THE EFFECT OF PALM OIL FUEL ASH (POFA) WITH LIMESTONE AS A PARTIAL CEMENT REPLACEMENT MATERIAL TOWARD CONCRETE MICROSTRUCTURE AND HYDRATION

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ABSTRACT

Malaysia as the world's largest exporter of palm oil has been facing problem in disposing palm oil fuel ash (POFA), a by-product of palm oil mills since many years ago. POFA is one of waste material that can be used as pozzolanic or fillers or replacement for the cement in concrete. This research is important to compare the effectiveness using POFA as a partial cement replacement material towards concrete microstructure and concrete hydration. The quality of POFA was improved by grinding until the median particles sizes is about 63 µm. At the first stage, each series of concrete test is design for grade 30. Four types of mixes are prepared. One consists of a control mix whereas another three consists of 20% of POFA, 20% of POFA with 5% of limestone and 20% of POFA with 10% of limestone respectively. For the compressive strength, concrete cubes 150 x 150 x 150 mm was tested due to 7 days, 28 days and 90 days of curing ages. From the testing carried out, it was found that, the compressive strength of POFA concrete was much lower than that of concrete without POFA. Although the strength of POFA concrete did not exceed the characteristic strength, the compressive strength of POFA concrete is slightly increased at 90 days. An analytical methods used to investigate the microstructure of the POFA include X-ray Diffraction (XRD), Thermogravimetric analysis (TGA) and Scanning Electron Microscopy (SEM).Based on XRD analysis leads to the fact that the existence of C-S-H increased with curing age indicating the progress of cement hydration reaction and pozzolanic reaction. From the microstructural analysis (SEM) shows the existing of C-S-H gel has lead to a densification structure and increase the strength of concrete. Hexagonal platelets of $Ca(OH)_2$ could be observed in some of samples. As a conclusion, it found that replacement of cement with 20% of POFA has achieved the pozzolanic reaction and also can improve the pore structure of the concrete.

ABSTRAK

Malaysia merupakan pengeksport terbesar di dunia minyak kelapa sawit setelah menghadapi masalah untuk menghapuskan abu bahan bakar minyak kelapa sawit hasil produk dari kilang minyak sawit sejak bertahun-tahun lamanya.Abu minyak kelapa sawit (POFA) adalah salah satu daripada bahan buangan yang boleh digunakan sebagai pozzolana atau mengisi atau menggantikan simen dalam konkrit.Kajian ini penting untuk membandingkan keberkasanan menggunakan POFA sebagai bahan pengganti separa simen terhadap mikrostruktur konkrit dan menghidratan konkrit. Kualiti POFA telah dipertingkatkan dengan mengisar sehingga zarah saiz median 63 µm. Pada peringkat pertama, setiap siri konkrit akan direka bentuk menggunakan gred 30. Empat jenis campuran telah disediakan. Satu daripadanya terdiri dari campuran kawalan manakala tiga lagi terdiri daripada 20% daripada POFA, 20% daripada POFA dengan 5% daripadanya batu kapur dan 20% daripada POFA dengan 10% daripadanya batu kapur masing-masing.Untuk kekuatan mampatan,kiub konkrit 150 x 150 x 150 mm telah direndam selama 7,28 dan 90 hari. Daripada ujian yang dijalankan, kekuatan mampatan konkrit POFA lebih rendah berbanding konkrit tanpa POFA. Walaupun kekuatan konkrit POFA tidak melebihi kekuatan yang dikehendaki, tetapi kekuatan mampatan konkrit POFA akan meningkat pada hari ke 90. Satu kaedah analisis yang digunakan untuk menyiasat mikrostruktur POFA adalah X-Ray Diffraction (XRD), analisis Thermogravimetric (TGA) dan Mengimbas Mikroskopi Electron (SEM). Berdasarkan analisis XRD, kewujudan CSH meningkat dengan menunjukkan kemajuan tindak balas penghidratan simen dan reaksi pozzolana.Dari analisis mikrostruktur (SEM) menunjukkan gel CSH telah membuatkan struktur pemadatan dan meningkatkan kekuatna konkrit. Platelet heksagon $Ca(OH)_2$ dapat diperhatikan didalam sampel. Kesimpulannya, kajian mendapati bahawa penggantian 20% daripada POFA telah mencapai reaksi pozzolana dan meningkat struktur simen.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
BS	British Standard
C-S-H	Calcium Silicate Hydrate
$Ca(OH)_2$	Calcium Hydroxide
LOI	Loss of Ignition
MS	Malaysian Standard
OPC	Ordinary Portland cement
POFA	Palm oil fuel ash
PFA	Pulverize fuel ash
w/c	water cement ratio
SO_3	Sulphur Oxide
Na_2O	Sodium Oxide
SiO_2	Silicon Dioxide
Al_2O_3	Aluminium Trioxide
Fe_2O_3	Ferric Oxide
C_2ASH_8	Calcium Aluminium Silicate Hydrate
C_4AH_{13}	Calcium Aluminate Hydrate
$CaCO_3$	Calcium Carbonate
SEM	Scanning Electron Microscopy
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDIES

Concrete is one of the oldest manufactured construction material used in construction of various structures globally until today. Concrete is a material where mixture by cement, water, and aggregate (fine and coarse) which must be workable, resistance to freezing, chemicals resistance, low permeability, wear resistance and economy (Metha et al.,2006).It is must environmental friendly construction materials with offer the stability and flexibility in designing all building structures.

However, the uses of these waste material products like fly ash, rice hush ash and silica fume is not only one of the solutions to the environmental and ecological problems. Some of this product also already shown a very effectively in improving the concrete microstructure and consequently achieved the durability properties of concrete by use the pure Portland cement (Galau et al., 1996)

Nowadays, the use of recycled materials as concrete ingredients is gaining popularity and development because of increasingly stringent environmental legislation. Furthermore, there is significant research on many different materials for cement usage substitutes and replacement such as palm oil fuel ash (POFA), pulverize fuel ash (PFA) and many others fibre and pozzolanic material. Since Malaysia is second largest producer in palm oil industry, the wastage of the palm oil can be used to replace in small amount of cement.

This industries produce waste from burning palm oil shell and husk that namely as POFA. POFA is one of waste that can be used as fillers or pozzolanic or replacement for cement in concrete. According to (Tangchirapat et al., 2009) POFA is one of agro waste ashes whose chemical composition contains a large amount of silica and high potential materials that can be used as a cement replacement. There are many experimental works that conducted by introducing recycled material likes palm oil fuel ash (POFA) as a replacement of cement with different percentage to improve the properties of concrete.

POFA is produced by the palm oil industry due to the burning of EFB, fibre and OPS as fuel to generate electricity and the waste, collected as ash to become POFA. About 3 million tons of POFA was produced in Malaysia at 2007 and 100,000 tons of POFA is produced annually in Thailand. In Thailand, POFA is produced from a biomass power and this by-product is still disposed of as waste in landfills. Due to the increasing disposal costs, the utilization of POFA is an important issue for the industry and the public to landfills environmental problems.

1.2 PROBLEM STATEMENTS

Generally, the waste of palm oil from the palm oil industries was increasing eventually. It is become a major problem to palm oil power plants because this wastage from palm oil are not reused and recycle in any works in order to utilize these waste materials as an active pozzolanic admixture. These pozzolanic admixtures are used for reducing the Portland cement content in mortar and concrete production. Many studies have been emphasized that the positive effects exerted by such pozzolanic admixtures on properties of Portland cement mortar and concrete. Besides that, when the admixtures is added is also could improve the sulphate resistance of the Portland cement mortar and concrete. However, what can be expected in a specific situation will depend on the mineralogical and chemical composition of the mineral admixture.

Therefore, the excess industrial ashes remain to disposed of in landfills which cause the environmental problems. The carbon dioxide emission from the production process can give greenhouse effect to the worldwide. So that, treated POFA on pozzolanic activity and microstructure can lead to be useful in protecting the environment by minimizing the volume waste disposed on the wasteland.

It is important to do research on the effect of POFA with the new replacement of cement materials that can reduce the amount of cement in the construction project. However, in general this research is very important in order to know whether the POFA concrete with lime added will produce a higher strength and higher workability of concrete towards concrete hydration and concrete microstructure.

1.3 OBJECTIVE OF STUDY

The objectives of the study are:

a) To investigate the effect of palm oil fuel ash (POFA) with limestone towards concrete hydration.
b) To investigate the effect of palm oil fuel ash (POFA) with limestone towards concrete microstructure.

1.4 SCOPE OF STUDY

This study concentrated on investigation of concrete microstructure and concrete hydration of palm oil fuel ash (POFA) concrete and plain concrete as a control mix. Each series of concrete will be design for grade 30 with constant water cement ratio (w/c) of 0.54 was conducted. For the plain concrete consist of cement, water, aggregate and sand was considered as a control mix without replacing with POFA (POFA – 0%). Three series of concrete mix design with POFA as cement replacement were consist as an unconventional mixes comprises of 20%, 20% POFA with 5% limestone and 20% with 10% limestone from the total weight of ordinary Portland cement. The POFA concrete was labelled as POFA-20%, POFA-20% + lime-5% and POFA-20% + lime-10% respectively.

After designation of the mix proportion, the concrete were cast and poured into the standard mould with dimension of 150 mm x 150 mm x 150 mm. The concrete was taken out from the mould after 24 hours concrete hardened. Then, the hardened concrete was cured in water for 7, 28 and 90 days for all mixes. The compressive strength tests were conducted after the specimens matured due to curing period for entire specimens. The testing is followed as accordance to BS1881: Part 119: 1983.

For the development of compressive strength of POFA will be investigated using three techniques which is Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Thermogravimetric Analysis (TGA). A small amount of the sample will be used during the experiment occurs. Other than that, analysis POFA concrete monitored by X-Ray Diffraction was applied to identify the peak pattern of C-S-H after 90 days. The hydration products were determined through the length intensity of C-S-H collected by X-Ray scans recorded as intensity in unit counts. For Scanning Electron Microscope is to determine the chemical compound and microstructure of POFA concrete. For Thermogravimetric Analysis used to measure weight loss were exposed gradually to temperature. From the microstructure analysis it proved that a change on the microstructure between control mixture and POFA concrete with 28 days and 90 days because of increases C-S-H. In hydration process, cement will react with water to form calcium silicate hydrate or simply defined as C-S-H and calcium hydroxide.

1.5 SIGNIFICANT OF STUDY

Concrete is one of the important materials used in construction. Many methods have been used to modification and developments the waste materials such as POFA as a cement replacement. This research is to investigate and proposed another way as an alternative to revealed that the replacements of POFA in Ordinary Portland cement can increases setting time of paste.

One of the main goals is sustainable development of the cement and concrete industry. Sustainable design and construction of structures have a small impact on the environment. Using of recycled materials can embodies low energy costs. High performance of cements and concrete can reduce the amount of cementations materials and total volume of concrete required. Reuse of post-consumer wastes and industry by-products in concrete is necessary to produce a replacement concrete. At the same time, recycled concrete also can improve air quality, minimizes solid wastes and leads to sustainable cement and concrete industry.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Palm oil industry is one of the most important an agro industries in Thailand. Besides that, the production of crude palm oil is a large amount of solid waste and also an output from the palm oil industry. Annually, more than two million tons of solid waste of palm oil residue such as palm fibre, shells, and empty fruit bunches are produced (Office of Agricultural Economics, 2002). Utilization of palm oil fuel ash (POFA) is minimal and unmanageable, while its quantity increase annually and most of the POFA is disposed of as a waste in landfills that can cause environmental problems.

Awal et al., (2011) was defined that the physical and chemical analysis POFA is a good pozzolanic material. It is because POFA sample contain higher percentage of silica which is two times the silica content of the OPC. Therefore, it is beneficial to the strength of development of POFA concrete. There are many experimental works conducted by introducing cycle material like POFA as a partial cement replacement of cement with different percentages to improve the properties of concrete.

2.2 ORIGIN OF POFA

Palm oil fuel ash is a by-product in palm oil mill. After palm oil is extracted from the palm oil fruit, both palm oil husk and palm oil shell are burned as fuel in the boiler of palm oil mill. Generally, after combustion about 5 % palm oil fuel ash by weight of solid waste is produced (Sata et al., 2004)The ash sometimes varies in tone of colour from whitish grey to darker shade based on the carbon content in it. In other words, the physical characteristic of POFA is very much influenced by the operating system in palm oil factory.

Besides that, POFA produced in Malaysia palm oil mill is dumped as waste without any profitable return (Sumadi et al., 1995). Either in 20th or 21st century, POFA is still considered as a nuisance to the environment and disposed without being put for any other use as compared to the other type of palm oil by-product. Since Malaysia is continuous to increase the production of palm oil, therefore more ashes will be produced and failure to find any solution in making use of this by-product will create severe environmental problems.

2.3 CHEMICAL COMPOSITION OF POFA

In Table 3 below the data presented that the OPC and POFA possess similar characteristics. It can be seen that the POFA sample contains higher percentage of silica which is two times the silica content of the OPC. Obviously, the presence of higher silica content influences the pozzolanic reaction when it reacts with free lime that can create extra C-S-H gels, which is beneficial to the strength of development of the POFA concrete. But the alumina content of the OPC appears to be twice those of POFA, while the iron content of OPC and POFA fall on the same percentage range. The sum of silica, aluminium and iron oxide of POFA is 67.18% which is below 70% and makes this pozzolanic material to be classified as Class C pozzolan in ASTM C618-05 (Sooraj, 2013; Awal et al., 1997; Tangchirapat et al., 2009 and Chindaprasirt et al. 2008). However, the higher percentage of LOI and low calcium oxide content of less than 5%, a maximum SO_3 content of 5% and maximum alkali content (expressed as Na_2O) of 1.5%, make this ash fall into class F but not class C, as enlisted in ASTM C618-05 (Awal et al., 2011). The main component of the treated POFA is Silicon Dioxide (SiO_2), Al_2O_3 and Fe_2O_3 which indicates that the chemical composition of treated POFA was well within the specification set by ASTM C618-05.

Table 2.1: Chemical composition of OPC and POFA

Chemical Composition	**Percentage (%)**	
	POFA	**OPC**
Silicon Dioxide (SiO_2)	42.24	23.00
Aluminium Trioxide (Al_2O_3)	4.48	4.00
Ferric Oxide (Fe_2O_3)	6.09	3.50
Potassium Oxide (K_2O)	7.76	0.51
Magnesium Oxide (MgO)	4.02	1.23
Calcium Oxide (CaO)	5.63	64.00

2.4 PARTICLES SIZE DISTRIBUTION

It is a well-known fact that the increase in the fineness of pozzolana material would lead to significant increase in strength. The extremely fine particles in concrete acts as lubricant in the concrete mix and permit a reduction in water content, thereby increasing strength. Therefore, the ashes spheres with their multi sized spherical morphology promote a high packing density of plastic concrete. The influence of ash fineness towards strength development of concrete has been investigated by many researches. The fineness of pozzolanic ash also tends to affect both the fresh and hardened state properties of concrete (Hussin, 2009). Generally, the ash used as pozzolanic materials need to produce in a finer size so that can function effectively in increasing the strength of concrete. The particles size distribution of materials is shown in Figure 2.1.

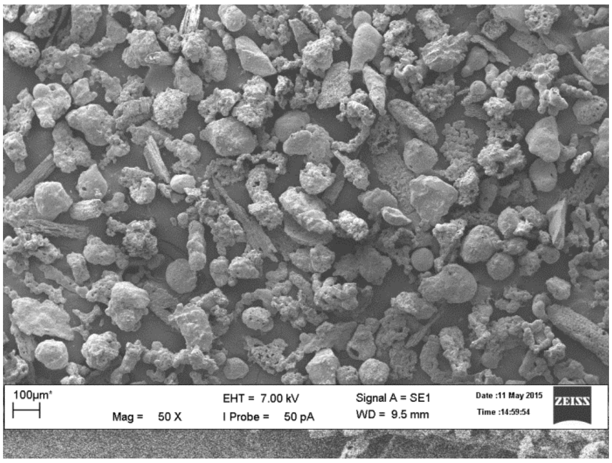

Figure 2.1: Scanning Electron Microscopy (SEM) of POFA

2.5 STRENGTH AND DURABILITY OF POFA

In this research, it was shown that the replacement of POFA's in concrete mixtures as binders will cause the rate of early strength increased and becomes slower at later age. This is because calcium hydroxide content from hydration process was diminished through reaction with silica dioxides compositions in pozzolans. The efficiency of this mechanism applies to the chemical compositions of pozzolans. This mechanism is clearly seen in earlier pozzonalans reaction observed by various researches. However, this mechanism is become more complicated and relies upon many factors such as microstructures and chemical composition. There are optimum amounts of cement replacement that can obtain a higher pozzolans concrete strength as another essential chemical composition and heat exerted from hydration process in OPC.

2.6 POZZOLANIC AS CEMENT SUBSTITUTES

Pozzolanic is a finely ground siliceous material which does not possess cementitious properties in itself but can be only take place with the existence of calcium hydroxide, $Ca(OH)_2$ that is produced from hydration process reacting with pozzolanic material in the presence of moisture. When the pozzolanic material reacts with calcium hydroxide, $Ca(OH)_2$ in the presence of moisture, Calcium Silicate Hydrate will be formed. Many studies have proven that the integration of pozzolanic materials as a partial cement replacement or filter material for production concrete can improves the properties of concrete in terms of strength and durability (Sivasundaran et al., 1999). Pozzolanic materials cause reaction which large particles fly ash physically because refinement of pore structures and result for the structure of the concrete become highly impermeable and denser than original. This material is commonly used as a partial replacement of cement which is to make concrete mixtures more economical, increase the strength and other concrete properties.

2.7 STRENGTH OF POZZOLANIC IN CONCRETE

Pozzolanic concrete has one of the primary benefits which are to increase compression strength of concrete and it is used essential to achieve a cost effective high strength concrete. For example, both slag and fly ash retard early hydration and reduce early to gain strength but it continues to hydrate and gain the strength for 90 days onwards. Silica fume contributes the most strength development between 3 and 28 days. It also can add fly ash cement mixes to improve early strength. Based on short-term investigation, the early ages of POFA concrete are weaker, but at the age of 28 days the development of compression strength is relatively high.

According to ASTM C618 (2001) defined that pozzolanic material as a material that contains siliceous or aluminous material by composition. POFA concrete gain maximum strength when 30% of cement was replaced with POFA. It is reported that the maximum strength gain occurred at the replacement level of 30% but further increase in the ash content wound reduce the strength of concrete gradually (Galau et al., 1996) . However, the result of POFA performance once added with lime in concrete still yet to study.

2.8 MICROSTRUCTURAL CHARACTERISTICS

Concrete microstructure was studied using Scanning electron microscopy (SEM), X-Ray Diffraction (XRD) and Thermogravimetric Analysis (TGA). The tests were conducted after 28 and 90 days of curing to estimate the hydration products. Analyses using SEM, XRD and TGA were performed to assess the reaction with Calcium hydroxide.

Scanning Electron microscopy (SEM) was used to investigate the present of the pozzolanic material (eg:POFA). The accelerating voltage of the SEM machine was operating at 10 kV and the magnification of X100 is used to capture photo of the samples. XRD analysis was carried out in terms of qualitative values. The analysis was based on the intensity of the peak corresponding to $Ca(OH)_2$ in the samples. Thermogravimetric analysis (TGA) is defined as the technique whereby the mass of a substance in a heated environment is recorded at a controlled rate as a function of time or temperature. In additional, TGA is more suitable for studying the hydration or pozzoalanic reaction that takes place at later stages. The hydration products were also examined by SEM to understand the paste morphology.

2.9 CURING LENGTH

Curing is one of the most important steps that need to be applied to exploit all potential of the cement used in the concrete mix. This process provide that an environment where temperature and moisture loss from and into the concrete is controlled. This process is essential for promoting the hydration of cement to ensure that the strength of development of concrete. The hydration of Portland cement is the chemical reaction between grains of Portland cement and water to form the hydration product and cement gel. Hydration also can proceed until all the hydration products are filled by cement gel until limit is reached first. However, curing pozzolanic concretes or mortars need more care compared with Portland cement. The strength development of concretes containing pozzolanas is more adversely affected by very short curing periods under water than the plain one (International & Specification 2000)

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

This chapter explains the materials used and the test methods followed in the conducting of various experimental investigations. At the beginning, the collection of Palm Oil Fuel Ash and its preparation are presented in detail. Following, the other materials such as cement are presented. Then this is followed by the preparations of control concrete and other POFA concrete. The test procedures for evaluating properties are also presented. It is important to mention that the methodologies followed in the current research are based on fully experimental investigations.