

PERPUSTAKAAN UMP



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EFFECTS OF PULVERIZED FUEL ASH AS CEMENT REPLACEMENT  
MATERIAL TOWARD CONCRETE MICROSTRUCTURE

NOR LIYANA BINTI SURAINI

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087850

Faculty of Civil Engineering and Earth Resources  
University Malaysia Pahang

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## ABSTRACT

The Pulverized Fuel Ash (PFA) is known as pozzolanic material and can be used as cement replacement material in the concrete in order to improve concrete properties. The use of PFA in concrete manufacture has reduced the disposal issue and can reduce cement consumption which is cut down the emission of the carbon dioxide, CO<sub>2</sub> as well as to reduce environmental problem caused by production of cement. This study has designed to determine the potential of PFA as cement replacement material in concrete, which are to determine the effectiveness of PFA toward compressive strength and its effect to concrete microstructure. X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM) were used to study the concrete microstructure development base on concrete age and curing period. The result of compressive strength indicates the optimum percentage of PFA as cement replacement is about 20% has increased the strength of concrete. The XRD and SEM have shown concrete with different percentage of PFA produced different intensity of C-S-H. It were shown that, the replacement of PFA as cement replacement can contribute to the different properties of concrete that can lead to concrete quality improvement. As conclusion, the PFA has the potential to be used as a cement replacement material in concrete because it will increase the strength and durability of concrete by improving the structure of the microstructure. However, the percentage of its replacement should be set and monitor to avoid a reduction in the level of quality required.

## ABSTRAK

Abu Bahan Api yang terhancur (PFA) telah dikenalpasti sebagai bahan pozolana dan boleh digunakan sebagai bahan gantian simen di dalam konkrit untuk memperbaiki kualiti konkrit. Penggunaan ini mampu mengurangkan masalah pembuangan sisa yang terhasil dan seterusnya mengurangkan pelepasan karbon dioksida, CO<sub>2</sub> yang menjadi masalah alam sekitar disebabkan oleh pengeluaran simen. Tujuan kajian ini ialah menggunakan PFA sebagai bahan gantian simen di dalam konkrit dan seterusnya mengkaji keberkesanan PFA terhadap kekuatan mampatan dan kesan terhadap mikrostruktur konkrit. Pembelauan sinar-X (XRD) dan Pengimbasan Mikroskop Elektron (SEM) digunakan untuk melihat dan menilai pembentukan mikrostruktur dan CSH di dalam konkrit. Hasil daripada kekuatan mampatan menunjukkan peningkatan dengan peratusan optimum PFA sebagai pengganti simen adalah 20%. Umur konkrit yang panjang telah meningkatkan aktiviti pozolana dengan mengurangkan keliangan konkrit. Keputusan XRD menunjukkan menunjukkan intensiti berbeza kristal CSH manakala SEM menunjukkan kandungan padat kalsium hidroksida dalam konkrit. Secara kesimpulannya, PFA mempunyai potensi untuk digunakan sebagai bahan gantian simen di dalam konkrit kerana ia akan meningkatkan kekuatan dan ketahanan lasakan konkrit dengan memperbaiki struktur mikrostrukturnya. Walaubagaimanapun, peratusan pengantiannya perlu ditetapkan bagi mengelakkan penurunan tahap kualiti yang diperlukan.

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Background of Study

The amount of pulverized fuel ash generated by electric power plant in Malaysia is increasing year by year in Malaysia. According to the statistic reported for years 1987 – 1989, 415 million tons of pulverized fuel ash ash (PFA) was produced all over the world. Only 16 % of the totals were utililised in construction sector (Baykal & Doven, 2000).

In this research is to study possibility of self healing concrete using PFA cement systems. Actually, PFA also known as fly ash. Fly ash is the particle of inorganic, incombustible matter present in the coal from the combustion of coal in electric generating plants. Fly ash is spherical and its size in range 2 $\mu$ m to 10 $\mu$ m and usually, fly ash consist of silicon dioxide (SiO<sub>2</sub>), Aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) and iron oxide (Fe<sub>2</sub>O<sub>3</sub>).

Coal fly ash or PFA is one of the by-products of coal-fired power plants. The coal fly ash produced by the power stations generally takes the form of an almost inert fine gray sand-like material deriving coal during deposition. Coal is burned at temperatures of around 1600°C in the power station boilers, and the ash thus formed

consists largely of glassy spherical particles of silica, alumina and iron oxide. (Thornely, 1988).

Fly ash is a pozzolanic materials that reacts with  $\text{Ca(OH)}_2$  for cement hydration. The factors are compressive strength, the hydration of cement and fly ash and hydrated products such as C-S-H gel and  $\text{Ca(OH)}_2$ . Concrete also has the ability in healing the cracks in its own. The gel produced seal the micro cracks and concrete made with cement and fly ash can show self-healing ability. Self healing concrete crack yield more durable long term concrete because concrete contains fly ash become denser, strong, compared to Portland cement mixtures. Concrete healing occurs in presence of water because chemical reaction of compounds vulnerable at cracks surface.

PFA improves various properties of concrete such as long term compressive strength, permeability and resistance to chloride diffusion. Strength improvement in the concrete in term of pozzolanic reaction and permeability because reduce the porosity and refinement of the microstructure. Reducing in porosity can reduce ingress water into the concrete. PFA also act as pozzolan to enhance the strength and durability properties. The hydration products like calcite, analcimes amd zeolites. The higher compressive strength of concrete is essential in improving the scaling resistance of concrete. Actually, at early age strength of concrete is decrease because of replacement of the pozzolana for Portland cement and addition of this pozzolana promotes the hydration of the Portland cement. (Gebler and Klieger,1986)

Formation of C-S-H particle in the concrete can tend the concrete heal the crack by itself. The cracks in the concrete are form from the formation of the etteringite. Self-healing means concrete is emphasizes that the concrete heals without any help from outside. The three main processes of autogenous healing according to Joseph (10) are (i) swelling and hydration of cement pastes; (ii) precipitation of calcium carbonate crystals, and; (iii) blockage of flow paths due to deposition of water impurities or movement of concrete fragments that detach during the cracking process.

The reaction products formed during the hydration of pozzolanic cements are the same as those occurring in portland cement pastes, although differing in content. They are:

- tetracalcium aluminate hydrate (often carbonated),
- monosulphoaluminate,
- C-S-H,
- $\text{Ca(OH)}_2$
- ettringite,

The hydration of alite is accelerated by the presence of pozzolanic materials. The formation of C-S-H is so rapid that is already visible after 24 hours and it is even more rapid if pozzolana is made up of microsilica. The hydration of both  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  is associated with the formation of portlandite. In pozzolanic cements, besides the C-S-H which is formed due to the hydration of clinker silicates, the C-S-H originating from the reaction between pozzolana and hydrolysis lime also occurs. The composition of this C-S-H is different from that originating from  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$ , the reason being due to different conditions of formation. In pozzolanic cements the C-S-H has a lower C/S ratio and alumina content greater than that of Portland cement pastes composition. This conclusion is supported by the different degree of polymerization of the silicate anion, greater in pozzolanic cement than in Portland cement pastes.

The presence of pores can adversely affect the material's mechanical properties such as failure strength, elasticity and creep strains. This is because of particle shape of fly ash very small make it able to fill the voids in concrete resulting increasing concrete's durability. Furthermore, fly ash in concrete also important for protecting of reinforcing steel. Fly ash can produce denser concrete that requires less water for installation, also produce more cementitious paste and concrete produced is stronger. Fly ash lowers the heat of hydration, reduce shrinkage and thermal cracking. By using fly ash in concrete can reduce environment impact because if sending it to a landfill, it is potential for the metal to leach into the environment.

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. SEM is a microscope that uses electrons instead of light to form an image. For this project, SEM used to examine and analysis the microstructure characteristics of the concrete. So, by using SEM, we can see the chemical compound such as C-S-H after some period. Formation of C-S-H proves that pozzolanic reaction occurs in the concrete.

X-ray Diffraction (XRD) used to study the mineral structural in the cracks. X-ray diffraction also used to determine the presence of a specific mineral in structure. XRD enables in identification of a crystal phases and more specifically enables the determination of interplanar spacing between parallel planes and thus the Miller indices of these finally it can be used for quantitative analysis. 100 p.p.m. The crystalline components in the powder provided that contain crystals can be identified using XRD. The patterns of XRD just like a finger print of a particular crystal. Based on this study is find the crystalline named calcium silicate hydroxide, XRD cannot be used to give quantitative analysis and very difficult to identify. So, XRD only can give the information from the crystalline components of cementitious materials like minerals and inorganic compounds.

In environment aspects, the utilization of cement causes pollution to the environment and reduction of raw material (limestone). The manufacturing of OPC requires the burning of large quantities of fuel and decomposition of limestone, resulting in significant emissions of carbon dioxide (Kong and Sanjayan, 2008). Based on other investigation, cement concrete also can emit nitrous oxide from burning of gasoline, coal and other fossil fuels, particulate air emissions, visual pollution resulting from quarries to gain raw material for cement production, adverse health effects and so on.

Many researches have been done about fly ash as cement replacement material in concrete. As the result, fly ash reduces environmental impacts of CO<sub>2</sub> production and air pollution by displacing a large percentage of cement in concrete.

## **1.2 Problem Statement**

Concrete is one of the most widely used materials in construction. In designing a concrete structure, one of the most important properties which have to be considered, besides the ability of the structure to resist all loads, is its durability. The service life and durability of a concrete structure strongly depend on its material transport properties, such as permeability, sorptivity, and diffusivity which are controlled by the microstructural characteristics of concrete. It is known that the porosity and pore size distribution are the critical components of the microstructure of hydrated cement paste that influence durability.

In order to achieve high strength, low permeability, and durable concrete, it is therefore necessary to reduce the porosity of cement paste. It is well known that the incorporation of pozzolanic materials as partial replacement of cement refines the porosity and pore size distribution of the paste. Fly ash is known to be a good pozzolanic material for use in concrete, and many researches have established its effect on the physical properties and pore structure of concrete.

### **1.3 Objective of Study**

The objectives of this study are

- i. To study the effect of concrete compressive strength of Pulverized Fuel Ash (PFA) as cement replacement material.
- ii. To study the effect of PFA as cement replacement material toward concrete porosity.
- iii. To determine the microstructure of the concrete containing PFA monitored by X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM).

### **1.4 Scope of Study**

This study is to investigate the compressive strength of the concrete containing PFA and control concrete mix. Water cement ratio is constant which 0.5 is. The control mix contains cement, water, aggregate and sand only. Control mixes not consist of PFA. The concrete containing PFA as cement replacement which are 10%, 20% and 30% of the total weight of Portland cement. The concretes are labeled as PFA-0%, PFA-10%, PFA-20% and PFA-30%.

The concrete are mix and hardened for 24 hours. After that, the concrete are taken out from the mould and cured in the water for 7, 28 and 90 days. The entire

specimens undergo compressive strength according to water curing period. The compressive strength test according to BS 1881 : Part 119 : 1983.

Durability test for these concrete is porosity test. The concrete age 28 days and 1 year are conducted for porosity test. The concrete are vacuum, submerged in water, dry in oven and buoyancy. This test is conducted accordance to ASTM C 642, 2002.

### **1.5 Significant of the Study**

CO<sub>2</sub> emitted almost a ton for every ton of cement produced. Major CO<sub>2</sub> emits causing global warming. 480 kg of CO<sub>2</sub> emitted per cubic meter of concrete or 20kg of CO<sub>2</sub> per 100kg of concrete produced. 7% of the total CO<sub>2</sub> of all of this amounts generated worldwide. Replacement of some the cement by cementing material or fly ash not associated with CO<sub>2</sub> emission significantly reduces these emissions.

It is generally recognized that the incorporation of pozzolanic materials as a partial replacement for Portland cement in concrete is an effective means for improving the properties of concrete. Pozzolanic materials react with calcium hydroxide during hydration reaction and forms calcium silicate hydrate. This can reduce the size of the pores of crystalline hydration products, make the microstructure of concrete more uniform and improve the impermeability and durability of concrete. These improvements can lead to an increase in the service life of a concrete structure

## **CHAPTER 2**

### **LITERATURE RIVIEW**

#### **2.1 Introduction**

Nowadays, there is an alternative way for the durability of the concrete which replace some cement with fly ash or known as Pulverized Fuel Ash. Pulverized Fuel Ash also contains some chemical to form C-S-H product in concrete and able to seal concrete cracks and as fill the pores in concrete. Cracks happen when shrinkage due to improper drying, contraction due to changing weathers patterns and the embedded metal in cement damage and pores in concrete is due to aggregates in concrete.

Fly ash is one of the most extensively used by-product materials in the construction field resembling Portland cement (Pfeifer, 1969). It is an inorganic, noncombustible, finely divided residue collected or precipitated from the exhaust gases of any industrial furnace (Halstead,1986). Most of the fly ash particles are solid spheres and some particles, called cenospheres, are Hollow (Kosmatka et al., 2002).

There are two reaction can happen in concrete which are hydration process and pozzolanic reaction. Hydration process is the reaction in the concrete to produce calcium

hydroxide ( $\text{Ca}(\text{OH})_2$ ) and Calcium Silicate hydrate (C-S-H). Then, pozzolanic reaction is the process involve  $\text{Ca}(\text{OH})_2$  and convert to C-S-H in presence of water. C-S-H product formed can make the concrete more durable and increase in strength.

## **2.2 Particle of Pulverized Fuel Ash (PFA)**

American Society for Testing and Materials (ASTM) C 618 defines two classes of fly ash based upon chemical and physical characteristics. ASTM C 618 Class F fly ash must contain a sum of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  contents equal to or greater than 70% by mass, while Class C fly ash must contain a sum of the same constituents equal to or greater than 50% by mass. However, the classes are commonly distinguished based solely upon CaO content, which may approach 20% for Class F ashes and 30 to 40% for Class C. The increased CaO content in Class C fly ashes may be attributed to the presence of lime, crystalline tricalcium aluminates, belite, and/or alite.

Schlorholtz et al. monitored the physical and chemical properties of fly ash produced at one electric generating station over a period of 2 years. The bulk chemical compositions of the ash samples did not differ greatly over the sampling period; however drastic differences in physical performance were observed. Hydrated specimens of fly ashes sampled at different dates yielded vastly different compressive strengths. These differences were assumed to be a function of phase mineralogy.

Because of their fly ash spherical morphology, when using fly ash admixtures as replacement for cement, workability and long-term strengths are achieved in concretes. In such cases, they act like small balls to reduce interparticle friction. Fly ashes are also used in concrete mixes in order to reduce the heat of hydration, permeability, and bleeding. The durability is improved by providing a better sulfate resistance, control of

the alkali-silica reaction, decreased chloride diffusion, and reduction of leaching from the reduction in calcium hydroxide (which is the most soluble of the hydration products) and changes in pore structure. However, there are some disadvantages related to the use of fly ash regarding the reduced air-entraining ability and early strength due to the influence of residual carbon from the ash (Gebler and Klieger, 1986).

Fly ash also present are plerospheres, which are spheres containing smaller spheres inside. The particle sizes in fly ash vary from less than 1  $\mu\text{m}$  to more than 100  $\mu\text{m}$  with the typical particle size measuring under 20  $\mu\text{m}$ . Their surface area is typically 300 to 500  $\text{m}^2/\text{kg}$ , although some fly ashes can have surface areas as low as 200  $\text{m}^2/\text{kg}$  and as high as 700  $\text{m}^2/\text{kg}$ . Fly ash is primarily silicate glass containing silica, alumina, iron, and calcium. The relative density or specific gravity of fly ash generally ranges between 1.9 and 2.8 and the colors are generally gray or tan (Halstead, 1986).

## **2.3 C-S-H in Concrete**

### **2.3.1 Pozzolana Effect**

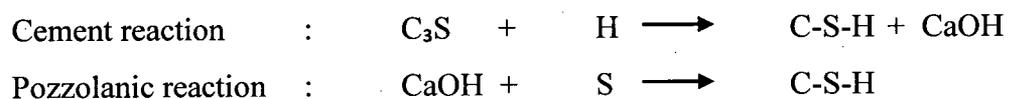
Pozzolanic reaction is the chemical reaction that occurs in hydraulic cement where the calcium hydroxides react with amorphous siliceous then forming non-soluble calcium silicate hydrates gel. Pozzolanic reaction occurs in water due to presence of fly ash in cement. Fly ash continues reaction of hydrate of cement. Ozer and Ozukul reported about the result of the influence of initial water curing on the strength development of ordinary Portland cement and pozzolanic cement concretes. They concluded that poor curing conditions more adversely affects the strength of concrete made from pozzolanic cement than that of ordinary Portland cement.

## Cement Hydration

Calcium hydroxide forms as a by-product in the hydration process of Portland cement. Calcium hydroxide (15-25 % by amount of cement) is a weak and soluble material that does not contribute to the strength or the durability of the concrete.

## Pozzolanic Reaction

Microsilica reacts with this calcium hydroxide. This creates an increased amount of CSH binder. Size of the micro silica particles is very fine. The microstructure formed by this reaction is also very fine and fills the void spaces within the matrix. This densifies the concrete, resulting in increased strength and a significant reduction in permeability.



*Figure 2.1: Chemical Equation of Pozzolana Hydration*

### 2.3.2 Mechanisms of C-S-H

Natural pozzolan heal or re-cement within the concrete which means of the continuation of pozzolanic reaction with the calcium hydroxides from cement hydration reaction. Then, the result is the filling up the most of the gaps in the hardened concrete matrix. Holt and Leivo have reported that both drying and autogenous shrinkage could be significant in certain early age scenarios.

The hydrated product, C-S-H gel can make the concrete denser, strong and durability.

#### Causes of self healing

- i. Formation of the calcium hydroxide or calcium hydroxide
- ii. Sedimentation of particles
- iii. Continuing hydration
- iv. Swelling of cement matrix

#### Condition for self healing

- i. Presence of water
- ii. Cracks width
- iii. Water pressure

### 2.4 Strength of Concrete containing PFA

Gopalan also evaluated the gel/ space ratios of fly ash concrete mixes from their compressive strength, assuming that the correlation between gel/space ratio and compressive strength for fly ash concrete was the same as for Portland cement

concrete. In addition to economic and ecological benefits, the use of fly ash in concrete improves its workability, reduces segregation, bleeding, heat evolution and permeability, inhibits alkali-aggregate reaction, and enhances sulfate resistance. Even though the use of fly ash in concrete has increased in the last 20 years, less than 20% of the fly ash collected was used in the cement and concrete industries (Helmuth 1987).

Strength of fly ash concrete is influenced by type of cement, quality of fly ash, and curing temperature compared to that of non-fly-ash concrete proportioned for equivalent 28-day compressive strength. Concrete containing typical Class F fly ash may develop lower strength at 3 or 7 days of age when tested at room temperature (Admixtures and ground slag for concrete, 1990; ACI Comm. 226 1987c). However, fly ash concretes usually have higher ultimate strengths when properly cured. The slow gain of strength is the result of the relatively slow pozzolanic reaction of fly ash. In cold weather, the strength gain in fly ash concretes can be more adversely affected than the strength gain in non-fly-ash concrete. Therefore, precautions must be taken when fly ash is used in cold weather (Admixtures and ground slag 1990).

## **2.5 Durability of the Concrete**

### **2.5.1 Decrease in Porosity**

The microstructure of concrete and natural building stones has significant influence on their physical and mechanical properties and on their durability.

The majority of pores in porous concrete are formed by the spaces left between coarse aggregates and they distinguished between porosity and air void content. In their

research, the fraction of measureable voids migrated by fluids in their experiments was termed porosity and the sum of measureable voids between aggregates plus entrained or entrapped air in the cement paste was termed air content. In other words, the porosity of porous concrete could be defined differently. In this study, for clarity, the measureable voids are defined as the effective porosity since this relates to permeability and the overall air content is accordingly defined as total porosity. (Ghafoori and Dutta)

### **2.5.2 Hydration in Concrete**

In a pioneering work, Powers and Brownyard (1948) were the first to systematically investigate the reaction of cement and water and the formation of cement paste. In the late 1940s they presented a thorough model of the cement paste, in which unreacted water and cement, the hydration product, and (gel and capillary) porosity were considered. Via extensive and carefully executed experiments major paste properties were determined such as the amount of retained water and the chemical shrinkage associated with the hydration reaction. These properties were furthermore related to the content of the four most important clinker phases, viz. alite, belite, aluminate and ferrite, in the cement. Locher (1975), Hansen (1986), Taylor (1997), Neville (2000) and Brouwers (2003) summarise the most important features of their work.

The hydration of cement-based materials leads to a continuous decrease in the amount of porosity due to the increase in hydration products. The degree of hydration and porosity in a hydration system are essentially correlated. Powers and Brownyard used a model to relate capillary pores in a cement paste to the degree of hydration and initial water to cement ratio.

Strength of concrete depends upon the gel/space ratio, which depends on the degree of hydration at a given age of the cementitious materials. Information on the degree of hydration of FC systems is also limited in other studies, except that by Ohsawa et al. and Li et al., who presented some data on the degree of hydration of fly ash and silica fume.

## **2.6 Environmental Effect**

The manufacturing of OPC requires the burning of large quantities of fuel and decomposition of limestone, resulting in significant emissions of carbon dioxide (Kong and Sanjayan, 2008).

Although fly ash offers environmental advantages, it also improves the performance and quality of concrete. Fly ash affects the plastic properties of concrete by improving workability, reducing water demand, reducing segregation and bleeding, and lowering heat of hydration. Fly ash also increases strength, reduces permeability, reduces corrosion of reinforcing steel, increases sulphate resistance, and reduces alkali-aggregate reaction. In addition, fly ash reaches its maximum strength more slowly than concrete made with only Portland cement. The techniques for working with this type of concrete are standard for the industry and will not impact the budget of a job.

## **2.7 Cracking in Concrete**