Faculty of Engineering and Science

Modified Cement Paste using Micro-fine POFA under Ammonium Nitrate condition

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ABSTRACT

In this research, micro-fine palm oil fuel ash (POFA) is used to control the degradation of cement paste in an ammonium nitrate condition. Ammonium nitrate is an odourless white solid mainly used as a plant fertilizer. However, ammonium nitrate is also an aggressive chemical, which causes degradation to concrete structures. The degradation of concrete in an ammonium nitrate environment occurs in two stages, which results in a reduction of calcium hydroxide in the cement paste, when the pH of the concrete drops as alkalinity declines and the volume increases. Therefore, the aim of this research is to apply micro-fine POFA as a pozzolanic material to control ammonium nitrate attack in cement paste and improve cements compressive strength and durability properties. This research has three objectives. The first objective is to examine the physical, chemical and micro-structural properties of raw POFA, treated POFA and Ordinary Portland Cement (OPC). The second objective is to investigate the compression strength and durability properties (VPV & Sorptivity) of cement paste at room temperature and in ammonium nitrate conditions. The third objective is to analyse the microstructure (TGA, SEM & EDX) of the cement paste at room temperature and in ammonium nitrate conditions.

The key difference between this research and previous studies is the use of micro-fine POFA in ammonium nitrate condition. Previous research had used POFA in an aggressive condition such as chloride, carbon dioxide, or sulphate but POFA has not been previously used against an ammonium nitrate condition. This research investigated the use of micro-fine POFA in cement paste to control ammonium nitrate attack by examining its compressive strength, durability and microstructure properties. The outcome of this research clearly can benefit the construction industry with improved economic value as the durability of the cement paste had increased. Therefore, the maintenance costs of the concrete in ammonium nitrate condition are reduced.

The results obtained from this research demonstrated that, the grinding and heat treatment process significantly improves the physical, chemical and microstructure properties of POFA. In addition, it was observed the compressive strength increased when OPC was replaced with 20% fine palm oil fuel ash. Similarly, it was found from the investigation, the sorptivity was the lowest when 20% POFA was used at room temperature and in ammonium nitrate

conditions. The volume of permeable voids was also lower when 20% fine POFA was used at room temperature and in ammonium nitrate conditions. As for the Thermo-gravimetric Analysis (TGA) studies, Ca(OH)₂ was reduced when OPC was replaced with POFA, due to the pozzolanic reaction and subsequently produced increased C-S-H. Through EDX analysis, it was found the Ca/Si ratio was the lowest for samples with 20% POFA. A low Ca/Si ratio is an indication of a pozzolanic reaction. Moreover, the SEM test also demonstrated a 20% POFA-based cement paste produced more C-S-H compared to the control sample and hence provided greater compressive strength, lower sorptivity and volume of permeable voids and better resistance in an ammonium nitrate solution.

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List of Abbreviations

NH4NO3	Ammonium Nitrate
Ca(OH) ₂	Calcium Hydroxide
C ₃ S	Alite
C_2S	Belite
C ₃ A	Aluminate
C4AF	Ferrite
С-S-Н	Calcium Silicate Hydrate
SF	Silica Fumes
POFA	Palm Oil Fuel Ash
RHA	Rice Husk Ash
XRF	X-ray Flourescences
VPV	Volume of Permeable Voids
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-ray Spectroscopy
TGA	Thermo-gravimetric Analysis
BS	British Standard
OPC	Ordinary Portland Cement
W/C	Water to Cement Ratio

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DECLARATION OF AUTHORSHIP

I, Sadia Tasnim declare that the thesis entitled:

Modified Cement Paste using fine POFA under Ammonium Nitrate condition is my own except for excerpts, diagrams, graphs, equations and references which have been acknowledged.

Signed: Sadia Tasnim

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Chapter 1

INTRODUCTION

1.1 Background

Concrete is one of the oldest known man-made construction materials used for various structures; such as bridges, dams, tunnels, buildings, sewerage systems, pavement, runways, roads and fertilizer plants. It has been in existence, in varying forms for thousands of years and is the second most consumed substance in the world after water Rajkumar (2014). Concrete is made by mixing water, cement, coarse aggregate, fine aggregates and sometimes special admixtures in specific proportions. Cement is the primary constituent of concrete and is produced and used in large quantities. In Malaysia, cement production was 1,846 thousand tonnes for the month of April 2016 (Trading Economics, 2016). Aggregates, both fine and coarse, are commonly considered as filler and they make the body of the concrete structure. Typically, in a concrete mix, cement occupies about 10 to 15% by volume, aggregates about 60 to 70% and water about 15 to 20%. Occasionally, about 5 to 8 percent of volume is made up by entrained air bubbles in concrete mixtures (PCA, 2016). Macroscopically, concrete consists of two phases; namely, (i) a mortar phase and (ii) a coarse aggregate phase. The coarse aggregate phase is generally stronger than the mortar phase and is responsible for the unit weight, dimensional stability and the elastic modulus of the concrete Naik (1997).

The mortar phase is interconnected from one end to the other while the coarse aggregate phase is disconnected. The mortar phase in concrete plays a crucial role in (i) workability, (ii) strength and (iii) durability of concrete. The mortar phase, in conventional concrete work, is made with fine aggregate, cement, and water. Concrete is defined as workable if it can be easily be placed, compacted, transported and finished without any segregation. The properties of fresh concrete is usually described by the workability of the concrete. The strength of the concrete is the ability of the material to resist stress without failure and is usually referred to the properties of hardened

concrete. Strength, especially compressive strength, is the property most often specified in quality control and design.

It is not common for concrete structures to fail because reinforced concrete structures are usually designed to a sufficiently high safety factor. However, over the last few decades, the lifespan of concrete structures has become a primary concern as many structures have collapsed, especially in buildings and transportation sectors. To repair such structures is expensive and it is therefore, imperative to improve the quality of construction, by improving the durability properties of concrete. The durability of concrete structures means the capacity of the structure to last a long time without any significant deterioration by resisting chemical attack, weathering actions and abrasion (PCA, 2016). Generally, the cause of concrete deterioration can be categorized into two categories i) physical and ii) chemical. Physical deterioration refers to the surface wear and cracking of concrete. Common chemical deterioration refers to (i) alkali-silica reactions, (ii) sulphate, (iii) chloride and (iv) carbon dioxide attack (PCA, 2016). The harmful chemicals enter the concrete through the mortar phase and triggers deterioration by causing cracking and degradation of the concrete.

Recently, it has been reported an ammonium nitrate solution is also responsible for the degradation of concrete. According to Hallaji et al. (2012), a small amount of an ammonium nitrate solution, approximately 0.5% by weight of the cement, is reported to be sufficient to cause damage to concrete structures. Ammonium nitrate attacks concrete in a two-stage reaction (Hallaji et al., 2012). In the first stage, in the presence of moisture and ammonium nitrate (NH₄NO₃), calcium hydroxide (Ca(OH)₂ in the cement paste is consumed and calcium nitrate, Ca(NO₃) is produced, thereby reducing the content of calcium hydroxide in the cement paste. The pH of the concrete drops as alkalinity declines. In the second stage, the calcium nitrate reacts with hydrated calcium aluminates, 3CaO·Al2O3·6H2O in the cement to form a new compound, calcium nitro-aluminates 3CaO·Al2O3·Ca(NO3)2·10H2O. As a result, the volume of the concrete increases and subsequently a busting of the contaminated layer occur leading to steel corrosion. Figures 1.1 to 1.3 show some examples of degradation of concrete structures when exposed to ammonium nitrate environments. This research aims to use POFA as a cement replacement to increase the resistance of the cement paste against aggressive ammonium nitrate conditions.



Figure 1.1: Internal view of prill tower of ammonium nitrate fertilizer plant, (Hallaji et al., 2012)



Figure 1.2: Deterioration of cantilever beams and accumulation of ammonium nitrate granulas, (Hallaji et al., 2012)



Figure 1.3: Deterioration of selected walls of ammonium nitrate and urea prill towers, (Hallaji et al., 2012)

1.2 Hydration of Cement

Hydration is the chemical combination of cement and water. In the anhydrous state, four key minerals exist in cement i) alite (C₃S) ii) belite (C₂S), iii) aluminate (C₃A) and iv) ferrite phase (C₄AF). When water is added to cement, an exothermic reaction occurs and two main hydration products, calcium hydroxide, Ca(OH)₂ and calcium silicate hydrate (C-S-H) are produced. Each of the four minerals tends to form different solid phases during hydration due to reactions at different rate. Alite is responsible for the initial setting and early strength while belite contributes to later-age strength beyond seven days. Aluminate contributes slightly to early strength development and usually produces a large amount of heat during the first few days of cement hydration. Ferrite hydrates rapidly and contributes little to the strength of the hydrated cement paste. The colour of the hydrated cement paste occurs due to the hydrate and calcium hydroxide while aluminate and ferrite form ettringite and monosulfoaluminate.

Most of the strength of the cement paste is due to the formation of the calcium silicate hydrate. It occupies about 50% by volume and is responsible for most of the engineering properties of the cement paste (Science of Concrete, 2008). This is because calcium silicate hydrate binds together the cement particles into a cohesive whole through the formation of a continuous layer. Calcium

hydroxide occupies about 15% by volume of the cement paste and contributes slightly to the impermeability and strength of the paste (Science of Concrete, 2008). It can easily be leached out though, increasing the porosity and thus making the paste more vulnerable to further chemical attack and leaching.

1.3 Pozzolanic Reaction

Pozzolanic reaction is a chemical reaction, which occurs in cement paste in the presence of pozzolans and moisture. According to ASTM C595 (1998), a pozzolan is defined as a material which contains high amount of silicon and aluminium. In presence of moisture, a pozzolanic material reacts with calcium hydroxide in cement paste to form compounds having cementing properties. When pozzolans are used in cement paste, the microstructure of the paste re-arranges itself due to the reaction between silicon in the pozzolans and calcium hydroxide Ca(OH)₂ in the cement paste to produce additional calcium silicate hydrate (C-S-H). As a result, the cement paste has a denser matrix, is more durable, less permeable and is relatively stronger. Equation 1.1 shows the pozzolanic reaction in cement paste.

The use of pozzolanic materials in concrete as a partial replacement of cement is gaining significant attention currently. This is because using this material in concrete improves the durability properties of concrete and accounts for some ecological benefits. When Portland cement is produced, there is a significant amount of carbon dioxide produced. If the amount of carbon dioxide can be reduced during construction, a project may be considered 'green' or in other words, if less cement is used in the concrete mix; it would make the concrete more 'green'. When concrete contains pozzolans, less cement is required to achieve the desired strength. A highly reactive pozzolan has more cementing properties than a lower reactive pozzolan. Therefore, less cement is required when a highly reactive pozzolan is used. The reactivity of a pozzolan depends on its mineralogical and chemical composition, the specific surface area, the ratio of lime to pozzolan, temperature, curing time and the amount of water. Fly ash, slag, silica fumes (SF), palm oil fuel ash (POFA) and rice husk ash (RHA) are some common pozzolans

used in concrete as a cement replacement. Recently the use of POFA as a cement replacement has caught the attention of many researchers due to it containing large amounts of silica.

1.4 Research Potential Using Palm Oil Fuel Ash (POFA)

Palm oil fuel ash (POFA) is generated during palm oil production. The combustion of oil palm shells and fibre in palm oil production has resulted in a secondary solid waste known as POFA. According to MPOB (2016), there are about 248 palm oil production sites in Peninsular Malaysia, 124 sites in Sabah and 57 in Sarawak. The annual capacity of these mills was 56.8 million tonnes, 32.1million tonnes and 13.1million tonnes respectively (MPOB, 2016). In palm oil mills, the palm fibre, shells and empty fruit brunches are usually burnt at around 700-1000°c for running the boiler, (Tanchirapat et al., 2007). The ash produced from the combustion process are discarded near the palm oil mill or in selected types of landfills such as i)swamp lands and ii) abandoned sand quarries (Al-Mulali et al., 2015). This disposal method contributes to air and land pollution. The amount of POFA produced after combustion is usually about 5% POFA-by weight of solid wastes (Sata et al., 2004). The color of the ash is based on the carbon content which usually varies from whitish grey to darker shades. POFA is a pozzolanic material, which has a high percentage of alumino-silicate content (Qyeleke et al., 2011).

Many attempts have been made to use POFA in concrete as a cement replacement material. Previous research has found the use of coarser POFA has had little effect on the strength of concrete (Al-Mulali et al., 2015). However, more recently, it was found that grinding the POFA to a smaller size could improve its quality. Raw POFA particles are usually of a large and angular size. The grinding process results in the POFA becoming a smaller and more irregular particle. As a result, the surface area increases and the finer POFA are more reactive than the coarser POFA (Sata et al., 2007). The amount of cement replacement can be increased by up to 60% with an improvement on the mechanical and durability properties of concrete (Hussin et al., 2015).

1.5 Aim and Research Objectives

The aim of this research is to investigate the performance of micro-fine palm oil fuel ash (POFA) on resistance to the ammonium nitrate effect on cement paste. The objectives can be categorized as follows:

- To characterize the physical properties and chemical compositions of raw POFA and treated POFA using a specific gravity test, a specific surface area test, SEM, a particle size analyser, EDX and XRF tests.
- To determine the effect of adding a replacement of cement a micro-fine POFA (0%, 10%, 20% and 30%) on the resistance to ammonium nitrate attack in cement paste using appropriate quantitative analysis (Compression test, VPV test and the Sorptivity test).
- To investigate the microstructure and hydration process of the cement paste by SEM, EDX and TGA tests to verify the outcomes from the experimental studies.

1.6 Scope of Work

The scope of this research is focused to fulfil the objectives presented in section 1.5. Based on the first objective, the physical, chemical and micro-structural properties of raw and treated POFA were investigated. A particle size test, specific gravity, and specific surface area test were carried out to determine the physical properties. A particle-size analyser machine was used to conduct the particle size test on raw POFA (directly from a palm oil mill) and treated POFA (after burning and grinding). For the chemical composition analysis, XRF (X-ray Fluorescence) test was carried out to determine the chemical composition of the POFA and their percentages. A SEM (scanning microscopy analysis) test was carried out to identify the differences between raw and treated POFA through an image produced from the analysis. Differences in particle size number of porous and shapes between the raw and the treated POFA was analysed through a SEM test. In addition, an EDX test was performed to determine the elements in the POFA.

Based on the second objective, the treated POFA (mean size about 10 microns) was used to replace cement at 0%, 10%, 20% and 30% proportions by volume and mechanical and the durability tests were carried out to verify results. The test was conducted in two different conditions, at room temperature, and in an ammonium nitrate solution. The mechanical test consisted of a compression strength test at the age of 3, 7, 28, 56 and 90 days. The durability test consisted of a Volume of Permeable Void, (VPV) and Sorptivity test at days 28, 56 and 90. 50mm cement cubes were cast and de-moulded after 24hours (±2 hours). The cubes were then kept in water for 28 days for a full-water curing. Tests for both mechanical and durability were carried out accordingly.

As for the third objective, three different tests, SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-ray spectroscopy) and TGA (Thermo- gravimetric analysis) were carried out. A SEM test was performed to produce an image to illustrate the morphological features of cement paste at 28, 56 and 90 days. To support further the SEM images, an EDX test was carried out to determine the Ca/Si and Si/Ca ratio of the samples. A TGA analysis was carried out at 28, 56 and 90 days to determine the hydration product such as calcium hydroxide, in the cement paste. The sample was heated from room temperature to 1050 degrees Celsius in a nitrogen gas atmosphere. The TGA test curves were used to estimate the amount of Ca(OH)₂ lost due to heating.

Although the research has reached its aim, there exist some unavoidable limitations. First because due to the fact that the research was for master studies and the objective of study was limited therefore the research was concluded only on one size of POFA which was below 10 microns. The research can be further by using POFA size of below 1 micron which is the smallest POFA size used so far in research and study its mechanical, durability and microstructure properties. Secondly, due to the limitation of the objective of the studies and limitation of resources, the concentration of ammonium nitrate used was only one concentration. The concentration of ammonium nitrate used can be further examined using few different concentrations. Thirdly, due to limitation of resources the investigation was only carried out on cement paste. The research can be further using POFA in mortar and concrete instead of just cement paste and examine its effect against ammonium nitrate solution.

1.7 Significance of Research

This present study aimed to investigate the performance of micro-fine palm oil fuel ash (POFA) to control the ammonium nitrate attack in cement paste. This research may likely lead to greater utilization of POFA in concrete. The outcomes from this research can benefit the construction industry with greater economic efficiency as the durability of the cement paste will have increased, which will result in reduced maintenance costs of the concrete in an ammonium nitrate condition. Subsequently, these research results could also be useful in protecting the environment by reducing the emissions of greenhouse gases and as well as the volume of waste needing to be disposed of. Furthermore, this study contributes to the knowledge base regarding the effectiveness of the POFA particle size and the most effective proportions required for substitution and finally, improving cement paste characteristics under ammonium nitrate conditions.

1.8 Thesis outlines

This thesis is composed of five chapters, following Chapter 1, the introduction. Chapter 2 reviews previous literature published related to the use of POFA as a cement replacement in concrete. This chapter discusses the i) physical, chemical and micro-structural properties of POFA, ii) the mechanical and durability properties of concrete containing POFA, iii) the microstructure analyses (SEM and TGA) of cement containing POFA and iv) the effect of the aggressive solution, ammonium nitrate on concrete.

Chapter 3 discusses materials and test methods used for this research. This chapter explains the properties of Ordinary Portland Cement (OPC), Palm Oil Fuel Ash (POFA) and an Ammonium Nitrate Solution. Fundamentally, the physical, chemical and microstructures properties of POFA are discussed in this chapter. In addition, this chapter also delivers the methodology of the compression test, the volume of permeable voids (VPV) test, the sorptivity test, the SEM test (scanning electron microscopy) and the TGA test.

Chapter 4 discusses the results from this research such as the mechanical, durability and microstructure tests. Results are analysed and compared with previous published works. Finally, Chapter 5 presents some conclusions as well as recommendations for further research.

Chapter 2

LITERATURE REVIEW

2.1 Introduction

This chapter gives background information regarding the use of palm oil fuel ash (POFA) as a cement replacement material. This chapter also discusses the i) physical, chemical and microstructure properties of POFA and cement, ii) compressive strength and durability properties of concrete containing POFA, iii) the microstructure tests (SEM, EDX and TGA) for cement containing POFA iv) the characteristics of ammonium nitrate and v) the effect of ammonium nitrate solution on concrete. The research gap is identified and conclusions are drawn.

2.2 Physical properties of POFA and Cement

The following sections discusses the physical properties of POFA and cement. The physical properties which will be discussed in detail are the median particle size, specific gravity and specific surface area.

2.2.1 Specific gravity and median particle size

POFA is produced due to the burning of the waste from the palm oil production process in palm oil mills. The burning temperatures used in the mill affect the properties of the produced POFA. Lower burning temperatures will produce a dark grey to black coloured POFA because of the amount of un-burnt carbon. Higher burning temperatures will produce a lighter coloured ash as the amount of un-burnt carbon is reduces. Generally, the solid wastes are burnt in the mill at temperatures ranging from approximately 700-1000 degrees Celsius (Tangchirapat et al., 2007; Tangchirapat et al., 2012; Sata et al., 2007). The POFA produced at palm oil mills have a large particle size with a porous texture, therefore in order to increase its reactivity in a concrete paste, the POFA are further ground to a smaller size. According to Tangchirapat et al. (2007), grinding

will produce POFA particles of a smaller size and a greater fineness. Furthermore, the grinding process will also increase the specific gravity of the POFA. Grinding is usually conducted using a ball mill or a Los Angeles Abrasion machine (Tangchirapat et al., 2009; Sata et al., 2010; Abdullah et al., 2006). Table 2.1 shows the physical properties of POFA investigated by several researchers. According to Deepak et al. (2014), Ordinary Portland cement (OPC) is made through the heating of a finely divided mixture of shale or clay and limestone or chalk in a kiln at a temperature of around 1500 degree Celsius. Based on Table 2.1, the median particle size (d_{50}) of OPC used in most research was 14.6 μ m and the specific gravity was 3.14.

	Un-grounded POFA		Grou	nded POFA	Cement		
Reference	Specific Gravity	Median Particle Size, d50 (µm)	Specific Gravity	Median Particle Size, d50 (μm)	Specific Gravity	Median Particle Size, d50 (μm)	
(Sata et al., 2004)	1.93	62.5	2.33	10.1	3.15	14.6	
(Abdullah et al., 2006)	-	45	-	-	-	-	
(Tangchirapat et al., 2007)	1.89	183	2.43	7.4	3.14	14.7	
(Sata et al., 2007)	-	-	2.33	10.1	3.15	14.6	
(Ahmad et al., 2008)	-	300	-	-	3.15	-	
(Tangchirapat et al., 2009)	1.97	65.6	2.33	10.1	3.14	14.6	
(Sata et al., 2010)	-	-	2.5	9.2	3.15	14.7	
(Bamaga et al., 2010)	-	45	-	-	-	-	
(Tangchirapat and Jaturapitakkul, 2010)		-	2.33	10.1	3.14	14.6	
(Budiea et al., 2010)	-	45	-	10	-	-	
(Kroehong et al., 2011)	-	-	2.48	2.1	3.14	14.6	
(Altwair et al., 2011)	-	74.29	-	2.99	-	-	

Table 2.1: Specific gravity and median particle size of Palm Oil Fuel Ash

(Tangchirapat et al., 2012)	-	-	2.53	10.7	3.14	14.6
(Johari et al., 2012)	-	-	2.56	2.06	3.1	6.79
(Soovraj et al., 2013)	1.65	300	-	-	-	-
(Deepak et al., 2014)	-	300	-	-	-	-
(Hidayati et al.,2015)	2.04	119.9	2.62	1.6	3.14	9.91
(Farzadnia et al., 2015)	-	32.16	-	-	-	-
(Munir et al., 2015)	1.48	4.75mm	-	-	-	-
(Hussin et al., 2015)	-	50-100nm	-	-	-	-
(Pourakbar et al., 2015)	2.13	21.89	-	-	-	-
(Usman et al., 2015)	2.42	45	-	-	3.15	-
(Ranjbar et al.,2016)	-	-	1.81	10	3.15	14.6
(Islam et al., 2016)	2.1	45	-	-	3.14	-

 $\overline{\text{Nil}}=(-)$

2.2.2 Specific surface area of POFA and OPC

Table 2.2 shows the specific surface area of POFA and OPC. The specific surface area of POFA increases as the particle size decreases. According to Kroehong et al. (2011) a POFA particle size of 15.6 μ m has shown a specific surface area of 6700 cm²/g while POFA of 2.1 μ m has a specific surface area of 14900 cm²/g. Altwair et al. (2011) have reported a similar pattern. The median size (d₅₀) of POFA before milling was around 74.29 μ m with a specific surface area of around 540cm²/g. For a median size (d₅₀) of approximately 2.99 μ m, the specific surface area of treated POFA was around 6200cm²/g.

	РО	OFA	0	РС
Reference	Median Particle Size, d50 (μm)	Specific surface area, (cm²/g)	Median Particle Size, d ₅₀ (μm)	Specific surface area, (cm²/g)
(Sata et al., 2004)	10	12440	14.6	3580
(Altwair et al., 2011)	74.29	540	-	-
(Altwair et al., 2011)	2.99	6200	-	-
(Kroehong et al., 2011)	15.6	6700	14.6	3600
(Kroehong et al., 2011)	2.1	14900	14.6	3600
(Johari et al., 2012)	2.06	17750	6.79	7850
(Yususf et al., 2014)	1.06	134000	-	-
(Farzadnia et al., 2015)	32.16	3570	-	-
(Hidayati et al., 2015)	1.6	8390	9.91	3500
(Ismail et al., 2016)	45	5060	-	-

Table 2.2: Specific surface area of POFA and OPC

Note: -, Nil

2.3 Chemical composition of POFA and OPC

Generally, POFA obtained from palm oil mills are sieved to remove unburnt fibres and larger particles. The main chemical composition of POFA is SiO₂ and is usually in the range of 50-60% by volume while other pozzolanic components present are Al₂O₃ and Fe₂O₃. (Bamaga et al., 2010; Tangchirapat et al., 2009; Kroehong et al., 2011). According to Johari et al. (2012), heat treatment significantly reduces the carbon content of POFA and lowers the loss of ignition (LOI) values. The loss on ignition (LOI) indicates the presence of unburned residue (Hidayati et al., 2015). Consequently, heat treatment also changes the total sum of SiO₂, Al₂O₃ and Fe₂O₃ and Fe₂O₃ and increases the value of SiO₂.

Table 2.3 shows the chemical composition of POFA. POFA can be classified as either a class C pozzolan (Hidayati et al., 2015), a class F pozzolan (Usman et al., 2015), a class N fly ash (Bamaga et al., 2010) or between class C and class F pozzolan (Awal and Nyuong, 2010). According to ASTM C 618 (2005), POFA can be classified as a class N pozzolan if the percentage of SiO₂, Al₂O₃ and Fe₂O₃ is greater than or equal to 70%, SO₃ is not greater than 4% and the LOI values are approximately 10%. For a class C pozzolan, the percentage of SiO_2 , Al_2O_3 and Fe_2O_3 should have a minimum value of 50%, and the maximum value of SO_3 and LOI should be 5% and 6% respectively. Meanwhile, for a class F pozzolan, the amount of SiO₂, Al₂O₃ and Fe₂O₃ should have a minimum value of 70%, and the maximum value of SO₃ and LOI should be 5% and 6% respectively (ASTM C 618, 2005). The primary difference between the Class C and Class F pozzolan is the amount of lime they contain. Typically, Class C fly ash contains over 20% calcium oxide while Class F contains a very small amount of CaO (less than 10% CaO). If the total percentage of SiO₂, Al₂O₃ and Fe₂O₃ is higher than 75% of the total chemical composition, than the pozzolanic material can be classified between class F and C pozzolan. However, the material should contain a small quantity of calcium oxide (CaO) in the range of 4-8% (ASTM C 618, 2005). The greater percentage of potassium oxide (K₂O) in POFA is because of the palm oil tree, which absorbs a large amount of potassium from the soil during cultivation (Karim et al., 2014).

The chemical composition of OPC is shown in Table 2.4. The relatively high percentage of CaO contained in cement compared to POFA, is because CaO tends to play a significant role in the

production of calcium hydroxide (Budies et al., 2010). Compounds found in OPC such as C_3S and C_2S are known to react with water to form calcium hydroxide and calcium silicate hydrates (Altwair et al., 2011). According to Tangchirapat et al. (2007) OPC used in their research contained 62.86% C_3S , 12.50% C_2S , 6.84% C_3A and 10.38% C_4AF .

Oxides	(Abdullah et al., 2006)	(Sata et al., 2007)	(Tangchirapat et al., 2007)	(Tangchirapat et al., 2009)	(Bamaga et al., 2010)	(Awal and Nguong, 2010)	(Budiea et al., 2010)	(Sata et al., 2010)	(Tangchirapat and Jaturapitakku l, 2010)
Silicon dioxide (SiO ₂)	55.2	65.3	57.75	65.3	58.3	49.2	48.99	42.5	65.3
Aluminium oxide (Al ₂ O ₃)	4.48	2.6	4.57	2.5	6.69	5.45	3.78	0.9	2.5
Ferric oxide (Fe ₂ O ₃)	5.44	2	3.3	1.9	9.77	5.73	3.5	2.4	1.9
Calcium oxide (CaO)	4.12	6.4	6.55	6.4	6.72	7.5	11.69	11	6.4
Magnesiu m oxide (MgO)	2.25	3.1	4.23	3.0	3.69	3.93	0.59	7.1	3
Potassium oxide (K ₂ O)	2.28	5.7	8.27	5.7	8.4	5.3	4.01	7	5.7
Sulfur oxide (SO ₃)	2.25	0.5	0.25	0.4	0.96	1.73	2.25	2.2	0.4
$\frac{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 + \text{Fe}_2\text{O}_3}{\text{Fe}_2\text{O}_3}$	65.12	69.9	65.62	69.7	74.76	60.38	56.27	45.8	69.7
LOI	13.86	10.1	10.52	10.0	7.34	13.85	10.51	-	10

Table 2.3 Chemical composition of Palm Oil Fuel Ash (POFA)

Oxides	(Kroehong et al., 2011)	(Johari et al., 2012)	(Tangchirapat et al., 2012)	(Soovraj ., 2013)	(Yusuf et al., 2014)	(Hidayati et al., 2015)	(Usman et al., 2015)	(Farzadnia et al., 2015)	(Ranjbar et al., 2016)	(Islam et al., 2016)
Silicon dioxide (SiO ₂)	55.7	65.01	55.5	21.81	60.42	45.5	63.7	47.37	64.17	63.4
Aluminium oxide (Al ₂ O ₃)	0.9	5.72	9.2	2.76	4.26	2.09	3.7	3.53	3.73	5.51
Ferric oxide (Fe ₂ O ₃)	2.0	4.41	5.6	3.2	3.34	2.82	6.3	6.19	6.33	4.2
Calcium oxide (CaO)	12.5	8.19	12.4	5.7	11	6.02	6	11.83	5.8	4.35
Magnesium oxide (MgO)	5.1	4.58	4.6	3.98	5.31	4.84	4.1	4.19	4.87	3.78
Potassium oxide (K ₂ O)	1.0	6.48	0	3.98	0.18	7.07	9.15	nil	8.25	6.35
Sulfur oxide (SO ₃)	11.9	0.33	2.3	1.28	5.03	0.19	1.6	1.22	0.72	0.93
$\begin{array}{c} \mathrm{SiO}_2 + \\ \mathrm{Al}_2\mathrm{O}_3 + \\ \mathrm{Fe}_2\mathrm{O}_3 \end{array}$	2.9	75.14	70.3	27.77	0.45	50.31	73.7	57.09	74.23	73.11
LOI	4.7	2.53	7.9	2.99	2.66	4.96	8	1.84	-	6.19

Table 2.3: Chemical composition of Palm Oil Fuel Ash (POFA) (Cont'd)

Oxides	(Sata et al., 2004)	(Sata et al., 2007)	(Tangchirapat et al., 2007)	(Tangchirapat et al., 2009)	(Tangchirapat and Jaturapitakkul., 2010)	(Sata et al., 2010)	(Budiea et al., 2010)
Silicon dioxide (SiO ₂)	20.9	20.9	20.9	20.9	20.9	20.9	21.45
Aluminium oxide (Al ₂ O ₃)	4.8	4.8	4.76	4.7	4.7	4.8	3.62
Ferric oxide (Fe ₂ O ₃)	3.4	3.4	3.41	3.4	3.4	3.4	4.89
Calcium oxide (CaO)	65.4	65.4	65.41	65.4	65.4	65.4	60.98
Magnesium oxide (MgO)	1.2	1.2	1.25	1.2	1.2	1.2	1.22
Potassium oxide (K ₂ O)	0.4	0.4	0.35	0.3	0.3	0.4	0.51
Sulfur oxide (SO ₃)	2.7	2.7	2.71	2.7	2.7	2.7	2.3

Table 2.4: Chemical composition of Ordinary Portland Cement

Oxides	(Kroehong et al., 2011)	(Tangchirapat et al., 2012)	(Johari et al., 2012)	(Farzadnia et al., 2015)	(Usman et al., 2015)	(Ranjbar et al., 2016)	(Ismail et al., 2016)
Silicon dioxide (SiO ₂)	20.8	20.9	19.01	21.3	19.8	17.6	22.7
Aluminium oxide (Al ₂ O ₃)	4.7	4.7	4.68	3.78	3.9	4.02	4.6
Ferric oxide (Fe ₂ O ₃)	3.4	3.4	3.2	3.75	3	4.47	1.4
Calcium oxide (CaO)	65.3	65.4	66.89	63.83	63.4	67.43	64.2
Magnesium oxide (MgO)	nil	1.2	0.81	1.77	2	1.33	3.4
Potassium oxide (K ₂ O)	0.4	0.3	1.17	nil	0.18	0.39	0.8
Sulfur oxide (SO ₃)	2.7	2.7	3.66	2.88	2.9	4.18	2.5

Table 2.4: Chemical composition of Ordinary Portland Cement (Cont'd)

2.4 Microstructure of POFA

The following sections discuss the microstructure of untreated and treated POFA. Tests, which have been discussed, are SEM (Scanning Electron Microscopy) and EDX (Energy-Dispersive X-Ray) tests.

2.4.1 SEM (Scanning Electron Microscopy) of POFA and Cement

Figures 2.1 to 2.7 show the particle morphology of raw POFA, treated POFA and OPC. In Figures 2.1 and 2.2, the raw POFA have large particle sizes and most particles are of a porous texture (Tangchirapat et al., 2007; Salih et al., 2014). There were many pores observed on the surface of the POFA. It was observed, most of the particles were round in shape. The porosity of raw POFA is high because of the presence of a large amount of voids.

In Figures 2.3 to 2.6, the treated POFA, due to the grinding process, were smaller in size with irregular and crushed shapes (Tangchirapat et al., 2007; Salih et al., 2014; Tangchirapat et al., 2012; Altwair et al., 2011). Fewer porous shapes were observed when the POFA became finer. Generally, the treated POFA have a wide range of sizes, but they are relatively spherical in shape. The grinding process reduces the size and porosity of POFA while increasing its specific gravity. Figure 2.7 shows the morphology of cement as reported by Ranjbar et al., (2016). The particle morphology of cement consists of agglomerated shapes; however, it has a less porous structure compared to POFA.



Figure 2.1: Original size of palm oil fuel ash (Tangchirapat et al., 2007).



Figure 2.2: Raw POFA before grinding (Salih et al., 2014).


Figure 2.3: Small size of palm oil fuel ash (Tangchirapat et al., 2007)



Figure 2.4: POFA after grinding (Salih et al., 2014)



Figure 2.5: Particle morphologies of the ground POFA (Tangchirapat et al., 2012)



Figure 2.6: SEM image of treated POFA (Altwair et al., 2011)



Figure 2.7: SEM image of cement (Ranjbar et al., 2016).

2.4.2 EDX (Energy-Dispersive X-Ray) Analysis

Figures 2.8 and 2.9 illustrate the EDX analysis of POFA together with SEM images. EDX analysis was carried out on raw POFA, ground POFA and fine POFA by Johari et al. (2012) and Figure 2.8 shows the test results for the fine POFA. EDX analysis was carried out at three different locations for the samples. In Figure 2.8, elements such as silicon, oxygen, magnesium, carbon, iron, potassium, phosphorus, aluminium and calcium were found. According to Johari et al. (2012), the raw POFA not subjected to heat treatment, showed carbon elements could be detected in relatively high intensity using SEM/EDX micrographs. Nonetheless, for the fine POFA sample which have been subjected to heat treatment, carbon element could still be detected but in a much lower intensity. However, in all the samples, the percentage of silicon was higher than other elements. In Figure 2.9, the ground POFA contains elements such as calcium, carbon, oxygen, potassium, magnesium and silicon. It was observed the ground POFA contained higher amounts of silicon compared to other elements Usman et al. (2015).



Figure 2.8: SEM micrographs with EDX analysis of POFA (Johari et al., 2012).



Figure 2.9: Field emission scanning electronic microscopy image of ground POFA and EDX Analysis (Usman et al., 2015).

2.5 Influence of POFA on Compressive Strength

Sections 2.5.1 and 2.5.2 discuss the influence of POFA on compressive strength. Table 2.5 summarizes the compressive strength of cement paste, mortar and concrete containing POFA. Factors that influence compressive strength are the median particle size and the percentage replacement of cement with POFA.

2.5.1 Influence of POFA particle size on Compressive Strength

Based on Table 2.5, the finest-size POFA used to replace cement, to study compressive strength, was $2.1\mu m$ while the largest size was 4.75mm. In most studies, the median particle size (d50) used were around $10\mu m$. (Sata et al., 2004; Tangchirapat et al., 2007; Sata et al., 2007).

Tangchirapat et al. (2007) investigated the replacement of three different sized POFA with cement. The original POFA size, 183.0 μ m was ground until the median particle size (d₅₀) were 15.9 μ m and 7.4 μ m. Test results demonstrated the compressive strength of samples containing POFA size 183.0 μ m were much lower than of control samples containing 100% cement. This is attributed to the fact that POFA of 183.0 μ m have large particles with high porosity. For samples containing POFA of 15.9 μ m, they produced higher compressive strength than samples containing POFA of 183.0 μ m. However, they still had lower strength values than the control sample. This is an indication that samples containing POFA of 15.9 μ m contributes to a better pozzolanic reaction than samples containing POFA of 183.0 μ m, which was the fineness POFA used in the study, the compressive strength was very close to the control sample. The authors concluded POFA might have a high potential for use as a pozzolanic material for a cement replacement, especially when the material is ground to a fine particle size of 7.4 μ m.

Tangchirapat and Jaturapitakkul, (2010) reported the compressive strength of the sample which used POFA increased with the fineness of the POFA. The POFA was ground to obtain two different median particle sizes (d_{50}) of 19.9µm and 10.1µm POFA. Based on test result samples containing POFA of 19.9µm the compressive strength was much lower than the control samples. The compressive strength of samples containing POFA of 10.1µm was close to the control samples for all the curing ages. Test results suggested the more fine the POFA, the greater the

pozzolanic reaction. The degree of fineness of POFA is very significant. When the particles are smaller, they fill the voids in the cement paste, and thus contribute to an increase in the compressive strength.

Kroehong et al. (2011) studied the effect of POFA on cement paste. POFA was ground to two different median particle sizes of 15.6 and 2.1 μ m. The compressive strength of concrete containing POFA of 15.6 μ m and cured at 90 days was slightly higher than of the OPC paste alone. However, for paste with smaller particle sizes of 2.1 μ m, the compressive strength after 90 days was much higher than OPC paste alone. The authors concluded the paste containing POFA with a greater fineness were denser and more homogeneous which resulted in improved compressive strength of the paste.

2.5.2 Influence of POFA replacement on the Compressive Strength

Based on Table 2.5, the minimum replacement rate of OPC with POFA is 5% while the maximum replacement rate is 60%. Generally, about a 20% replacement rate of OPC with POFA gives the highest compressive strength.

Several researchers have studied compressive strength incorporating 10%, 20% and 30% of POFA into the mix (Sata et al., 2004; Tangchirapat et al., 2009; Tangchirapat and Jaturapitakkul, 2010; Sata et al., 2010). According to Sata et al., (2004), after 28 days, the compressive strength of samples containing 20% POFA achieved a higher compressive strength than those with 10% and 30% replacement rates. This is due to the high percentage of SiO₂ in POFA which reacts with Ca(OH)₂ to produce additional calcium silicate hydrate. Tangchirapat et al. (2009) concluded that after 28 days, the compressive strength of samples containing POFA were greater than of control samples containing 100% cement. Among all the samples tested in the study it was found out that samples containing 20% POFA had the highest compressive strength. Tangchirapat and Jaturapitakkul (2010), recommended about 20% to 30% replacement rate of cement with POFA. According to Sata et al., (2010), after 28 days, when OPC was replaced with 10% POFA, this paste produced lower compressive strength. When OPC was replaced with 30% POFA, this paste produced lower compressive strength values at all testing ages. This is because of the low OPC content in the 30% POFA replacement rate.

Abdullah et al. (2006) investigated the replacement rate of OPC with 10%, 20%, 30%, 40% and 50% of POFA. Based on the test results, the authors concluded as the replacement level increased, the compressive strength declined. A 50% replacement rate of cement with POFA had the least compressive strength after 28 days. Consequently, a 20% replacement rate of OPC with POFA exhibited compressive strength approximately the same as the control sample. According to Tangchirapat et al. (2007), OPC was replaced at rates of 10%, 20%, 30% and 40% of POFA. It was found that, the compressive strength was the lowest for 40% of POFA sample at all testing ages and all POFA sizes. At 10% and 20% replacement rates of OPC with POFA compressive strength was approximately the same as the control sample. Kroehong et al. (2011) studied compressive strength incorporating 20 % and 40% of POFA into the mix. At 90 days, the compressive strength of the paste containing 20% POFA showed the greatest compressive strength compared to the control sample and the 40% OPC replacement rate. The compressive strength of the paste with 40% OPC replaced with POFA was the lowest value at 90 days. Johari et al. (2012) investigated the compressive strength of a paste containing up to 60% POFA. OPC was replaced with a 20%, 40% and 60% rate of POFA. At 28 days, samples containing 40% POFA showed the highest compressive strength. Tangchirapat et al. (2012) studied compressive strength by replacing 20%, 35% and 50% OPC with POFA. The authors concluded when 20% of the OPC was replaced by ground POFA, the compressive strength of the samples at 90 days was greater than the control samples.

Sooraj (2013) studied the use of POFA as an OPC replacement up to a 40% rate. OPC was replaced with 10%, 20%, 30% and 40% of POFA. It was recommended that the optimum replacement level of OPC with POFA would be at 20% for the maximum strength in a compressive test. Deepak et al. (2014) investigated compressive strength incorporating rates of 5%, 15%, 25%, 35% and 45% POFA. The authors concluded greater compressive strength was achieved when OPC was replaced with a 15% rate of POFA. Munir et al. (2015) studied the compressive strength by replacing 10%, 20%, 30%, 40% and 50% of OPC with POFA. It was found that the compressive strength decreased linearly, with the addition in the percentage of POFA in the mix. However, the incorporation of 10% POFA had a compressive strength close to the control sample containing 100% OPC. Nonetheless, a 50% replacement rate of OPC with POFA had the lowest compressive strength.

Islam et al., (2016) studied compressive strength by replacing 5%, 10%, 15%, 20% and 25% of OPC with POFA. It was recommended a 10-15% replacement rate of OPC with POFA would achieve the best results. However, a decrease in compressive strength was noticed when the POFA replacement level increased to 20% and 25%.

Reference	POFA Particle Size (µm)	Replacement of cement with POFA (%)	Recommended Replacement Level (%)
(Sata et al., 2004)	10	10, 20 & 30	20
(Abdullah et al., 2006)	45	10, 20, 30, 40 & 50	20
(Tangchirapat et al., 2007)	183.0, 15.9 & 7.4	10, 20, 30 & 40	10, 20
(Sata et al., 2007)	10.1	10, 20, 30 & 40	20, 30
(Ahmad et al., 2008)	300	5, 10 & 15	15
(Tangchirapat et al., 2009)	10.1	10, 20 & 30	20
(Tangchirapat and Jaturapitakkul, 2010)	19.9 & 10.1	10, 20 & 30	20 & 30
(Sata et al., 2010)	9.2	10, 20 & 30	10 & 20
(Kroehong et al., 2011)	15.6 & 2.1	20 & 40	20
(Johari et al., 2012)	2.06	20, 40 & 60	40
(Tangchirapat et al., 2012)	10.7	20, 35 & 50	20
(Sooraj., 2013)	300	10, 20, 30 & 40	20
(Deepak et al., 2014)	300	5, 15, 25, 35, & 45	15
(Munir et al., 2015)	4.75mm	10, 20, 30, 40 & 50	10
(Islam et al., 2016)	45µm	5, 10, 15, 20 & 25	10-15

Table 2.5: Compressive strength of concrete, mortar and cement paste containing POFA

2.6 Influence of POFA on Durability

There are different types of tests carried out to measure concrete durability. Some of the common ways to measure the durability of the concrete, mortar and cement paste are the surface absorption, water absorption, water permeability or chloride permeability tests. Section 2.6.1 discusses the influence of POFA on water permeability. Table 2.6 summarizes the water permeability of concrete, mortar and cement paste containing POFA.

2.6.1 Influence of POFA on Water Permeability

Tangchirapat et al. (2009) studied water permeability when cement was replaced with POFA as a supplementary cementation material. The original POFA was ground to a median particle size of 10.1µm and was substituted at 10%, 20% and 30% levels. The water permeability test was carried out at the 90-day cured stage. Based on the test results, the authors observed the use of POFA had reduced the water permeability of the samples. Samples replaced with POFA resulted in greater impermeability of water than the control sample. Samples containing 20% POFA had higher impermeability of water compared to samples containing POFA at other replacement rates. In addition, all the samples containing POFA had water permeability about half of the control sample. This was because POFA can refine the porosity and pore size in cement paste to produce an impermeable and dense matrix. However, the above researchers have recommended replacing cement at a 20% POFA level.

Tangchirapat et al. (2010) investigated water permeability when cement was replaced with two different POFA sizes. The two POFA particle sizes used were 19.9µm and 10.1µm and were replaced at rates of 10%, 20% and 30%. At 28 days the water permeability of samples containing the 19.9µm sized POFA at 10% and 20% rates had higher values of water permeability than the control sample containing 100% OPC. However, at 90 days, the water permeability of the samples containing 19.9µm sized particles of POFA at 10% and 20% rates, had lower water permeability than the control sample. Samples containing 30% POFA had higher water permeability than ordinary Portland cement at both 28 and 90 days. The higher values of water.

The water permeability of the sample containing the 10.1µm sized POFA particles were lower than both the sample containing the 19.9µm POFA sized particles and the sample containing 100% OPC at both 28 and 90 days. This was attributed to the fact the more fine the POFA particles, the lower the water permeability. The low water permeability is influenced by the pozzolanic reaction and the packing effect of small particles. The authors concluded the replacement of 10% POFA accounted for the improved results in water permeability. Subsequently, they have recommended using a 10% POFA replacement rate.

Tangchirapat et al. (2012) studied water permeability at 28 and 90 days when cement was replaced with POFA. The median size of POFA used was 10.7µm and the OPC was replaced at rates of 20%, 35% and 50% with POFA. Based on the test results, when OPC was replaced with 20% and 35% POFA, the water permeability values of samples were lower than the control sample. However, when the OPC was replaced by POFA at up to a 50% rate, the samples had higher water permeability than the control sample. Table 2.8 summarizes the water permeability of samples containing POFA. The researchers have recommended using POFA at 20% and 30% replacement rates.

Reference	POFA Particle Size (μm)	Replacement of cement with POFA (%)	Recommended Replacement Level (%)	
(Tangchirapat et al., 2009)	10.1	10, 20 & 30	20	
(Tangchirapat and Jaturapitakkul, 2010)	19.9 & 2.33	10, 20 & 30	10	
(Tangchirapat et al., 2012)	10.1	20, 35 & 50	20 & 35	

Table 2.6: Water Permeability of concrete, mortar and cement paste containing POFA

2.7 Influence of POFA on Microstructure Study

The following sections discuss the influence of POFA on the microstructure properties of cement paste and mortar. The microstructure studies that have been discussed are TGA Analysis (Thermo-gravimetric Analysis), SEM Analysis (Scanning Electron Micrographs) and EDX Analysis (Energy-Dispersive X-Ray).

2.7.1 TGA Analysis

Kroehong et al. (2011) studied the Thermogravimetric analysis (TGA) of cement paste containing 20% and 40% POFA by volume. The TGA analysis was carried out at 7, 28, 60 and 90 days and the median particle size of the POFA was 15.6µm and 2.1µm. Based on the analysis, three step mass loss were found. The first step loss showed the mass loss of ettringite which was detected between 105-450 degrees Celsius. The second step loss of calcium hydroxide was detected between 450-580 degrees Celsius and the third step loss was that of calcium carbonate at temperatures between 580-1000 degrees Celsius. Based on the test results, there was an increase in the mass loss of calcium hydroxide in the cement paste from the 7 to 90 days samples due to the hydration of the cement. The total amount of calcium hydroxide in pastes containing POFA was much lower than that of the pure cement pastes. The total amount of calcium hydroxide in paste containing POFA decreased with an increase in the curing age. This reduction of calcium hydroxide in the cement paste is an indication of the pozzolanic reaction. In addition, cement paste containing POFA particle sizes of 2.1µm showed lower mass loss of calcium hydroxide content than of POFA with a particle size of 15.6µm. The authors observed that the cement paste containing 40% POFA had a lower mass loss of calcium hydroxide than of the 20% POFA mix. This is attributed to the fact that the mass loss of calcium hydroxide decreased with an increase in the POFA content.

Altwair et al. (2011) applied the TGA analysis to a paste containing POFA sized 2.99µm. They used seven POFA samples and one control sample to study the hydration products at 90 days. A POFA/cement ratio from 0.1 to 0.8 was used to study the microstructure characteristic. Three, considerable endothermic shifts took place. The first shift was broad and was due to the removal of water molecules and decomposition of ettringite. The second shift was due to dehydroxilation of calcium hydroxide and the third shift was due to calcium carbonate decomposition. The mass

loss of calcium hydroxide was highest for the control sample. However, when the POFA content was at 0.8 (POFA/ cement ratio) the loss of calcium hydroxide was at the lowest level of all samples.

2.7.2 Scanning Electron Microscopy Analysis (SEM)

Hussin et al. (2015) studied the microstructure of mortar using the SEM technique. The POFA particle size used was from 50-100nm and was used at replacement rates of 60%, 80% and 100% of cement. The SEM test was carried out at both 28 days and 365 days with an 80% cement replacement mix. The authors observed that after increasing the age of curing, the total amount of calcium silicate hydrate crystals increased. Moreover, samples at 365 days had fewer voids compared with samples at 28 days. Kroehong et al. (2011) applied SEM analysis on cement paste containing 20% POFA of a median size 2 μ m at 7 days and 28 days. At 7 days, hydrated products such as calcium silicate hydrates, calcium hydroxide and ettringites were observed. The microstructures of the cement paste at 7 days had many voids and were porous. However after 28 days, the paste had a denser structure.

Altwair et al. (2011) studied the particle morphology of the hardened paste using SEM techniques. The median particle size of the POFA used was 2.89µm. Cement paste with 0, 0.3 and 0.8 POFA/cement ratios were chosen for the SEM test which was carried out at 90 days. Based on the results, the paste containing pure cement was coated with calcium silicate hydrate and calcium hydroxide (lime). The samples containing POFA/C with a ratio of 0.3, had a structure containing small pores, and the fractured surface was almost completely covered by calcium silicate hydrate. Most of the larger spaces had been coated by calcium silicate hydrate, forming a dense structure. When the POFA/C with a ratio of 0.8 was examined, many un-reacted particles of POFA could be observed.

2.7.3 Influence of Ca/Si Ratio on Energy-Dispersive X-Ray (EDX)

According to Wu and Ye, (2015), in cement paste the Ca/Si ratio is about 1.5-1.9. The addition of supplementary cementitious material results in the formation of additional C-S-H and Ca/Si values decrease. Dolado et al. (2007) stated the Ca/Si ratio usually ranges from 0.7 to 2.3 for cement paste and C-S-H gel is often described by its Ca/Si ratio. Liu et al. (2015) reported that SiO₂ in pozzolanic material reacts with the C–S–H gel and lowers the Ca/Si ratio. The Ca/Si ratio of C-S-H gel in cement paste with pozzolanic material is from 0 to 1. Rishav at al. (2016) used EDX analysis to determine the Ca/Si ratio. If the Ca/Si ratio is greater than 1.7 than it is an indication of higher presence of CH while a Ca/Si ratio smaller than 1.7 is an indication of higher the presence of C-S-H. As the amount of CH increases, the Ca/Si ratio increases. Additionally, the Ca/Si ratio decreases while the amount of CSH increases.

2.8 Concrete in Ammonium Nitrate Solution

Various studies on the microstructure of concrete have been carried out by researchers using an ammonium nitrate solution. Jauberthie and Rendell, (2002) studied mortar structures (40x40x160mm) which were immersed in a 0.25 mol/l (2.3%) ammonium nitrate solution for a period of 2 years. Based on the test results, it was observed that, there was cracking on the mortars after one year of immersion in the ammonium nitrate solution. Schneider and Chen, (2005) conducted an experiment for concrete prisms (40x40x160 mm) which were immersed in the ammonium nitrate solution. The concentrations of ammonium nitrate were 0.1%, 1%, 5% and 10%. The results showed that the highly concentrated ammonium nitrate solutions led to a very rapid decline in the strength of the test objects. The effective life of the concrete decreased significantly with an increase in the concentration of the ammonium nitrate solution, irrespective of loading or without loading. Demir et al. (2010) investigated the effects of exposing cement mortar to three different aggressive conditions with different percentages of ground waste brick. The 28-day compressive strength test results were the lowest for all the samples immersed in 5% ammonium nitrate solution containing different percentages of ground waste brick.

Wong et al. (2012) studied the effect of a 20% concentration of ammonium nitrate on the engineering properties of G50 (50N/mm²) and G60 (60N/mm²) concrete. The authors investigated the durability properties consisting of the water absorption, volume of permeable voids and sorptivity. The compressive strength, degradation depth and pH value were investigated for up to 90 days. It was concluded the pH value decreased and the degradation depth increased over time. Arafa et al. (2015) studied the effects of ammonium nitrate on the physical and mechanical properties of mortars. After 28 days of full water curing, samples were immersed in 5%, 20% and 50% ammonium nitrate concentration. The samples were tested at 10, 20, 40, and 60 days. The authors observed that as the concentration of ammonium nitrate increased, the compressive strength decreased. Samples immersed in a 50% ammonium nitrate solution had the lowest compressive strength. As for the porosity test, the higher the concentration of the ammonium nitrate, the higher the porosity. The samples immersed in the 50% ammonium nitrate solution had the highest porosity. This increase could be due to the removal of calcium hydroxide and the progressive decalcification of the calcium silicate hydrate compounds. The bulk density of the cement mortar decreased when it was exposed to the ammonium nitrate solution. The loss in bulk density increased as the concentration of the ammonium nitrate solutions increased.

2.9 Conclusions

From the present literature review, it is understood the particle size of POFA has a significant effect on its physical properties. As the POFA particle size decreases, the specific gravity and specific surface area increases. Currently the finest size POFA that has been used by researchers has been 50-100nm. Additionally, the microstructure properties of POFA also improve as the particles become finer. According to this literature review, the original, unground POFA particles are of large size and have many pores on their surface. However, after the grinding process, the POFA particles become finer and fewer pores are observed. In general, POFA contain high amounts of silicon dioxide, which is responsible for the pozzolanic reaction with cement paste.

The mechanical and durability properties of concrete containing POFA are influenced greatly by the particle size and the percentage replacement. Finer POFA particles exhibited better performance in the compressive strength of concrete when compare to coarser POFA particles. Moreover, the percentage replacement o plays a significant role in compressive strength and durability of concrete containing POFA. It was observed that, at about a 10% to 20% replacement level of cement with POFA gave the highest compressive strength and durability values.

Based on TGA analysis, it was concluded the mass loss of calcium hydroxide in cement paste was lower when it was replaced with POFA. However, in a pure cement paste, the mass loss of calcium hydroxide content increased with the curing age process. It was observed by SEM analysis, that as the curing period increased, the microstructure of the cement paste containing POFA formed a denser structure.

This author is unaware of any past research published using micro-fine POFA in cement paste to counteract an ammonium nitrate condition. Previous studies have used POFA of various sizes as a cement replacement to analyze and compare compression, tension, flexural, setting time, workability, heat evolution, dry shrinkage, water absorption, porosity, and permeability. POFA has also been investigated as a cement replacement and its effect on aggressive solutions such as chloride, carbon dioxide, and sulfate. The particle size of POFA used has ranged from 300µm-50nm. However, studies have yet to be done using POFA against aggressive ammonium nitrate solutions to control deterioration. Therefore, the aim of this research is to use micro-fine POFA of less than 10 micron as a partial cement replacement in an ammonium nitrate condition and then analyze the mechanical, durability and microstructure properties. POFA size less than 10 micron was used due to several factors. Firstly because the main purpose of this research is to investigate the effect of POFA against ammonium nitrate solution. Investigation of different POFA size or the smallest POFA size was not the objective of the study. Therefore POFA size below 10 micron was chosen because according to previous studies POFA size around 15-8 micron was mostly used. According to previous research, there had already been studies done regarding the use of POFA against other aggressive solutions such as, chloride, sulphate and carbon dioxide. There had not been any studies done regarding the use of POFA against ammonium nitrate solution. The main purpose of this research is to control degradation of concrete in ammonium nitrate environments such as the ammonium nitrate fertilizer plant. This is because the durability properties of concrete are affected in such conditions.

Chapter 3

MATERIALS AND TEST METHODS

3.1 Introduction

This chapter discusses the properties of Ordinary Portland Cement (OPC), Palm Oil Fuel Ash (POFA) and Ammonium Nitrate Solution. Consequently, the curing age, moulds and mix proportions used in various tests have been discussed in detail. Test procedures such as compressive strength, volume of permeable voids, sorptivity, TGA, SEM and EDX tests have also been elaborated in detail.

3.2 Material and properties

The materials used in this study were all available locally. They included OPC as the binder, POFA as the pozzolanic material used as a cement replacement and Ammonium Nitrate as the aggressive chemical. Potable tap water was used for mixing and curing throughout the research. Detailed descriptions of each material are presented in the following sections.

3.2.1 Cement

Ordinary Portland cement was used in this research. It was obtained from a local manufacturer, Cahaya Mata Sarawak (CMS) Sdn. Bhd. The cement fulfilled the requirements set under ASTM C-150 Type 1 Ordinary Portland Cement (OPC) as well as meeting the Malaysian standard MS 522: Part 1-2007, ISO 9001 and 14001 quality requirements.

3.2.2 Palm oil fuel ash

Palm oil fuel ash (POFA) is a by-product of the palm oil mill manufacturing process. The POFA used in this study was collected from a local palm oil mill in Kuching, Malaysia. In order to improve its reactivity, the POFA was further treated. The POFA was burnt using a furnace at 600^odegrees Celsius for one hour to remove any remaining carbon. Figure 3.1 shows the furnace used for the burning of the POFA. The POFA was then ground using a grinder operating at 25, 000 rpm for ten minutes to produce POFA particles smaller than 10 microns. A particle-size analyser machine was used to test the size of the POFA. Figure 3.2 shows the grinder used to process the POFA. Figure 3.3 shows the particle-size analyser machine.

The raw, black POFA obtained from the palm oil mill had a median particle size (d50) of 161.92 microns. Figures 3.4 and 3.5 show images of the raw POFA and the treated POFA. Figure 3.4shows the darker colour of raw POFA, due to the amount of unburned carbon. In Figure 3.5, the colour of the POFA is lighter due to the combustion effect, which reduced the amount of carbon.



Figure 3.1: Muffle furnace used for burning black POFA



Figure 3.2: Grinder used to reduce the size of raw POFA to medina particle size (d₅₀) below 10micron.



Figure 3.3: Particle Size Analyser.



Figure 3.4: Black POFA received from Palm oil mill (POFA partly burnt at palm oil mill).



Figure 3.5: Desired POFA produced after burning of black POFA in furnace at 600^o C for 1 hour.

3.2.3 Ammonium nitrate

Ammonium nitrate was obtained in pellet form from a local market. A 20% Ammonium nitrate solution was prepared by mixing the pellets with water. After 28 days of water curing, the test samples were immersed in the 20% ammonium nitrate solution for 90 days. The container holding the samples and solution was closed in order to keep the concentration constant. The highest percentage of ammonium nitrate which had been used in research is 50% Arafa et al. (2015) while the lowest percentage is 0.1%, Schneider and Chen, (2005). Since the concentration of the ammonium nitrate was not the main target of the investigation, therefore 20% ammonium nitrate was chosen since it was the median value used according to previous study.

3.3 Curing

The curing ages for the testing was 3, 7, 28, 56 and 90 days. The method of curing used in this research was a water curing. Fresh cement paste was cast in 50mm moulds and demolded on the next day. The cement cubes were then immersed in water for 27 days for full water curing. After the desired cuing age was achieved, some of the samples were left at room temperature and some were placed in an ammonium nitrate solution for 90 days. Table 3.1 shows the curing conditions of the cement pastes.

Table 3.1:	Curing	Condition
------------	--------	-----------

Maulda	Watara	Ammonium	Room
woulds	waters	Nitrates	Temperatures
1 Davi	27 davia	50% immersed till	50% left in room
I Day	27 days	90 days	temperature

3.4 Moulds

Fifteen moulds were used to cast the cement pastes. The moulds were 50mm cubes as shown in Figure 3.6.



Figure 3.6: Moulds used for casting

3.5 Mix proportion

The cement paste was prepared according to the BS standard. Table 3.2 describes the mix proportion used in this study. According to the 1997 Uniform Building Codes, a maximum water to cement ratio of 0.45 was chosen for concrete exposed to severe conditions; therefore, for this study, a water cement ratio of 0.4 was chosen. The water cement ratio of 0.4 was chosen based on several trial mix method. Additionally, cement was replaced at rates of 0%, 10%, 20%, 30% and 40% of ground POFA having a median particle (d₅₀) size of below 10 microns. Cement paste was chosen instead of mortar and concrete for this research because the reaction of ammonium nitrate only occurs with calcium hydroxide which is found in cement only. Therefore it would be wastage of material and money if mortar and concrete is chosen for this research.

Mix. No	Symbol	OPC, (gram)	POFA (gram)	W/C ratio	Water (gram)
1	Control	200	0	0.4	80
2	10%POFA	180	20	0.4	80
3	20%POFA	160	40	0.4	80
4	30%POFA	140	60	0.4	80

Table 3.2: Mix amount of cement paste for each batch

3.6 Specific Gravity Test for POFA

A specific gravity test for POFA was conducted using the Pycnometer method. This procedure was done in accordance with the ASTM D-854 standards. First, an empty Pycnometer bottle with its stopper was weighed and its mass was recorded (W1). Then, 20 grams of POFA was added into the Pycnometer bottle and weighed (W2). After that, kerosene was added into a flask until it had filled three-fourths of the Pycnometer. The samples were kept in a vacuum desiccator for 1 hour to remove any entrapped air. After vacuuming, kerosene was added into the same flask until it reached the graduated mark. The outer surface of the bottle was cleaned and the bottle was weighed (W3). The bottle was then emptied and kerosene was added until it reached the bottle line mark. The bottle with kerosene was weighed (W4). Lastly, the bottle was rinsed using methanol to remove any remaining kerosene before washing it with distilled water.

3.7 Compressive Strength Test

The compressive strength test is carried out to determine the maximum amount of compressive load which can be applied to a material before fracturing. The test piece is usually compressed between the plates of the compression-testing machine by gradually

applying load. The test pieces are usually in the form of a cube, prism or cylinder. Compressive strength is one of the most important engineering properties used to classify concrete. Compressive strength tests were carried out in accordance with BS1881: Part 116: 1983 Standards. Five samples were tested and an average result was calculated. The calibrated compression machine was used for a 50 mm cube test at a loading rate of 700 N/sec., which was within a loading range between 0.2 N/mm²/sec and 0.4 N/mm²/sec. Figure 3.7 shows the compression machine used to test the samples.



Figure 3.7: Compression test machine used for testing

3.8 Volume of Permeable Voids (VPV)

Permeability is a major factor for the long-term durability of concrete. Low permeability means a high resistance to moisture into the concrete matrix and less damage from harmful chemicals. One of the simplest ways to measure the permeability of concrete is by a volume of voids test. Volume of permeable void means the amount of voids present in a sample.

The test was conducted on 50 mm cubes at 28, 56 and 90 days curing age following the ASTM C642 Standard. A sample was oven-dried for 24 hours at 100 degrees Celsius. Afterwards, it was removed from the oven and cooled at room temperature and the oven dry-mass A of the sample was recorded. The same sample was then fully immersed in water for 48 hours then heated for 5 hours and finally left to cool for 14 hours. The mass of the sample

was recorded as B after it was taken out of the water and wiped clean. In the final stage, the same sample was immersed in water, and the apparent mass C was recorded. The VPV values of the sample were then calculated. Figures 3.8 and 3.9 show the sample weighed for the VPV test and samples boiled for 5 hours. All the mix number of samples in Table 3.2 was used in the test.



Figure 3.8: Sample weighted for VPV



Figure 3.9: Sample boiled for 5 hours.

3.9 Sorptivity Test

Sorptivity is defined as the rate of absorption under capillary force. It is measured using dry concretes samples. It is used to measure dry concrete samples which rest on small supports with a few millimetres of the bottom of the sample are submerged in the wetting liquid.

The sorptivity test was conducted in accordance with ASTM C 1585 Standards at 28, 56 and 90 days. The sorptivity test determines water absorption through capillary action and is quantified by the time rate of water intake per unit of the cross-sectional area. A test sample of a 50mm cube was oven dried for 24 hours at 100 degrees Celsius. Afterwards it was cooled at room temperature, and adhesive tape was used on its sides of immersion and mass A was recorded. Later, the sample with the surface where the adhesive tape was stuck was partially immersed in a tray with water in it where immersion was maintained between 1 to 3 mm. The increase in weight of the sample was then recorded at 30 min. Graphs of water uptake, I versus \sqrt{t} were plotted and the slope was calculated using linear regression. All the mix number of samples in Table 3.2 was used to carry out the test. Figure 3.10 shows the sorptivity test setup.



Figure 3.10: Sorptivity test setup

3.10 TGA (Thermo-gravimetric Analysis)

In TGA analysis method, the change in chemical and physical of the material are measured as a function of increasing temperature. The mass gain or loss of a material due to oxidation, decomposition or losses of volatiles are measured through the TGA method.

The thermo-gravimetric analysis was carried out using STAR Software (METTLER TOLEDO). About 50 grams of the test sample was inserted into the crucible and weighed using an external balance. The TGA/DSC1 machine and a PC were switched on. While waiting for the module to establish communication with the PC, the circulator was turned on. To create a new test on the PC, the start icon was clicked, a file was opened, and a new test was added. In the dynamic section of the new test, the start temperature upon insertion was 35°C and the ending temperature was 1100°C. In the gas segment of the test, nitrogen gas was applied and the volume entered was 50m³. The pan size was entered by clicking on the appropriate pan. To save the test results, the test name was keyed in and then clicked OK. On the TGA machine, the TARE button was adjusted to zero the balance and the furnace was opened. The crucible containing the sample was inserted into the machine when the temperature was suitable. The furnace was then closed and the 'Proceed' button was pressed

to increase the temperature and start the analysis. Figure 3.11 shows the TGA machine used in this test. All the mix samples in Table 3.2 were used to carry out the test.



Figure 3.11: TGA Machine

3.11 Scanning Electron Microscopy (SEM) and Energy-Dispersive X-Ray (EDX) Test

A scanning electron microscope (SEM) is a special type of microscope, which produces images of samples by scanning the samples. The electrons connect with the atoms in the sample and produce signals regarding the sample's composition and surface topography. The element analysis and chemical characterization of a sample is determined through EDX technique. The analysis is accomplished by the interaction of some source of x-ray excitation and sample.

In this research, SEM was carried out on cement pastes with POFA using a SEM machine. Samples were placed on a double-sided adhesive conductive carbon tape to prevent the scattering of loose particles. The samples were then coated with gold to increase the electrical conductivity in the samples. Samples were placed in the SEM machine, and the analysis was carried out. Several SEM images were made of different aspects of the sample. The SEM machine was set to produce images at 10µm and 1µm.

EDX analysis was carried out in the same machine as the SEM. After producing the SEM images, the samples were further analysed in the EDX test. Each sample was analysed for 10 minutes to determine the all of the elements present in the samples. The EDX test was carried out on the same sample aspect as the SEM image taken. All the mix samples in Table 3.2 were used to carry out the test. Figures 3.12 to 3.14 show the samples and the machine used for the tests.



Figure 3.12: SEM samples preparation



Figure 3.13: Gold Plating Machine



Figure 3.14: SEM Test Machine

3.12 Summary

This chapter discussed the materials used throughout the research and their properties. For this research, a cement paste with 100 % OPC, acted as the control sample. Micro-fine POFA of below 10 μ m was used to replace OPC at 10%, 20% and 30%. A constant water to cement ratio of 0.4 was used for all the samples. The control samples and samples replaced with 10%, 20% and 30% POFA were cured in water for 28 days. Then, half of the samples were left in

room temperature and the remaining samples were immersed in a 20% ammonium nitrate solution for 90 days. A compressive strength test was carried out at 3, 7, 28, 56 and 90 days on both groups of samples. Similarly, durability tests, consisting of a sorptivity and a volume of permeable void test were carried out at 28, 56 and 90 days for both groups of samples Finally, a micro-structural test, consisting of a TGA, SEM and EDX test was carried out at 28, 56 and 90 days as well.

Chapter 4

RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter presents the results and discussion of the entire set of tests mentioned in chapter 3. The physical properties test results, which consisted of a median particle size (d50), specific surface area, specific gravity and the colour of OPC and POFA are presented and discussed. The chemical properties and micro-structural test results of OPC and POFA are also presented in this chapter. The mechanical and durability test results of the modified cement paste are analysed and discussed in detail. Results are compared with previous research findings. The TGA, SEM and EDX test results are presented, analysed and compared.

4.2 Physical Properties of POFA and OPC

The physical properties test consisted of median particles of (d_{50}) examined through a particle-size analyzer, a specific gravity test in accordance to ASTM D-854 standards and a specific surface area test through the particle size analyzer. Table 4.1 presents the physical properties of OPC, raw POFA and treated POFA. Raw POFA refers to the POFA obtained directly from the palm oil mill. Meanwhile, treated POFA refers to the raw POFA, which was burnt in an electric furnace at 600 degrees C for one hour and then ground for 10 min. in a grinder. For this research, 10 minutes grinding duration of POFA was adopted because the target POFA size which was less than 10 micron was obtain when POFA was grounded for this duration.

As shown in Table 4.1, the colour of raw POFA is black due to the presence of excess carbon. This is attributed to the incomplete burning at the palm oil mill. As observed in this study, the colour of treated POFA changed from black to grey after being heated in an electric furnace. Similar observations were also reported by previous researchers. The colour of raw POFA, as collected from the palm oil mill, was black in colour but became grey after

heat treatment (Hussin et al., 2015; Islam et al., 2016). According to Table 4.1, the particle size D_{10} , D_{50} and D_{90} of raw POFA were 96.19µm, 149.22µm and 246.6µm respectively. D_{10} means 10% of the samples tested in the particle size analyzer had a median particle size of 96.19µm. The mean diameter, which refers to the average value of all the particles at 10%, 50% and 90% for raw POFA was 161.92 µm. For treated POFA, the particles were 0.81µm, 4.92µm and 22.79µm at D_{10} , D_{50} and D_{90} . The mean diameter was 8.7µm. Sata et al. (2004) reported using raw POFA of 62.5µm and treated POFA of 10.1 µm. Tangchirapat et al. (2007) used raw POFA of 183 µm and treated POFA of 7.4 µm.

Table 4.1 shows the specific gravity of POFA increased as the size decreased. The specific gravity of raw POFA was 1.89 while treated POFA was 2.50. The increase of the specific gravity is due to the grinding process, which produces finer POFA particles. As a result, the treated POFA are denser and highly packed and have a higher specific gravity value. Similar results have been reported by Sata et al. (2004) and Tangchirapat et al. (2007).

Table 4.1 also demonstrates the specific surface for raw POFA was 447.68 cm²/g while treated POFA had a specific surface area of 53206.33 cm²/g. The increase in the specific surface area is due to the reduction of the POFA into finer particles having a higher surface area. For OPC, the particles were of 3.19 μ m, 20.22 μ m and 52.52 μ m at D₁₀, D₅₀ and D₉₀. The mean diameter was 24.67 μ m. The specific gravity and specific surface area were 3.10 and 10667.40 cm²/g respectively.

Table 4.2 demonstrates the grinding duration of POFA. It is observed that, as the grinding time increased, the size of the POFA particles decreased. The raw POFA had a median particle size (D_{50}) of 149.22µm at zero minutes of grinding. This size however decreased to 8.03 µm after 1 minute of grinding. At 2, 3, 4, 5 and 10 minutes of grinding, the median particle sizes (D_{50}) were 6.87µm, 6.88µm, 6.19 µm, 5.46µm and 4.92µm respectively. It was also observed, the particles at (D_{10}) also decreased in size as the grinding time increased. At 0 minutes of grinding for raw POFA, the (D_{10}) was 96.19µm. This value however decreased to 1.34µm at 1 minute, to 1.28µm at 2 minutes, 1.25µm at 3 minutes, 1.22 µm at 4 minutes, 1.16 µm at 5 minutes and 0.81 µm at 10 minutes. A similar pattern was also observed for particles at (D_{90}). The sizes at 0, 1, 2, 3, 4, 5 and 10 minutes were 246.6 µm, 35.71 µm, 29.44 µm, 29.97 µm, 26.92 µm, 22.59 µm and 22.79 µm respectively. For this study, 10 minutes of grinding was selected as the mean diameter of the POFA produced was 8.7µm.

Figure 4.1 shows the particle size distribution of OPC and POFA. Based on Figure 4.1, the distribution of ground POFA fell within the same range. However, for the raw POFA, which was not ground, the distribution was further from the ground POFA because it had a higher particle size. The distribution of OPC fell between the ground POFA and the raw POFA. This was attributed to the fact the OPC had a median particle (D_{50}) size of 24.67µm which was finer than raw POFA but bigger than the ground POFA. A similar distribution was also reported by Tangchirapat et al. (2007) and Pourakar et al. (2015).

Physical Properties	OPC	Raw POFA	Treated POFA
Colour	grey	black	grey
Particle Size D ₁₀ (µm)	3.19	96.19	0.81
Median Particle D ₅₀ (µm)	20.22	149.22	4.92
Particle Size D ₉₀ (µm)	52.52	246.6	22.79
Mean Diameter (µm)	24.67	161.92	8.7
Specific Gravity	3.10	1.89	2.50
Surface Area (cm ² /g)			
(Particle Size Analyser)	10667.40	447.68	53206.33

Table 4.1: Physical properties of OPC and POFA

Table 4.2: Particle size of POFA with grinding time

Grinding Time	D ₁₀ (µm)	D ₅₀ (µm)	D ₉₀ (µm)	Mean Diameter (µm)	Value Selected
Raw POFA(0min)	96.19	149.22	246.6	161.92	
POFA-1min	1.35	8.03	35.71	13.57	
POFA-2min	1.28	6.87	29.44	11.35	N
POFA-3min	1.25	6.88	29.97	11.45	Not-selected
POFA-4min	1.22	6.19	26.92	10.35	
POFA-5min	1.16	5.46	22.59	8.87	
POFA-10min	0.81	4.92	22.79	8.7	selected



Figure 4.1: Particle size distribution of OPC and POFA
4.3 Chemical Composition of POFA and OPC

The chemical composition of OPC and treated POFA was determined using the X-ray fluorescence (XRF) technique shown in Table 4.3. Table 4.3 shows the percentage of SiO₂, the major oxide of POFA, in samples was 58.1%, and the total sum of SiO₂, Al₂O₃ and Fe₂O₃ was 62.37%. The loss of ignition of the POFA was 6.78% and SO₃ was 0.7%. The treated POFA however had lower amounts of CaO, 10.8% compared to OPC. In addition, the treated POFA contained 6.1% MgO and 6.45% of K₂O by volume. The POFA in this study is classified as a class N pozzolanic, as the total sum of SiO₂, Al₂O₃ and Fe₂O₃ was close to 70%, SO₃ was lower than 4% and LOI values are close to 10% following ASTM C 618 standards. A similar class was also grouped by Tangchirapat et al. (2009) and Tangchirapat et al. (2012). According to Tangchirapat et al. (2009), the total amount of SiO₂, Al₂O₃ and Fe₂O₃ was 70.3%, while the percentage of LOI and SO₃ was 7.9% and 2.3% respectively.

A low percentage of CaO in POFA signifies the POFA has no cementing properties and therefore the addition of Ca(OH)₂ in cement is required for a pozzolanic reaction. A high percentage of silica indicates the pozzolanic characteristic of the POFA. According to Table 4.3, the percentage of Al₂O₃ and Fe₂O₃ in the POFA was lower than in OPC while, the percentage of K₂O and MgO in the POFA was higher than the OPC. It was reported high K₂O content in POFA is responsible for the increase in the alkali silica reaction damage when reactive aggregate is present Malvar et al. (2006). The SO₃ content in POFA and OPC are almost the same. The LOI in POFA indicates the presence of unburned carbon due to the improper burning process in the palm oil mill. According to Johari et al. (2012), heat treatment influences the LOI values of POFA and is therefore required to ensure compliance with the requirements specified in ASTM C618.

Based on Table 4.3, it was observed OPC had a high amount of lime (CaO) content, 65.9%. The percent of silica in OPC was relatively low, 19.28% compared to POFA. In addition, according to Table 4.3, the OPC contained 4.67% Al_2O_3 , 3.3% Fe2O3, 1.7% MgO, 0.5% K_2O and 0.3% SO₃ by volume. Generally, OPC should contain the following ranges of compounds, about 60-67% CaO, 17-25% SiO₂, 3-8% Al_2O_3 , 0.5-6% Fe₂O₃, 1-4.0% MgO,

1.3-3.0 SO₃ and 0.4-1.3% alkalis (K₂O & Na₂O) according to ASTM C 150. The chemical composition of OPC in Table 4.3 however satisfies the required percentage. Similar values were reported by previous researchers (Johari et al., 2012; Usman et al., 2015; Ranjbar et al., 2016).

The raw materials used to manufacture cement mainly consist of lime, (CaO), silica (SiO₂), alumina (Al₂O₃) and iron oxide (Fe₂O₃). This iron oxide interacts with the other compounds in the kiln to form compounds that are more complex. The percentage of CaO must be within the acceptable limit as too much will make it difficult to combine the cement with other compounds and free lime will exist. This will cause unsoundness in the cement. K₂O and Na₂O in cement are referred to as alkalis in cement and are considered as minor oxides formed in a kiln during the manufacturing process. Large amounts of these alkalis can cause difficulties in regulating the setting times of cement. The amount of SO₃ present is an indirect measurement of the amount of gypsum in cement. Gypsum is added to cement primarily to regulate setting times. Adding too much gypsum can cause expansion. The percentage of MgO in cement comes from the Magnesia compound and must be correctly measured to control for expansion from hydration of this oxide in hardened concrete.

Chemical Composition	Treated POFA (%)	OPC (%)
Silicon Dioxide, (SiO2)	58.1	19.28
Aluminium Oxide, (Al ₂ O ₃)	2.6	4.67
Iron Oxide,(Fe ₂ O ₃)	1.67	3.3
Calcium Oxide, (CaO)	10.8	65.9
Magnesium Oxide, (MgO)	6.1	1.7
Potassium Oxide, (K ₂ O)	6.45	0.5
Sulphur Trioxide, (SO3)	0.7	0.3
S+A+F	62.37	27.25
LOI	6.83	0.9

Table 4.3: Chemical composition of POFA and OPC

4.4 Microstructure analysis on POFA and OPC

The microstructure analysis consisted of a Scanning Electron Microscopy (SEM) and an Energy-Dispersive X-Ray (EDX) testing process. SEM and EDX tests were carried out on raw POFA (directly from the mill), treated POFA (burned and ground) and OPC. The SEM test was carried out to study the morphologies, particle shapes, particle size and agglomeration of POFA and OPC. The EDX analysis was carried out to study the elements such as silicon and calcium in raw POFA, treated POFA and OPC.

4.4.1 Scanning Electron Microscopy (SEM) of POFA and OPC

Figure 4.2 shows the SEM images of raw POFA. The median particle size (d50) of the raw POFA was 161.92 μ m. Based on Figure 4.2, the raw POFA had a large particle size and most of the particles were porous. Due to the large particle size, both the specific surface area and specific gravity were lower than the treated POFA. Most of the particles were observed to be round in shape with a porous surface. A large porous surface on the POFA particles will result in a greater amount of water used during mixing and increase the porosity. Tangchirapat at el. (2007) reported a similar observation for POFA having a median particle size (d₅₀) of 183.0 μ m. The author reported the POFA had a large particle size and most particles were of a porous texture.

Figure 4.3 shows the SEM image of treated POFA. The median particle size (d_{50}) of the treated POFA was below 10µm. It was observed that the treated POFA are smaller in size and shape compared to raw POFA. The particles were less porous in treated POFA compared to raw POFA. The treated POFA had a wide range of sizes but they were generally irregular and crushed shaped. Both the specific gravity and specific surface area of the treated POFA due to a less porous texture. Tangchirapat et al. (2007) reported, when the POFA size was reduced to 15.9µm and 7.4µm, the particles were irregular and crushed shape. A similar observation was also reported by Tangchirapat et al. (2012) for a POFA of median particle size (d_{50}) 10.7µm. The observation of treated POFA in this study agrees with the findings of the previous research.

Figure 4.4 shows the SEM image of OPC. The median particle size (d_{50}) of the OPC is 24.67µm. The particle morphology of cement consists of a wide range of shapes and sizes but

is generally agglomerated shaped. However, it is less porous compared to raw POFA. OPC consists of four main minerals: i) alite (C₃S), ii) belite (C₂S), iii) aluminate (C₃A) and iv) ferrite (C₄AF). When water is added, these minerals react and form few hydration products. Ranjbar et al. (2016) reported the particle morphology of cement consists of an agglomerated shape; however, it has a less porous structure compared to POFA. The median particle size (d_{50}) of the OPC used by the author was 14.6µm



Figure 4.2: SEM image of Raw POFA



Figure 4.3: SEM image of treated POFA



Figure 4.4: SEM image of OPC

4.4.2 EDX Analysis of OPC and POFA

The EDX test results of raw POFA, treated POFA and OPC are shown in Table 4.4 and Figures 4.5 to 4.7. According to Table 4.4 and Figure 4.5, the elements found in raw POFA were carbon, oxygen, magnesium, aluminium, silicon, potassium and calcium. It was observed, silicon made up the highest percentage at 30.94% compared to the other elements. The higher percentage of silicon presents the pozzolanic characteristic of POFA. Consequently, the raw POFA particles consisted of 19.97% carbon, 15.93% oxygen, 4.71% magnesium, 2.3% aluminium, 9.88% potassium and 16.26% calcium by volume.

According to Table 4.4 and Figure 4.6, the percentage of silicon in treated POFA was 36.9%, which was an increase of 19.26% compared to raw POFA. The percentage of oxygen was 25.17% and magnesium 5.24%. Both of these elements showed an increase of 58% and 11.25% respectively compared to raw POFA. As shown in Table 4.4, the elements carbon, aluminium, potassium and calcium had values of 15.65%, 1.07%, 6.54% and 9.42% respectively in treated POFA. It was observed carbon, aluminium, potassium and calcium decreased by 21.63%, 53.47%, 33.80%, and 42.07% respectively compared to raw POFA. It was observed the percentage of silicon and reduced the amount of carbon. These findings agree with previous researchers as explained in the following paragraph.

According to Johari et al. (2012), heat treatment had increased the percentage of silicon dioxide by 27% and reduced the carbon percentage by 99.5%. In addition, the elements found in the POFA in these test results also agree with the findings of previous researchers. Johari et al. (2012) carried out an EDX test at three different locations on raw and treated POFA. It was reported by the author, the elements carbon, oxygen, aluminium, magnesium, potassium, silicon, and iron were detected in raw and treated POFA. It was concluded by the author, in raw POFA, the percentage of carbon was higher than in treated POFA. Similarly, the percentage of silicon was lower in raw POFA compared to treated POFA. Usman et al. (2015) also reported finding the elements oxygen, calcium, potassium, magnesium, oxygen and carbon in treated POFA. The author concluded the percentage of silicon was the highest compared to the other elements.

Table 4.4 and Figure 4.7 illustrate the EDX analysis of OPC. It is noted the elements carbon, oxygen, silicon and calcium were detected in OPC. The percentage of silicon was 5.85%, which was much lower than raw and treated POFA. It was observed calcium had the highest percentage at 56.07% compared to the other elements. Other elements detected were carbon at 7.35% and oxygen at 30.73%. The lower percentage of silicon in OPC is because it does not have any pozzolanic characteristics. The higher percentage of calcium in OPC is required so hydration and a pozzolanic reaction can occur when water and pozzolanic material are added.

Flomont	Atom (%)						
Liement	Raw POFA	Treated POFA	POFA OPC				
Carbon 19.97		15.65	7.35				
Oxygen 15.93		25.17	30.73				
Magnesium	4.71	5.24	-				
Aluminium	2.3	1.07	-				
Silicon	30.94	36.9	5.85				
Potassium	9.88	6.54	-				
Calcium	16.26	9.42	56.07				
Total	100	100	100				

Table 4.4: EDX test result of OPC and POFA



Figure 4.5: EDX analysis of raw POFA



Figure 4.6: EDX analysis of treated POFA



Figure 4.7: EDX analysis of OPC

4.5 Mechanical Properties Test of Modified Cement Paste

The mechanical properties test consisted of a compressive strength test. The compressive strength tests were carried out in accordance with BS1881: Part 116: 1983 standards. The tests were carried out at 3, 7, 28, 56 and 90 days for control samples (containing 100% OPC) and with samples replaced with 10% POFA, 20% POFA, and 30% POFA. The compressive strength test was carried out on samples in room temperature and in ammonium nitrate conditions. The test was conducted with a constant water to cement ratio of 0.4. Sections 4.5.1 and 4.5.2 discuss the compressive strength test results obtained at room temperature and in ammonium nitrate conditions. Section 4.5.3 compares the compressive strength at room temperature and in an ammonium nitrate solution.

4.5.1 Influence of POFA on the compressive strength at room temperature

. The compressive strength and normalized compressive strength of the cement paste at room temperature are shown in Table 4.5. Figure 4.8 shows the graph of the compressive strength of the cement paste at room temperature. Normalized compressive strength is explained as the ratio (in percentage) between the compressive strength of the control sample and the compressive strength of cement paste containing various percentages of POFA.

Based on the Table 4.5, the compressive strength of the control sample at 3 days and 7 days had the highest compressive strength values compared to the samples containing POFA. The compressive strength of the control sample at 3 days and 7 days was 37.7 MPa and 47.8 MPa respectively. The compressive strength for the samples with 10% POFA, 20% POFA and 30% POFA at 3 days were 26.2 MPa, 20.9 MPa and 20 MPa respectively. The percentage decrease in the compressive strength between the control sample and the 10% POFA, 20% POFA and 30% POFA were 70%, 55% and 53% respectively. The compressive strength for the samples with 10% POFA, 20% POFA and 30% POFA at 7 days were 41.9 MPa, 34.4 MPa, and 24.4 MPa, respectively. The percentage decrease between the control sample and the 10% POFA, 20% POFA and 30% POFA were 88%, 72% and 51% respectively. At 28 days, the compressive strength of the samples containing 10% and 20% POFA exhibited a higher compressive strength than the control samples. The compressive strength of the control sample was 50.2 MPa, while the 10% POFA and 20% POFA had compressive strength values of 52.7 MPa and 52.0 MPa, respectively. This was about a 105 % and a 104 % increase in the compressive strength values compared to the control samples. However, the compressive strength of the samples with a 30% POFA replacement had a compressive strength value of 83MPa. This was about an 83% decline in the compressive strength values compared to the control samples. Similarly, at 56 days and 90 days, the compressive strength values for 10% POFA and 20% POFA increased compared to the control samples. At 56 days, the compressive strength values for 10% POFA and 20% POFA were 101 MPa and 106 MPa, which was about a 101% and a 106% increase compared to the control samples. At 90 days, the compressive strength values for 10% POFA and 20% POFA were 63.7 MPa and 69.5 MPa respectively. This was about a 106% and 115% increase compared to the control samples. At 56 days, the compressive strength of the 30% POFA mix was 45.7 MPa, which was about 80% less than the control sample. At 90 days, the compressive strength for 30% POFA was 57 MPa. This was about 94% less than the control samples.

Based on the test results obtained, it was observed the compressive strength increases with the curing age. This is because more calcium silicate hydrate (C-S-H) and calcium hydroxide Ca(OH)₂ are produced with an increase in age. Calcium silicate hydrates and calcium hydroxide are responsible for the strength in the cement paste. The decrease in the compressive strength with an increase in the cement replacement percentage with POFA at 3 and 7 days is due to the lack of CaO in the mix to produce Ca(OH)₂ and C-S-H. At this age, the presence of SiO₂ in POFA is insignificant due to the absence of the pozzolanic reaction. However, the higher compressive strength after 28 days for the 10% and 20% POFA samples was due to the pozzolanic reactions. The greater fineness of the POFA particles and the silicon dioxide (SiO₂) content in the POFA, reacted with Ca(OH)₂ to produce additional secondary calcium silicate hydrates(C-S-H). The higher strength of the 10% and 20% POFA cement paste was mainly due to the formation of calcium silicate hydrates. As a result, the compressive strength had improved at the later age.

In addition, according to Abdullah et al. (2006) too much POFA added as the cement replacement will result in very low strength compared to samples consisting of a lower percentage of POFA. This is because there is less CaO present to produce $Ca(OH)_2$ for the pozzolanic reaction to occur. This agrees with the test results, as the compressive strength was lowest for samples with 30% POFA as a replacement. In addition, the compressive strength values obtained from the control samples in the test agree with the previous literature. According to Chindaprasirt et al. (2004), the compressive strength obtained from control samples was 60.9 MPa, 77.6 MPa, 84.5 MPa and 84.8 MPa for 7, 28, 56 and 90 days respectively. These values are similar to the test results obtained in Table 4.5. According to Tangchirapat et al. (2007) and Sata et al. (2010), a mix with 10% and 20% a POFA replacement had the highest compressive strength values, with a median particle size of 7.4 μ m and 9.2 μ m.

Therefore, it is recommended to replace cement with 20% of POFA as it exhibited higher compressive strength than the control at 56 and 90 days. These findings agree with the previous literature.

Mixes	Compressive strength (MPa) - normalized compressive strength (%)						
	3-days	7-days	28-days	56-days	90-days		
Control	37.7 - 100	47.8 - 100	50.2 - 100	57.5 - 100	60.4 - 100		
10%POFA	26.2 - 70	41.9 - 88	52.7 - 105	57.9 - 101	63.7 - 106		
20%POFA	20.9 - 55	34.4 - 72	52.0 - 104	60.7 - 106	69.5 - 115		
30%POFA	20.0 - 53	24.4 - 51	41.8 - 83	45.7 - 80	57 - 94		

Table 4.5: Compressive strength and normalized strength in room temperature



Figure 4.8: Compressive strength in room temperature

4.5.2 Influence of POFA on the compressive strength in ammonium nitrate conditions

The compressive strength and normalized compression values for samples in an ammonium nitrate condition at 56 and 90 days are presented in Table 4.6. Figure 4.9 shows the compressive strength of samples immersed in an ammonium nitrate solution up to 90 days. Based on the test results, the compressive strength at 56 days for the control sample was 42.7 MPa. Samples replaced with 10% POFA and 20% POFA had compressive strength values of 47.4MPa and 44.2MPa, which was about 111% and 104% higher than the control samples. The compressive strength values for 30% POFA was 36 MPa which is about 85% less than the control samples. At 90 days, the compressive strength of the control sample, 10% POFA, 20% POFA and 30% POFA were 39.2 MPa, 37.4 MPa, 42.4 MPa and 31.8 MPa respectively. Samples with 20% POFA exhibited an increase in the compressive strength values of about 108% compared to the control sample. However, the compressive strength of 10% POFA, 30% POFA and 40% POFA had 95%, 81% and 88% lower values than the control samples. The loss of compression strength after 28 days of water curing is due to the removal of calcium hydroxide. According to Pepenar (2013), when cement is exposed to an ammonium nitrate solution, the calcium hydroxide in the cement paste reacts with the ammonium nitrate. As a result, the calcium hydroxide is removed from the paste causing the development of voids and pores in the cement paste. Therefore, the compressive strength is lower. Removal of calcium hydroxide also results in a less conducive environment for the pozzolanic reaction to take place with silicon dioxide in the POFA. Similar compressive strength patterns were reported by Arafa et al. (2015) and Wong et al. (2013). Both authors observed the compressive strength decreased when it was immersed in an ammonium nitrate solution.

Based on these test results it is recommended replacing about 20% of cement with POFA would achieve a better compressive strength value in ammonium nitrate conditions.

Mixos	Compressive strength (MPa) - normalized compressive strength (%)						
WIIXes	3-days	7-days	28-days	56-days	90-days		
Control	37.7 - 100	47.8 - 100	50.2 - 100	42.7 - 100	39.2 - 100		
10%POFA	26.2 - 70	41.9 - 88	52.7 – 105	47.4 - 111	37.4 - 95		
20%POFA	20.9 - 55	34.4 - 72	52.0 - 104	44.2 - 104	42.4 - 108		
30%POFA	20.0 - 53	24.4 - 51	41.8 - 83	36.1 - 85	31.8 - 81		

Table 4.6: Compressive strength and normalized compressive strength in ammonium nitrate solution



Figure 4.9: Compressive strength of concrete in ammonium nitrate solution

4.5.3 Difference in compressive strength of samples in room temperature and in ammonium nitrate conditions

Table 4.7 compares the percentage difference between samples in room temperature and samples in an ammonium nitrate solution. Table 4.7 shows, at 56 days, the percentage loss of compressive strength in an ammonium nitrate solution and summarized thus: at control, 10% POFA, 20% POFA and 30% POFA the loss of compressive strength was 74%, 82%, 73% and 79%. This comparison was done with the samples in room temperature. Similarly, there was a loss of compressive strength shown in the data at 90 days: of control, 10% POFA, 20% POFA and 30% POFA there was a loss of 65%, 59%, 61% and 56% respectively. There was no difference at 3, 7 and 28 days because samples were in the same water curing condition. After 28 days, samples were subjected to room temperature and an ammonium nitrate solution. It was observed the percentage decrease in compressive strength at 56 days in an ammonium nitrate solution was almost 25% compared to samples at room temperature. The strength however continued to decrease to about 50% at 90 days in an ammonium nitrate solution.

Wong et al. (2013) reported similar differences between samples in water and in an ammonium nitrate solution. The author reported that samples immersed in a 20% ammonium nitrate solution had a percentage decrease of 75% and 53% at 56 and 90 days respectively for G50 concrete. For G60 concrete, the decrease in compressive strength was 77% at 56 days and 58% at 90 days.

Mixes	Compressive strength (MPa) - Normalized compressive strength (%)							
	3 days	56days	90days					
Control	37.7 - 100	47.8 - 100	50.2 - 100	57.5 – 100	60.4 - 100			
Control (AN)	37.7-100	47.8 - 100	50.2 - 100	42.7 – 74	39.2 - 65			
10%POFA	26.2 - 100	41.9 - 100	52.7 - 100	57.9 – 100	63.7 - 100			
10%POFA (AN)	26.2 - 100	41.9 - 100	52.7 - 100	47.4 - 82	37.4 - 59			
20%POFA	20.9 - 100	34.4 - 100	52.0 - 100	60.7-100	69.5 - 100			
20%POFA (AN)	20.9 -100	34.4 - 100	52.0 - 100	44.2 - 73	42.4 - 61			
30%POFA	20.0 - 100	24.4 - 100	41.8 - 100	45.7 – 100	57.0 - 100			
30%POFA (AN)	20.0 - 100	24.4 - 100	41.8 - 100	36.1 – 79	31.8 - 56			

Table 4.7: Comparison of compressive strength

4.6 Durability Properties Test on Modified Cement Paste

The durability properties test consisted of a sorptivity and volume of permeable voids test (VPV). The sorptivity test was carried out in accordance with the ASTM C 1585 standards as explained in chapter 3. Meanwhile the VPV test was carried out in accordance with the ASTM C642 standard as explained in chapter 3. The durability test was carried out for the control sample and samples replaced with 10% POFA, 20% POFA and 30% POFA. A constant water to cement ratio of 0.4 was used for all the samples. In addition, the durability test was carried out for samples at room temperature and in ammonium nitrate conditions. Sections 4.6.1 and 4.6.4 discuss the sorptivity and volume of permeable voids test results

4.6.1 Sorptivity of Modified Cement Paste

The sorptivity test is a widely used method to assess the capillary rise of the water absorption rate. Table 4.8 demonstrates the sorptivity of the control sample, and samples replaced with 10%, 20% and 30% POFA at 28, 56 and 90 days respectively, at room temperature and in an ammonium nitrate solution. Figure 4.10 shows the sorptivity of samples with different percentages of POFA at room temperature and in an ammonium nitrate solution at different curing ages. The soptivity of the samples were calculated based on the formula as attached in Appendix D.

Based on Table 4.8, the sorptivity at 28 days for the control sample was 0.8mm/min^{0.5}. The sorptivity value for samples replaced with 10% POFA, 20% POFA and 30% POFA at 28 days was 0.37mm/min^{0.5}, 0.29mm/min^{0.5} and 0.66mm/min^{0.5} respectively. It was observed that at 28 days, the sorptivity value was highest for the control sample and lowest for samples with 20% POFA replaced. The sorptivity value for the control sample at room temperature at 56 days was 0.73mm/min^{0.5}. The sorptivity value for the 10% POFA, 20% POFA and 30% POFA at 56 days at room temperature was 0.29mm/min^{0.5}, 0.22mm/min^{0.5} and 0.66mm/min^{0.5} respectively. Table 4.8 shows, the sorptivity value of the test samples at 56 days at room temperature have decreased compared to the 28 days samples. There was a loss of 8.75%, 21.62% and 24.14% for the control sample, the 10% POFA and 20% POFA respectively, compared to the 28 days samples. However, for samples replaced with 30% POFA, there was no difference in the sorptivity value between 28 days and 56 days at room temperature. In addition, the 20% POFA had the lowest sorptivity value.

The sorptivity value at 90 days at room temperature for the control sample, 10% POFA, 20% POFA and 30% POFA was 0.51mm/min^{0.5}, 0.07mm/min^{0.5}, 0.15mm/min^{0.5} and 0.15mm/min^{0.5} respectively. There was a loss of 30.14%, 75.86%, 31.9% and 77.27% for the control sample, the 10% POFA, 20% POFA and 30% POFA compared to the 56 days samples at room temperature. However if compared with the 28 days sample, there was a decrease of 36.25%, 81.09%, 48.28% and 77.27% for the control sample, and the 10% POFA, 20% POFA and 30% POFA and 30% POFA samples respectively. At 90 days, the 10%POFA sample had the lowest sorptivity value, meanwhile the control sample had the highest sorptivity value.

The sorptivity value at 56 days for samples immersed in ammonium nitrate conditions for the control sample, and the 10% POFA, 20% POFA and 30% POFA were 0.73mm/min^{0.5}, 0.29mm/min^{0.5}, 0.43mm/min^{0.5} and 0.73mm/min^{0.5}respectively. It was observed the sorptivity values for the samples immersed in an ammonium nitrate solution were higher than at room temperature. The sorptivity values for samples with 20% POFA and 30% POFA had an increase of 95.5% and 10.61% respectively. At 56 days in an ammonium nitrate solution, the sorptivity value for 10% POFA was lowest while the control sample and the 30% POFA had the highest sorptivity values.

The sorptivity value at 90 days for samples immersed in an ammonium nitrate solution was 0.80mm/min^{0.5}, 0.58mm/min^{0.5}, 0.51mm/min^{0.5} and 0.88mm/min^{0.5} respectively, for the control sample, the 10% POFA, 20% POFA and 30% POFA. There was an increase of 56.86%, 87.93%, 70.59%, and 10% in the sorptivity values for the control, 10% POFA, 20% POFA and 30% POFA respectively compared to the 90 days samples at room temperature. Consequently, if compared with the 56 days samples in an ammonium nitrate solution, the sorptivity value increased by 9.6%, 50%, 18.61% and 20.55% for the control sample, 10% POFA, 20% POFA and 30% POFA respectively. For the test samples of 90 days in an ammonium nitrate solution, the sorptivity value was highest for the 30% POFA while the 20% POFA had the lowest sorptivity values.

The lower sorptivity values for the control samples at room temperature and with an increase in the curing age were due to the hydration of the cement, which produced more calcium silicate hydrate. However, for samples replaced with POFA, the lower sorptivity values are mainly due to the filler effect of POFA particles in addition to the pozzolanic reaction between the silicon dioxide in the POFA and the calcium hydroxide in cement. When POFA is added to concrete the pozzolanic reaction occurs between the silicon in the POFA and Ca(OH)₂ in the cement paste which then produces additional calcium silicate hydrates. As a result the cement matrix becomes denser due to the formation of additional calcium silicate hydrates and thus the sorptivity value decreases. However, the higher sorptivity values for the samples in ammonium nitrate compared to the samples at room temperature is due to the leaching of the calcium hydroxide from the paste. Therefore, the sorptivity value was higher as there are more numerous voids in the structure.

Similar findings have been reported by previous researchers. According to Sivakumar and Mahendran (2014), pozzolanic materials result in a decrease of the pore space of the cement paste and therefore the sorptivity value decreases. Adam et al. (2010) reported the sorptivity value of the control samples at 90 days is lower than the control sample at 56 days. In addition, the author also mentioned the sorptivity decreased when pozzolanic material was used in the cement paste. Kumar et al. (2016) reported the sorptivity was lowest when samples were replaced with 15% of pozzolanic material.

Therefore based on the test results, it is recommended to replace cement with 20% of POFA for lower sorptivity values at room temperature and in an ammonium nitrate solution. The findings in these tests however agree with the test results in the previous sections.

Age	Samples	Dry Weight (g) (W1)	Wet Weight (g) (W2)	Sorptivity (mm/min ^{0.5})
	Control	209	220	0.8
29 dava	10%POFA	211	216	0.37
28 days	20%POFA	211	215	0.29
	30%POFA	199	208	0.66
	Control	210	220	0.73
56 days (Room	10%POFA	220	224	0.29
Temperature)	20%POFA	218	221	0.22
	30%POFA	210	219	0.66
	Control	206	216	0.73
56 days	10%POFA	200	204	0.29
Nitrate)	20%POFA	206	212	0.43
	30%POFA	214	224	0.73
	Control	221	228	0.51
90 days (Room	10%POFA	212	213	0.07
Temperature)	20%POFA	216	218	0.15
	30%POFA	205	207	0.15
00.1	Control	234	245	0.80
90 days	10%POFA	215	223	0.58
(Annoniulli Nitrate)	20%POFA	215	222	0.51
initiate)	30%POFA	212	224	0.88

Table: 4.8: Sorptivity of samples with different percentage of POFA



Figure 4.10: Sorptivity of samples with different percentage of POFA

4.6.2 Volume of Permeable Voids (VPV)

The volume of permeable voids (VPV) test is carried out to determine the amount of voids in a sample. The permeable void affects the transport properties and durability of concrete. Table 4.9 illustrates the VPV test results of the control sample, and samples replaced with 10%, 20% and 30% POFA at 28, 56 and 90 days at room temperature and in an ammonium nitrate solution. Figure 4.11 shows the VPV values of samples with different percentages of POFA at room temperature and in an ammonium nitrate solution at different curing ages. The volumes of permeable voids of the samples were calculated according to the formula as attached in Appendix D.

According to Table 4.9, the VPV values, for the control sample, and 10% POFA, 20% POFA and 30% POFA at 28 days was 20.98%, 20.47%, 20% and 20.41% respectively. It was observed the VPV values at 28 days for the control sample were the highest and for the sample with 20% POFA the results were the lowest. At 56 days at room temperature, the VPV results for the control sample, 10% POFA, 20% POFA and 30% POFA was 20.77%, 19.63%, 18.01% and 20.35% respectively. Consequently, there was a decrease of 1%, 4.1%, 9.95% and 0.29% of VPV values for the control sample, 10% POFA, 20% POFA, 20% POFA and 30% POFA and 30% POFA and 30% POFA respectively, compared to the 28 days test results.

The VPV values for 90 days at room temperature for the control sample, 10% POFA, 20% POFA and 30% POFA was 19.96%, 18.68%, 16.67% and 20.25% respectively. Compared to the 56 days samples at room temperature, there was a decrease of 3.9%, 4.8%, 7.4% and 0.49% for the control sample, 10% POFA, 20% POFA and 30% POFA. However, if compared to the 28 days samples, there was a reduction of 4.9%, 8.7%, 16.65% and 0.78% for the control sample 10% POFA, 20% POFA and 30% POFA respectively.

In addition, the VPV values for the 56 days sample, immersed in ammonium nitrate was 22.36%, 22.27%, 20.61% and 20.72% for the control sample, 10% POFA, 20% POFA and 30% POFA respectively. It was observed for samples immersed in an ammonium nitrate solution at 56 days had higher VPV values compared to samples at room temperature and at the same curing age. There was an increase of 7.7%, 13.45%, 14.44% and 1.81% of VPV

values for the control, 10% POFA, 20% POFA and 30% POFA for samples immersed in the ammonium nitrate compared to the 56 days samples at room temperature.

Similar patterns were also observed for the 90 days samples in ammonium nitrate compared to the samples at room temperature. The VPV values for the 90 days samples immersed in an ammonium nitrate solution was 23.50%, 25.84%, 23.85% and 23.72% for the control sample, 10% POFA, 20% POFA and 30% POFA respectively. Compared to the 90 days samples at room temperature there was an increase of 17.73%, 38.32%, 43.07% and 17.14% for the control sample, 10% POFA, 20% POFA and 30% POFA and 30% POFA respectively. However, if the samples were compared with the 56 days samples immersed in an ammonium nitrate solution, there was an increase of 5.1%, 16.03%, 15.7% and 14.5% for the control sample, 10% POFA, 20% POFA respectively.

Based on these test results, the void percentage in the cement paste decreased as the curing age increased. This is because more calcium silicate hydrate and calcium hydroxide is produced during the cement hydration process. Calcium silicate hydrate is responsible for decreasing the void percentages as the cement paste becomes denser. A lower void percentage is an indication the sample has a denser matrix and would give increased durability. The lower void percentage in samples with 10% and 20% POFA is due to the pozzolanic reaction, which produced additional calcium silicate hydrates. Therefore, the cement paste has a denser matrix and the void percentage is lower compared to the control sample and the 30% POFA sample. The higher void percentage in samples with 30% POFA can be explained due to a lower amount of CaO present in the cement, which will affect the pozzolanic reaction process. The higher void percentage in the ammonium nitrate solution was due to the dissolution of the calcium hydroxide. Calcium hydroxide is a hydrated product, which fills the pore system within the cement paste. As a result, the concrete becomes more permeable.

According to previous research, similar test results were reported. Wong et al. (2012) reported the VPV values decreased with an increase in the duration of the curing age. However, the VPV values increased when immersed in an ammonium nitrate solution. Bashar et al. (2016) reported the VPV value is influenced by the paste/aggregate ratio. As the paste/aggregate ratio increases, the void ratio in the hardened concrete decreases. Jitendra et al (2015) reported that the VPV value was lower for the 56 days samples compared to the 28

days samples. In addition, the author also stated the VPV values decreased as the cement replacement percentage with pozzolanic material increased.

Based on the test results, it is recommended to replace OPC with 20% of POFA if at room temperature and in an ammonium nitrate conditions. These findings agree with previous research.

Age	Samples	Ma(g)	Mb(g)	Mc(g)	Md(g)	Void (%)
	Control	618	725	704	294	20.98
19 days	10%POFA	645	755	733	303	20.47
28 days	20%POFA	650	753	736	306	20.00
	30%POFA	625	731	714	278	20.41
	Control	630	740	716	302	20.77
56 days	10%POFA	634	737	720	282	19.63
(KOOM Temperature)	20%POFA	650	753	728	295	18.01
	30%POFA	626	731	719	262	20.35
	Control	625	720	718	302	22.36
56 days	10%POFA	617	727	713	282	22.27
(Ammonium Nitroto)	20%POFA	630	751	717	295	20.61
(iti acc)	30%POFA	637	720	735	262	20.72
00.1	Control	680	775	768	327	19.96
90 days	10%POFA	683	771	765	326	18.68
(NUUIII Temperature)	20%POFA	673	752	744	318	16.67
	30%POFA	630	739	712	307	20.25
	Control	659	765	761	327	23.50
90 days	10%POFA	657	777	772	327	25.84
(AIIIIIONIUM Nitroto)	20%POFA	633	744	737	301	23.85
	30%POFA	630	738	732	302	23.72

Table: 4.9: VPV of samples with different percentage of POFA



Figure 4.11: VPV of samples with different percentage of POFA

4.7 Microstructure studies on Modified Cement Paste

The microstructure studies consisted of the Thermo-gravimetric Analysis (TGA), Energydispersive X-ray (EDX) and Scanning Electron Microscopy (SEM) tests. The tests were carried out according to the procedures mentioned in chapter 3. A constant water to cement ratio of 0.4 was used for all the samples. The test was carried out for the control samples, 10% POFA, 20% POFA and 30% POFA samples, at room temperature and in ammonium nitrate conditions. Sections 4.7.1, 4.7.2 and 4.7.3 discuss the TGA, EDX and SEM test results.

4.7.1 Thermo-gravimetric Analysis (TGA) of Modified Cement Paste

Thermogravimetric Analysis (TGA) is a widely accepted technique to assess Ca(OH)₂ content in hydrated cement paste. For this study, the TGA test was carried out to determine the total percentage of Ca(OH)₂ present in the control samples and in samples replaced with 10%, 20% and 30% POFA at different curing ages and conditions. The TGA test was carried out at 28, 56 and 90 days for samples at room temperature and in ammonium nitrate conditions. Sections 4.7.1.1 discuss the hydration phase of OPC paste and paste containing POFA. Section 4.7.1.2 discusses the Ca(OH)₂ content in OPC paste and paste containing POFA.

4.7.1.1 Hydration phase of OPC paste and paste containing POFA

The Thermogravimetric analysis (TGA) results of OPC paste (the control) and cement paste containing 10% POFA, 20% POFA and 30% POFA at 28 days is shown in Figure 4.12 to 4.15. According to Figures 4.12 to 4.15, it was observed three steps mass loss transitions were found. In the first step mass loss, water molecules are removed Altwair et al. (2011). Figures 4.5 to 4.6 show this step loss occurred at around 0-250 degrees Celsius. The second weight loss at approximately 400-500 degrees Celsius is due to the Ca(OH)₂ dehydroxilation. The second weight loss is because of the following reaction:

$$Ca(OH)_2 \rightarrow CaO + 2OH^-$$
 (1)

The third shift at 500-750 degrees Celsius is due to the calcium carbonate ($CaCO_3$) decomposition. The endothermic shift is caused by the following reactions:

$$CaCO_3 \rightarrow CaO + CO_2$$
 (2)

Nevertheless it was also observed in Figures 4.12 to 4.15 the second weight loss curve, which is due to the decrease of $Ca(OH)_2$ during the dehydroxilation process as the percentage

replacement of cement increases. This is attributed to the lower loss of $Ca(OH)_2$ as the replacement of OPC with POFA increases. Similar patterns were also observed for TGA curves at 56 days and 90 days at room temperature and 56 and 90 days in an ammonium nitrate solution as attached in Appendix A.



Figure 4.12: TGA curve of control at 28 days



Figure 4.13: TGA curve of 10%POFA sample







Figure 4.15: TGA curve of 30% POFA sample

4.7.1.2 Ca(OH)₂ content in OPC paste and paste containing POFA

The total $Ca(OH)_2$ content in the OPC paste and paste containing POFA is summarized in Table 4.10. Figure 4.16 shows the $Ca(OH)_2$ values for samples with different POFA percentages at room temperature at different curing ages. Figure 4.17 compares the $Ca(OH)_2$ content for samples at room temperature and in an ammonium nitrate solution.

Table 4.10 shows the Ca(OH)₂ contents of the control sample and paste containing 10%POFA, 20% POFA and 30% POFA at 28 days were 21.07%, 18.92%, 16.82% and 19.37% respectively. At 56 days at room temperature, the Ca(OH)₂ content in the control sample, 10% POFA, 20% POFA and 30% POFA were 23.61%, 21.05%, 17.82% and 16.81% respectively. It was observed there was an increase in the percentage of Ca(OH)₂ in the control sample by 12.05% compared to the 28 days control sample. Similarly 10% POFA and 20% POFA also show an increase of 11.26% and 5.95% respectively, compared to the, 10% and 20% POFA samples at 28 days. However, for samples with 30% POFA, there is a decrease of 13.21% compared to the 30% POFA sample at 28 days. According to Table 4.10, the values of Ca(OH)₂ at 90 days at room temperature for the control sample, 10% POFA, 20% POFA and 30% POFA were 27.99%, 22.25%, 18.40% and 15.78% respectively. There was an increase of 18.6% of Ca(OH)₂ content in the control sample compared to the 56 days control sample at room temperature. Consequently, there was an increase of 32.8% compared to the 28 day control sample. Similarly, for 10% and 20% POFA, the Ca(OH)₂ content at 90 days at room temperature was 22.25% and 18.40%. There was an increase of 5.71% and 3.25% compared to 56 days at 10% and 20% POFA samples at room temperature. Nevertheless, there was an increase of 17.6% and 9.39% in the Ca(OH)₂ content compared to the 10% and 20% POFA samples at 28 days.

The Ca(OH)₂ content in the control sample, 10% POFA, 20% POFA and 30% POFA samples immersed in an ammonium nitrate solution for 56 days was 22.97%, 19.38%, 16.82% and 16.25% respectively. It was observed this was a decrease of 2.71%, 7.93%, 3.25%, 6.13% compared to the control, 10% POFA, 20% POFA and 30% POFA at 56 days at room temperature. The Ca(OH)₂ content in the control sample, 10% POFA, 20% POFA and 30% POFA and 30% POFA at 90 days, immersed in an ammonium nitrate solution was 23.86%, 19.79%, 18.06% and 15.21% respectively. Consequently, it was observed, there was a decrease of 14.76%, 11.06%, 1.85%, 3.6% compared to the control sample, 10% POFA, 20% POFA and 30% POFA and 30% POFA samples at 90 days at room temperature.

Based on the test results, it was observed the $Ca(OH)_2$ content in the control was the highest compared to samples containing POFA. This is attributed to the fact that there is a high amount of $Ca(OH)_2$ present in the paste due to the absence of the pozzolanic reaction. The $Ca(OH)_2$ content in the control samples however increased with an increase in the duration of the curing age. This is due to hydration of the cement paste which releases more $Ca(OH)_2$ in the paste, hence the content of $Ca(OH)_2$ is higher. It was also observed $Ca(OH)_2$ content in the 10% and 20% POFA samples increased with an increase in the duration of the curing age. However, the percentage of $Ca(OH)_2$ in 10% POFA, 20% POFA and 30% POFA was lower than the control samples. This is attributed to the fact that the $Ca(OH)_2$ content decreases as the replacement of POFA increases. Hence, the higher the amount of cement replaced with POFA, the higher the consumption of the $Ca(OH)_2$ due to the pozzolanic reaction. As a result, the $Ca(OH)_2$ content in the paste decreases with an increase in the percentage replacement of POFA.

However, according to the test results, it was observed for samples containing 30% POFA, the Ca(OH)₂ content decreased as the curing age increased. This lower Ca(OH)₂ content in the 30% POFA sample can be explained due to the low amount of CaO present in the paste as too much of the pozzolanic material was used to replace OPC. As a result there is a smaller amount of CaO present for the pozzolanic reaction to occur and therefore the Ca(OH)₂ content is less. Nonetheless it was observed the Ca(OH)₂ content for samples in an ammonium nitrate solution were lower compared to samples at room temperature. This is attributed to that fact some of the Ca(OH)₂ had reacted with the ammonium nitrate solution and hence its percentage is lower.

Similar findings were reported by previous researchers. According to Kroehong et al., (2011), the weight loss of Ca(OH)₂ content was calculated between 450-580 degrees Celsius. It was observed by the author Ca(OH)₂ content in the control sample increased with an increase in the duration of the curing age. The Ca(OH)₂ content was 19.02%, 19.64%, 20.22% and 20.46% for the control sample at 7, 28, 60 and 90 days respectively. It was reported by the author the Ca(OH)₂ content of the paste decreased when POFA, having a median particle size (d_{50}) 15.6µm was used. It was also observed by the author the Ca(OH)₂ loss was higher in the sample containing 20%POFA compared to the sample with 40% POFA. Altwair et al (2011) also reported similar observations. When the percentage replacement of cement with POFA increased, the Ca(OH)₂ loss decreased.

Therefore, it is recommended to replace OPC with 20% of POFA if at room temperature and in an ammonium nitrate solution. This finding agrees with previous research.

				dh- Loss (400-	dc-Loss	
Age	Sample	Weight (mg)	Moisture (mg)	500)	(500-750)	Total (%) Loss Ca(OH) ₂
28 days	Control	84	13.56	2.89	1.77	21.07
	10% POFA	79	13.51	2.46	1.35	18.92
	20% POFA	80	16.99	2.10	1.17	16.82
	30% POFA	74	12.99	0.88	4.91	19.37
56 days	Control	96	15.4	3.91	1.76	23.61
(Room	10%POFA	77	12.35	2.22	2.67	21.05
Temperat	20%POFA	86	14.48	2.42	1.67	17.82
ure)	30%POFA	71	10.21	0.78	4.18	16.81
56 days	Control	92	16.53	3.17	2.57	22.97
(Ammoni	10%POFA	74	13.16	1.99	2.15	19.38
um	20%POFA	78	15.38	1.58	2.40	16.82
Nitrate)	30%POFA	66	10.19	0.50	4.17	16.25
90 days	Control	75	13.09	2.51	4.18	27.99
(Room	10%POFA	83	3.73	2.79	3.67	22.25
Temperat	20%POFA	86	16.93	2.48	1.50	18.40
ure)	30%POFA	67	10.57	1.07	2.68	15.78
90 days	Control	81	14.82	3.02	2.00	23.86
(Ammoni	10%POFA	76	13.75	2.12	2.16	19.79
um	20%POFA	86	16.78	2.16	2.15	18.06
Nitrate)	30%POFA	67	10.78	1.00	2.65	15.21

Table 4.10: Mass loss of Ca(OH)₂ with different percentage of POFA



Figure 4.16: Ca(OH)₂ content for samples with different POFA percentage at different curing age



Figure 4.17: Ca(OH)₂ content for samples in room temperature and in ammonium nitrate solution

4.7.2 Energy-dispersive X-ray spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy (EDX) is a technique used for conducting element analysis. It depends on interaction of some source of X-ray excitation. EDX analysis was carried out to identify the total atomic percentage mass of calcium and silicon in the samples. The atomic percentage mass of these two elements is used to calculate the Ca/Si ratio. C-S-H gel is often defined by its Ca/Si ratio, which usually ranges from 0.7 to 2.3 from its compositional point of view (Chen et al., 2004). Generally, the typical Ca/Si ratio of C-S-H in OPC is about 1.5–1.8, but reduced ratios has been observed when pozzolanic material is used (Shirazi et al., (2014). The EDX test was carried out with samples at 28 days, 56 days and 90 days, at room temperature and in an ammonium nitrate solution.

Table 4.11 illustrates the Ca/Si ratio of samples at room temperature and in an ammonium nitrate solution at different curing ages. Figures 4.18 to 4.21 demonstrate the EDX test results for the control sample, 10% POFA, 20% POFA and 30% POFA at 28 days. Test results for the 56 and 90 days samples, at room temperature and in an ammonium nitrate solution are attached in the as Appendix B.

Based on Table 4.11, the Ca/Si ratio for the control sample, 10% POFA, 20% POFA and 30% POFA at 28 days was 3.07, 2.97, 2.17 and 3.91 respectively. At 56 days at room temperature, the Ca/Si ratio of the samples has decreased compared to the 28 days sample. The ratio was 2.72, 2.32, 2.71 and 2.90 for the control, 10% POFA, 20% POFA and 30% POFA respectively. Similarly, at 90 days at room temperature, the ratio for the control, 10% POFA, 20% POFA and 30% POFA, 20% POFA and 30% POFA was 3.79, 2.13, 1.86 and 1.97 respectively. It was observed 10% POFA, 20% POFA and 30% POFA had lower ratio values compared to the 28 days and 56 days samples at room temperature.

The ratio for samples immersed in an ammonium nitrate solution at 56 days was 2.16, 1.17, 1.72 and 2.03 for the control, 10% POFA, 20% POFA and 30% POFA respectively. Based on the test results, the Ca/Si ratio for samples at 56 days in an ammonium nitrate solution was lower than the 56 days at room temperature samples. A similar pattern was also observed for the 90 days samples in an ammonium nitrate solution compared to the 90 days samples at room temperature. The Ca/Si ratio was 0.74, 0.69, 0.61 and 0.73 for the control, 10% POFA, 20% POFA and 30% POFA for 90 days in an ammonium nitrate solution. The lower Ca/Si ratio for the 90 days samples in an ammonium nitrate solution was due to the lower amount
of calcium hydroxide present in the paste. This is attributed to the consumption of $Ca(OH)_2$ by the ammonium nitrate solution. In addition, it was also observed with an increase in the curing age, the atomic percentage mass of silicon increases. This is an indication there is more silicon in the paste for the pozzolanic reaction to occur as the curing age increases.

The lower Ca/Si ratio for the 10% POFA and 20% POFA at all curing ages and conditions is due to a higher pozzolanic reaction having occurred in the paste compared to the control sample and the 30% POFA. Nevertheless, it was observed the Ca/Si ratio at 56 days at room temperature was lower than in the 28 days samples. Similarly, the Ca/Si ration for the 90 days samples at room temperature was lower than the 28 days and 56 days samples at room temperature. This is attributed to the fact the pozzolanic reaction in the paste increases with an increase in the duration of the curing age.

Moreover, the Ca/Si ratio also has an influence on the surface charge of C-S-H. When, the Ca/Si ratio is low, the surface charge of C-S-H is negative. When the Ca/Si ratio is high, anions are absorbed on the C-S-H fibes and the surface charge of C-S-H is positive Sutan et al. (2015). According to Wonko et al. (2011), the Ca/Si ratio of OPC was 3.08 and the ratio decreased when pozzolanic material was used. The Ca/Si ratio was 0.88 when 60% of OPC was replaced with a pozzolanic material as published.

Therefore, based on the test results, it is recommended to replace OPC with 20% of POFA for a lower Ca/Si ratio at room temperature and in ammonium nitrate conditions.

Age	Sample	Atomic Mass (%) Silicon	Atomic Mass (%) Calcium	Ca/Si Ratio
28 days	Control	12.84	39.49	3.07
	10% POFA	13.81	41.02	2.97
	20% POFA	16.4	35.61	2.17
	30% POFA	12.45	48.76	3.91
56 days (Room Temperature)	Control	16.09	43.92	2.72
	10% POFA	15.35	35.64	2.32
	20% POFA	15.8	42.94	2.71
	30% POFA	17.61	51.15	2.90
	Control	19.09	41.26	2.16
56 days (Ammonium	10% POFA	26.94	31.68	1.17
	20% POFA	20.06	34.60	1.72
Nitrate)	30% POFA	22.15	45.16	2.03
	Control	13.48	51.20	3.79
	10% POFA	15.73	33.52	2.13
90 days (Room	20% POFA	17.23	32.19	1.86
Temperature)	30% POFA	17.95	35.41	1.97
	Control	30.55	22.74	0.74
90 days (Ammonium	10% POFA	31.19	21.80	0.69
	20% POFA	32.26	19.76	0.61
Nitrate)	30% POFA	34.15	25.00	0.73

Table 4.11: Ca/Si ratio of samples with different percentage of POFA



Figure 4.18: EDX for 28 days control



Figure 4.19: EDX for 28 days 10% POFA



Figure 4.20: EDX for 28 days 20% POFA



Figure 4.21: EDX for 28 days 30% POFA

4.7.3 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) provides sample images which include the chemical composition, orientation and external morphology (texture).Generally, data are collected over a selected area of the surface of the sample. A SEM test was carried out to detect the Ca(OH)₂ and C-S-H in the control sample and in samples replaced with 10%, 20% and 30% POFA. Figures 4.22 to 4.25 show the SEM image of the control sample, 10% POFA, 20% POFA and 30% POFA at 28 days. The SEM images for samples at 56 days and 90 days at room temperature and in an ammonium nitrate solution are attached in the Appendix C.

For the 28 days control sample, the SEM image in Figure 4.22 illustrates there is a crystal solid hexagonal plate like morphology. This structure is referred to as Ca(OH)₂. In addition, there is also a flowery-like morphology found in the sample. This structure is known as C-S-H. Both Ca(OH)₂ and C-S-H are the by-products of cement hydration and are responsible for its strength. It was also observed there are rod-like crystal structures in the 28 days control samples. These rod-like structures are known as ettringite and are usually present in the early stage of the hydration reaction.

According to Figures 4.23 to 4.25, it was observed there is an absence of the rod-like structures in the 10% POFA, 20% POFA and 30% POFA samples. However, it was also observed there is comparatively more hexagonal plate like morphology $Ca(OH)_2$ and flowery-like morphology (C-S-H) in the samples compared to the control sample. This is evidence of the pozzolanic reaction. Moreover, it was observed there was a higher amount of flower-like morphology in the 20% POFA compared to the 10% and 30% POFA. This can attribute to a higher pozzolanic reaction in the 20% POFA sample.

A similar pattern was also observed for the 56 days samples at room temperature and in an ammonium nitrate solution. However, for the 56 days control samples at room temperature and in an ammonium nitrate solution, there is an absence of ettringite. This is attributed to the fact ettringite is only present during the early stages of curing and disappear as the curing age increases. However, for the 56 days samples, it was observed, there was more flowery like structures (C-S-H) and the matrix was denser. This is attributed to a higher pozzolanic reaction with an increase in the duration of the curing age.

In addition, it was also observed there was less $Ca(0H)_2$ present in the 56 days samples, immersed in an ammonium nitrate solution. This is due to the consumption of the calcium hydroxide in the cement paste by the ammonium salt.

Nevertheless, the 90 days samples at room temperature and in an ammonium nitrate solution also show similar results. However, the matrix was denser as more flowery-like morphology (C-S-H) was found.

The findings in this study agree with the previous research studies. According to Hussin et al. (2015), when increasing the age of curing, the total amount of calcium silicate hydrate crystal increased. Kroehong et al. (2011) applied SEM on a cement paste containing POFA. At 7 days hydrated products such as calcium silicate hydrates, calcium hydroxide and ettringites were observed. However, at 28 days, the paste had a denser structure.



Figure 4.22: SEM of control at 28 days



Figure 4.23: SEM of 10%POFA at 28 days



Figure 4.24: SEM of 20%POFA at 28 days



Figure 4.25: SEM of 30%POFA at 28 days

4.8 Summary

Based on the results and analysis presented in this chapter, the main findings are:

- (a) The physical, chemical and microstructure of POFA depend on the heat treatment and grinding duration. When the size of POFA decreases, the specific gravity and specific surface area increases. Heat treatment influences the chemical composition of the POFA. Due to the heat treatment, the percentage of silicon increases while the carbon percentage in the POFA decreases.
- (b) The compressive strength was highest for samples replaced with 20% POFA at room temperature and in an ammonium nitrate solution. Moreover, 20% POFA also exhibited greater durability results. The sorptivity value was lowest for samples replaced with 20% POFA. Similarly, the void percentage was lowest for samples replaced with 20% POFA.
- (c) Micro-structural studies on the modified cement paste showed the 20% POFA samples had better results compared to the control samples, 10% and 30% POFA. According to the TGA test results, it was concluded the Ca(OH)₂ content decreased as

the percentage of OPC replaced with POFA increased. The EDX test results showed the Ca/Si ratio was lowest for the 20% POFA samples at room temperature and in ammonium nitrate conditions. Similarly, SEM images concluded there was more calcium silicate hydrate in the 20% POFA samples

Chapter 5

CONCLUSIONS

5.1 Introduction

This chapter concludes the investigation of modified cement paste using micro-fine POFA under an ammonium nitrate condition. There have been many reports clearly showing the damages caused to concrete structures in a nitrates-based environment. This is due to the fact the nitrates- based environment presents a more complex and aggressive environment compared to other aggressive chemical environments. Therefore, the purpose of this research was to investigate the performance of a modified cement paste containing fine POFA and its resistance to ammonium nitrate attack. Properties such as mechanical, durability and the microstructure of the modified cement paste were studied. The main reason for using POFA as a pozzolanic material is that a large amount of POFA is produced by the palm oil industry in Malaysia. The POFA in the palm oil mill is usually dumped haphazardly in the surrounding area, which leads to further environmental problems. Therefore, POFA was chosen as the pozzolanic material as there has not been any investigation into using such pozzolanic material in an ammonium nitrates condition.

The following objectives of the research were achieved:

- (a) The physical properties, consisting of median particle size, specific surface area and specific gravity of raw POFA, treated POFA and OPC was investigated. The chemical properties of treated POFA and raw POFA were analyzed. The micro-structural properties were also determined using microscopy imaging and EDX testing of raw POFA, treated POFA and OPC.
- (b) The mechanical properties consisting of the compressive strength of the modified cement paste were determined in different percentages of POFA at room temperature and subject to an ammonium nitrate condition.

- (c) The durability properties consisting of the sorptivity and the volume of permeable voids (VPV) of the modified cement paste were verified in different percentages of POFA at room temperature and in ammonium nitrate conditions.
- (d) The microstructure properties were ascertained using the TGA, EDX and SEM tests of the modified cement paste in different percentages of POFA at room temperature and in ammonium nitrate conditions.

5.2 Conclusions

Based on objective one, the following conclusions were drawn:

- 1. Grinding significantly improves the specific gravity and specific surface area of POFA. The specific gravity and specific surface area are highly influenced by the size of the POFA. The finer the POFA, the higher the specific gravity and specific surface area, when compared to coarser POFA. Finer POFA particles have fewer voids, which cause the POFA particles to be denser and more packed compared to coarser POFA.
- 2. Heat treatment has no effect on the specific gravity and specific surface area of the POFA. However, heat treatment does influence the chemical composition of POFA. Heat treatment at 600 degrees Celsius for one hour increased the main oxides of POFA, particularly silica and reduced the carbon content. Based on its chemical composition, the treated POFA is classified as an N class pozzolan.

Based on objective **two**, the following conclusions were drawn:

- Cement paste containing 20% micro-fine POFA at room temperature at 28 days and 90 days curing age, results in a compressive strength of 52.0MPa and 69.5MPa respectively, which is higher than the control sample by 104% and 115% respectively. At the early stage of curing, POFA works as a filler material. However, after 28 days, the higher compressive strength in cement, which had been replaced with 20% POFA, is due to the pozzolanic reaction.
- 2. The compressive strength decreased when samples were immersed in an ammonium nitrate solution due to the decalcification reaction. The calcium hydroxide in the cement paste had been consumed by the nitrate in the ammonium nitrate solution, therefore the compressive strength decreased. Cement paste containing 20% POFA in

an ammonium nitrate solution exhibited compressive strength of 42.4MPa at 90 days, which was 108% higher than the control sample.

3. The sorptivity and the volume of permeable voids of the cement paste increased when samples were immersed in an ammonium nitrate solution. This is attributed to the decalcification reaction. There were more voids in the cement paste due to the consumption of calcium hydroxide by the nitrate. As a result, sorptivity and the volume of permeable voids increased. Cement paste containing 20% micro-fine POFA exhibited lower sorptivity and volume of permeable voids due to a higher pozzolanic reaction.

Based on objective three, the following conclusions were drawn:

- Cement paste containing POFA showed a decrease in Ca(OH)₂ with a corresponding increase in the POFA replacement level. The decrease of Ca(OH)₂ in the POFA paste was due to the pozzolanic reaction. The Ca/Si ratio decreased when cement was replaced with POFA.
- Calcium silicate hydrate (C-S-H) is classified by the Ca/Si ratio. The Ca/Si ratio decreased when the volume of calcium silicate hydrate increased while the Ca/Si ratio increased when the volume of calcium hydroxide increased. Cement replaced with 20% POFA exhibited a lower Ca/Si ratio due to a higher pozzolanic reaction.
- 3. As the curing age increased, the total amount of calcium silicate hydrate (C-S-H) crystals increased which consequently, decreased the calcium hydroxide content. This is attributed to the ability of POFA to reduce the amount of calcium hydroxide content in the paste.
- 4. The SEM test results also demonstrated a 20% POFA -based cement paste produced more C-S-H compared to the control sample and hence it provided higher compressive strength, lower sorptivity and volume of permeable voids and greater resistance to weakening in an ammonium nitrate solution.

5.3 Recommendation for Future Work

This research has met all the objectives stated in the introduction, and from the findings presented, it is recommended to:

- (a) Replace cement with POFA below 1µm in size and study the effects on the mechanical, durability and microstructure properties at room temperature and in ammonium nitrate conditions.
- (b) Use different concentrations of ammonium nitrate solution and study the mechanical, durability and micro-structural properties of modified cement paste containing microfine POFA.
- (c) Further study of various mortar and concrete mixes containing POFA against ammonium nitrate attack.

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APPENDIX A – Thermogravimetric Analysis Curves



Figure A 1.1: TGA control 56 days in room temperature



Figure A 1.2 : TGA 10% POFA 56 days in room temperature



Figure A 1.3: TGA 20% POFA 56 days in room temperature



Figure A 1.4: TGA 30% POFA 56 days in room temperature



Figure A 1.5: TGA control 90 days in room temperature



Figure A 1.6: TGA 10% POFA 90 days in room temperature



Figure A 1.7: TGA 20% POFA 90 days in room temperature



Figure A 1.8: TGA 30% POFA 90 days in room temperature



Figure A 1.9: TGA control 56 days in ammonium nitrate solution



Figure A 1.10: TGA 10% POFA 56 days in ammonium nitrate solution



Figure A 1.11: TGA 20% POFA 56 days in ammonium nitrate solution



Figure A 1.12: TGA 30% POFA 56 days in ammonium nitrate solution



Figure A 1.13: TGA control 90 days in ammonium nitrate solution



Figure A 1.14: TGA 10% POFA 90 days in ammonium nitrate solution



Figure A 1.15: TGA 20% POFA 90 days in ammonium nitrate solution



Figure A 1.16: TGA 30% POFA 90 days in ammonium nitrate solution

APPENDIX B – Energy Dispersive X-ray Spectroscopy Curves



Figure B 1.1: EDX control 56 days room temperature



Figure B 1.2: EDX 10% POFA 56 days room temperature



Figure B 1.3: EDX 20% POFA 56 days room temperature



Figure B 1.4: EDX 30% POFA 56 days room temperature



Figure B 1.5: EDX control 56 days ammonium nitrate solution



B 1.6: EDX 10% POFA 56 days ammonium nitrate solution



Figure B 1.7: EDX 20% POFA 56 days ammonium nitrate solution



Figure B 1.8: EDX 30% POFA 56 days ammonium nitrate solution



Figure B 1.9: EDX control 90 days room temperature



Figure B 1.10: EDX 10%POFA 90 days room temperature



Figure B 1.11: EDX 20% POFA 90 days room temperature



Figure B 1.12: EDX 30% POFA 90 days room temperature



Figure B 1.13: EDX control 90 days in ammonium nitrate solution



Figure B 1.14: EDX 10% POFA 90 days in ammonium nitrate solution



Figure B 1.15: EDX 20% POFA 90 days in ammonium nitrate solution



Figure B 1.16: EDX 30% POFA 90 days in ammonium nitrate solution

APPENDIX C- Scanning Electron Microscopy of Modified Cement Paste



Figure C 1.1: SEM control 56 days in room temperature



Figure C 1.2: SEM 10% POFA 56 days in room temperature



Figure C 1.3: SEM 20% POFA 56 days in room temperature



Figure C 1.4: SEM 30% POFA 56 days in room temperature


Figure C 1.5: SEM control 56 days in ammonium nitrate solution



Figure C 1.6: SEM 10% POFA 56 days in ammonium nitrate solution



Figure C 1.7: SEM 20% POFA 56 days in ammonium nitrate solution



Figure C 1.8: SEM 30% POFA 56 days in ammonium nitrate solution



Figure C 1.9: SEM control 90 days in room temperature



Figure C 1.10: SEM 10% POFA 90 days in room temperature



Figure C 1.11: SEM 20% POFA 90 days in room temperature



Figure C 1.12: SEM 30% POFA 90 days in room temperature



Figure C 1.13: SEM control 90 days in ammonium nitrate solution



Figure C 1.14: SEM 10% POFA 90 days in ammonium nitrate solution



Figure C 1.15: SEM 20% POFA 90 days in ammonium nitrate solution



Figure C 1.16: SEM 30% POFA 90 days in ammonium nitrate solution.

APPENDIX D- Sample Calculations

		Dry Weight	Wet Weight (g)		Soptivity	
Age	Samples	(g) (W1)	(W2)	I (mm)	(mm/min0.5)	
	Control	209	220	4.4	0.802919708	
28 dava	10%POFA	211	216	2	0.364963504	
28 days	20%POFA	211	215	1.6	0.291970803	
	30%POFA	199	208	3.6	0.656934307	
	Control	210	220	4	0.729927007	
56 days	10%POFA	220	224	1.6	0.291970803	
	20%POFA	218	221	1.2	0.218978102	
	30%POFA	210	219	3.6	0.656934307	
	Control	206	216	4	0.729927007	
56 days	10%POFA	200	204	1.6	0.291970803	
(ammonium	20%POFA	206	212	2.4	0.437956204	
nitrate)	30%POFA	214	224	4	0.729927007	
	Control	221	228	2.8	0.510948905	
90 days	10%POFA	212	213	0.4	0.072992701	
(room	20%POFA	216	218	0.8	0.145985401	
temperature)	30%POFA	205	207	0.8	0.145985401	
	Control	234	245	4.4	0.802919708	
90 days	10%POFA	215	223	3.2	0.583941606	
(ammonium	20%POFA	215	222	2.8	0.510948905	
nitrate)	30%POFA	212	224	4.8	0.875912409	

Table D1: Soptivity of Modified Cement Paste

The sorptivity is calculated based on the following formula:

 $S = I/(t)^{0.5}$

Where *S* is sorptivity, *I* is the cumulative infiltration at time, *t*. Where; S = sorptivity in mm, t = elapsed time in minute. $I = \Delta w/Ad$ $\Delta W = \text{change in weight} = W2-W1$ W1 = Oven dry weight of the cylinder in grams W2 = Weight of cylinder after30 minute capillary suction of water in grams. A = surface area of the specimen through which water penetrated.d = density of water.

Sample Calculation:

Control 28 days sample

Dry Weight (g) = 209

Wet Weight (g) = 220

 $\Delta W = 220-209 = 11g$

I = 11/2.5 = 4.4

 $S = 4.4/(30)^{0.5}$

=0.81mm/min

Age	Samples	Ma(g)	Mb(g)	Mc(g)	Md(g)	Void (%)
	Control	618	725	704	294	20.98
19 days	10%POFA	645	755	733	303	20.47
20 uays	20%POFA	650	753	736	306	20.00
	30%POFA	625	731	714	278	20.41
	Control	630	740	716	302	20.77
56 days (Room	10%POFA	634	737	720	282	19.63
Temperature)	20%POFA	650	753	728	295	18.01
	30%POFA	626	731	719	262	20.35
	Control	625	720	718	302	22.36
56 days	10%POFA	617	727	713	282	22.27
(Ammonium Nitrate)	20%POFA	630	751	717	295	20.61
	30%POFA	637	720	735	262	20.72
	Control	680	775	768	327	19.96
90 days (Room	10%POFA	683	771	765	326	18.68
Temperature)	20%POFA	673	752	744	318	16.67
	30%POFA	630	739	712	307	20.25
00.1	Control	659	765	761	327	23.50
90 days	10%POFA	657	777	772	327	25.84
(Ammonium Nitrate)	20%POFA	633	744	737	301	23.85
	30%POFA	630	738	732	302	23.72

Table D2: Volume of Permeable Voids (VPV)

A= mass of oven-dried sample in air, g

B = mass of surface-dry sample in air after immersion, g

C = mass of surface-dry sample in air after immersion and boiling, g

D = apparent mass of sample in water after immersion and boiling, g

 $VPV = \{C-A/C-D\} * 100$

Sample Calculation:

Control -28 days

Ma- 681g

Mb - 725g

Mc - 704g

Md - 294g

VPV = [(704-618)/(704-294)] * 100= 20.98

Thermo-gravimetric

Thermo-gravimetric Analysis (TGA)

Calculation of the CH Content:

The CH content of the hydrated paste samples is calculated as at time t, CH1(t)

CH 1(t): 74/18*{m400(t)-m500(t)}/ms

where m420(t) and m540(t) are the mass of the sample recorded at 400°C and 500°C during the TGA test, and ms is the anhydrous mass of the sample. (74/18) is the molar mass ratio between CH and H₂O.

Due to the carbonation reaction, the CH produced within the mix can react to produce CaCO₃ as in the following reaction:

 $Ca(OH)_2 + CO_2 - CaCO_3 + H_2O$

The CaCO₃ content of the cement paste at time t, CO(t), is calculated as:

CO(t) = 100/44* m500(t) - m750(t) / ms

CH(t) : CH1(t) + 74/100 * CO(t)

Sample Calculation:

Control 28 days sample:

Weight: 84mg

Moisture: 13.57mg

CH loss (400-500): 2.88mg

CC loss (500-750): 1.78mg

Ms = 84 - 13.57 + 70.43

d CH + 2.88/70.43 = 0.041 * 100= 4.1

d CC = 1.78/70.43 = 0.025 * 100 = 2.5

d ch = 4.1 * (74/18) = 16.85

d cc = 2.5 * (74/44) = 4.2

Total Ca(OH)₂ loss: 16.85 + 4.2 = 21.05

	~ .		Moisture	CH(t400-	CC t(500-	~ .					Total (%)
Age	Sample	Weight (mg)	(mg)	500))	700)	Sample	d CH	d CC	d ch	d cc	Loss
28 days	Control	84	13.5753	2.8861	1.7697	70.4247	4.098136	2.5129	16.8479	4.2262354	21.07412799
	10% POFA	79	13.5076	2.4609	1.3506	65.4924	3.7575352	2.06222	15.4476	3.4682858	18.91593066
	20% POFA	80	16.9938	2.1019	1.1647	63.0062	3.3360209	1.84855	13.7148	3.108922	16.82367462
	30% POFA	74.2	12.9881	0.8757	4.9089	61.2119	1.4306042	8.01952	5.88137	13.487373	19.36874574
56 days	Control	96	15.3951	3.9071	1.764	80.6049	4.8472239	2.18845	19.9275	3.6805793	23.60805546
	10%POFA	77	12.3486	2.2195	2.6673	64.6514	3.433027	4.12566	14.1136	6.9386179	21.05217327
	20%POFA	86	14.4753	2.4155	1.672	71.5247	3.377155	2.33765	13.8839	3.931509	17.81536852
	30%POFA	71	10.2123	0.7757	4.1808	60.7877	1.2760805	6.87771	5.24611	11.567053	16.81316178
56 days (AN)	Control	92	16.5293	3.1658	2.5708	75.4707	4.1947405	3.40636	17.245	5.7288699	22.97391403
	10%POFA	74	13.1576	1.9874	2.1511	60.8424	3.2664721	3.53553	13.4288	5.946115	19.37494463
	20%POFA	78	15.3833	1.58	2.4016	62.6167	2.5232885	3.8354	10.3735	6.450443	16.82396246
	30%POFA	77	12.8243	0.9157	5.6525	64.1757	1.4268641	8.80785	5.866	14.813204	20.67920057
90 days	Control	75	13.0853	2.5058	4.1796	61.9147	4.047181	6.75058	16.6384	11.353245	27.99165545
	10%POFA	83	3.7342	2.7905	3.6649	79.2658	3.5204338	4.62356	14.4729	7.7759834	22.24887784
	20%POFA	79	14.3036	1.8746	1.8284	64.6964	2.8975337	2.82612	11.9121	4.7530255	16.6651085
	30%POFA	67	10.5732	1.0685	2.6831	56.4268	1.8936037	4.75501	7.78482	7.9970623	15.78187774
90 days (AN)	Control	91	10.2058	3.5762	1.9254	80.7942	4.4263078	2.38309	18.197	4.0079272	22.20497051
	10%POFA	76	13.7475	2.1147	2.1557	62.2525	3.396972	3.46283	13.9653	5.8238552	19.78918456
	20%POFA	86	16.781	2.1611	2.1513	69.219	3.1221196	3.10796	12.8354	5.2270265	18.06240725
	30%POFA	67	10.7773	0.9976	2.6453	56.2227	1.7743723	4.70504	7.29464	7.9130203	15.20766182

Table D3: Thermogravimetric Analysis of Modified Cement Paste