortar represents a small proportion of the total volume area in the concrete construction, however, it affects on the performance of a concrete significantly. Mortar serves many important functions: it bonds units together into an integral structural assembly, seals joints against penetration by air and moisture, accommodates small movements within a wall and a concrete, accommodates slight differences between unit sizes, and bonds to joint reinforcement, ties and anchors so that all elements perform as an assembly (Adesanya, 1996; Bagel, 1998; Boubitsas, 2001; Chindaprasirt & Rukzon, 2008; Mehta & Monteiro, 2006). The proper selection of raw materials, mix design and curing methods will produce a high quality mortar: not only in term of the strength of mortar, but also the effectiveness of mortar applications.

This chapter describes the experimental procedures which include the explanations characteristics of the materials, the process and the type of testing methods used for this research. It also develops the criteria for assessment of workability, which will be used as a reference throughout the following two chapters. In order to establish these criteria with a sufficient reliability, it was decided to do experiments with making groups of mortar containing high volume cementitious materials. Furthermore, the microstructure of hardened mortar was examined using SEM (Scanning Electron Microscopy) test. The research study also focuses on classifying supplementary cementitious material (SCM), raw materials and the process involved in manufacturing cement based materials. The important

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part of this research is to test the engineering properties of mortar containing high volume cementitious materials (HVCM).

## 3.2 MATERIALS

### 3.2.1 CEMENT

The cement used in all mixes was ordinary Portland cement (OPC). The specific gravity of cement was about 3.14. Based on particle size analysis (PSA) tests, the specific surface area (SSA) by BET method for OPC was determined to be 2667.24 $m^2$/kg. The chemical composition of OPC was determined by ''X-ray fluorescence spectrometry (XRF)'' testing method. The compositions of OPC are given in Table 3.1.

Table 3.1 Chemical composition of OPC (% by mass)

| Oxides | Chemical composition (% by mass) |
|--------|----------------------------------|
| $SiO_2$ | 20.14 |
| CaO | 60.82 |
| $Al_2O_3$ | 3.89 |
| MgO | 3.10 |
| $Fe_2O_3$ | 3.35 |
| $P_2O_5$ | 0.064 |
| MnO | 0.14 |
| $K_2O$ | 0.24 |
| $TiO_2$ | 0.16 |
| $SO_3$ | 2.25 |
| SrO | 0.02 |
| LOI* | 2.33 |

*LOI = Loss on Ignition

### 3.2.2. Supplementary Cementitious Materials (SCMs)

Sometimes, supplementary cementitious materials (SCMs) often called as mineral admixtures and should satisfy the requirements of established standards for use in concrete or mortar. The utilization of any SCMs will turn on its output, such as hydraulic factors, permeability, strength, unit weight, durability and volumetric constancy in a long time. Several SCMs used in this experiment are as follows:

### 3.2.2.1 Ground Granulated Blast-Furnace Slag (GGBFS)

The specific gravity of GGBFS is approximately 2.87, with its bulk density varying in the range of 1180–1250 kg/m$^3$. The color of GGBFS is whitish (off-white). GGBFS is derived from Malaysia. Based on PSA tests, the SSA for GGBFS has been determined at 3197.2 m$^2$/kg. It can be seen that SSA GGBFS was 1.90 times of OPC, which means that particles of GGBFS are 90% finer than those of OPC. The chemical compositions of GGBFS are given in Table 3.2. As with all cementing materials, the reactivity of the GGBFS is determined by its SSA. In general, increased fineness results in better strength development, however, in practice; fineness is limited by economics, performance considerations and factors such as setting time and shrinkage (Agarwal, 2006).

Table 3.2 Chemical composition of GGBFS (% by mass)

| Oxides | Chemical composition (% by mass) |
|---|---|
| $SiO_2$ | 36.01 |
| CaO | 40.54 |
| $Al_2O_3$ | 13.17 |
| MgO | 5.42 |
| $Fe_2O_3$ | 0.42 |
| $P_2O_5$ | 0.011 |
| MnO | 0.18 |
| $K_2O$ | 0.34 |
| $TiO_2$ | 0.57 |
| $SO_3$ | 1.77 |
| SrO | 0.05 |
| LOI* | 0.59 |

*LOI = Loss on Ignition

### 3.2.2.2 Fly Ash 1

Fly ash is the most common source material for geopolymer because it is available in abundance throughout the world. It also contains amorphous alumina silica. The specific gravity of the fly ash used in the study is approximately 2.28, with its bulk density of 994 kg/m$^3$. The color of fly ash was whitish grey. Based on PSA tests, the SSA for fly ash has been determined at 2858.6 m$^2$/kg by BET method. The chemical properties of fly ash 1 are shown in Table 3.3.

Table 3.3 Chemical composition of FA 1 (% by mass)

| Oxides | Chemical composition (% by mass) |
|---|---|
| $SiO_2$ | 39.86 |
| CaO | 12.72 |
| $Al_2O_3$ | 17.10 |
| MgO | 6.79 |
| $Fe_2O_3$ | 14.98 |
| $P_2O_5$ | 0.20 |
| MnO | 0.18 |
| $K_2O$ | 1.03 |
| $TiO_2$ | 0.89 |
| $SO_3$ | 0.58 |
| SrO | 0.06 |
| LOI* | 0.70 |

*LOI = Loss on Ignition

### 3.2.2.3 Rice Husk Ash (RHA)

Rice husk was obtained from Muhairi Resources Sdn. Bhd. Enterprises, Selangor, Malaysia. The raw rice husk was burnt in the manual incinerator. The combustion process was performed using a simple furnace designed and built at the University. The temperature of incineration is up to $700^{o}C$ and the burning duration was for 24 hour. It should be emphasized that the silica is in amorphous form and silica-crystals grew with time of incineration. The combustion environment affects the SSA of RHA. Hence, the time, temperature and environment must be considered in the processing of rice husks to produce ash with maximum reactivity. After burning, RHA was grind for 16,000 cycling. The specific gravity of RHA was approximately 2.11. Based on particle size analysis (PSA) tests, the specific surface area (SSA) by BET method for RHA was determined to be 7667.8 $m^2$/kg. The color of rice husk ash was grey. The chemical composition of RHA is shown in Table 3.4.

Table 3.4 Chemical composition of RHA (% by mass)

| Oxides | Chemical composition (% by mass) |
|---|---|
| $SiO_2$ | 93.25 |
| CaO | 0.41 |
| $Al_2O_3$ | 0.62 |
| MgO | 0.42 |
| $Fe_2O_3$ | 0.91 |
| $P_2O_5$ | 0.86 |
| MnO | 0.09 |
| $K_2O$ | 2.29 |
| $TiO_2$ | 0.12 |
| $SO_3$ | 0.10 |
| SrO | 0.02 |
| LOI* | 3.42 |

*LOI = Loss on Ignition

### 3.2.2.4 Fly Ash II

Fly Ash II produced in Selangor, Malaysia, was used. It is mainly contains amorphous alumina silica, iron, and calcium. The specific gravity of the fly ash used in the study is approximately 2.8. Based on PSA tests, the SSA for fly ash II has been determined at 2576.4 m$^2$/kg by BET method. The color of fly ash was grey. The chemical characteristics of fly ash 2 are given in Table 3.5.

Table 3.5 Chemical composition of FA 2 (% by mass)

| Oxides | Chemical composition (% by mass) |
|---|---|
| $SiO_2$ | 36.43 |
| CaO | 12.71 |
| $Al_2O_3$ | 17.10 |
| MgO | 6.79 |
| $Fe_2O_3$ | 18.66 |
| $P_2O_5$ | 0.271 |

| | |
|---|---|
| MnO | 0.179 |
| $K_2O$ | 1.025 |
| $TiO_2$ | 0.891 |
| $SO_3$ | 0.579 |
| SrO | 0.063 |
| LOI* | 4.70 |

*LOI = Loss on Ignition

### 3.2.2.5 Palm Oil Fuel Ash (POFA)

Palm oil fuel ash is the product of burning palm oil husk and palm kernel shell in the palm oil mill. POFA obtained from Oil Palm Company, in Malaysia was used in the investigation. The specific gravity of Palm oil fuel ash was 1.65. Based on PSA tests, the SSA for POFA has been determined at 2960.3 $m^2$/kg by BET method. The chemical composition of POFA was tested at Department of Mining & Geology, University of Malaya, and the results are given in Table 3.6.

Table 3.6 Chemical composition of POFA (% by mass)

| Oxides | Chemical composition (% by mass) |
|---|---|
| $SiO_2$ | 60.17 |
| CaO | 5.23 |
| $Al_2O_3$ | 3.25 |
| MgO | 4.60 |
| $Fe_2O_3$ | 5.22 |
| $P_2O_5$ | 3.35 |
| MnO | 0.12 |
| $K_2O$ | 7.94 |
| $TiO_2$ | 0.18 |
| $SO_3$ | 0.11 |
| SrO | 0.01 |
| LOI* | 3.46 |

*LOI = Loss on Ignition

### 3.2.3 FINE AGGREGATE

The fine aggregate used in the mixes was mining sands with specific gravity and fineness modulus of 2.65 and 2.72, respectively. The maximum grain size of sand was 4.75 mm.

### 3.2.4 SUPERPLASTICIZER

In order to have appropriate consistency with low water to binder (W/B) ratio, superplasticizer (SP) was required. The specific gravity of SP used was approximately 1.195. It was dark brown in color, with a pH in the range of 6.0–9.0. The consumed content of SP in the mortar depends on the replacement level of cementitious material. For a flow of 140±10 mm, the SP used was 0.5-1% of total binder.

### 3.2.5 WATER

The water used in all mixes was water in pipeline of the lab. It was assumed that the specific gravity of the used water was about 1.

### 3.3. METHODS

Experimental procedures applied for mortar are shown in Figures 3.1. First of all, the preparation of materials such as cement, water, fine aggregate and cementitious materials (GGBFS, RHA, FA1, FAII, and POFA). Scan electron microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), X-Ray Fluorescence (XRF) and X-Ray Diffractometry (XRD) are the methods applied for identifying and defining the properties of cementitious materials in powder form. Then, start to mixing materials and put them into the mould (Cube and Prism).

```
┌─────────────────────────────────────┐                    ┌─────────────────────────────┐
│ Preparation of cementitious materials│───────────────────▶│     FINE AGGREGATE           │
│ (GGBFS, RHA, FA1, FAII and POFA):    │                    └─────────────────────────────┘
│                                       │                               ▲
│   1.  Burning process                 │                    ┌─────────────────────────────┐
│   2.  SCM, FTIR, XRD and XRF test     │                    │         WATER                │
│                                       │                    └─────────────────────────────┘
│ Cement + SCM (the mixes vary with     │                               ▲
│ different level of OPC-SCM combinations)│                  ┌─────────────────────────────┐
│                                       │                    │    SUPERPLASTICIZER          │
│ SCM is used as partial replacement of OPC.│                └─────────────────────────────┘
└─────────────────────────────────────┘
```

**MIXING**

(Mix OPC and SCM (based on percentage level of combination explain in Table 3.8), add Fine aggregate and water then stirring all combinations while add superplasticizer step by step) then put in the vibration machine

MOULDING and CURING

(After mixing materials and reach the desired flow 140±10 cm, the mixing result then moulded into prism and cube, after few days (vary with age) demoulded)

(specimens cured with the different temperature of curing conditions)

TESTING

(The specimens were test using compressive strength test, flexural strength test, porosity and water absorption test)
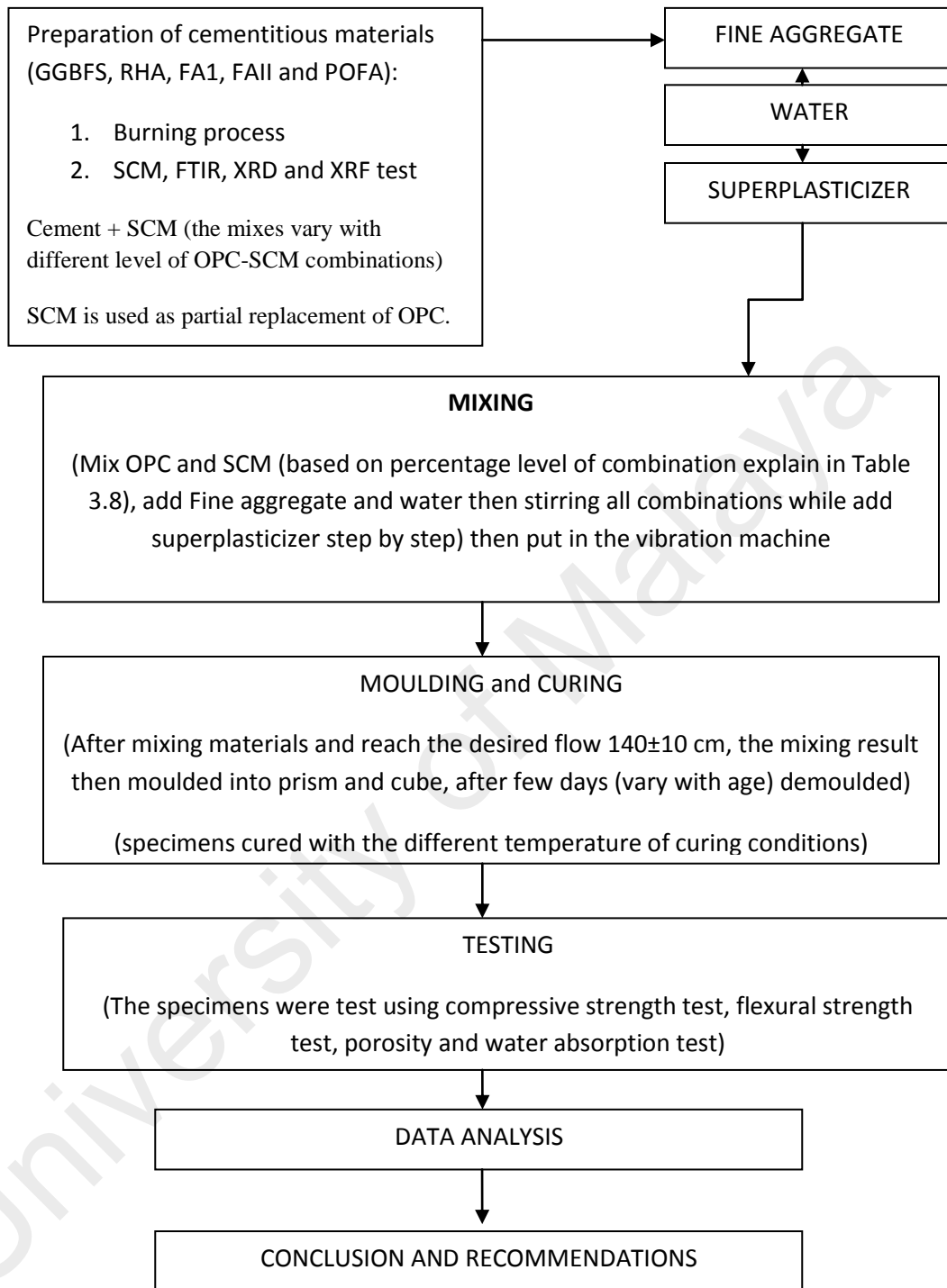
DATA ANALYSIS

CONCLUSION AND RECOMMENDATIONS

Figure 3.1 Flow chart for mortar containing high volume cementitious materials

### 3.3.1 Scan Electron Microscopy (SEM)

The scanning electron microscopy (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that are derived from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample (Shivakumar et al., 2009). The SEM is also capable of performing analyses of selected point locations on the sample.
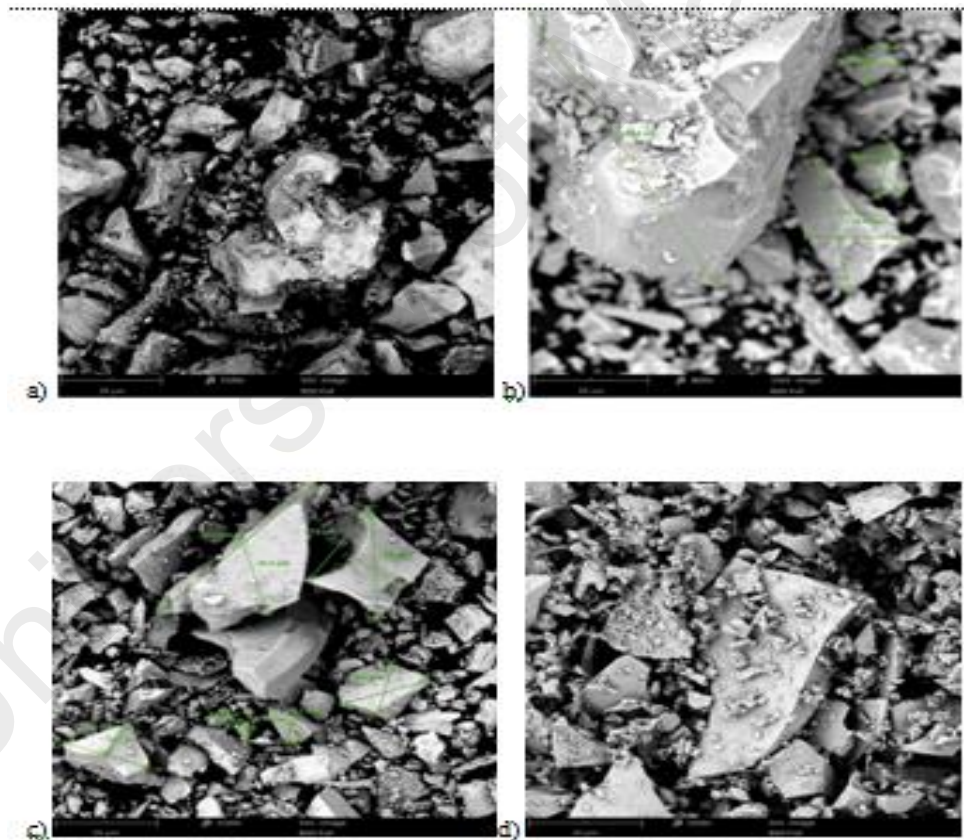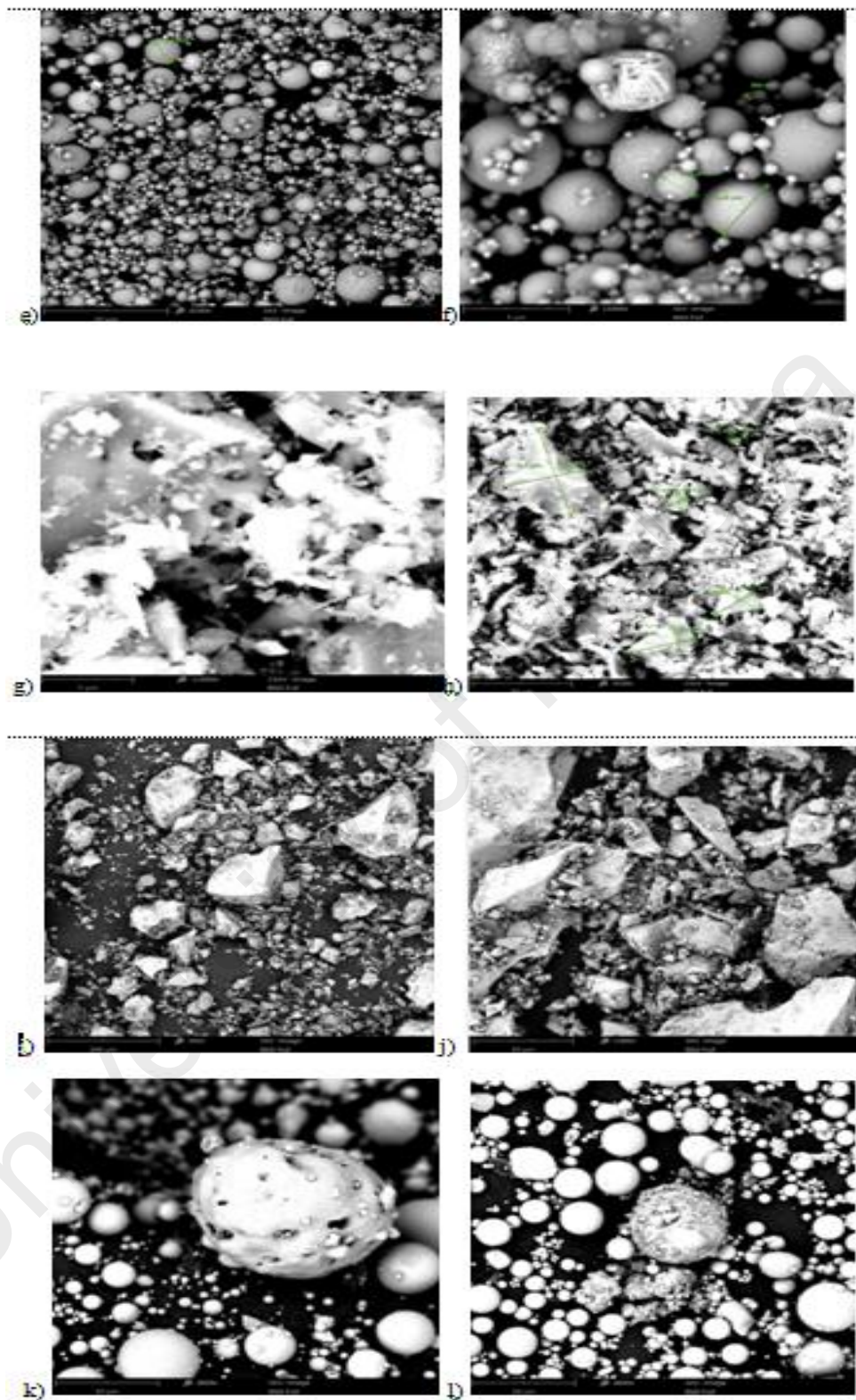
Figure 3.2 SEM result for a,b) OPC; c.d) GGBS; e,f) FA1; g,h) RHA; i,j) POFA; k,l) FA2

SEM micrographs of OPC and SCMs samples are shown in Figure 3.2. The samples used are in powder form. They are OPC, GGBFS, FA, POFA, FA II and RHA. It can be seen that OPC (Figure 3.2a) and GGBFS (Figure 3.2c) have a similar shape resembling an irregular prism. Furthermore, Figure 3.2e shows that all FA grains are in the spherules shape. Due to the spherules shapes of fly ash, the use of this SCM will increase the workability of mortar/concrete. While SEM of RHA (Figure 3.2g), display prism elements with many porous on it. Due to these porosities in RHA and consequently higher specific surface area, it can be used as SCM in low or moderate volume. The use of high volume RHA causes mixture to be dried. However, when it is used by other type of SCMs, the workability of mixture could be good or satisfactory. Therefore, RHA together with FA were used in this study.

### 3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a technique used to obtain an infrared spectrum of absorption, emission, photo-conductivity or Raman scattering of a solid, liquid or gas. FTIR can identify unknown materials and determine the quality or consistency of a sample. It can also determine the amount of components in a mixture. The Infrared spectra are recorded using Perkin Elmer model RX-1 FTIR spectrometer for the powdered samples which are made to a pellet by mixing with KBr. FTIR spectra of the hydrated OPC, GGBFS, two type of FAs and RHA are shown in Figure 3.3.

a)



b)

c)

d)

96

e)



f)
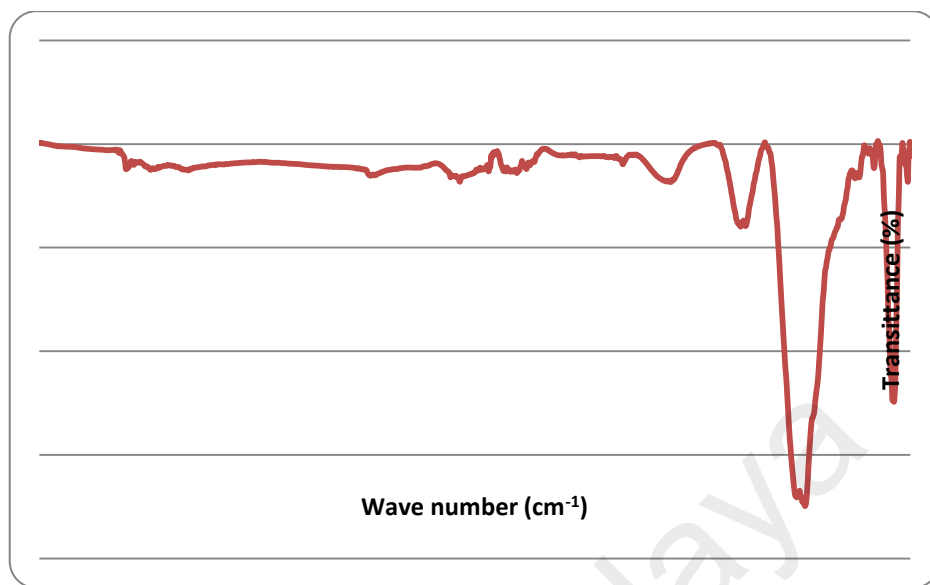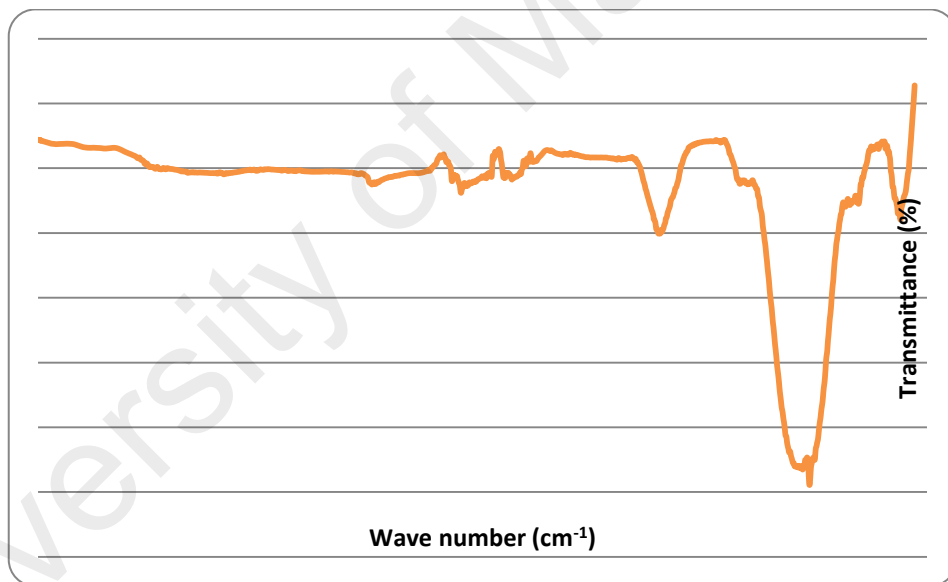
Figure 3.3 FTIR results of a) OPC, b) GGBFS, c) Fly Ash1, d) Fly AshII, e) RHA and f) POFA

The way to read the FTIR spectra:

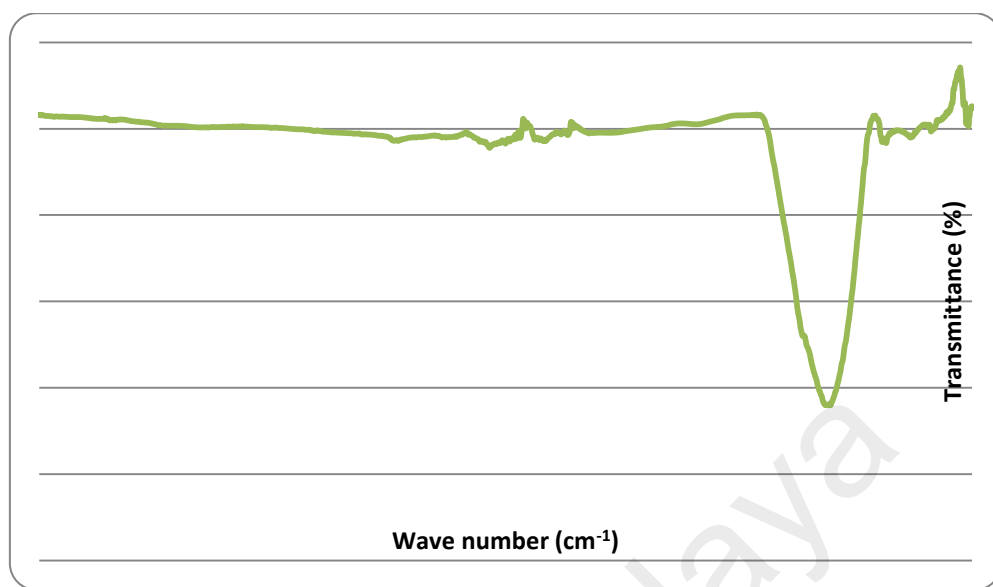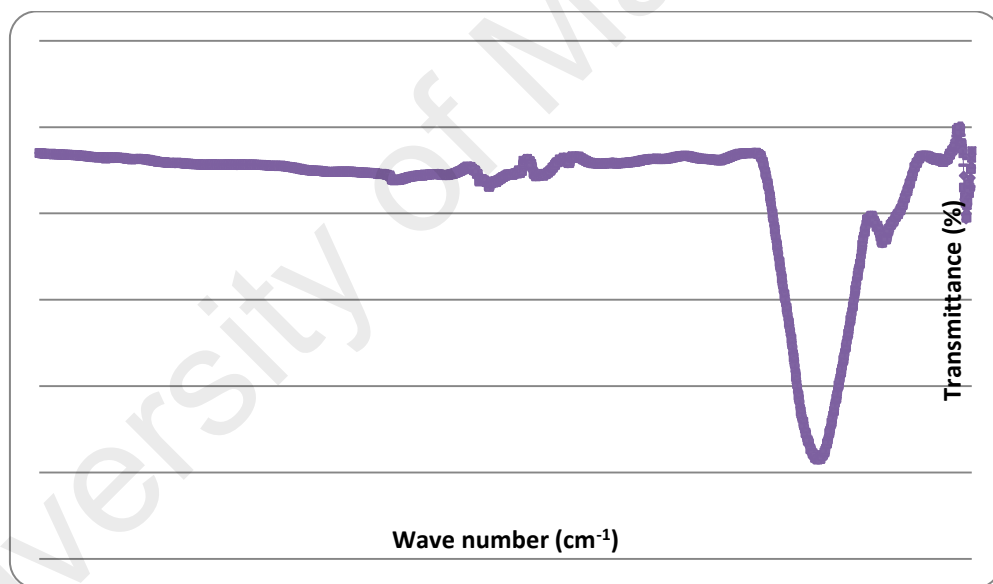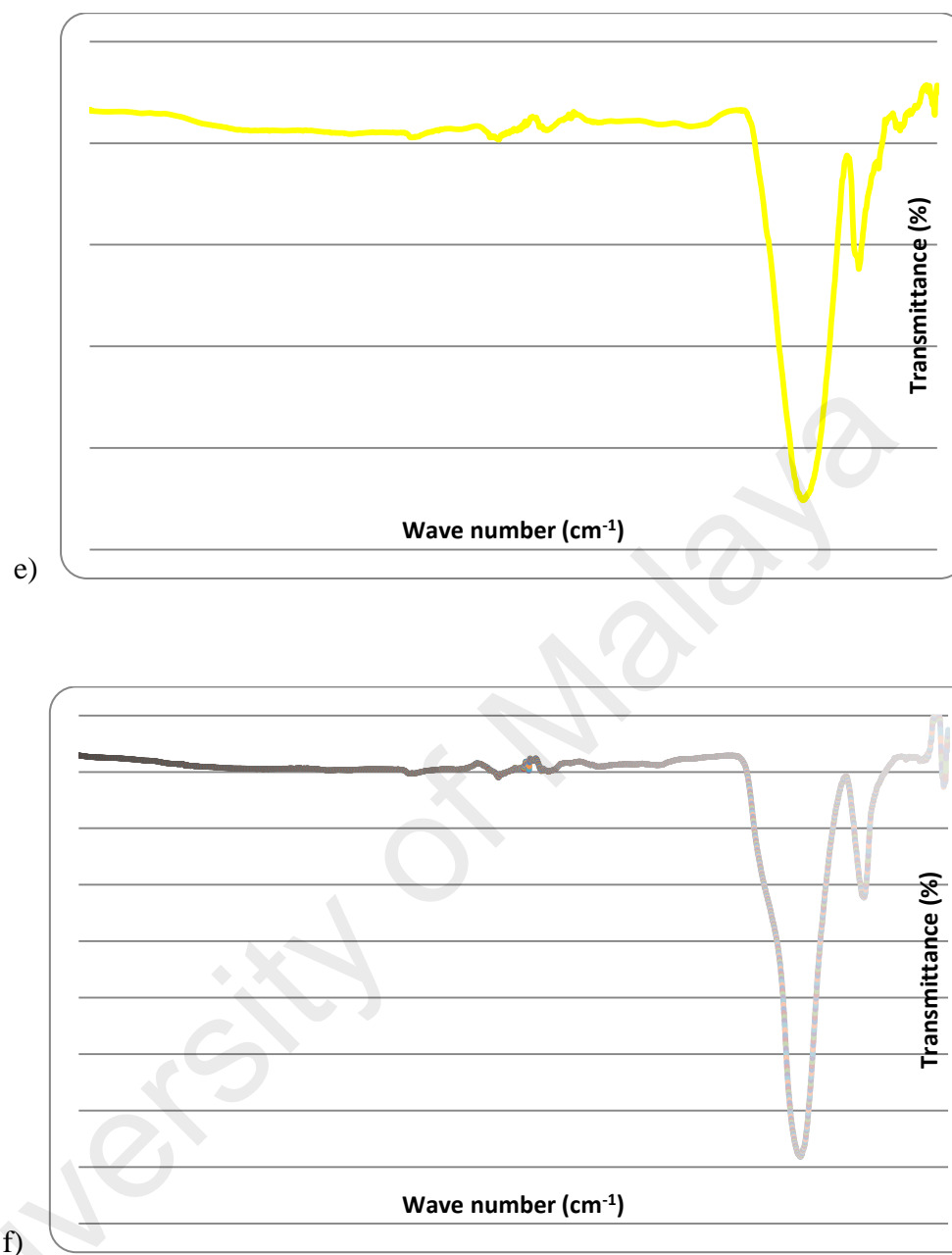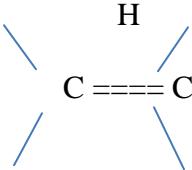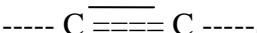1) Determine the X-axis and Y-axis of the spectrum. X axis of the IR spectrum labeled as "wave numbers" and the amount ranges from 400 to 4,000 in the far right on the far left. X axis provides a number of absorption. The Y-axis is labeled as

"Transmittance Percent" and the amount ranges from 0 at the bottom and 100 above.

2) Determine the characteristic of peaks in the IR spectrum. All infrared spectrums contain many peaks. Furthermore, looking at the data area of the functional groups required to read the spectrum.

3) Specify the region of the spectrum where there are characteristic peaks. IR spectrum can be separated into four regions. The first area range from 4,000 to 2,500. The second area range from 2,500 to 2,000. The third area range from 2,000 to 1,500. The fourth area ranges from 1,500 to 400.

4) Determine the functional groups absorbed in the first region. If the spectrum has a characteristic peak in the range of 4,000 to 2,500, according to the absorption peak caused by NH, CH and OH single bonds.

5) Determine the functional groups absorbed in the second area. If the spectrum has a characteristic peak in the range of 2,500 to 2,000, according to the absorption peak caused by a triple bond.

6) Determine the functional groups absorbed in the third region. If the spectrum has a characteristic peak in the range of 2,000 to 1,500, according to the peak of the absorption caused by bond like $C = O$, $C = N$ and $C = C$.

7) Compare peak in the fourth region to peak in the fourth region of another IR spectrum. The fourth is known as the fingerprint region of the IR spectrum and contains a large number of absorption peaks that account for a wide range of single bonds. If all the peaks in the IR spectrum, including those in the fourth, are identical to the other spectral peaks, then you can be sure that the two compounds are identical. The type of bond agent and compounds are shown in Table 3.7.

Table 3.7 Principle of Instrumental Spectra Analysis (Skoog et al., 1998)

| Bond | Types of compound | Frequencies area | Intensity |
|---|---|---|---|
| **C – H** | Alkana | 2850 – 2970 | Strong |
| | | 1340 - 1470 | Strong |
| **C – H** | Alkene H \ / C ==== C / \ | 3010 – 3095 | Moderate |
| | | 675 – 995 | Strong |
| **C – H** | Alkuna ----- C ==== C ----- | 3300 | Strong |
| **C – H** | Aromatic Ring | 3010 – 3100 | Moderate |
| | | 690 – 900 | strong |
| **O – H** | Phenol, Alcohol monomer | 3590 – 3650 | Fluctuate |
| | Alcohol hydrogen bond, Phenol | 3200 – 3600 | Fluctuate, sometimes widen |
| | Carboxylic acid monomer, | 3500 – 3650 | Moderate |
| | Hydrogen bonding carboxylic acid | 2500 – 2700 | Widen |
| **N – H** | Amine, Amide | 3300 – 3500 | Moderate |
| **C ==== C** | Alkene | 1610 – 1680 | Fluctuating |
| **C ==== C** | Aromatic Ring | 1500 – 1600 | Fluctuating |
| **C ==== C** | Alkune | 2100 - 2260 | Fluctuating |

| C - N | Amine, Amide | 1180 - 1360 | Strong |
|-------|--------------|-------------|--------|
| C $\equiv$ N | Nitrile | 2210 - 2280 | Strong |
| C – O | Alcohol, Ether, Carboxylic Acid, Ester | 1050 - 1300 | Strong |
| C $\equiv$ O | Aldehyde, Ketone, Carboxylic Acid, Ester | 1690 – 1760 | Strong |
| NO$_2$ | Nitro Compounds | 1500 – 1570 | Strong |

FT-IR analyzes for RHA illustrated the bands observe at about 3440 cm$^{-1}$. It shows the chemically or physically absorbed water. Peaks in the range of 750 to 900 cm$^{-1}$ are the characteristic of O-Si-O bond as described by Colthup spectra structure correlation charts for infrared frequencies (Palva et al., 2009). These peaks confirm the presence of silicate in the samples. Bands observed in the range of 900-1100 cm$^{-1}$can are attributed due to Si-O-Ca bonds (Meiszterics & Sinko, 2008).The peaks in the range of 1600-2500 cm$^{-1}$show the presence of unreacted calcium oxide in the samples. This is a finger print evidence for the higher degree of silicate polymerization of the precipitated CSH. It indicates the completion of hydration in this stage and well coincide with the compressive strength results (Palva et al., 2009). Therefore, it can be concluded from this figure that the pozzolanic reaction is higher in rice husk ash cement which accelerates the rate of reaction and enhances the strength.

In Figure 3.3 also described spectrometry of OPC. High intensity peaks can be seen in the range of 750 to 900 cm$^{-1}$ which are the characteristic of O-Si-O bond. These peaks confirm the presence of silicate in the samples. It is indicative of early faster dissolution of gypsum

and other alkali sulphates and ettringite formation. Water stretching band at 3640 cm-1 has grown in intensity with a shift ($3688\text{cm}^{-1}$). The shift of water stretching band may be due to conversion of ettringite to monosulphate(Sivakumar et al., 2009; Chindaprasirt&Rukzon, 2008; Pandey & Sharma, 2000). Low intensity peaks of GGBFS can be seen in the same range. The FTIR of GGBFS showed little or no shift in the characteristic peaks clearly depicting that the interactions between the components are physical in nature and prevented the leakage of GGBFS from the building materials during phase transition of the mortars.

In Figure 3.3 for fly ash, no peak has been observed in the same range indicating absence of calcium oxide. Disappearance of peaks represents the disappearance of calcium oxide or coating of silica on calcium silicates. It is noted that the relative intensities of the bands at around 1000, 970 and $800\,\text{cm}^{-1}$ are much higher in fly ash with higher reactivity. FTIR spectroscopy in combination with particle size analysis provides a fast approach to predict the reactivity of fly ash, from the perspective of alumino-silicate glass chemistry.

In all four spectra, the peaks of calcium silicate are different indicating presence of various types of calcium silicates but exact type could not identified only by FTIR.

### 3.3.3 X-Ray Diffractometry (XRD)

X-rays are electromagnetic waves, similar to light, but with a much shorter wave length ($\lambda$=0.2-200 A) (Pandey & Sharma, 2000). Diffraction is a physical phenomenon that consists in electromagnetic waves avoiding of obstacles when obstacles have a size that compares to the wavelength (Palva et al., 2009). So, X-ray diffraction (XRD) is a rapid

analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The samples analyzed are OPC, GGBFS, Fly Ash, RHA, Fly Ash II and POFA in powder form.



a)



b)

c)



d)



e)

f)
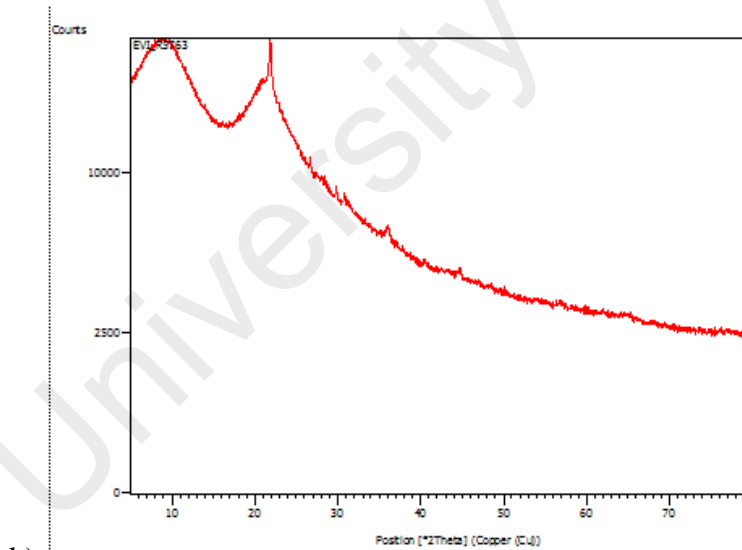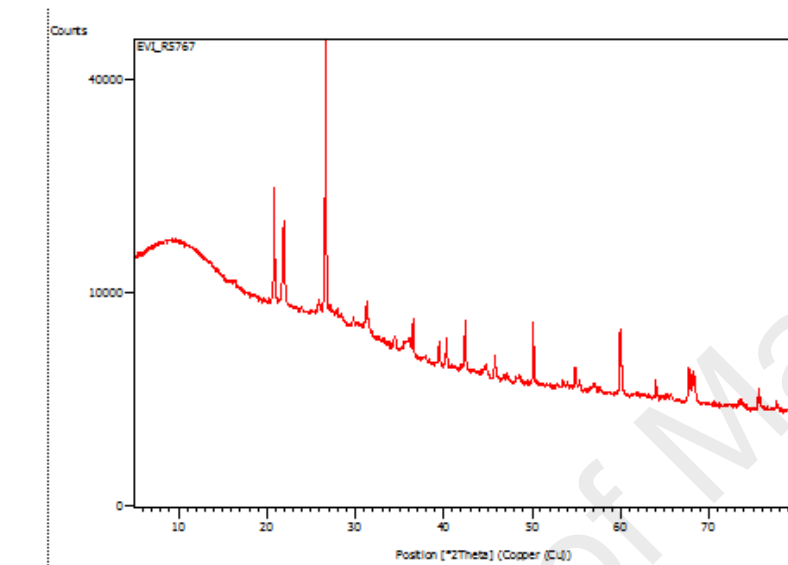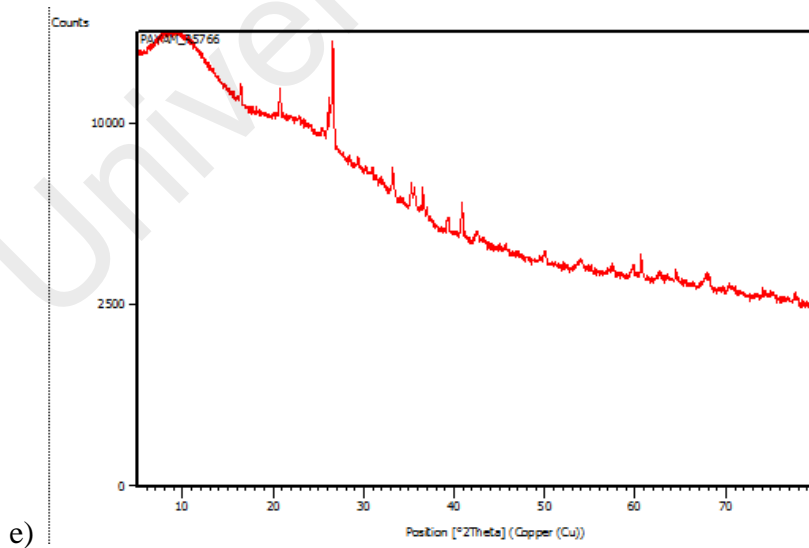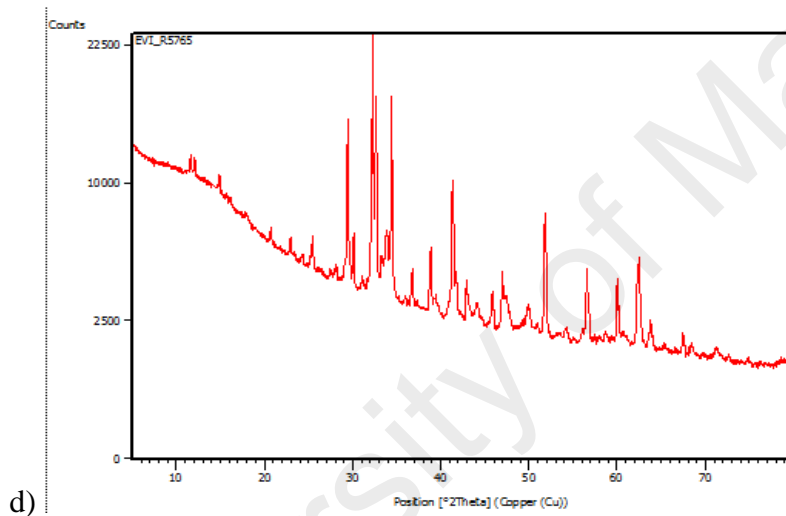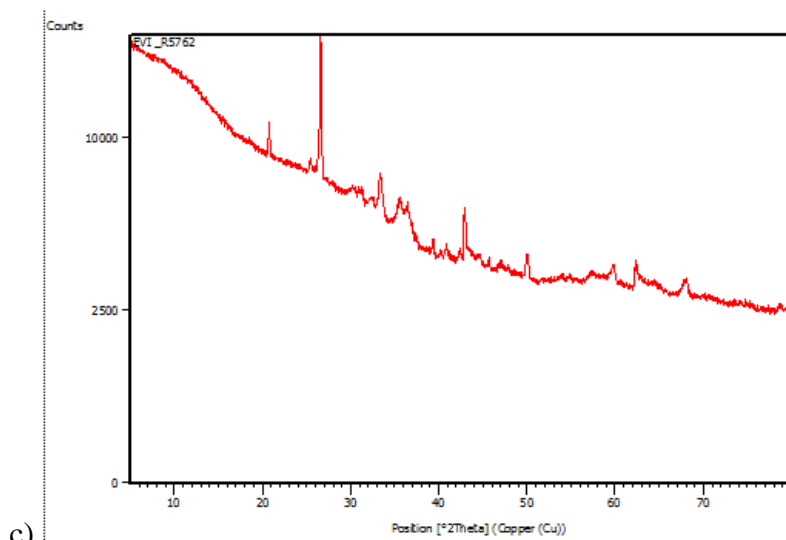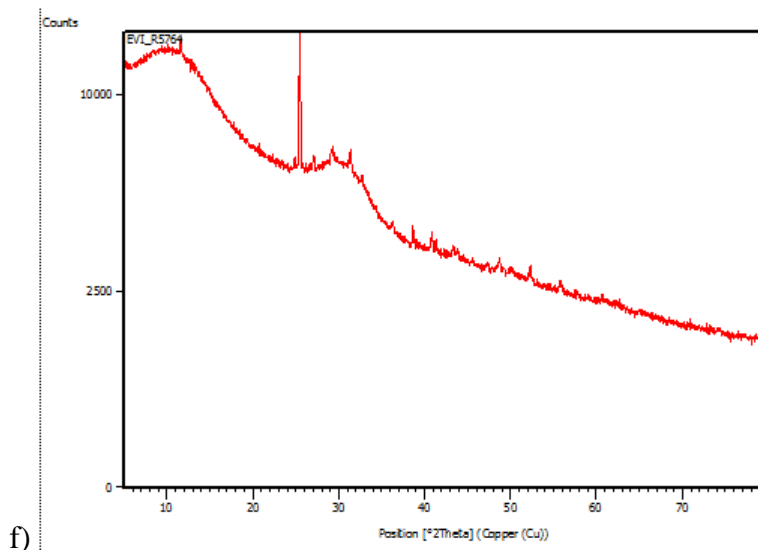
Figure 3.4 XRD results for a) OPC, b) GGBFS, c) Fly Ash, d) RHA, e) Fly Ash II and f) POFA

As seen in Figure 3.4, XRD results appeared in the form of peaks. The peaks appeared corresponding to the crystallinity of materials. If the intensity of some peaks is high, it indicates the abundance concentration of those crystalline planes (Malami&Kaloidas, 2003; Khan, 2003). The narrow sharper peaks mean larger crystallite size or more crystallinity. The XRD pattern for GGBFS in Figure 3.4b showed a diffuse band due to its amorphous and poor crystalline composition. If FA (Figure 3.4c) absorbed water, the mixture will be dry while it increases workability. It is due to FA having higher amorphous structure than OPC (Figure 3.4a). As displayed in Figure 3.4, OPC has more peaks than FA which was dominated by the crystal structure. RHA is absolutely amorphous due to the wider sharper peaks that were shown in Figure 3.4d. It should be noted that micromolecular phase and reactivity level of OPC, GGBFS, FA, and RHA classified as crystal and amorphous. Crystal has a regular and repeatedly structure of atom while amorphous has an irregular structure (Malami & Kaloidas, 2003). Amorphous structure can

easily soluble in water due to weak bonds between molecules (flexible). Karim et al., (2014) reported that generally, crystal structure has a strong reaction between compounds rather than the amorphous structure viewed from their bonding structure. However in the most cases, reactivity is primarily due to the subatomic properties of the compound (Karim et al, 2014; Ahmari et al., 2012; Li et al., 2013; Castaldeli et al., 2013). Therefore, OPC and GGBFS will activated if be in crystal form, while reactivity of FA and RHA when be in amorphous form as shown in Figure 3.4. Generally, pozzolanic material contains crystalline and amorphous. It can be filler if not react with calcium hydroxide $Ca(OH)_2$ (Li et al., 2013). Crystalline has a coarse grain called crystal whereas amorphous in a finer granule likely similar to flour form. So, when react with water, materials in amorphous form is better than crystalline due to their fineness.

## 3.4 MIX PROPORTION AND MIXING PROCEDURE

Table 3.8 represents the mix proportions for different mortars. In all mixes w/c ratio was maintained 0.32. PC contains 100% ordinary Portland cement (OPC). While in the rest mixes, 50% of OPC was substituted by one or two types of cementitious materials. PG, PF, PGF and PRF represent mortar containing 50% GGBFS; 50% FA; 25% GGBFS with 25% FA and 25% RHA with 25% FA, respectively. On the other hand, PF II and PF II-5 are mortar containing 50% FAII. PPF and PPR are ternary blended cement consists of 25% POFA with 25% FA and 25% POFA with 25% RHA, respectively. Otherwise, PGF II is ternary blended cement containing low Portland cement.

At first, sand were put in as a mixture and mixed for 5 minutes. After that the cement and supplementary cementitious material (SCMs) were added and mixing was done for 5–8 minutes. Later on, the calculated water was poured into the mix and the mixing continued for 2 minutes. Then, the superplasticizer was added and mixing continued for 2-3 minutes. Afterward, the flow test was performed and the specimens were moulded. The moulds were filled with fresh mortar and compacted with a vibration table.

Table 3.8 Mix proportion of mortars (Kg/m$^3$)

| Mix Code | Binder | | | | | | Water | w/c | SP (%) | Sand | Flow |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | OPC | GGBFS | FA | RHA | POFA | FA II | | | | | |
| PC | 550.0 | 0 | 0 | 0 | 0 | 0 | 213.40 | 0.32 | 0.60 | 1537.6 | 140±10 mm |
| PG | 275.0 | 275.0 | 0 | 0 | 0 | 0 | 213.40 | 0.32 | 0.55 | 1537.6 | |
| PF | 275.0 | 0 | 275.0 | 0 | 0 | 0 | 213.40 | 0.32 | 0.50 | 1537.6 | |
| PGF | 275.0 | 137.5 | 137.5 | 0 | 0 | 0 | 213.40 | 0.32 | 0.60 | 1537.6 | |
| PRF | 275.0 | 0 | 137.5 | 137.5 | 0 | 0 | 213.40 | 0.32 | 1.00 | 1537.6 | |
| PF II - 5 | 275.0 | 0 | 0 | 0 | 0 | 275.0 | 213.40 | 0.32 | 0.10 | 1537.6 | |
| PF II | 275.0 | 0 | 0 | 0 | 0 | 275.0 | 213.40 | 0.32 | 0.10 | 1537.6 | |
| PPF | 275.0 | 0 | 137.5 | 0 | 137.5 | 0 | 213.40 | 0.32 | 0.65 | 1537.6 | |
| PGF II | 137.5 | 275.0 | 137.5 | 0 | 0 | 0 | 213.40 | 0.32 | 0.75 | 1537.6 | |
| PPR | 137.5 | 0 | 0 | 275.0 | 137.5 | 0 | 213.40 | 0.32 | 1.00 | 1537.6 | |

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### 3.5 TEST FOR FRESH MORTAR

In order to have appropriate consistency for each mortar, a flow table test according to ASTM C230/C230M-08 was performed. The range of flow amounts were $140\pm10$ mm. First, some mortar was put in the truncated brass cone in two layer sand each layer was compacted $10\pm5$ times by a steel rod of 16 mm diameter till it solid. The cone was then lifted and the mortar was collapsed on the flow table. Following that, both the flow table and mortar were jolted 15 times in a period of 60 s. The jolting of the table allowed the mortar to spread out and the maximum spread to the two edges of the table was recorded. The average of both records was calculated as flow in mm.

### 3.6 CURING CONDITION

The specimens were demoulded 24 h after casting. After demoulding, the specimens were divided to five groups to consider four conditions on properties of mortars containing high volume cementitious materials. Some specimens were directly cured in normal water (WC) with $23 \pm 3^{o}C$ temperature and also cured in air (AC) under room temperature of $27 \pm 4^{o}C$ with $70 \pm 10\%$ relative humidity. The rest of specimens were heated in water at $60^{o}C$ for 24 h first, and then they were divided into two groups to be cured in air (HAC) under room temperature as well as water curing (HWC) until the test day. In addition, to investigate early hot water curing on the early strength of mortar, 3 cube specimens were heated for 2½ h and also 5 h. In this condition, the compressive strength at 1 day age was conducted.

Hardened mortars can reach their maximum strength within several hours through elevated curing temperature. However, the ultimate strength of hardened mortars and concretes has been shown to decrease with curing temperature. It was found that by increasing the curing temperature up to $60^{\circ}$C and the heating time to 24 h, a continuous increase in compressive strength could be noted (Kim et al., 2002). Therefore, this temperature was selected in this study.

## 3.7 TEST FOR HARDENED MORTAR

### 3.7.1 COMPRESSIVE AND FLEXURAL STRENGTH TEST

All of the specimens within four conditions were cured until they were used for compressive strength tests at 3, 7, 14, 28, 56 and 90 days age. The compressive strength measurements were carried out using an ELE testing machine press with a capacity of 2000 kN and a loading rate of 0.5 kN/s. Compressive tests were done according to BS EN 12390-3-09. While, for flexural strength test conducted at 7 and 28 age days two curing conditions of HWC and HAC. For flexural strength test, the specimens were put the specimen above 2 equal pedestals then saddled with a load evenly located in the middle span, as well as the addition of the load gradually until it reaches the fracture and obtain the maximum load value ($P_{maks}$) was shown at Figure 3.5.
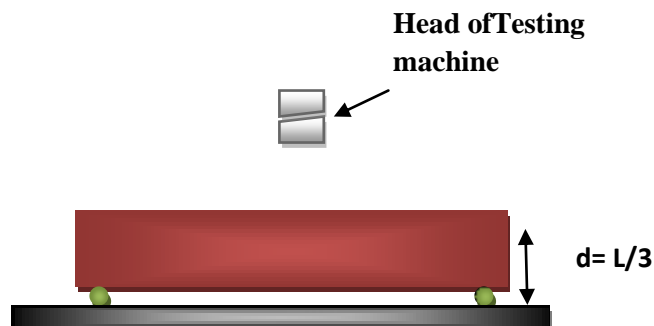


**Head ofTesting machine**

**d= L/3**

Figure 3.5 The illustrated test for flexural strength of mortar

### 3.7.2 WATER ABSORPTION

Water absorption test conducted at 56 days age. Water absorption was determined using a mortar cube of 50 mm $\times$ 50 mm $\times$ 50 mm. In this regard, cube specimens were dried in oven at $110^{o}$C for $24\pm2$ h until constant weight. Then they were weighted in air immediately (*W*a) after removing from oven and also after immersion periods of 30 min and 72 h. Thus, water absorption of the specimen was calculated as $100 \times (Wa - Wd)/Wd$.

### 3.7.3 POROSITY

The porosity test for hardened mortar conducted when the mortar reach 56 days age. Porosity tests were carried out on cubical samples with the size of 50x50x50 mm. The purpose of this test is to determine the percentage of pores of the concrete/mortar to the volume of solid concrete/mortar. As it is known that the compressive strength of mortar/concrete is influenced by the porosity (Chindaprasirt & Rukzon, 2008; Malami & Kaloidas, 2003; Khan, 2003). More porous present in the mortar specimen, the lower compressive strength produced (Khan, 2003). The porosity test set up was shown in Figure 3.8. The steps of the test are as follows:

1.  Samples of each condition at 56 days removed from the curing tubs and aerated.

2.  Prepare the specimens and then put in the oven at $100\pm5°$C for 24 hours.

3.  The specimens were removed from the oven and aerated at room temperature ($25^{o}$C) and then weighed. The weight of the mortar obtained was oven dry condition (C).

4.  The specimens were put in a dessicator to vacuum process using a vacuum pump as mentioned in Figure 3.6. The vacuum process of the specimen as long as $24\pm2$ hours.

After that, the specimen immersed in water until all sides of the specimens completely submerged in water. Immersion process of the specimens also in vacuum conditions and performed for 24 hours. Then, weighed and obtained the weight in water (A).



Figure 3.6 Porosity test using SMART-CL vacuum dessicator with moisture trap

5. The specimens were removed from the water and wipe the surface to get a SSD condition then the samples were weighed. The weight of the mortar conditions of SSD obtained after immersion (B).

From the above test results, the porosity value was calculated based on the following formula:

**Porosity** $= \left(\frac{B-C}{B-A}\right) x 100\%$

Where, A is the weight of the specimens in water, B is the weight of the specimens in SSD condition and C is the weight of the specimens in oven dry condition.

# CHAPTER 4

## RESULTS AND DISCUSSION

As discussed earlier, the experimental work on the properties of mortar containing cementitious materials was carried out. The results for investigation of raw materials have been described in chapter 3. Furthermore, this chapter presents the compressive strength of cementitious mortar, the flexural strength of cementitious mortar, porosity and water absorption of mortar.

### 4.1 The compressive strength in normal and under early hot-water curing conditions

The results obtained in the study for compressive strengths, based on heating time, are given in Table 4.1. The data inventory in this table examined two subjects. The compressive strengths obtained for different short time heat durations and also provided the result for 1 day test immediately after demoulding.

**Table 4.1** The 1-day compressive strength test results in normal and early hot-water curing condition

| Type of mixes | 1 day without heating process | **% Reduction as compared to PC** | 2.5 hour in hot water | **% Increased as compared to PC** | 5 hour in hot water | **% Increased as compared to PC** |
|---|---|---|---|---|---|---|
| PC | 32.53 | **26.35** | 41.10 | **20.85** | 41.60 | **21.80** |
| PG | 20.17 | **48.98** | 30.05 | **32.88** | 34.67 | **41.82** |
| PF | 15.57 | **9.82** | 17.10 | **8.95** | 19.50 | **20.15** |
| PGF | 13.44 | **25.75** | 16.90 | **20.47** | 21.60 | **37.78** |
| PRF | 16.40 | **0.61** | 16.50 | **0.61** | 18.94 | **13.41** |
| PF II - 5 | 14.51 | **24.19** | 18.02 | **19.48** | 23.54 | **38.36** |
| PF II - 24 | 14.50 | **24.20** | 18.01 | **19.49** | 23.50 | **38.30** |
| PGF II | 9.98 | **88.78** | 18.84 | **47.03** | 20.12 | **50.40** |
| PPF | 17.08 | **20.37** | 20.56 | **16.92** | 23.89 | **28.50** |
| PPR | 11.23 | **33.75** | 15.02 | **25.23** | 17.22 | **34.79** |

As expected, substitution of OPC by cementitious materials up to 50% significantly reduced the 1-day compressive strength. The lowest reduction was observed in PRF mix by a reduction about 0.61%. While, the great reduction was observed in mixes containing GGBFS and FA II (PGF II mix) by a reduction about 88%. It shows that contribution of FA II (from 25%-50%) in high volume substitution level can significantly reduce the compressive strength of mortar.

The data inventory shows that on heating process for 5 hours, substitution of OPC by 50% GGBFS significantly increased the compressive strength by 41.82% and the result is equal to PC mix. This is due to crystalline effect from GGBFS which accelerated inner to gain more strength under heating process. The reduction was observed for mixes contain fly ash, by an average reduction about 22.18%. Reversely, when rice husk ash (RHA) combine with FA or POFA, the strength is lower than other mixes, this is due to the high silica content from RHA and FA or POFA slowly react under heating process. As can be seen from PF II − 5 and PF II − 24 gained equal strength. Hereafter, combinations of OPC and FA for both mixes mitigated compressive strength of 57 % compared to PC when cured in hot water within 2.5 h. It means that the margin is only 1% in average between 1 day without heating process and curing in hot water for 2.5 h. It shows that contributions of 50% FA will slowly obtaining the compressive strength of mortar compared to control mix (PC). It shows that the PF mortar did not get enough heat to complete the pozzolanic reaction at earlier heating process therefore the reaction may took place at longer time of heating process. The results are also indicated that high fineness and low carbon content in FA will result in high-early strength. Other benefits

that FA did not generate any heat of hydration unlike OPC (Berry et al., 1994). Moreover, the 1-day strength without heating process and 2.5 hour heating process behaved similarly with 5 hour heating process. The results obtained show that both of PF II-5 and PF II-24 had the same tendencies to gain the strengths during accelerated heating process. Whereas, the PC mortar still have better strength than other mixes mortar.

However, test results of early heating curing show that the reduction on the compressive strength can be compensated by using early hot water curing. The results indicated that early hot water curing is an effective method in order to gain 1-day strength for cement based materials. In general, it can be specified that early hot water curing is more effective to enhance the compressive strength if the sum of CaO content of the binder is more than $SiO_2$ content.

## 4.2 The compressive strength result for all ages at different curing conditions

Figure 4.1 shows the compressive strengths development of all mortars containing 50% of pozzolan. Based on the results, it can be seen generally that at 3, 7 and 14 days strengths, for specimens cured in the water (WC) is greater than the specimens cured under room temperature (AC). This reality has proven for binary blended cement. Conversely, the aforementioned statement is reversed for ternary blended cement containing RHA (Mix PRF) at the same ages. The strength of ternary blended cement mortar containing RHA and cured under room temperature (AC) was higher compared to the strength of specimens cured in water. It may be due to two reasons: first, as observed

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in the chapter 3 that RHA is a porous material. This porosity can absorb the free water at the time of casting. This absorbed water may have a significant role for internal curing.
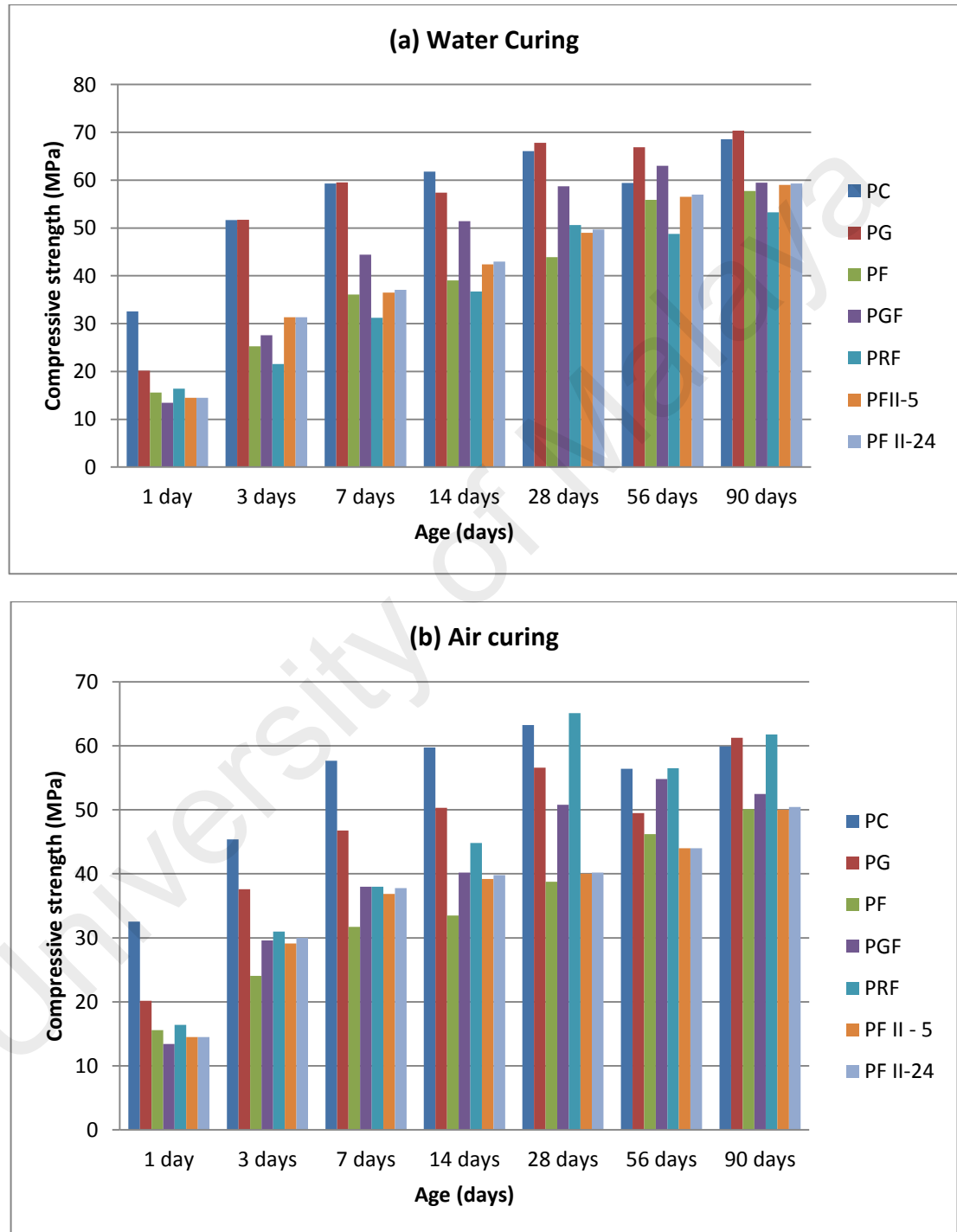


**Figure 4.1** The compressive strength of mortar without heating process at early ages for WC (a) and AC (b) conditions

This role of RHA was already reported by other researchers (Anthiohos et al., 2014; Schmidt et al., 2012; Hasparyk et al., 2000). They confirmed that RHA particles are finest and porous appeared to be most effective in mitigating process. RHA particles obviously best prepared to absorb a certain amount of water into its pores. Then, in the lack of available water, the absorbed water can be released to maintain hydration of cement (induced). The pores structure of RHA which is induced called internal curing of mortar. Second, it was shown in the FTIR and XRD test that RHA has high reactivity potential in the form of silica amorphous. In addition, it has high specific surface area. Therefore, mortar containing a combination of RHA and FA gain better strength under AC condition compared to WC condition.

At 3 days age, compared to PC, the results revealed that PGF and PRF showed the lower strength under WC in the decrease about 15% and 33%, respectively, while in AC condition about 9% and 4%, respectively. The greater incremental strength was observed in mixes containing GGBFS. It is due to the crystalline content from GGBFS. While, the highest strength loss was found in PF mixes by a total reduction about 23% and 26% for WC and AC, respectively. It is due to the high volume of fly ash will cause the delay on C-S-H reaction while curing process. This fact shows that the type of binder plays a major role in strength improvement of the mortars in different curing conditions.

Further detail discussion of compressive strength result can be seen in Figure 4.2. As can be described in Figure 4.2, the compressive strength of mortar containing 50% FA depends on the curing conditions.
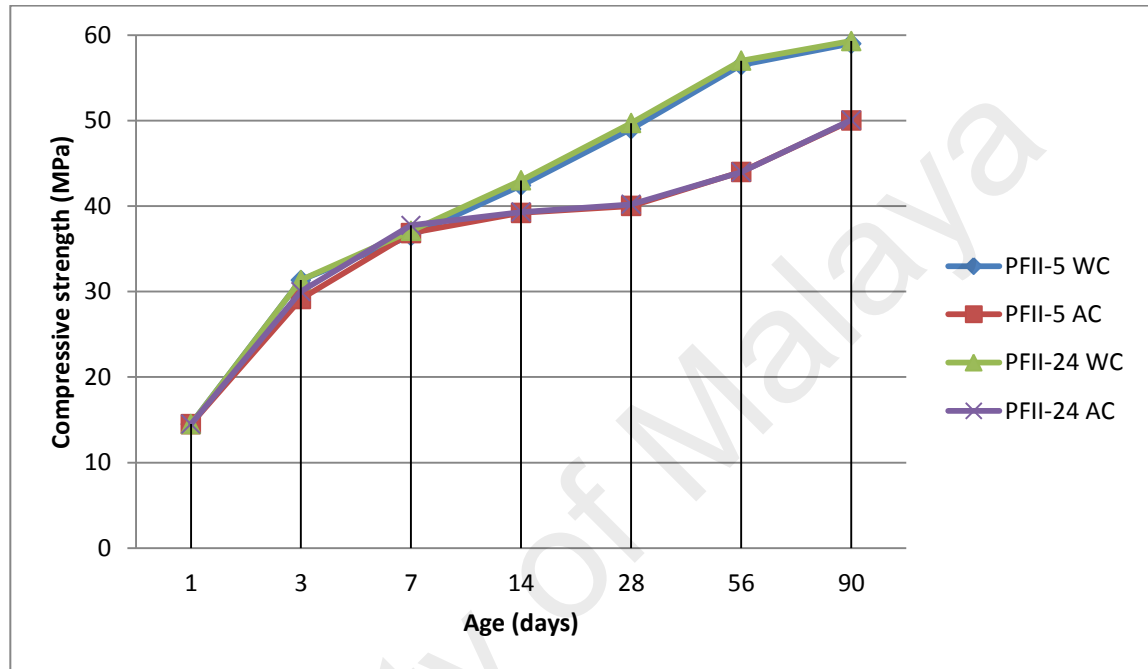


**Figure 4.2** Compressive strength of PFII-5 and PFII-24 in WC and AC conditions

Figure 4.2 shows that in WC and AC conditions, both PFII-5 and PFII-24 are almost in the same line. It indicates that for WC conditions, mortar containing 50% FA exhibit higher strength compared to AC conditions. Compared to AC conditions, the compressive strength of PFII-24 increases about 7%, 16%, 18% and 11% for 14 days, 28 days, 56 days and 90 days, respectively. In addition, the compressive strength of PFII-5 in AC conditions decreases about 7%, 15%, 17% and 12% for 14 days, 28 days, 56 days and 90 days, respectively. Based on the incremental results, it can be concluded that PFII-5 and PFII-24 have the similar tendencies towards WC and AC conditions.

Variations of compressive strength for the specimens cured in HWC and HAC conditions are shown in Figure 4.3.



**(a) Hot-water curing (HWC) condition**



**(b) Hot- air curing (HAC) condition**

**Figure 4.3** The compressive strength of mortar without heating process at early ages for HWC (a) and HAC (b) conditions

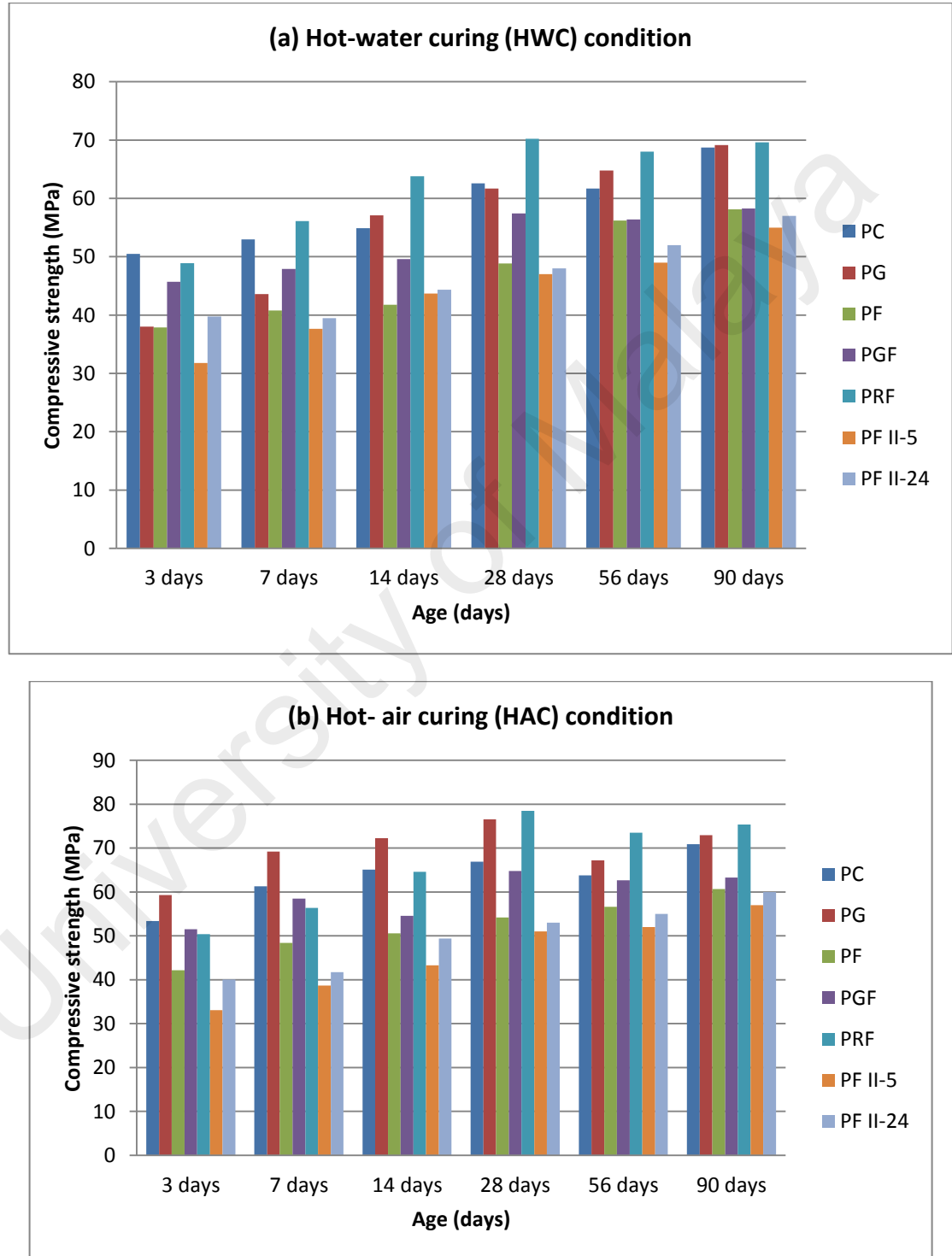From the data in Figure 4.3, it can be seen that in the most cases, the strengths of mortars cured in HAC are higher than those of mortars cured in HWC in all early ages. The results revealed that with the use of heating process, the compressive strength of PC mortar under room temperature (HAC) increased by on average 14% compared to PC mortar cured in water (HWC). In addition, when 50% GGBFS is used in mortar (PG), the strength increased by on average 12% compared to PC mortar under HAC condition at all early ages. Reversely, when PG mortars cured in HWC condition obtained lower strength by 24% and 18% compared to PC mortars for 3 days and 7 days, respectively. Crystalline effect will react faster under room temperature after initial heating process.

Meanwhile, the strength rate of PF and PGF compared to PC at all early ages, for both in HWC and HAC conditions, decreased by 24% and 10%, respectively. It was reported (Li et al., 2013; Ahmari et al., 2012; Peter et al., 2011; Karim et al., 2014) that the appearances of the strength was slowed in the early ages and continuously for a long curing period by adding FA for more than 30%. It is due to the chemical reaction in mortar, in terms of hydration process.

Other case for mortar containing RHA with FA (PRF) compared to PC at 3 days, the strength decreased by 4% and 6% in HWC and HAC condition, respectively. However, this strength is increased by 6% and 16% at 7 and 14 days age, respectively for HWC condition. Surprisingly, PRF mortar obtained the equivalent compressive strength at 14 days as much as 65 MPa in HAC condition. This results show that there is continuity in the

hydration progress of PRF mortar from 7 days to 14 days, while the whole latent potential of PRF mortar released during early ages due to the heat effect.

Compared to PC at 3 days, compressive strength of PFII-5 and PFII-24 decreases about 39% and 38%, respectively for WC condition. Furthermore, compressive strength of PFII-24 exhibited higher values than PFII-5, whereas the incremental strengths of PFII-24 are 1.5%; 1.4%; 1.3%; 0.9% and 0.5% for 7 days, 14 days, 28 days, 56 days and 90 days, respectively. It can be concluded that PFII-24 obtained the average incremental strength about 1.2% compared to PFII-5 in WC condition. Compared to PFII-5, the compressive strength of PFII-24 shows gained the strength about 3%, 2%, 2%, 5%, 7% and 6% at 3 days, 7 days, 14 days, 28 days, 56 days and 90 days, respectively for AC condition. It shows that when cured under room temperature, PFII-24 was higher than PFII-5 about 4% on average. Moreover, the compressive strength results for PFII-24 are 7%, 12%, 4%, 6% and 5% at 7 days, 14 days, 28 days, 56 days and 90 days, respectively, compared to PFII-5. In addition, the compressive strength of PFII-24 mortar is decreased by on average 20.25% compared to PC mortar under HAC condition at all early ages. It could generally be said that the initial heating time influenced the compressive strength of mortar containing 50% fly ash.

It shows that the PF mortar did not get enough heat to complete the pozzolanic reaction at earlier heating process therefore the reaction may took place at longer time of heating process. The detail micrograph images of mortar containing fly ash will discuss further in Figure 4.4 to prove the influence of thermal duration.
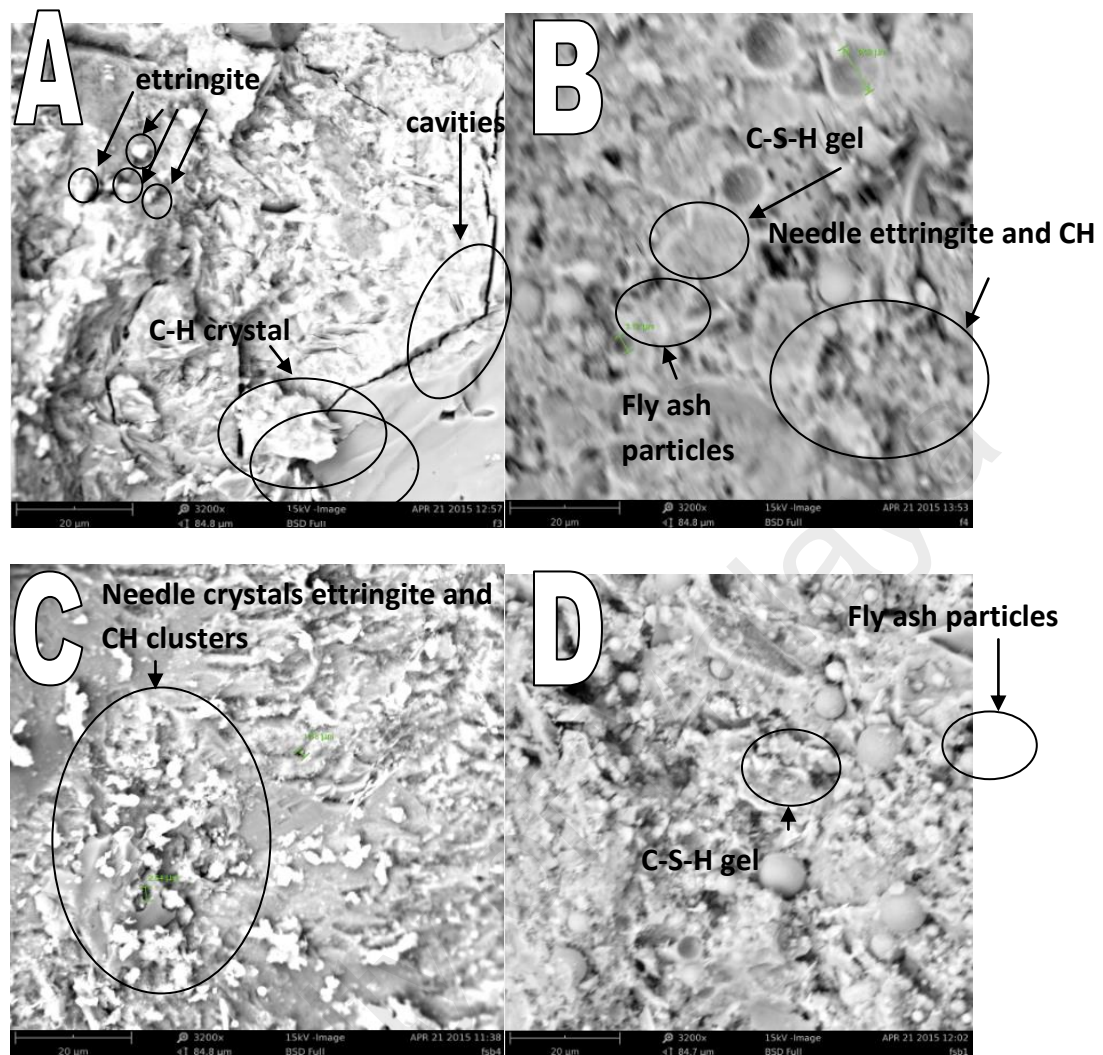
**Figure 4.4** SEM results of PF II-5 and PF II-24 mortar at HWC and HAC

It can be seen generally that Figure 4.4 (a) and (b) shows many cavities and less needle crystals. Reversely, Figure 4.4 (c) and (d) shows more crystals and less of cavities between interface zone from fly ashes particles. It also can be seen that the microstructures of PF II-5 mortars in Figures 4.4 were porous and had many voids (cavities) compared to PFII-24 for HWC and HAC conditions. As can be seen in HWC conditions (Figure 4.4a and Figure 4.4c), PF II-24 has less porous than PFII-5. Under reduced or negative pressure, such surface gas may expand into visible bubbles called cavities (Bremond et al., 2005). It can be seen that the hydration products on the fly ash surface hardly proceeded, some of the

surfaces of fly ash particles were found to be coated with layers of small amounts of hydration products. It is found that the CH products in PFII-5 much higher than PFII-24. The CH products cause deterioration which known as a sulphate attack (Hewlett, 2003). Therefore, the mechanical strength of PFII-5 is lower than PF-II-24. Xu et al., (1994) noted that FA particles have both enhancement and retardation effects on the hydration process. The retardation process is often happen in FA mixtures due to LOI and subjected to the different curing conditions. As can be seen in Figure 4.4b and Figure 4.4c, some of the ettringite needles, which grow in vacant areas in paste, were occurring. Significantly, the pozzolanic reaction of fly ash when mixed with cement paste started after one or more weeks (Gopalan, 1993; Montgomery, 1981). In this period, two mechanisms of hydration and nucleation occupied simultaneously (Xu &Sarker, 1994; Berry et al, 1994). Considering PFII-5 and PF II-24 mortars at 56 days, as the FA substitution increases, the setting times increase. To overcome this problem, the use of heating process under optimum temperature of $60^{o}C$ and probable durations will improve the strength significantly, for both early and later ages of mortar containing high volume of FA.

The results are also indicated that high fineness and low carbon content in FA will result in high-early strength. Other benefits that FA did not generate any heat of hydration unlike OPC (Berry et al., 1994). A rise in temperature greatly accelerates the cement hydration reactions and affects advantageously the properties of mortar (Alamri, 1988). It also reduces the dormant period of hydrates and the overall structure of the hydrated mortar is running at an advanced time. This reality has proven for binary blended cement. As observed in the Chapter 3 that FA is a spherical material which is advantageous from

the water requirement point of view (Sybertz, 1989). This spherical can observe the free water at the time of casting. This absorbed water may have a significant role for internal curing. So, FA particles are finest and spherical appeared to be most effective in mitigating process. when the pozzolanic materials in the form of fly ash are added to the cements, the C-H of hydrated cement is consumed by the reactive $SiO_2$ portion of these pozzolanas. This pozzolanic reaction improves the microstructure of cement composites as additional C-S-H gel is formed and also the pore size refinement of the hydrated cement occurs. Hydration of tri-calcium-aluminate in the ash provides one of the primary cementitious products in many ashes. The rapid rate at which the hydration of the tri-calcium-aluminate results in the rapid set of these materials and is the reason for the delay in lower strengths of the stabilized material. In a simple sentences, the higher strength of PFII, both PFII-5 and PFII-24 in WC conditions due to C-H contents which are higher in fly ash specimens caused by the rapid free CaO hydration by water.

Overall, HAC condition showed the highest strength results compared with other three conditions at later ages. It was cleared that under WC condition, PC mortar gave lower strength than PG mortar but shows higher strength than PF, PGF and PRF mortars. It is related to the presence of crystalline structure from GGBFS which can improve strengths at later ages (Sajedi & Razak, 2011). Generally, from the results obtained for AC condition, it was observed that the strength of PRF mortars were higher than those of PC, PG, PF and PGF mortars in all later ages. The results revealed that compared to PRF mortar, PC mortar and PG mortar under AC condition showed strength loss about on average 4% and 8%, respectively. Otherwise, PC mortar shows higher strength when compared to PGF mortar with incremental on average about 23% at all later ages. It should

be noted that for the specimens cured at room temperature, the maximum relative humidity was 85% and air temperature of $27\pm3^{o}$C whereas for the specimens cured in water is 100% with temperature by on average $23^{o}$C. High relative humidity and air temperature may be the reasons for strength gain for some mortars under AC condition and also for the most mortars under HAC condition.

Based on reaction, the reactivity of RHA is attributed to its high content of amorphous silica, and to its very large surface area governed by the porous structure of the particles as shown in XRD and SEM results (Chapter 3). RHA have the highest $SiO_2$ content but when mix with OPC in high volume, it will dry. At the stage of hydration process, the fly ash performed faster than GGBFS. It is due to the fineness particle and containing silica amorphous. The hydration process result indicates that chemical composition such as $SiO_2$ and CaO (in the vicinity of the interface) is one of the major factors for the increase in bond strength (Peter et al., 2011). Therefore, as mentioned from XRD results (chapter 3), the other cementitious material which has a high reactivity similar to FA in silica amorphous form is RHA. So that, RHA combine with fly ash and produced the better flow and good workability. The combination of OPC, RHA and FA to be composite binder exhibit as the best mix compare to all combinations. It is due to the chemical and physical properties of these cementitious materials.

It can be said that by using combination of RHA with FA as partial substitute cement, several benefits provided such as reduced materials costs due to cement savings (Peter et al., 2011) and environmentally friendly related to the utilization of waste materials as well as reduced $CO_2$ emissions from cement exploitation.

Based on curing conditions criteria, the strength of the specimens cured in air at room temperature after heat process (HAC) is the highest. The second level of strength is attributed to the specimens cured in water after the heating process (HWC). The third level is for those cured in water without the use of heating (WC) and the last is attributed to the specimens cured in air under room temperature without the use of heat process (AC). This result also shows that the thermal technique like HAC is a feasible and efficient method for the activation of ordinary Portland cement with high volume cementitious materials in mortars and concretes without the use of water to cure the specimens after heating process. It could generally be said that whenever OPC-cementitious mortars are heated, it is preferred to cure under HAC condition than cured in water (HWC). It is due to the OPC-cementitious mortar will accelerate reactions to obtain the strength under initial thermal curing process.

As conclusion, it seems that whenever mortars cured under room temperature after heating (HAC), the strengths increase with the curing duration. Moreover, the results prove that a proper combination of cementitious materials in binder plays a main role in the strength improvement of mortars. In addition, it can be said that by using combination of cementitious materials as partial substitute cement, several benefits provided such as reduced materials costs due to cement savings and environmentally friendly related to the utilization of waste materials as well as reduced $CO_2$ emissions from cement exploitation. This result is the break solution to face one of the concrete industry challenges that is towards the achievement of sustainable development.

## 4.3 Evaluation of compressive strength of ternary blended cement using different curing conditions

The effect of hot water curing on the mechanical properties of ternary blended cement of cementitious mortar was investigated. The main purpose is to evaluate the performance of ternary blended cement containing POFA by incorporating RHA and FA. The used of POFA and RHA due to the huge availability in Malaysia. The research focuses on ternary blended cement mixes incorporating municipal wastes which are available on a huge amount in Malaysia. Furthermore, the effect of hot water curing on cementitious mortar containing low Portland cement (25%) is also investigated. An evaluation was conducted to determine the effect of using thermal process and different curing conditions as a cost-reducing in mortar.

The results of ternary blended cement mortars in different curing condition at early age can be seen in Figure 4.5 and Figure 4.6.
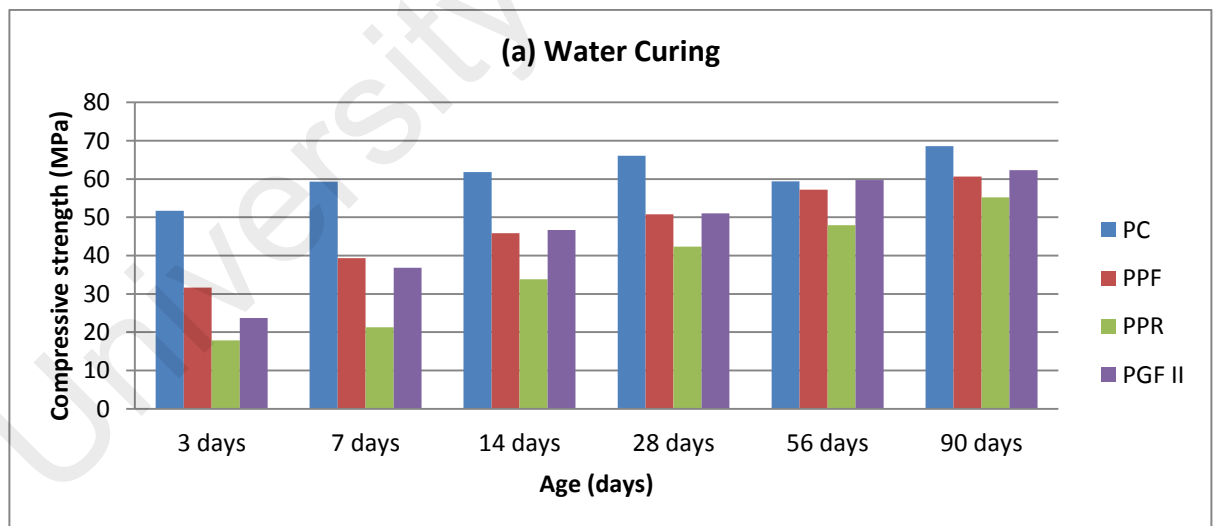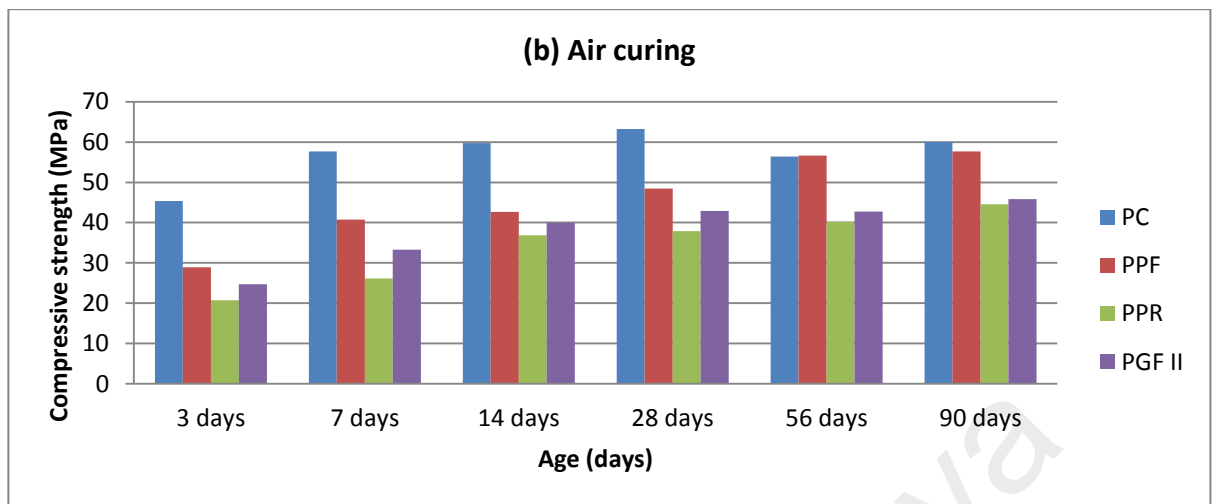
**Figure 4.5 The compressive strength result of mortar in a) WC & b) AC conditions.**
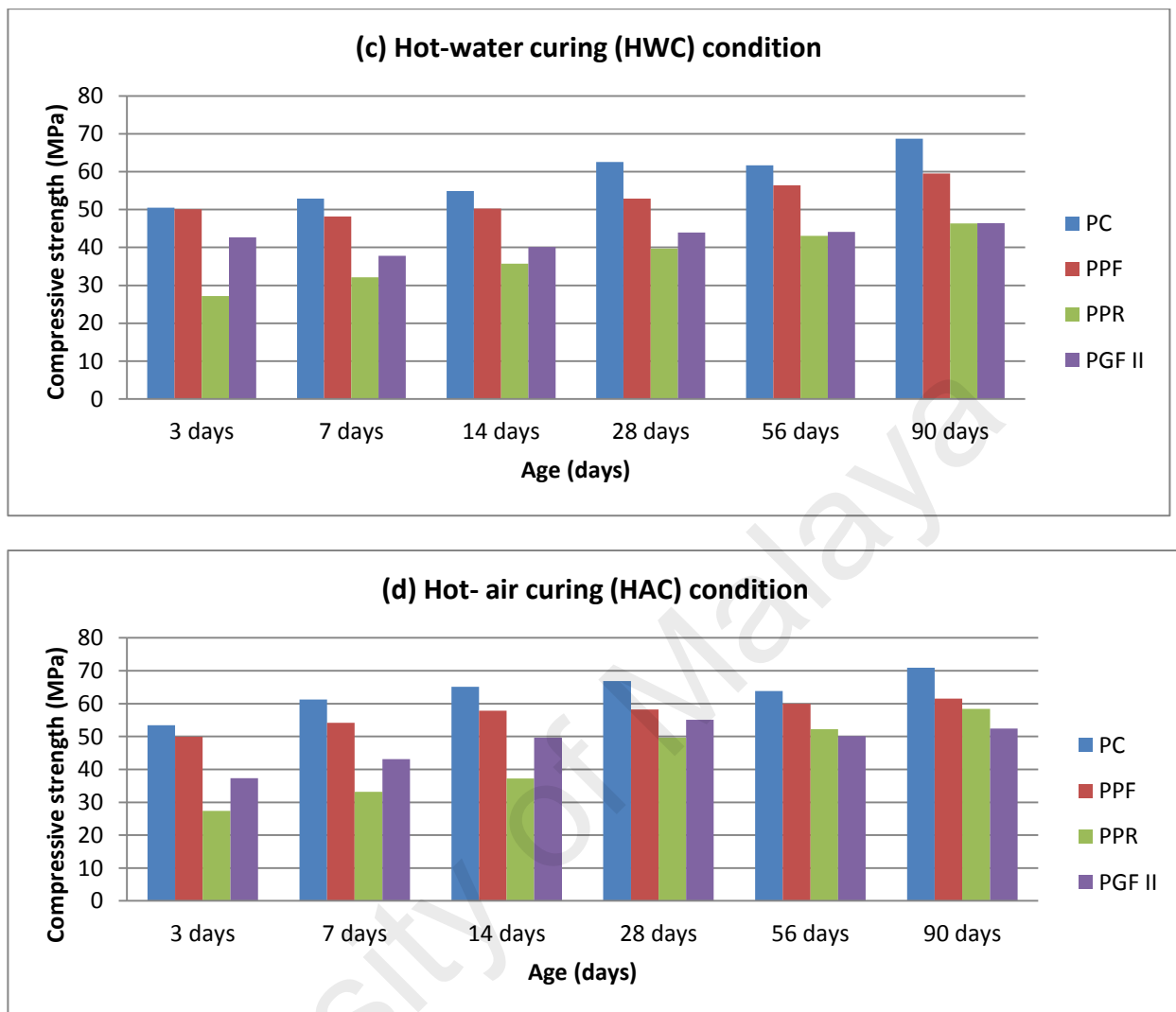
**Figure 4.6 The compressive strength result of mortar in c) HWC & d)HAC conditions.**

The comparison begins from water curing conditions with and without heating process. Comparing the compressive strengths of PGF II mortar, the significant differences are observed for both curing conditions of strength. The compressive strength of PGFII mixes using initial heating process gained the strength of 44% and 3% at 3 days and 7 days, respectively, compared to PGFII without heating process. Reversely, PGF II in HWC condition decreased about 17% at 14 days compared to WC condition. Based on the results, it can be seen generally that at 3 and 7 days strengths, for specimens cured in the HWC condition, the compressive strength is higher than the specimens cured without

heating process (WC). Contrarily, the strength of PGFII mixes were cured in WC condition at 14 days show better performance than cured in HWC condition for about 17%. The delayed strength gain between 3 days to 7 days due to retardation clusters consist in FA under heating process. Other than that, mortar containing FA sets faster in WC condition, so that the strength at 7 days to 14 days increase much higher than in HWC conditions.

When PGFII mixes cured in HAC conditions, the compressive strength was slightly higher than those were cured without heating process at all early ages. As detail, the compressive strength of PGFII cured under room temperature without heating process decreases for about 50%, 30% and 25% at 3 days, 7 days and 14 days, respectively. It can be seen that particularly under room temperature, ternary blended cement consist of 25% GGBFS and 25% FA will show better performance using initial heating process compared to PGFII mixes in AC conditions. The initial thermal process at $60^{o}$C for 24 h has an adverse effect on inner and outer microstructure of hydration product particularly in the case of calcium silicate hydration consists of fly ashes particles. Meanwhile, initial heating process will bring benefit effects on hydration product and the strength performance of mortar when after heating process followed by cured under room temperature, particularly for the mortars containing fly ash.

The evaluation of ternary blended cement mortar containing of 25% POFA was investigated. PPR mix compared to PPF mix in WC condition, the strength obtained decreased by 14%, 18% and 35% for 3 days, 7 days and 14 days, respectively. When HWC condition compared to WC condition, the strength of PPR and PPF mortar increased on average of 25% and 21%, respectively. As conclusion, the combination of OPC and 25%

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POFA with 25% RHA (PPR) and PPF are suitable to cure in water after heating process (HWC) at early ages. Meanwhile, the control mortar or PC mix is better cure in water, due to the chemical reaction of pure 100% Portland cement going faster at the early ages. Continuously, POFA when used in a high volume, it was shown in the trial mix that the result failed (dry/bad flow).

Researchers have conducted experimental work regarding this matter in mortar and concrete production. Awa1 et al., (2011) investigated that high volume palm oil fuel ash concrete, like concrete made with other pozzolanic materials, showed a slower gain in strength at early age. Safiuddin et al., (2010) reviewed that the use of POFA is limited to a partial replacement, ranging from 0-30% by weight of the total cementitious material in the production of concrete. In addition, it has a filler effect similar to FA. Therefore, mortar containing a combination of POFA and FA gain better strength compared to POFA-RHA condition.

Variations of compressive strength for the specimens cured in HAC conditions. It can be seen that in the cases of PPF, the strengths of mortars cured in HAC are higher than those of mortars cured in AC in all early ages. The results revealed that with the use of heating process, the compressive strength of PPF mortar under room temperature (HAC) increased by on average 30% compared to PPF mortar cured in water (AC). The results obtained from PPR mortars were cured in AC decreased by 32%, 27% and 5% compared to PPR mortar cured in HAC condition at 3 days, 7 days and 14 days, respectively. This trends show that at early ages, ternary blended cement consists of 25% POFA and 25%

RHA is suitable to cure in HAC condition. Comparing the compressive strength of PPR in HAC and HWC condition, no significant differences are observed for both conditions.

In addition, when 50% GGBFS and 25% FA are used in mortar (PGF II), the strength decreased by on average 20% compared to PPF mortar under HAC condition at all early ages. Reversely, when PGF II mortars cured in HWC condition obtained lower strength by 14% and 23% compared to PGF II mortars in HAC condition for 7 days and 14 days, respectively. The strength of ternary blended cement mortar containing low volume OPC (PGFII) cured under room temperature after heating process (HAC) was higher compared to the strength of specimens cured in water after initial thermal process (HWC). It may be due to the low portion of OPC used but the volume of GGBFS-FA is higher (up to 75%). As observed in the Chapter 3 that FA is fineness and has a high surface area, so it needs water to react well. Furthermore, the actual reactivity of GGBFS depends on its composition, glassy content as well as similarity behavior to fly ash (Thomas et al, 1999; Roy, 1987). It could generally be said that whenever PGF II mortars are heated, it is prefer to cure under HAC condition than cured in water (HWC).

As can be seen from Figure 4.5 without heating process (AC) compared to Figure 4.6 with heating process (HAC), PPF mix, PPR mix and PGFII mix increased the strength on average 10%, 24% and 16%, respectively. PC mortar at 56 days gave lower strength than PGF II mortar but shows higher strength than PPF and PPR mortars. It is related to the presence of crystalline structure from GGBFS and enhancement clusters from Fly ash which can improve strengths at later ages. Generally, from the results of PPF and PPR obtained for HAC condition, it was observed that the strength of PPF mortars were higher

than those of PPR mortars in all later ages. The results revealed that compared to PPF mortar, PPR mortar under HAC condition showed strength loss about on average 13%. Otherwise, in WC condition, PGFII mortar shows higher strength when compared to PPF and PPR mortar with incremental on average about 3% and 16% at all later ages. PGF II mortars used low volume of OPC in mixture. The results obtained in WC condition at later ages show a better performance than other curing conditions. As reported before (Sajedi&Razak, 2011), the OPC and GGBFS make mortar become more sensitive to air curing condition (AC).

This fact can be attributed to high consistency of GGBFS nearby water. At the stage of hydration process, the fly ash performed faster than GGBFS. It is due to the fineness particle and containing silica amorphous. So that, 50% GGBFS combine with fly ash and produced the better flow and good workability when immersed in water. It can concluded that when mortar cured in water after demoulding without heating process, the use of 25%OPC combine with 50% GGBFS and 25% fly ash shows a good strength than PPF and PPR mixes. Whilst, it should be noted that for the specimens cured at room temperature, the maximum relative humidity was 85% and air temperature of $27\pm3^{o}C$ whereas for the specimens cured in water is 100% with temperature by on average $23^{o}C$. High relative humidity and air temperature may be the reasons for strength gain for some mortars under AC condition and also for the most mortars under HAC condition.

Overall, the strength comparison of two group mortars containing POFA (PPR, and PPF) at the later ages showed that PPF mortars gave the highest strengths cured under HAC condition. The lowest strengths are related to PPR mortars almost in all curing

conditions and PG mortar has medium strengths and improve steadily in all curing conditions. According to the results obtained in the study, it can be said that thermal activation with air cured (HAC) is one of the effective methods for the activation of OPC-cementitious materials. Otherwise, PC mixes as the control mortar (reference) still the highest among all ternary blended cements. It can be seen generally that HAC condition showed the highest strength results compared with other three conditions at later ages. It was cleared that the strength of ternary blended cement mortar using heating process (HWC and HAC) shows better strength compared to WC and AC conditions.

The use of multiple by products from agriculture and industries with more economic curing design will reduce the use of Portland cement and eventually cutting down the cost of construction project. At the same time, it resulting in profit incremental, easier to be handled and maintaining due to the no more spaces needed to cure specimens.

**4.4 The mechanical properties results for mortar containing cementitious materials.**

**4.4.1 The Flexural Strength**

The effect of two curing conditions with heating process (HWC and HAC) on the flexural strength of mortars containing 50% cementitious materials are shown in the Table 4.2. As shown in Table 4.2, flexural strength results under HAC condition are higher than HWC condition.

Table 4.2 The Flexural strength results of mortar under heating process at 7 and 28 days age in HWC and HAC conditions.

| MIX | FLEXURAL STRENGTH (MPa) | | | | | | | |
| | 7 DAYS | | | | 28 DAYS | | | |
| | HAC | % reduction as compared with HAC | HWC | % increased | HAC | % reduction as compared with PC | HWC | % increased |
|---|---|---|---|---|---|---|---|---|
| PC | 4.6 | **13** | 4.0 | **-** | 12.7 | **5** | 12.0 | **-** |
| PG | 5.2 | **15** | 4.5 | **-** | 12.2 | **9** | 11.0 | **-** |
| PF | 11.2 | **24** | 8.5 | **-** | 14.1 | **11** | 12.5 | **-** |
| PGF | 11.6 | **17** | 9.6 | **-** | 15.1 | **11** | 13.4 | **-** |
| PRF | 13.4 | **21** | 10.6 | **-** | 17.8 | **28** | 12.7 | **-** |
| **PFII-5** | **7.5** | **-** | **8.9** | **18** | **13.5** | **-** | **15.2** | **28** |
| PFII-24 | 9.0 | **4** | 8.6 | **-** | 13.3 | **12** | 11.7 | **-** |
| PPF | 9.8 | **11** | 8.7 | **-** | 13.2 | **12** | 11.7 | **-** |
| PGFII | 5.1 | **25** | 3.8 | **-** | 8.8 | **9** | 8.0 | **-** |
| PPR | 8.7 | **-** | 9.0 | **3** | 12.1 | **9** | 10.9 | **-** |

At 7 days, flexural strength of mortar under HAC condition, compared to the control mix (PC), increases by 13%, 143%, 152% and 190% for PG, PF, PGF, and PRF, respectively. Moreover in HWC condition at 7 days age, compared to PC mortar, the flexural strength also increased by 12%, 112%, 140% and 165% for PG, PF, PGF and PRF mortars, respectively. Generally under HAC condition, the flexural strength from ternary blended cement mortar was better than binary blended cement mortar. Particularly, mortar containing RHA and FA (PRF) obtained the highest flexural strength. Furthermore, from five group mortars investigated, the average incremental strength obtained under HAC increase by 10%, 14%, 23%, 22% and 34% when compared to HWC condition, for PC, PG, PF, PGF and PRF, respectively.

The flexural strength of PF II-24 mortars compared to the control mix (PC), increases by 48.88% and 53.48%, for HAC and HWC, respectively. Moreover, at 28 days, the flexural strength also increased by 6% and 21% for PF II-5, in HAC and HWC conditions, respectively. At 7 days age, flexural strength of mortar under HAC condition, compared to the control mix (PC), increases by 53%, 47% and 9% when POFA with FA, POFA with RHA, and 50% GGBFS with FA are used, respectively. Moreover in HWC condition at 7 days age, compared to PC mortar, the flexural strength also increased by 54% and 55%, for PPF and PPR mortars, respectively. Conversely, PGF II mortar show the strength loss by 5% compared to PC mortar under HWC condition. It is due to the low OPC used in the combination of PGF II mortar, which is only 25% of the total volume of binder. Generally under HAC condition, the flexural strength from ternary blended cement mortar was better than control mortar. Particularly, mortar containing RHA and FA (PRF) obtained the highest flexural strength.

The silica amorphous released due to the large specific surface area. Amorphous material produced high flexibility due to the rubbery domain structure. The increase in flexural strength could be due to the improvement of the bond between the cement and fine aggregate in the presence of RHA with FA which are finer than OPC (Anthiohos et al., 2014; Schmidt et al., 2012; Hasparyk et al., 2000). On the other hand, RHA and FA have a high reactivity in the form of silica amorphous as shown in SEM, XRD and FTIR tests. The silica amorphous released due to the large specific surface area. Amorphous material produced high flexibility due to the rubbery domain structure. Hydration process of pozzolan materials particularly in amorphous form reached high strength under thermal conductivity when react with calcium hydroxide (Sajedi&Razak, 2011).

Therefore, compared to the other four groups of mortar containing cementitious materials, the rate of flexural strength gained by PRF under HAC was better. Finally, as conclusion that the highest flexural strength for cementitious mortar could be only achieved under HAC condition by using combination of OPC and RHA with FA.

**4.4.2    The Water Absorption**

In order to evaluate the effect of curing conditions on the water absorption of mortar containing high volume cementitious material, a bar graph represent the results of initial (30 minutes) and final (72 hours) water absorptions at 56 days age are depicted in Figure 4.5. It has been reported that mortar with high quality usually has water absorption lower than 5% (Jumate & Manea, 2011; Castaldelli et al. 2013). In addition, it was specified that cement based materials can be classified as poor, average and good for initial water absorption values of 5% and above, 3–5% and 0–3%, respectively (CEB-FIP, 1989). Sajedi and Razak (2011) already reported that cementitious material-cement mixtures displayed lower water absorption than the OPC control mix. Therefore, It can be seen from Figure 4.7. that in the most curing conditions PC mortar absorbed water more than mortar containing cementitious materials at the beginning of the sorption.
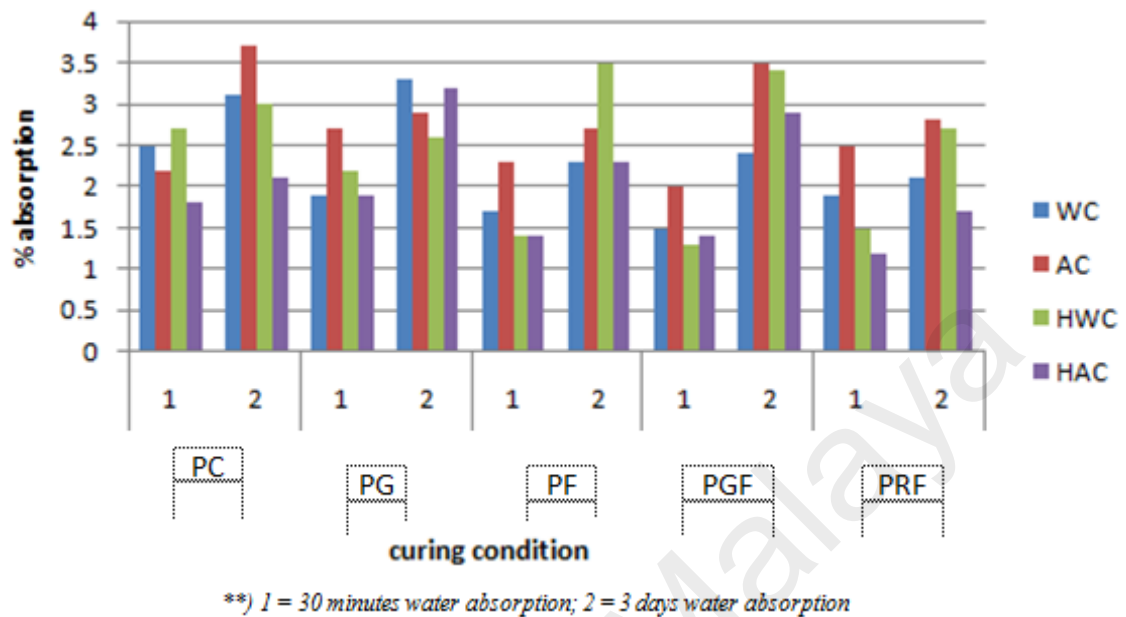
**\*\*)** *1 = 30 minutes water absorption; 2 = 3 days water absorption*

**Figure 4.7 Water absorption results of mortars in four curing conditions at 56 days**

In general, mortars containing SCMs have lower water absorption in all curing conditions compared to control mortar (PC). According to the CEB-FIP (1989) criterias, all mortars containing high volume SCMs can be considered as good quality. As can be seen from Figure 4.5 that during the initial period of water absorption, WC condition show the highest result about 2.5% for PC mortar whereas the lowest result about 1.5% for PGF mortar. The water absorption of mortars in HAC condition is lower than mortars cured under WC and AC conditions for initial absorption.

Therefore, HAC method is the effective technique to produce a denser microstructure. It is due to the heating process is one of the methods for increases the degree of hydration which caused interlocking between cement and pozzolan then released the dense mortar

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(Chindaprasirt & Rukzon, 2008; Malami & Kaloidas, 2003; Pandey & Sharma, 2000; Anthiohos et al., 2014; Schmidt et al., 2012; Hasparyk et al., 2000; Palva et al., 2009). It means that the incorporating of fineness cementitious material and HAC condition produced the dense microstructure of mortar which results better compressive strength and lower water absorption.

### 4.4.3 The Porosity

The porosity is one of the factors that affect the strength of the mortar. The number of pores contained in the mortar will greatly affect the density of the mortar itself. The porosity test results are shown in Figure 4.8.



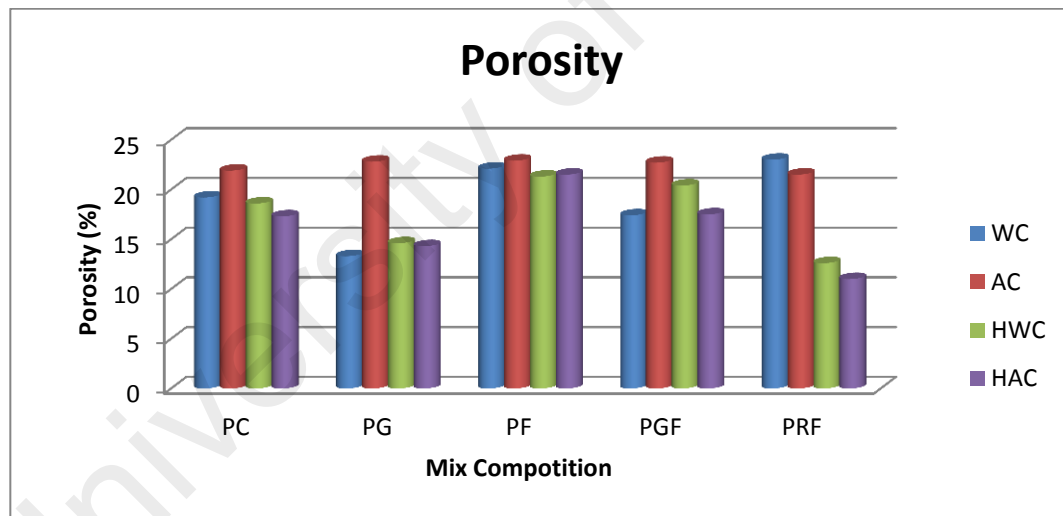**Figure 4.8 The relationship between type of mixes and percentage (%) porosity of mortar**

It can be seen that PC mortar both in water and air curing conditions without heating process have a porosity about 20% and 22%, respectively. Furthermore, mortar containing 50% of fly ash (PF) tend to obtained porosity more than 20% in all curing conditions. Malami and Kaloidas (2003) reported that the factors such as the curing

conditions, age and the degree of hydration significantly affected the total porosity of mortars, particularly in the case of OPC-cementitious mortars. Khan (2003) recommended that the particle size of cementitious materials should be finer than OPC to achieve the better performance.

The lowest porosity was attributed to PRF under HAC about 11%. While, the highest porosity results were observed in mortar containing FA by an average about 23%. It is due to the use of high volume replacement level of FA in mortar, so the interfacial zone between cement and aggregate increased and become thick. The thickness of interfacial zone will cause low dense mortar. Pandey and Sharma (2001) reported that a good compressive strength has the high dense mortar. In addition, other researchers also reported (Pandey & Sharma, 2001; Khan, 2003) that ternary blended cement produces mortars with higher strengths using heating process. Furthermore, the porosity of mortar containing two cementitious materials like RHA and FA was decreased due to the filler effect from the fineness particle of RHA and FA used. The particle size of materials influenced to the filler effect of mortar which is reduce the volume of void space between cement and aggregate. Test results show that the mortars containing any type of cementitious materials have lower porosity and consequently the strength improved when specimens cured in HAC condition. It means that HAC condition is the effective way to reactivate pozzolan in hydration process and significant reduction on the total of porosity.

Figure 4.9 represented the porosity results for PC mix, PF II-24 mix and PF II-5 mix. Mortars containing the same type of Fly ash (Type C) but they were cured under different time (duration).
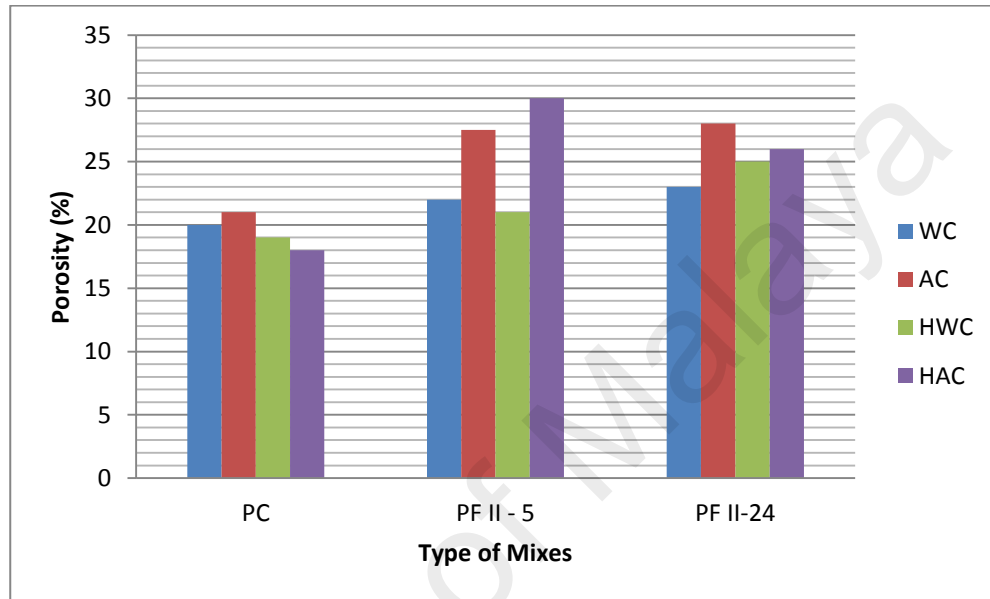


**Figure 4.9 The porosity results of mortar containing fly ash (PF II-24 and PF II-5)**

It can be seen from Figure 4.9 that PC mortar both in water and air curing conditions without heating process have porosities about 20% and 22%, respectively. Furthermore, mortar containing 50% of fly ash tend to obtained porosity more than 20% in all curing conditions. PF II-5 has lower porosity than PF II-24 under WC condition, about 5%. While, the highest porosity results were observed in PF II-5 mix by an average about 7% in AC and HAC conditions. It is due to the use of high volume replacement level of FA in mortar followed by hot water curing for short time, so the interfacial zone between cement and aggregate increased and become thick. The thickness of interfacial zone will cause low dense mortar. The particle size of materials influenced to the filler effect of mortar which is reduce the volume of void space between cement and aggregate. The presence of internal

pores in the mortar particles was mentioned in connection with the characteristics of this pores/void is very important in order to study of its properties. Malami and Kaloidas (2003) reported that the factors such as the curing conditions, age and the degree of hydration significantly affected the total porosity of mortars, particularly in the case of OPC-cementitious mortars. Hydrates consist of C-S-H and $Ca(OH)_2$ are generated through chemical reaction with cement particles and water (Ishida et al., 2007).

Neville (1995) stated earlier that the porosity of cement paste also depends on the porous of raw cementitious materials. As mentioned in Chapter 3, that the micrographs display of fly ash type II has porous spherical form after SEM test. Unfortunately, SEM results of Fly Ash type II displayed many cavities in each particles of FA. As conclusion, the relation between strength of mortar and the total voids (porosity) is found influenced by the volume of porous in cementitious materials and the exposure time (duration) when the specimens were cured under hot water of $60^{o}C$. However, it is found that the porosity performances in cementitious mortar significantly decrease with increasing age of curing. Due to the hydration process will set properly over the time, either in counting days nor months.

It can be assumed that porosity with various pore distributions which are generated in the heating process can be the main route of water and gas. Test results show that the strength improved when specimens accelerated cure in hot water for 24 hours followed by air curing condition (HAC). The effects of thermal curing time has performed that at optimum 24 h heating process, the strength of mortar increased necessarily have lower number of cavities indeed. It means that HAC condition is the effective way to reactivate pozzolan in hydration process and significant reduction on the total of porosity.

# CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

In this chapter, we tried to come up with several conclusions based on the results obtained in this study. The results from the first objective showed that local waste and by-product materials, such as ground granulated blast furnace slag (GGBFS), fly ash, rice husk ash (RHA) and palm oil fuel ash (POFA) can be used as supplementary cementitious materials (SCM) due to the required materials are rich in silicon (Si) and aluminium (Al). An increase in $SiO_2$ or $SiO_2+Al_2O_3$ content will lead to the improvement of pozzolanic reaction. The variations in the number of Si and Al were influenced by the differences in the relative amounts of carbon, ash in the samples, geographical condition and original sources. Overall, GGBFS, fly ash, RHA and POFA possesses great potential pozzolanic cementing materials with possibly superior engineering properties in proper mixing and curing systems. Furthermore, by minimizing the volume of local waste, which is disposed of landfill, will protect the environment, reduce the emission of GAGs (greenhouse gases $CO_2$) and contributes to the sustainability of eco-constructions.

The results from the second objective concluded that among ten types of mixtures, the best combination for binary blended cement is attributed to PG mix which combine 50% OPC and 50% GGBFS. OPC and GGBFS showed a similar effect in order to gain the strength due to crystalline form. While, the PRF mix which combine 50% OPC and 25% RHA with 25% fly ash is the proper combination for ternary blended cement. The appearances of the strength were slowed in the early ages and continuously for a long curing period by adding FA for more than 30%. Moreover, the utilization of RHA up to 30% will not set properly and produce a dry mix due to the pores structure of RHA. Other than that, FA and RHA

have a high reactivity in silica amorphous form. Therefore, the combination of 25% RHA with 25% FA as partial cement replacement gained the higher strength for a long period of curing. The fact shows that the type and combination of binder plays a major role in order to produce high strength mortar containing high volume cementitious materials. It is due to the chemical reaction in mortar, in terms of hydration process, which indicates that chemical composition such as $SiO_2$ and CaO (in the vicinity of the interface) is one of the major factors for the increase in bond strength. It should be noted that POFA cannot be used as binary blended cement due to its pores structure.

The result from the third objective concluded that whenever mortars cured under room temperature after initial heating process (HAC), the strengths of all mortar mixes increased with the curing duration. It is due to high relative humidity for about 85% and air temperature of $27 \pm 3^0C$ for gain the better strength. Furthermore, the thermal technique like HAC is a feasible and efficient method for accelerated the activation of ordinary Portland cement with high volume cementitious materials in mortars without utilized much water and large places to cure the specimens. This result also shows that initial heating process then following air curing (HAC) is the effective way to produce a denser microstructure of mortar containing high volume cementitious materials and consequently to achieve the higher compressive strength with lower water absorption.

In addition, the results of the fourth objective concluded that parameters such as the type of binder, initial heating process, curing conditions and curing period have important role on the mechanical and physical properties of mortar containing high volume supplementary cementitious materials. Among them, initial heating process and curing conditions were found to be the most significant variable.

In this study, ten types of mixture were analyzed to determine the optimum curing conditions in order to gain the better properties of mortar containing high volume cementitious materials. Generally, the compressive strength of mortar containing high volume cementitious material which was cured in WC is greater than cured in AC condition at early ages. The greater incremental strength was observed in PG mortar, both in WC and AC conditions. PG and PC mortars showed similarity effect in order to gain the strength at early ages when cured in WC condition. Whereas, the compressive strength of mortar containing high volume cementitious materials which was cured in HAC are higher than those of mortar cured in HWC. It is found that PRF mortar gave the highest compressive strength cured under HAC condition. While, the lowest strength is PF mortar in all curing conditions.

**5.2 Recommendations**

Based on the results of this study, there are several works that we recommend for future research. Some potential topics are:

1) We recommend the use of the waste materials as supplementary cementitious materials in increasing the value of solid waste and municipal wastes in Malaysia. If possible, the future research or study can improve the volume of SCM with more than 50% of the total volume of binder.

2) Further investigation of the possibility of using other types of siliceous waste materials for producing artificial cement/binder. The waste can be originated from many resources such as baggase ash, wood waste ash, bamboo leaf ash and so on.

3) Further work regarding the energy conservation and energy consumption should be done, due to the burning process of converting the raw waste materials to be cementitious materials. It also contributes to reducing the landfill and air pollution needed, decreasing the cost of construction as well as maintenance product, and solving several environmental problems.

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