Department of Civil Engineering

Carbonation of Concrete Incorporating High Volume of Micro and Low Volume of Nano Palm Oil Fuel Ash

Wei Le Tang

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
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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

In regards to Human and Animal Ethics:-

No humans or animals were used for this research project. In this research work, materials such as cement, palm oil fuel ash and aggregates were used. Safety measures in using carbon dioxide ad phenolphthalein solution were as prescribed individually in Material Safety data Sheet carefully. Procedures were followed in accordance with standards mentioned at "Section 3.0 Methodology".

Signature: _____

Date: _____30/7/2018_____

Title: **Carbonation of Reinforced concrete Incorporating High Volume of Micro and Low Volume of Nano Palm Oil Fuel Ash**

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Date: 30th July 2018

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ABSTRACT:

Carbonation induced corrosion affects the structure of reinforced concrete by reducing the serviceability and durability. This has become a major concern in industries in design of reinforced concrete structures. A proper design of concrete may slow down the effect of carbonation, in other words, decreased the rate of carbonation effect, hence, the total service lifespan can be increased. The rate of carbonation is influenced by several parameters known as the temperature, relative humidity and concentration of CO_2 in the atmosphere. In this research project, it is to produce high resistance of carbonation concretes by incorporating treated palm oil fuel ash (POFA) using accelerate carbonation testing. Variations of 10% to 30% of micro POFA (mPOFA) and 0.5% to 1.5% of nano POFA (nPOFA) were used to determine which proportion would produce the best carbonation resistance. Normally, it would take several months or more to determine the carbonation depth of concrete if occurred naturally. Therefore, accelerated carbonation testing was preferred in this research. The carbonation effect can be accelerated easily by controlling the three parameters mentioned. In addition, phenolphthalein solution was used to determine the carbonation depth. Microstructures were studied using XRF, XRD and SEM. Workability and sorptivity rate were also tested. The test results show that 10% mPOFA with 0.5% nPOFA had the highest carbonation resistance. Further increasing the amount of POFA would decrease the carbonation resistance of concrete. The result also showed that the rate of carbonation decreased as the time elapsed, this has also already been proven by other researchers. There were two reasons causing this trend. Firstly, the POFA had slower pozzolanic reaction and this would mean that the concrete would have lower resistivity of carbonation. Secondly, as the carbonation effect was an ongoing process, there was the formation of calcium carbonated causing the porosity size to reduce.

Indexing terms: carbonation effect, carbonation depth, parameters, nano, micro, palm oil fuel ash, microstructure, morphology phases, accelerated method

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To whom may concern,

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Kind Regards,

Wei Le Tang

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ABBREVIATIONS

OPC	Ordinary Portland Cement
POFA	Palm Oil Fuel Ash
mPOFA	Micro Palm Oil Fuel Ash
nPOFA	Nano Palm Oil Fuel Ash
FA	Fly Ash
SF	Silica Fume
RHA	Rice Husk Ash
SCM	Supplementary Cementitious Material
HPC	High Performance Concrete
HSC	High Strength Concrete
XRD	X-Ray Diffraction
XRF	X-Ray Fluoresces
SEM	Scanning Electron Microscopy
CSH	Calcium Silicate Hydrate
CH	Calcium Hydroxide
RH	Relative Humidity
LOI	Loss on Ignition
w/c ratio	Water-cement Ratio

CHAPTER 1   INTRODUCTION

1.1 BACKGROUND

Durability properties of concrete define its service lifespan that has implication in the structural integrity and its life cycle cost.   Durability depends on the surrounding environmental conditions and how concrete is affected by the detrimental effect caused by the exposure to those conditions.   Corrosion in concrete is a common problem which is inevitable over time.   Therefore, studying corrosion effects is the main research area when determining durability properties of concrete.   Chlorination and carbonation are the common attacks that induced corrosion in concrete.   Chlorination can be found in almost all concrete after its surface is losing the water and is left with dry and porous matrix that makes it vulnerable to chloride attacks (Margalit 2016). Carbonation occurs due to a prolonged exposure of concrete to carbon dioxide (CO_2) in the atmosphere.   Carbonation could cause corrosion in steel reinforcement inside the concrete.

In the past, the major effect that caused corrosion was chlorination; hence, plentiful of researches had done to evaluate and understand in order to counter the chlorination effect. However, due to modern technologies now especially in developing countries, the carbonation effect can be said to have almost the similar percentage occurrence with chlorination due to the increase of the greenhouse effect (J. Collado et al. 2015). Therefore, it is crucial to search for a way to encounter the carbonation effect inducing corrosion using different supplementary cementitious materials (SCM) with good justifications. Many testings have been performed to test for chlorination and carbonation effects using different types of SCM. The one of the most potential recycle materials is known as the Palm Oil Fuel Ash (POFA) which have been introduced decades ago to act as the SCM (Sooraj V.M. et al. 2013). Further testing of chlorination effect using POFA have been conducted but not carbonation (Zeyad et al. 2017). It essential that the carbonation testing should be done too using the POFA. Therefore, this research project is mainly focusing on the carbonation effect only by incorporating POFA.

Carbonation induced corrosion is a major concern for durability of reinforced concrete structures in the industries. The concentration of CO_2 has been increasing throughout the decades due to the growth of urban population density producing an abundance of carbon dioxide in the air; therefore, the rate of carbonation effect is dramatically higher compared to the past (Mohammed Tarek Uddin1 et al. 2011). The parameters controlling carbonation effect are the concentration of CO_2, the relative humidity, and the temperature. Carbonation in concrete is the reaction between CO_2 and CH (calcium hydroxide) contents to form calcium carbonate (A.A. Ramezanianpour et al. 2014). This reaction can only occur in the presence of

water; hence, relative humidity and temperature are the major factors influencing the carbonation (Mohammed Tarek Uddin1 et al. 2011).

When the carbonation effect is initiated in the concrete, it can induce corrosion at the steel reinforcement. Originally the concrete is in alkali forms and consists of a passive film layer that surrounds and protects the steel reinforcements. Since CO_2 is acidic, it can cause the pH value of concrete to drop causing the passive film layer to dissolve (Jack M. Chi et al. 2002). This can lead to the steel reinforcement being more vulnerable to corrosion effect. Furthermore, corrosion occurred at the steel reinforcement can build up pressure internally because the corroded steel has a higher volume than the un-corroded part (Ming-Te Liang et al. 2011). Eventually, the cracking will occur and spalling of cover concrete can be seen.

Blended cement has now been very popular because it shows better performance compared to ordinary Portland cement (OPC). As a result, the trend of utilizing pozzolanic materials as partial replacement of cement is expanding (Blessen Skariah Thomas et al. 2017). In this case, palm oil fuel ash (POFA) could be one of the supplementary cementitious materials. POFA has a very good potential for incrementing the concrete's properties due to the chemical compositions presence inside the POFA (Ul Islam et al. 2016).

The three largest producers of POFA are Indonesia, Malaysia, and Thailand. An industry is generating electricity by burning the wastes such as palm oil kernel, palm oil shell, palm oil fiber and empty fruit brunch through 1000˚C (Blessen Skariah Thomas et al. 2017). The end product of this burning process is known as the palm oil fuel ash, which will be thrown into the landfill causing environmental impact. Moreover, when the wind is blown through the landfill, it could cause the health hazards as it is toxic to breathe it in (Aprianti S. et al. 2017). Hence reusing the POFA from the landfill is a good opportunity to reduce the environmental and health effect at the same time achieving better performance of concrete.

1.2 RESEARCH AIM AND OBJECTIVES

The aim of this research project is to achieve the desired carbonation resistance of concrete by incorporating palm oil fuel ash (POFA). There are two types of POFA are used known as micro and nano POFA. Incorporate both of these POFA at a time has a good possibility to increase the carbonation resistance. Several different mix proportions of POFA will be tested for carbonation testing. The carbonation testing is done by conducting the accelerated carbonation method. Three parameters that control the carbonation are the concentration of CO_2, relative humidity, and temperature; hence, these parameters are controlled to accelerate the carbonation effect. Otherwise, for the carbonation effect to occur naturally would be taking too long for the experiment to end. The main mechanism for the carbonation

is the porosity. Generally, the carbonation does not occur in the same way in all mixes, nor does it occur in all circumstances.

The objectives of this research are listed below:-

    i.   To incorporate micro POFA and nano POFA in concrete and examine how different portions of micro and nano POFA contribute to durability properties of concrete in terms of exposing to carbon dioxide.

    ii.   To investigate the carbonation of concrete by evaluating the carbonation depth using accelerated carbonation method.

    iii.   To improve the concretes' porosity by using POFA in order to achieve desired carbonation resistance.

1.3 RESEARCH SIGNIFICANCE

It has been reported that the reinforced concrete structures do not last long in the high exposure of carbon dioxide especially in the urban or industrial areas. The carbon dioxide initiated the carbonation reaction inducing the corrosion effect causing detrimental effect to reinforced concrete structures. In the developed countries, there are many technologies that output the carbon dioxide in the air, as a result, higher chance of carbonation effect to occur. Therefore, by doing this research, it will bring benefits to the structures in industries or marine environment. The reinforced concrete structures will have desired carbonation resistance that can achieve a longer lifespan even with the high exposure of carbon dioxide. Furthermore, understanding the parameters that can accelerate the carbonation induced corrosion effect and counteract it.

1.4 RESEARCH SCOPE

This project was undertaken in five stages. During the first stage of the project, it was to do the material preparation. The materials such as cement, palm oil fuel ash, aggregates, and tools are important for casting and testing so that no delays would occur.

At the second stage, concrete specimens are needed to be cast. A total of 30 concrete prism specimens and 20 concrete cylinder specimens were cast and cured for 28 days. The prism specimens' size is 280 mm x 70 mm x 70 mm and cylinder specimens' size is 50 mm height x 100 mm in diameter. After finishing casting, cover the exposed surface with polythene or any impermeable sheeting to prevent drying.

The concrete's mould was stripped out after (20 ± 4) hours and placed it into the water curing tank. At this stage, it is known as the third stage. The water curing tank should have temperature control (20 ± 2) ˚C. After 28 days, removed all the concrete specimens from the water tank. The concrete cylinder specimens were ready for sorptivity testing, but concrete

prism specimens required further air drying conditioning. These concrete prism specimens were transferred to a laboratory air drying environment (between 18 ˚C to 25 ˚C, between 50% and 65% relative humidity) for 14 days. After 14 days conditioning, seal top and bottom longitudinal faces and the two end faces of prisms using paraffin wax or similar material that can prevent diffusion of carbon dioxide. As a result, carbonation can take effect on the other two cast longitudinal surfaces only. The purpose of sealing other faces was to prevent the carbonation effect to occur in order to minimize any corner effect from multi-directional carbonation. After the sealing, the third stage can proceed.

During the fourth stage, all specimens were removed from the laboratory air drying environment and placed into the carbonation chamber for 70 days. The measurement of carbonation depth of prisms was recorded after the exposure period of 56 days, 63 days and 70 days. Sliced 50mm of the concrete prism and sprayed phenolphthalein solution to indicate the carbonation depth. Use any measurement apparatus to measure the carbonation depth and re-seal the sliced surface with paraffin wax again. Overall, the total lab experiment required to conduct is 112 days.

During the final stage, sorptivity testing was conducted on all of the specimens to determine which had the best porosity. At the same time, XRF, XRD, and SEM were performed to obtain the chemical composition of POFA, morphology phases of POFA and microstructure of POFA and the sample specimens to justify the results got from the accelerated carbonation testing.

CHAPTER 2   LITERATURE REVIEW

2.1 INTRODUCTION

2.1.1 Introduction of Palm Oil Fuel Ash

There are large quantities of palm oil fuel ash (POFA) have been produced annually. Furthermore, the rate of production of POFA has been increasing throughout the decades due to the increment of urban density population. With the increase of the urban density population, it can lead to higher demand for palm oil thus palm oil plantation will be substantially increased. In Malaysia, the oil palm cultivation was limited to 54,000 ha in the year of 1960; however, it has been dramatically increased to 4.85 million hectares in 2010 and 5.39 million hectares in 2014. Moreover, in Indonesia, the oil palm cultivation was 6.5 million hectares in 2012. A statistic has been module indicating the world's production of palm oil, Indonesia = 48%, Malaysia = 38%, Thailand = 3%, Columbia = 1%, Papua New Guinea = 1% and others = 7% (Awalludin MF et al. 2016).

The main concern of oil palm cultivation is the huge portions of biomass wastes like oil palm fronds, palm oil mill effluent, oil palm leaves, oil palm trunks, oil palm kernel shell, mesocarp fibre and empty fruit brunches are generated after harvesting of oil palm fruits, palm oil processing and re-plantation of palm oil trees. A rough estimation has been made, the production of 1kg of palm oil can generate about 4kg of dry biomass (Vakili M et al. 2015). Approximate 75% of dry biomass have been left rotten to act as mulching and nutrient recycling for the future. However, almost 25% of dry biomass is dried and used in power plants to generate electricity through combustion at 800 ˚C to 1000 ˚C (Umar MS et al. 2013).

2.1.2 Introduction of Carbonation

Durability property of concrete is a major consternation when it comes to exposure of aggressive environments. There are many environmental phenomena which can greatly influence the durability of reinforced concrete. Previously, chlorination is considered as the most common deterioration effect that can induce corrosion. However, carbonation can now be found almost in every concrete structure due to increasing greenhouse gas emissions especially the carbon dioxide. Therefore, the carbonation induced corrosion can be as crucial as chlorination effect (G. Kakali et al. 2000).

Carbonation induced corrosion increases the crack development and decreases the service lifespan of reinforced concretes. The ability to cause detrimental to concrete is due to the reaction of hydration products dissolved in pore water with the carbon dioxide in the air, as a result, reducing the pH from 12.6 to 9. This outcome has led to the de-passivation of steel passive oxide film and accelerates the uniform corrosion.

Chapter 3   Methodology

The carbonation process can be complex in reality. The simplest understanding of the carbonation effect is basically, calcium hydroxide ($CaOH$) reacts with carbon dioxide (CO_2) to form calcium carbonate ($CaCO_3$) (Mobin Raj T. et al. 2016). Earlier mentioned, carbonation decreases the pH value of concrete is due to the consumption of $CaOH$. Initial concrete's state is in alkali phase, but due to the reaction of carbonation which then eventually causes the cement paste/pore solution to drop and all the other hydrates will break down.

Normally, carbonation does not occur similarly in all circumstances; different exposure condition environments will influence the rate of carbonation differently (Neves R. et al. 2012). The atmosphere contains a substantial amount of carbon dioxide but this gas cannot directly react with the hydrates of the cement paste (Mobin Raj T. et al. 2016). The first step for the carbonation to occur is when the carbon dioxide dissolved in water and formed carbonate ions that in turn will react with Ca ions of the pore water. The type of carbonate ions formed is depending on the pH value of the concrete pore solution. As mentioned earlier that the pH may decrease due to the dissolution of calcium hydroxide. In neutrality (pH = 7), CO_2 comes in contact with water to form bicarbonate ions and since inside concrete, the pH value is high (pH not equal to 7) therefore the bicarbonate dissociates to form carbonate ions (Mobin Raj T et al. 2016).

The carbonation process can be described by the following chemical equations:

Equation 1. Chemical equations of the carbonation process:-

$$CO_2\ (g) + H_2O\ (l) = HCO_3^-\ (bicarbonate\ ions) + H^+$$

$$HCO_3^- = CO_3^{2-}(carbonate\ ions) + H^+$$

$$Ca^{2+} + CO_3^{2-} = CaCO_3\ (s) \tag{1}$$
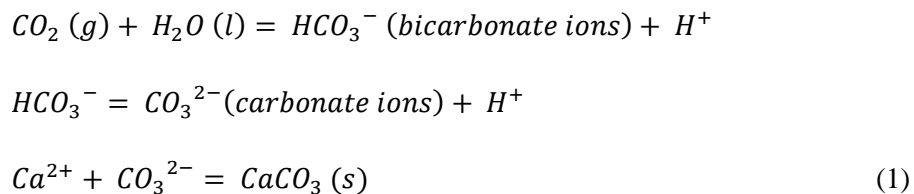
2.2 CARBONATION CONTROL PHENOMENA

There are three controlling agents that influenced the rate of carbonation occurred in reinforced concretes. The formation of calcium carbonate is the process of the carbonation. The precipitation and transformation of calcium carbonate strongly dependant on these three parameters known as the relative humidity, the temperature and the concentration of carbon dioxide in the surrounding (Shanmukhaprasad Gopi et al. 2013).

2.2.1 Relative Humidity

This relative humidity mainly influences the phases of the calcium carbonate. There are at least three different phases of anhydrous crystalline polymorphs known as calcite, aragonite and vaterite. There are three fundamental steps for the formation of calcium carbonate.

During the first step, physical adsorption of the water held within the atmospheric humidity at the $Ca(OH)_2$ grains' surface. The next step is to allow $Ca(OH)_2$ to dissolve into Ca^{2+} and OH^- ions. The final step is the dissolution of CO_2 under a certain pH condition (pH = 10), yields $CO_3{}^{2-}$ ions to contribute to the precipitation of calcium carbonate (Shanmukhaprasad Gopi et al. 2013).

XRD quantification of portlandite and calcium carbonate polymorphs depending on RH (relative humidity) and exposure time (days).

RH (%)	Time (days)	Portlandite (%)	Calcite (%)	Vaterite (%)	Aragonite (%)	MHC (%)
33	7	96	4	N/d	N/d	N/d
	28	84	8	N/d	N/d	8
54	7	92	N/d	8	N/d	N/d
	28	36	N/d	52	7	5
75	7	N/d	3	20	41	36
	28	N/d	11	39	23	27
90	7	N/d	32	37	N/d	31
	28	N/d	37	25	24	16

N/d (No detected);

Table 1 Percentage Formation of Anhydrous Crystalline Polymorphs in different Relative Humidity

The Table 1 shows the best carbonation effect can occur is in between 75% to 90% of relative humidity. There is a faster rate of carbonation and larger particles size with higher crystallinity compared to lower relative humidity (33% to 54%). In this lower relative humidity, it gives rise mainly to portlandite and vaterite. In other words, it has slower carbonation and smaller particles sizes with lower crystallinity (Shanmukhaprasad Gopi et al. 2013).

The results above mainly represent the formation of calcium carbonate in the non-concrete structures. Therefore, if concrete structures are to be considered, porosity or the permeability should be taken into account. In other words, if the surrounding is too wet (high relative humidity), it tends to slow down the penetration of carbon dioxide. Although CO_2 diffuses into the capillary pores, it cannot dissolve into the thin layer of water covering the pores.

Therefore, reaching peak relative humidity can slow down the carbonation effect due to the water present in the pores. The highest occurrence of carbonation effect will be in between 50% to 70% relative humidity (J. Collado et al. 2015).

2.2.2 Temperature

The diffusivity of gaseous CO_2 is directly proportional to the temperature. As the temperature increases, there will be a higher rate of diffusivity of the CO_2 due to the increased molecular activity (J. Collado et al. 2015). Furthermore, Kolio mentioned that as the temperature rises, the solubility of chemical compounds increases inducing a higher rate of corrosion of the steel reinforcement (Kolio et al. 2014). Temperature is a significant parameter as it influences the rate of both nucleation and crystal growth (E. Altay et al. 2007).

Among the three different phases of the three crystalline polymorphs, the thermodynamically most stable is calcite and least stable is vaterite. Hence, it would be better as there is more calcite phase than vaterite. According to Shanmukhaprasad Gopi et al. aragonite is observed at 60 ˚C and 80 ˚C, pure calcite at 100 ˚C and 130 ˚C and coexistence of calcite and vaterite at 150 ˚C to 200 ˚C by using X-ray diffraction (XRD) (López-Arce et al. 2011). The appearance of calcite, aragonite and vaterite are rhomboidal, needle/rod and spherical respectively.

Shanmukhaprasad Gopi et al. have done an experiment to prove the influence of temperature is valid by applying an inhibitor. The Figure 1 above summarised the effect of temperature on the crystallization of calcium carbonate. The presence of diethylenetriaminepentaacetic acid (DTPA) will act as an inhibitor to kinetically stabilize the formation of different polymorphs of calcium carbonate. It has proven that the three crystalline polymorphs can be influenced by thermodynamically. Overall, with the rise in temperature, there will be more effective for the carbonation effect to occur.
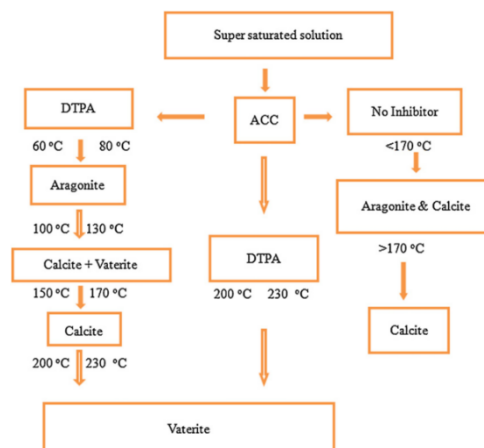
Figure 1 Indication of Anhydrous Crystalline Polymorphs using DTPA as Inhibitor

2.2.3 CO_2 Concentration

Obviously, the CO_2 concentration can dramatically influence the rate of carbonation. When there is a high concentration of CO_2, the carbonation effect will definitely be increased as diffusivity of CO_2 penetrates into the concrete structures is faster. The speed of diffusion can be defined by using the Fick's Law (Woyeiechowski et al. 2015). The rate of diffusion is related to the difference between the gradient of concentration from both sides. As there is a larger difference of gradient of concentration, higher speed of diffusion can be found.

Furthermore, naturally in the surrounding will have estimated 0.3% to 0.4% of CO_2 concentration in the urban area. However, by using an accelerated carbonation method, the CO_2 concentration has been increased to 3% to 4% (McGrath et al. 2015). This is applied to all standards that can be found to conduct accelerated carbonation method. Increasing the CO_2 concentration is the most effective way to accelerate the carbonation effect. While for the relative humidity and the temperature, it is only to ensure that carbonation effect can occur in that condition. Moreover, it affects the crystallization forms of calcium carbonate.

2.3 CARBONATION INDUCED CORROSION

Aggressive environments have high impacts to the durability of the reinforced concretes especially environment with a substantially high content of carbon dioxide in the surrounding. Therefore, understanding different states of environment well enough to provide the suitable hindrance to the concretes.

Deterioration of concrete structures can be caused by carbonation. This carbonation effect is more probable especially in the urban and marine environment, where the rate of carbonation is enormous. Generally, carbonation is known as a physiochemical process which involves the diffusion of CO_2 dioxide in the gaseous phase of the concrete pores/pastes and the dissolution of CO_2 in the pore water as carbonic acid (H_2CO_3) (Shaik Hussain et al. 2016). Due to this certain process, the carbonation is able to induce corrosion because as the pH of pore solution is reduced caused by carbonic acid and the consumption of $Ca(OH)_2$ to react with the CO_2. Once the pH value is decreased, it will dissipate the passive film layer surrounding the steel reinforcement leading it to be vulnerable to corrosion. Carbonation-induced corrosion can increase the crack development and hence, decrease the service lifespan of concretes. This concludes that every concrete structure will have different service lifespan depending on the effectiveness of the carbonation effect to occur. There is one model of the service life design for reinforced concrete structures known as Tutti's model.

One case study in Dhaka City has taken 70 in-situ concrete samples for carbonation coefficient measurement. These samples have taken from different structural members such as the slab, beam, column and others. These samples were exposed to both outdoor and indoor exposure. It has concluded that carbonation coefficient in outdoor condition is more severe compared to indoor exposure. Generally, due to a high concentration of carbon dioxide in the outdoor environment. The result is shown in Table 2.

Table 2. Carbonation Coefficient at Different Structural Elements

Structural Element	Coefficient of Carbonation (K)		
	Outdoor Exposure	Indoor Exposure	Average
Slab	4.12	3.83	3.98
Beam	4.03	3.14	3.59
Column	3.90	3.54	3.72
Others	4.13	3.23	3.68
Average	4.16	3.36	3.75

Irrespective to the table above, the carbonation coefficient in the outdoor is 4.16 while the indoor is 3.36. In conclusion, the indoor has a lower rate of carbonation than outdoor.

Relatively, a higher rate of carbonation is found in slab compared to the other structural member (Mohammed Tarek Uddin1 et al. 2011).

2.3.1 Service Lifespan of Concrete Structures

Tutti's model is shown in Figure 3. This model shows that the total service lifespan of concrete consists of initiation and propagation time (fib model 2006). During the initiation time, the substance such as CO_2 will penetrate into the concrete cover. In other words, the time taken required by CO_2 to reach the steel reinforcement and eliminate the "protective passive film layer" of reinforcement because it loses thermodynamic stability (Xu et al. 2016). During the propagation time, it is where the actual corrosion process takes place at the steel reinforcement. The solid formation of the corrosion products will exert pressure at the steel/concrete interface. This is because the corrosion forms take up more volume than the steel consumed hence internal pressure will be built up causing damage to the concrete. Propagation time will undergo into three phases which are "Damage", "Cracking" and "Spalling" (Tuutti Model and fib Model code 2013).

"Damage" phase occurs when the formation of tiny cracks is found inside the concrete cover. While the "Cracking" phase refers to the formation of those tiny cracks together causing an opening cracks on the surface of the concrete. Lastly, "Spalling" phase refers to the phenomenon of concrete cover is repelled away from each other leading to a huge gap [Michel K et al. 2011]. The transition from each phase to another is when the width of the crack get further apart. For example, the time for damage phase is when the crack width reaches 50μm. The size of 50μm is the smallest crack that can be seen by naked eye which is also the so-called the hairline crack [DuraCrete. 2000]. The duration of the crack phase is from W=50μm till the crack can be seen on the concrete cover. As the crack on the concrete surface getting wider is the duration of the spalling phase. The spalling phase ends when the concrete finally reaches in the final stage where it collapsed.
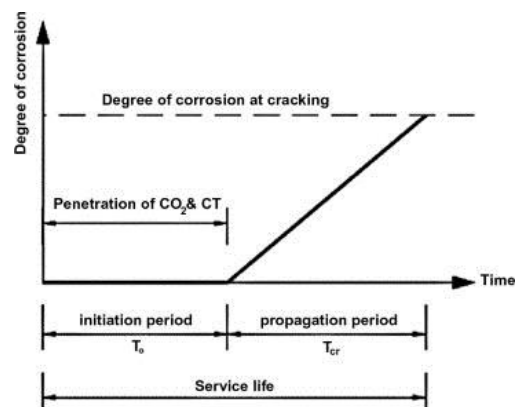
Figure 3 Total Service Lifespan of Reinforced Concrete (fib model, 2006)

2.3.2 Effect of Corrosion Products

Figure 4 shows the internal formation of steel in the concrete structures due to the damage, cracking and spalling phases [Solgaard et al. 2013]. The cracks inside the concrete get bigger is because of the formation of corrosion products. Once the corrosion products are formed surrounding the steel reinforcement, radial internal pressure at the steel/concrete interface is built up causing expansion of the concrete [Bhargava et al. 2006]. Hence, the concrete will be damage. This will create hoop tensile stresses in the surrounding. If this exerted tensile stress has exceeded the limit of the tensile strength, cracking phase will occurs as shown in Figure 4. The continuation of the formation of corrosion products will lead from cracking to spalling phase, as the width of the crack is getting wider. During this phase, the concrete is starting to fall apart or collapse.

Figure 4 Internal Cracking due to Corrosion Effect

2.4 COMPARISON BETWEEN NATURAL AND ACCELERATED CARBONATION METHOD

There are two ways of the method for testing of carbonation which is known as "Natural" and "Accelerated" carbonation method. The carbonation test in the natural environment is the most realistic method thus produced the most reliable results, which can be used to assess the carbonation resistance of concrete with different supplementary cementitious materials blended into the concrete (Yaodong Jia et al. 2012). Unfortunately, this method is proved to be slow and unfeasible compared to the accelerated carbonation testing method. Normally, researchers will consider using the accelerated carbonation method due to less time consuming com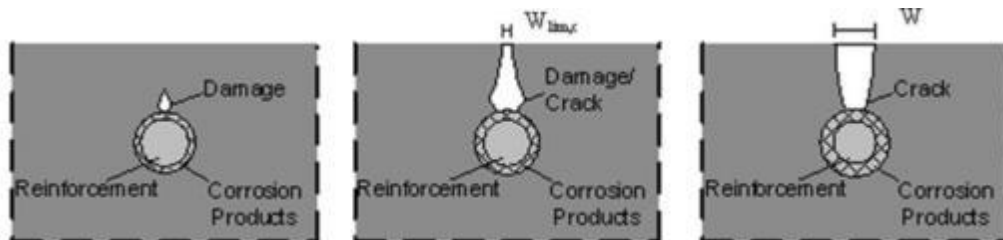pare to natural carbonation method. This method is an important tool for laboratory studies, as far as its limitations are taken into account (M. A. Sanjuan et al. 2003).

The way to accelerate the carbonation testing is by using a relatively high carbon dioxide concentration atmosphere, which is normally done by using a so-called "carbonation chamber". It is demonstrated that the accelerated testing changes the ranking of concrete's carbonation resistance (Sanjuan et al. 2003). Moreover, it also changes the microstructure of concrete when it is subjected to high concentrations of carbon dioxide (Yaodong Jia et al, 2012).

Despite much research have been carried out regarding the carbonation of cement pastes, mortar and concrete, there are too many parameters taking into account when conducting the carbonation testing. Therefore, there exist many doubts about the validity of the extrapolation from the accelerated testing to real-life conditions (M. A. Sanjuan et al. 2003). In practice, the chances to reproduce the real conditions by doing a simple test method is nearly impossible. Hence, it is normally treated as a source of information, either for simple predictive models recognizing its low accuracy or as tools to compare different concrete qualities (M. A. Sanjuan et al. 2003).

There are several case studies regarding the accelerated carbonation method. One of the examples is the conducted in China by following the Chinese standards GB175-2007, analogous with ASTM C 150. They have used the accelerated carbonation chamber with RH = 70 ± 5%, Temperature 20 ± 3°C, CO_2 concentration = 20 ± 3%. The measurement of carbonation depth is at 3, 7, 14 and 28 days. The results ranges from 0mm to 25mm (Xu et al. 2016). Next case study is conducted in South Korea by using accelerated method. The conditions inside the carbonation chamber is RH = 60 ± 5%, Temperature 20 ± 3°C, CO_2 concentration = 5 ± 3%. The measurement of carbonation depth is at 28, 56, 91 and 180 days. The results range from 12.33mm to 41.10mm (Ho Jae Lee et al. 2012). There are other case studies using different standards with different accelerated carbonation chamber. This has

proven that the actual objective of using accelerated method is to produce an idea or trend on how does the carbonation affects the concrete in the long run. However, it is almost impossible to extrapolate the accelerated results to natural conditions.

2.5   THEORETICAL FOUNDATION OF CARBONATION MODELLING

Many years in various research centres have been conducting researches on the development of universal models of carbonation in terms of changes in time and taking into account different technological and material variables. The main key issue of understanding the mathematical modelling of carbonation is to determine the intensity of the flow of carbon dioxide through the concrete. The starting point of the understanding of the theoretical foundations of carbonation modelling is by understanding the Fick's Law. In accordance to Fick's first law (eq. 2), it describes the diffusion flux in one-dimensional space under a constant, unchanging in time.

Equation 2. Fick's first law is shown below:-

$$Q = -D\frac{\partial \varphi}{\partial x}, \mid \tag{2}$$

Where   Q = the flow (mol/m^2)

      D = the diffusion coefficient (m^2/s)

      ϕ = the concentration of the diffusing substance (mol/m^3)

      X = the way of diffusion (m)

In terms of changing in time, the density of diffusion flux can be defined by using Fick's second law (eq.3).

Equation 3. Fick's second law is shown below:-

$$\frac{\partial Q}{\partial t} = D \cdot F_D \frac{\Delta \varphi}{x}, \tag{3}$$

Where t = time (s)

      F_D = surface through which the diffusion occurs (m^2)

      $\frac{\Delta \phi}{x}$ = the concentration gradient on the concrete surface and on the depth x.

If x is taken as the depth of carbonation, thus simplifying it can be assumed that ϕx, i.e. the concentration on the depth x is 0 and the eq. 3 becomes the form of eq.4.

Equation 4 is shown below:-

$$\frac{\partial Q}{\partial t} = \frac{D \cdot F_D \cdot \varphi_{\text{ext}}}{x} \tag{4}$$

Where $\phi_{ext} = CO_2$ concentration in the air

Assuming 100% of CO_2 will be used up completely during the carbonation. This leads the diffusion dQ through a given volume is equal to the maximum potential amount of carbon

dioxide that can bind due to carbonation in this volume of concrete. This characterizes the equation 5:-

Equation 5 is shown below:-

$$\partial Q = a \cdot F_D \dot{\partial} x \qquad (5)$$

Where a = coefficient determining the amount of CO_2 bound In the way of carbonation by unit volume of concrete (kg/m^3)

In accordance to Bulletin CEB, (Woyeiechowski et al. 2015) the value of "a" can be calculated using equation 6

Equation 6 is shown below:-

$$a = 0.75 \cdot \text{C} \cdot [\text{CaO}] \cdot \alpha_H \cdot (M_{CO2}/M_{CaO}) \qquad (6)$$

Where C = content of cement (kg/m^3)

  CaO = CaO content in the cement composition (kg/m^3)

  αH = the degree of hydration of cement

  M_{CO_2} and M_{CaO} = molar mases

By comparing all the equations listed above, substitute eq. 5 into eq.4 to form eq. 7:- This model has been used by many researchers. (Yaodong Jia et al. 2012)

Equation 7 is shown below:-

$$x = \sqrt{\frac{2D\varphi_{\text{ext}}}{a}} \cdot \sqrt{t}. \qquad (7)$$

In practice, the model that is greatly been used is normally simplified. It relates to the certain parameters that affect the carbonation such as the average constant of relative humidity and concentration of carbon dioxide in the environment. The simplified equation is shown in equation 8:-

Equation 8 is shown below:-

$$x = k\sqrt{t} \qquad (8)$$

Where x = carbonation depth (m)

  K = the diffusion coefficient (m^2/s)

  T = time $(year)$

Also, a formula (eq. 9) in the following form is often used.

Equation 9 is shown below:-

$$x = \sqrt{\frac{2Dt[CO_2]}{[Ca(OH)_2]}}$$

(9)

Where $[CO_2]$ and $[Ca(OH)_2]$ = molar concentration of carbon dioxide and calcium hydroxide concentration

   D = the diffusion coefficient

   t = time of exposition

The equations from 7 to 9 are the equations for the mathematical modelling for the concretes exposed to an environment containing carbon dioxide and unlimited in time. This model has mainly taken into account of the diffusion of carbon dioxide resulting from different concentration gradient in both concrete and the surrounding. However, this model has excluded the consideration of the microstructure of the concrete. Hence, there are several factors that have not been taken into accounts such as the changes in diffusivity as a function of humidity, changes in atmospheric concentration of carbon dioxide in the climatic year, participation in the carbonation of CSH phase and residual of non-hydrated cement. These factors will change from the changes in time of the concrete microstructure (Woyeiechowski et al. 2015).

2.6 FACTORS AFFECTING CARBONATION

Carbon dioxide is always present in ambient air and the internal atmosphere of buildings. The course of carbonation is also significant to be studied. There are several factors that can affect the course of carbonation. Concrete carbonation is not only dependent on the amount of CO_2 presence in the surrounding but also the intensity. These factors have been classified as the external and internal factor for easier understanding. The external factors are relating to the ambient and the internal factors are relating to the composition and microstructure of concrete. In the group of external factors, there are environmental factors and exploitation conditions of concrete and technological factors shaping the concrete properties during its execution are standing out. While for the internal factors, there are the properties of concrete components and their proportions in concrete as well as hardened concrete properties. These both factors are the results of the qualitative and quantitative composition.

The time of carbonation is strongly dependant on the relationship of CO_2 and Ca^{2+} ions. If the speed of diffusion Ca^{2+} ions is faster than CO_2, carbonation crystallization such as calcite, aragonite and vaterite may form on the surface of CSH and most likely reducing the porosity of the concrete as carbonation crystallization may also form in the capillary pores. On the other hand, if the speed of diffusion of CO_2 is faster than Ca^{2+} ions, the carbonation products crystallize on the surface of portlandite which may then benefits the concrete as a new protective layer is formed that can slows down the process. This layer is not completely sealed; therefore, the carbonation process is delayed instead of stopped. This mechanism is particularly significant in the case of Portland cement concretes or blended cement concretes (B. Lagerblad et al. 2005).

Figure 5 above shows the classification of factors affecting the carbonation. Almost all of the above are time dependent factor, especially for the external factors. As for the concentration of CO_2, air humidity and air temperature have been discussed earlier in the section 2.2 carbonation control phenomena. As the "structure condition" seen in Figure 5 under exploitation, it is referring to the cracking, stress state such as tensile stresses and compressive stresses and freeze/ thawing destruction. All of the factors mentioned in the "structure condition" increased, the rate of carbonation will also increase except for the compressive stress. For example, if the concrete has been found more cracks occurred, this could lead to a higher carbonation rate because higher rate of diffusion of carbon dioxide penetrates into the concrete. However, if the compressive stress increased, the rate of carbonation will still decrease. This is because the formation of carbonation crystallization formed can cause the concrete to become stronger in terms of compressive strength. The formation of calcium

carbonate will cause the concrete to become denser and compact; hence, achieving higher compressive strength (Woyeiechowski et al. 2015).
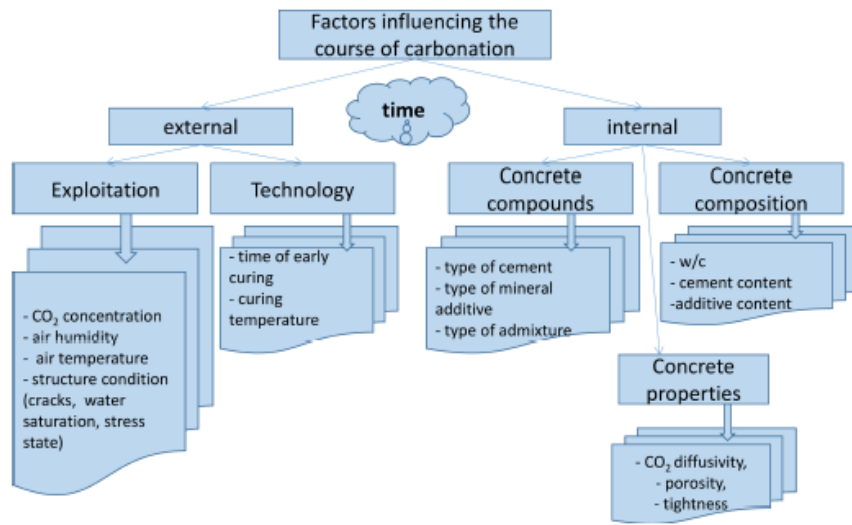
Figure 1 Factors Influencing the Course of Carbonation

With the effect of carbonation, it definitely influenced the main properties of concrete (Woyeiechowski et al. 2015). The summarisation of properties of concrete due to carbonation is shown in Table 3.

Table 3. Influence of Carbonation on Different Properties

Property of Concrete	Influence: "+" (positive) or "-" (negative)	Remarks
Passivation of reinforcement	-	As carbonation will decrease the pH value of the concrete, the passivation of reinforcement will dissipate and induced higher corrosion rate.
Water absorption	+	Small decrease as a consequence of microstructure tightening.
Compressive strength	+	Small increase as the formation of calcium carbonate causing the concrete to become denser and compact.
Frost resistance	-	Decrease, due to the fact that small pores can easier full with water.
Shrinkage	-	Carbonation shrinkage is an element of total shrinkage
Susceptibility on chloride penetration	-	Increase of susceptibility

2.7 THE PHASE TRANSITION OF CALCIUM CARBONATE DUE TO RELATIVE HUMIDITY AND TEMPERATURE

The calcium carbonate has three phases of anhydrous crystalline polymorphs known as calcite, aragonite and vaterite; and three hydrated forms are known as amorphous $CaCO_3$ (ACC) hydrate, monohydrocalcite ($CaCO_3.H_2O$) and crystalline hexahydrate or ikaite ($CaCO_3.6H_2O$) (A. Antony et al. 2011). Among the anhydrous crystalline forms, the most stable is the calcite while the least stable is the vaterite. This crystallization of calcium carbonate can be influenced by several parameters such as the morphology, size, structure, chemical purity and the specific surface area which depends on the method of preparation (I. Raluca et al. 2010). Normally, the hydrated forms are unstable and therefore have the tendency toward transformation into anhydrous crystalline forms (calcite, aragonite and vaterite) (Shanmukhaprasad Gopi et al. 2013). However, the most important parameters are the temperature, relative humidity, and the concentration of CO_2. These are the ones responsible for the rates of both nucleation and crystal growth (Q. Shen et al. 2005).

2.7.1 Due to Relative Humidity

Relative humidity is one of the known factors and condition that control the precipitation of these crystalline polymorphs (López-Arce et al. 2011). Relative humidity is referring to the percentage saturation of atmosphere. There are three sequential steps when the calcium carbonate is exposed to the humid atmosphere. In this first step, physical absorption of the water held within the atmospheric humidity at the $Ca(OH)_2$ grains' surface. In the second step, the water will cause the $Ca(OH)_2$ will dissolve into Ca^{2+} ions and OH^- ions. In addition, there is a possibility yielding CO_3^{-2} during the dissolution of CO_2 under the condition of pH = 10. In the third step, the production of Ca^{2+} and CO_3^{-2} in the previous step will then react and contribute to the precipitation of calcium carbonate (R.M. Dheilly et al. 2002).

An experiment was done by a researcher named P. Lopez-Arce. He had exposed the calcium hydroxide nanoparticles to 33%, 54%, 75% and 90% relative humidity. The main mineralogical phase found in the different humid atmosphere; 33%, 54%, 75% and 90% relative humidity are "portlandite", "vaterite and portlandite", "aragonite and vaterite" and "calcite" respectively. Take note that all of the calcium carbonate polymorphs have the different structure. The calcium hydroxide nanoparticles were analyzed by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS), X-Ray Diffraction Analysis (XRD) and Micro Raman Spectroscopy (López-Arce et al. 2011).

The purpose of TEM is to identify the mineralogical phases and to study the shape and size of the calcium carbonate polymorphs nanoparticles. SEM was performed to study the

morphology, size and distribution of the nanoparticles including the spaces between the particles. XRD is to identify the mineralogy and crystallinity. Micro Raman spectroscopy can be used to obtain the value of wavelength in a particular point to determine the carbonation of the carbonation calcium hydroxide nanoparticles.

At higher relative humidity, portlandite will start to dissolve and transformed into calcium carbonate. The form of calcium carbonate transformed will be depending on the relative humidity. If the relative humidity is high, calcite will formed while vaterite will be forme if the relative humidity is low. The reason why portlandite will still remaine at low relative humidity is that at lower RH, the dissolution and transformation process is slowed (López-Arce et al. 2011).

2.7.2 Due to Temperature

The calcium carbonate polymorphs are definitely influenced by the factor of temperature. Few researchers had done experiments regarding this particular issue. They had done it by subjecting the calcium carbonate polymorphs precipitation in spring systems. Hence, one of the controlling factors is the water temperature. The idea that "temperature" played an important role in the precipitation of aragonite and calcite have been proven by Faivre, Togari, Zeller and etc. (Jones 2017b). Few studies have been found introducing that the calcite may transforme into aragonite precipitation once it reached a critical temperature. For example, calcite forms when T < 50, whereas aragonite forms if T >50 (Jones 2017b). However, another researcher mentioned that aragonite forms when T >60. In addition, past researchers also demonstrated that $CaCO_3$ phase changed from vaterite to calcite and lastly to aragonite as temperature increased (Jones 2017a). There are many different results from the past; however, it is proven that the factor of temperature evidently influenced the calcium carbonate phases.

2.8 SUPPLEMENTARY CEMENTITIOUS MATERIALS AND POZZOLANIC REACTION

There are various different chemical elements present in the Ordinary Portland Cement (OPC). The main four elements that influenced the properties of concrete are the silica dioxide (SiO_2), aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3) and calcium oxide (CaO). However, the significant elements among the four are the calcium and silica ions. The reason why the trend of using blended cements is very popular because of these chemical elements present in different supplementary cementitious materials (SCM) can benefit the concrete's properties in different ways (Zeyad et al. 2017). Some SCM can benefits the concrete by improving the heat of hydration, permeability, early or later strength and etc.

Palm Oil Fuel Ash (POFA) as the SCM is considerably good in terms of enhancing the concrete's durability. The origin of POFA is a by-product waste produced by burning the palm oil husk or fiber and palm kernel shell as fuel in palm oil mill boiler to produce electricity in the industry. The main reason for incorporating into the concrete is because it might favour the concrete's properties (Ul Islam et al. 2016).

It is well-known that POFA acts as SCM in concrete can improve the mechanical and durability properties due to the "filler effect" and the "pozzolanic reaction" (Aprianti S. et al. 2017). SCM can be considered as pozzolan material which in generally contain higher siliceous materials compare to ordinary cement products. Many researchers have published the compared chemical composition of OPC and POFA. One of the results is shown at Table 4

Chemical composition of OPC, G-POFA, and T-POFA (%).

| Oxide composition	OPC	G-POFA	T-POFA
Silicon dioxide (SiO_2)	17.60	59.17	69.02
Aluminum trioxide (Al_2O_3)	4.02	3.73	3.9
Iron oxide (Fe_2O_3)	4.47	6.33	4.33
Calcium oxide (CaO)	67.43	5.80	5.01
Magnesium oxide (MgO)	1.33	4.87	5.18
Sodium oxide (Na_2O)	0.03	0.18	0.18
Potassium oxide (K_2O)	0.39	8.25	6.9
Sulfur trioxide (SO_3)	4.18	0.72	0.41
$SiO_2 + Al_2O_3 + Fe_2O_3$	–	69.23	77.25
Loss on ignition (LOI)	2.4	16.1	1.8

Table 4. Chemical Composition of Different Binders.

When the siliceous materials combined with the calcium hydroxide, it can exhibit cementitious properties depending on the constituents of the pozzolan. On the basis of the pozzolanic reaction stands a simple acid-base reaction between Portlandite ($Ca(OH)_2$) and
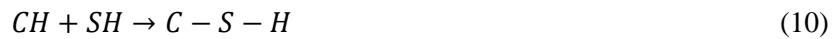
silicic acid ($Si(OH)_4$) (Aprianti S. et al. 2017). The formation of this two components forms C-S-H material. This reaction is simplified represented in the equation 10.

Equation 10 is shown below:-

$$Ca(OH)_2 + Si(OH)_4 \rightarrow Ca^{2+} + H_2SiO_4{}^{2-} + 2H_2O \rightarrow CaH_2SiO_4 + 2H_2O$$
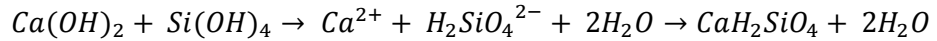
A similar abbreviated notation is shown below:

$$CH + SH \rightarrow C - S - H \qquad\qquad\qquad (10)$$

As the density of this C-S-H products is lower than the Portlandite and pure silica; hence, the concrete can be more densified. In other words, the permeability of the concrete can be reduced. One of the most important consequences incorporating POFA is the early strength of the concrete is reduced significantly. However, in the long run, the total strength of the will eventually overhead the normal concrete. The reason for lower early strength is due to the calcium content has been reduced. When replacing the cement usage to POFA, the calcium contents used is also reduced because cement has high calcium but low silica while POFA has low calcium but high silica. Since the calcium is responsible for the early strength hence incorporated POFA in concrete is degraded in terms of early strength of concrete. On the other hand, later strength will increase dramatically due to the formation of CSH products causing the concrete to become more densified. It is also discussed that the pozzolanic reaction of POFA increased with arising particle fine-ness, cement replacement rate and age of concrete (Aprianti S. et al. 2017).

2.8.1 Mineralogical composition of clinker

There are varieties of chemical compounds present in the cement. Chemical compounds with calcium sulfate sources such as gypsum can illustrate good effect for the concrete. These can improve the regulation of the early hydration reactions to prevent flash setting, improve strength development and reduce drying shrinkage. Moreover, there are more compounds present inside the cement such as the sulfate and aluminate (Association 1998).

The four main mineralogical composition of clinker are (Tricalcium silicate) C_3S, (Dicalcium Silicate) C_2S, (Tricalcium Aluminate) C_3A and (Tetracalcium Aluminoferrite) C_4AF. The total addition of C_3S and C_2S may consist of more than 60% of the cement weight as shown in Figure 5 (Kakali et al. 2000). Each of these compounds affect the concrete in several ways.

(Tricalcium silicate) C_3S : This compound will be hydrated and hardens rapidly. It is responsible for the initial set and early strength of the concrete. Normally, with the increased percentage of the C_3S can increase the early strength of the Portland cement concrete.

(Dicalcium Silicate) C_2S : By comparing to C_3S, this particular compound will hardens slowly and usually contributes dramatically to the later strength of the concrete at the ages beyond 7 days.

(Tricalcium Aluminate) C_3A : It is responsible for the setting times. This is because it influences by liberating a large amount of heat during the first few days of hardening concrete.

(Tetracalcium Aluminoferrite) C_4AF : Minor affection of the strength gain only. Generally, this acts as a flux during manufacturing and contributes to the colour effects visualizing cement in grey colour.

Chemical composition of clinker and limestone. Mineralogical composition of clinker

Chemical composition (%)			Mineralogical composition of clinker (%)	
	Clinker	Limestone		
SiO_2	21.79	0.61	C_3S	65.15
Al_2O_3	5.13	0.15	C_2S	13.32
Fe_2O_3	3.59	0.17	C_3A	7.54
CaO	66.42	53.36	C_4AF	10.92
MgO	1.71	1.47		
K_2O	0.55	0.02		
Na_2O	0.09	0.00		
SO_3	0.52			
LOI		43.54		

Figure 5 Chemical and Mineralogical Composition of Clinker

2.8.2 Hydration products
The three major cement hydration products are calcium silicate hydrate (C-S-H), calcium sulfoaluminate (ettringite) and monosulfate. Amorphous C-S-H can contribute to 50% of the paste volume and classified as a high sorption potential ascribed to high specific surface area and variability in structure and composition. Moreover, the ettringite and monosulfate is favouring the crystallochemical substitution reactions (Baur et al. 2004).

The C-S-H gel is known to have disordered nanostructure arranged in layers that resemble the pattern found in crystalline calcium silicate hydrates such as 1.4 thick of tobermorite and jennite (Baur et al. 2004). This C-S-H gel carries a huge responsibility for the engineering properties of cement paste because it forms a continuous layer that binds all the cement particles together into one cohesive whole. It has the strongest binding component when compared to other hydration products. C-S-H gel can produce an internal system of tiny pores known as gel pores. This is almost 100 times smaller than capillary pores. This is due to the nano size of the C-S-H gel producing tiny voids in the concrete.

Ettringite is another form of hydration product. It is a needle-like structure with chemical formula known as 3CaO•Al2O3•3CaSO4•32H2O. It is formed when the sulfate compounds

react with calcium aluminate under saturated condition. Ettringite crystal in air voids or cracks has size of 2 to 4 micrometres in cross-section and roughly 20 to 30 micrometres long. This indeed is larger size compare to C-S-H gel. Furthermore, if the concrete is exposed to water for long period, the primary ettringite (formed at the early stage) can slowly dissolve and reform into micro-cracks. Research has also proven that the secondary ettringite (formed by dissolution and recrystallization in voids or cracks) is not detrimental to the concrete.

2.9 CASES WHEN INCORPORATING PALM OIL FUEL ASH

All of the Supplementary Cementitious Material (SCM) products are widely used to act as potential pozzolanic materials. Particles size, large surface area, low carbon content, loss of ignition and high amorphous content contribute to superior pozzolanic properties (Zeyad et al. 2017). Mostly the SCM are known as by-product wastes come from different origin and usually unused SCM are thrown into the landfill which eventually causes serious environmental pollution or human hazards. Therefore, utilizing the wastes as the pozzolanic material would be the most viable reason. This could bring huge benefits to the civil and construction development.

Many researchers have been doing research on the POFA in terms of concrete's properties. This product has been proven that the mechanical and durability properties of concrete will be improved the mechanical properties include the compressive strength, flexural strength and tensile strength while the durability properties include porosity, the heat of hydration and workability.

Generally, researchers seldom used raw POFA because it does not have a good pozzolanic reaction. However, after treating the raw POFA into ground POFA by heating, it would change into a high potential SCM. Heating the raw POFA decrease the carbon content, loss of ignition and improve the chemical composition (Lim et al. 2015). The improvement is shown in Table 5. Furthermore, the sorptivity of concrete incorporated POFA can be improved as well because it decreases the critical pore size and average pore diameter (Kroehong et al. 2011).

Table 5. Comparison of Carbon Content and Loss of Ignition (LOI)

Properties	Raw POFA	Treated POFA
Carbon Content	18.9%	0.41%
Loss of Ignition (LOI)	20.9%	1.3%
Chemical Composition	59.21%	75.14%

2.9.1 Micro Size of Palm Oil Fuel Ash

As one of the criteria to have a better pozzolanic reaction is to obtain smaller particle size; hence, achieving micro size particle is significant. This can provide huge benefits for the concrete's properties. A lot of testing have been conducted to verify the advantage of using micro POFA. There are different results from different researchers because there will not be exactly the same POFA collected from the different location. However, it has been summarised that incorporating more 30% micro POFA is the optimum mix to achieve the highest mechanical strength such as the compressive strength, flexural strength and tensile strength. Using more than 30% will cause detrimental to the concrete (Lim et al. 2015). Moreover, incorporating more than 30% of POFA can bring incremental to the durability of

concrete. Hence, the amount of POFA used is depending on the research point of view rather of obtaining High-Strength Concrete (HSC) or High-Performance Concrete (HPC).

The influence of POFA in term of mechanical properties of concretes in 28 days is summarised in Table 6 below (Sooraj V.M. et al. 2013).

Table 6. Comparison of Mechanical Properties

Properties	0% POFA	10% POFA	20% POFA	30% POFA	40% POFA
Compressive Strength (MPa)	36.89	35.63	32.70	28.44	23.48
Flexural Strength ($N/mm^{1/2}$)	2.62	2.69	2.62	2.33	1.99
Tensile Strength (($N/mm^{1/2}$))	5.71	5.71	6.12	4.89	4.28

In 28 days, increasing POFA will decrease the mechanical properties of concrete. This is due to the slower reaction at the early stage due to higher silica content in the POFA. After sometimes, the strength will eventually go more than the control mix after 28 days. The percentage increase of strength in more than 28 days by incorporating 10% and 40% POFA is shown at Table 7. (Wunchock Kroehong et al. 2011)

Table 7. Comparison of different percentage of Palm Oil Fuel Ash in terms of strength

POFA	7 days	28 days	60 days	90 days
10%	4%	9%	11%	12%
40%	16%	21%	25%	28%

The amount of incremental strength is highly dependent on the particle size of POFA. The smaller particles used will have higher strength due to the packing and filler effect. Using large particle of POFA (30.8μm) will not have gained as much strength as the small particle of POFA (12.3μm). In other words, using the larger particle of POFA will not have higher strength than the control mix. Hence, it is crucial to use the micro size of POFA (Jaturapitakkul et al. 2011).

The results of POFA in terms of heat of hydration of concrete is shown in Table 8.

Table 8. Comparison of different percentage of Palm Oil Fuel Ash in terms of Heat of Hydration

POFA	Temperature	Duration of peak hour
0%	50°C	9hrs
30%	34.1°C	11hrs

The POFA decreases the peak temperature and delays the temperature rise. This is due to the slower pozzolanic reaction at the early stage. As the peak temperature has been decreased, it has minimized the chance of internal cracking due to the heat pressure build-up inside the concrete (Lim et al. 2015).

The results of POFA in terms of workability of concrete is shown in Table 9.

Table 9. Comparison of different percentage of Palm Oil Fuel Ash in terms of the Slump test

POFA (%)	Slump (mm)
0%	160 mm
50%	115 mm
60%	90 mm
70%	80 mm

The POFA decreases the workability of concrete. Without POFA has better workability than 70% of POFA. One of the main reason is that the particle size of micro POFA is smaller than the OPC. This has increased the effect of large surface area. Due to this, it increased higher demand of water for concrete (Blessen Skariah Thomas et al. 2017).

2.9.2 Nano Size of Palm Oil Fuel Ash

There are only a few case studies regarding the nano size of POFA contributing to concrete's properties. Only in the size range of 1nm to 100nm is said to be nano size. According to Lim et. al., with 80% inclusion level of nano POFA can achieve high strength at the later age (Lim et al. 2015). Rajak et. al also mentioned that the nano particle has higher potential to fill the pore system of cement pastes when compared to micro particle. This is because the nano POFA can fill in the voids created by the micro POFA. Furthermore, it enhanced the durability by producing extra C-S-H gel (Mohammed Zuhear Al-mulali et al. 2015).

2.10 PREVIOUS MODELLING OF CARBONATION

There have been made statistical modelling created to predict the rate of carbonation. Most carbonation models are semi-empirical, their development starts from a theoretical basis (Fick's First Law) and is completed by fitting the required parameters to experimental results. In other words, most of the carbonation prediction models are generally assume that the carbonation depth can be estimated through the product of carbonation coefficient by the square root of time.

2.12.1 Statistical Modelling of Concrete Carbonation

The statistical modelling of the concrete carbonation phenomenon was performed using multi-linear regression. The several factors that are included in this modelling are distinguished into three conditions:-

1) Factors inherent to concrete such as the type of cement, percentage of pozzolanic additions, percentage of latent hydraulic, binder & clinker content, water/cement ratio, 28-days mechanical strength and type of admixture.
2) Curing and moulding conditions such as relative humidity, the temperature of the curing environment and compaction type.
3) Exposure condition such as relative humidity, the temperature of the exposure environment, carbon dioxide concentration, exposure class and protection from the action of rain.

By performing multiple linear regression graph required huge amount of data. Silva et. al has conducted this statistical modelling of the concrete carbonation phenomenon by using a large number of results collected (964 case studies) in the literature review (A. Silva et al. 2014). The concluded mathematical formula presented are:-

$$k_w = 3.355\,c - 0.019\,C - 0.042\,f_c + 10.83$$ --- eq. 1

   k_w = carbonation coefficient for RH > 70% $(mm/year^{0.5})$

   c = $CO_2\ content$ (%)

   C = clinker content kg/m^3

   f_c = 28-day compressive strength (MPa)

$$k_d = 0.556.\,c - 3602.\,X - 148f_c + 18.734$$ --- eq. 2

   k_d = carbonation coefficient for RH < 70% $(mm/year^{0.5})$

   c = $CO_2\ content$ (%)

   X = exposure class

The determination coefficient for both equation 1 and equation 2 are 0.917 and 0.712 respectively. Since both of these numbers are close to 1, thus, it indicates that the values are relatively close in most case studies.

2.12.2 New-Meta Modelling of Concrete Carbonation
A more advanced statistically modelling of concrete carbonation has been created known as new-meta modelling. This new presented metal model has been validated using data from the literature on short and long-term natural carbonation exposure conditions. Many existing models have limitation such as numerical models are difficult to use because they require accurate and complete data and semi-empirical models are quite simple because they generally developed to match specific application cases.

This new-meta modelling improves the calculation part such as the amount of carbon dioxide absorbed and carbon dioxide diffusion coefficient. There are certain assumptions have been made to develop the meta-model:

1)   Carbonation is modelled as a sharp carbonation front moving inwards.
2)   Carbonation is controlled the carbon dioxide diffusion under a steady-state.
3)   The amount of carbon dioxide absorbed per volume of concrete is determines as the required amount of carbon dioxide gas for making completely carbonate concrete.

The above Figure 6 shows the newly developed formula to determine the carbonation front of concrete. The results have been validated with the experimental ones. It shows that most results are within a +30%/-20% margin error. The prediction obtained is said to be satisfactory accurate (Ta et al. 2016).
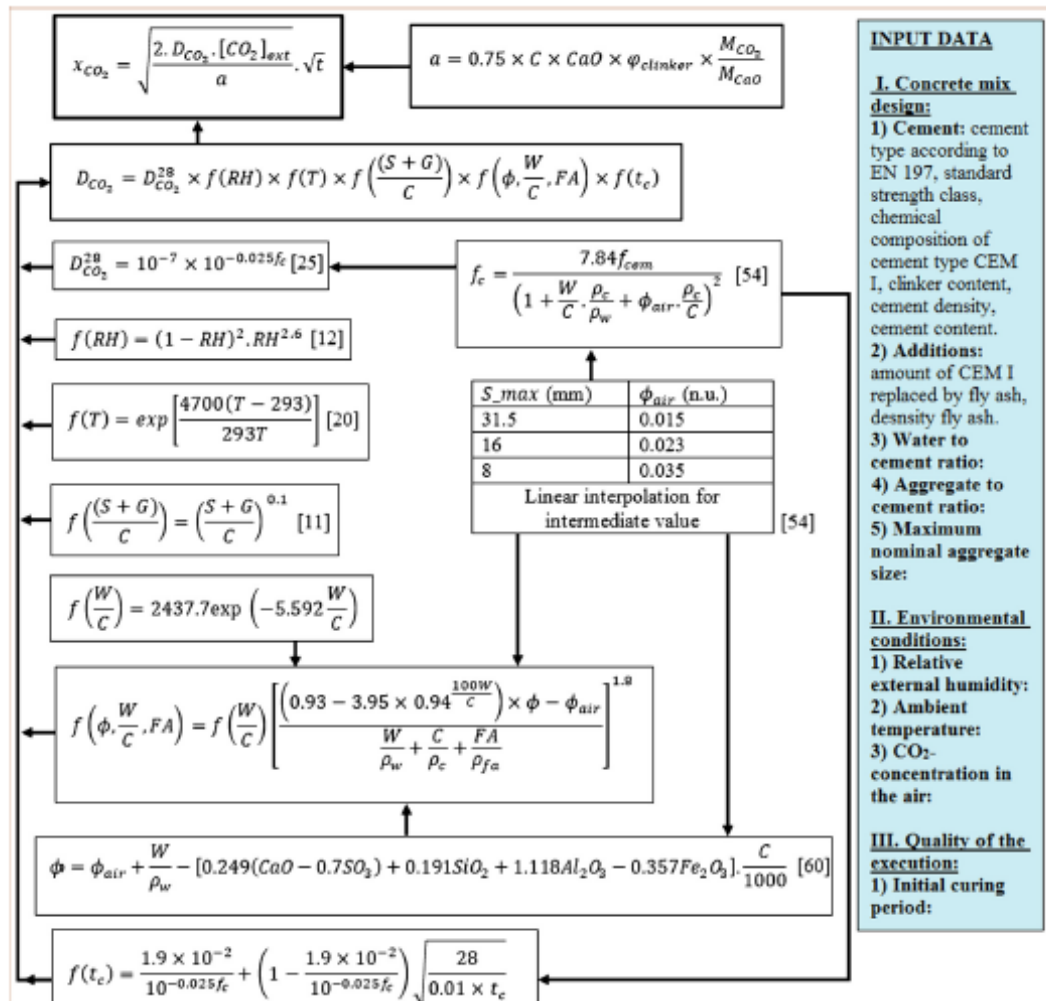
Figure 6 Formula for the new-meta modelling of concrete carbonation

CHAPTER 3   METHODOLOGY

This chapter presents the methods and procedures used to test carbonation and porosity in concretes containing palm oil fuel ash (POFA) using a carbonation chamber by the accelerated method. There were several phases in this experiment; the first was materials preparation, secondly was casting of concrete samples for carbonation and sorptivity testing, the third phase was curing of concrete samples and performed air drying concrete, the fourth phase was performing accelerated carbonation method, while the fifth phase was conducting sorptivity test, scanning electron microscopy, x-ray diffraction and x-ray fluoresces.

3.1 PREPARATION OF THE MATERIALS

At the first phase, it was important to prepare all the required materials for casting concrete specimens. Therefore, before commencing any castings, it was more appropriate to obtain all the materials from suppliers in Malaysia as the casting was taken place in Miri, Sarawak. The required materials were Portland cement, coarse aggregates, fine aggregates, superplasticizers, palm oil fuel ash and concrete prism moulds with the size of 70mm x 70mm x 280mm.

There are two kinds of design mix of concrete, which are known as the "High-Strength Concrete" (HSC) and "High-Performance Concrete" (HPC). HSC is highly depending on the "mechanical property" of concrete while HPC highly depending on the "durability property" of concrete. As for this research, High-Performance Concrete (HPC) was taken into consideration, as the main aim of this research project was to achieve the desired carbonation resistance of concrete. This HPC depends heavily on the high performance of the durability properties with optimum strength (High-Performance Concrete 2002).

The standard used to design the mix of the concrete for HPC was in accordance to ACI 211-4R. This standard allowed us to obtain the initial amount of the density of the materials required for concrete casting. However, this standard was specifically used for designing HSC. Therefore, another guideline is known as Chapter 17 – High-Performance Concrete was required to refer so that HPC could be designed (High-Performance Concrete 2002).

3.1.1 Coarse Aggregates

The standards used for designing the coarse aggregates were ACI 211-4R and ASTM C33-16. The ACI 211-4R was used to obtain the density of coarse aggregates in the concrete content. While the ASTM C33-16 was used for grading requirement of coarse aggregates. These standards allow us to obtain the sieve analysis range for the coarse aggregates to ensure that the coarse aggregates used were within the range of the grading requirement.

Using the standards, the obtained value of the density of coarse aggregates inside the concrete content was 1093kg/m^3. Furthermore, the coarse aggregates used in this research were

crushed granite from a local source with nominal sizes ranging from 9.5 mm to 12.5 mm. The fineness modulus, specific gravity and water absorption of the coarse aggregates were 2.3, 2.71 and 0.5% respectively. The method used to obtain the required coarse aggregates size of 9.5 mm to 12.5 mm in diameter was through sieving.

3.1.2 Fine aggregates

The standards used for designing the fine aggregates were ACI 211-4R and ASTM C33-16. The ACI 211-4R was used to obtain the density of fine aggregates in the concrete content. While the ASTM C33-16 was used for grading requirement of fine aggregates. These standards allow us to obtain the sieve analysis range for the fine aggregates to ensure that the fine aggregates used were within the range of the grading requirement.

Using the standards, the obtained value of the density of fine aggregates inside the concrete content was 536 kg/m^3. The fine aggregates were obtained as river sand and produced from a local source in Sarawak. The casting of concrete specimens was conducted in Malaysia and the sand in Malaysia had a fine modulus of 1 unit, which did not meet the requirement in accordance with the standards. The quarry dust has come into the mix due to the low fineness modulus of sand. Hence, the method used to resolve this issue was to use both sand and quarry dust to increase the fine modulus of fine aggregates. The requirement of fine modulus was 2.8 to 3.2 for designing the HPC.

3.1.3 Superplasticizer

The superplasticizer used in the present study was Master Clenium Ace 8538. The BASF Chemical Petronas supplied this superplasticizer (SP). This type of superplasticizer contains polycarboxylate ether polymers and free of chloride that comply with the requirements of standards ASTM C494-16. The ability of this SP was to work with low water-cement ratio and still be able to obtain extended slump retention. The advantage of using SP was to have higher flowability, superior workability, reduced slump loss, minimal bleed water, high elastic modulus and low shrinkage and creep.

The normal dosage of this SP was between 400 ml and 1400 ml per 100 kg of cementitious materials. The actual SP dosage was determined by doing trial mixes in this research. The trial batches showed that SP 0.2% of cementitious materials should be used.

3.1.4 Palm Oil Fuel Ash

Palm oil fuel ash (POFA) was acted as a supplementary cementitious material (SCM) in this research. This material could be easily obtained locally. As from past researches, POFA was collected in different oil palm plantations showed variation from each other (Nurdeen M. Altwair et al. 2013). The reason was that the nutrition absorbed by oil palm plantation was

different. Moreover, the wastes produced from the oil palm plantation such as palm oil husk, palm oil shell and others were burnt in an industry to produce electricity while the end-product of the burnt waste was POFA. As the initial nutrition consumption absorbed by the different location of POFA were different, the chemical compositions of the palm oil fuel ash produced in the industry were varied.

In the present work, POFA was collected from three different locations and was differentiated the best among the three POFA sources. The method used to choose the best POFA was by using the X-Ray Fluoresces, to choose the POFA which had the lowest contents of carbon, silica, calcium and iron elements (Sooraj V.M. et al. 2013).

After the comparison of all POFA sources, the best POFA was obtained from the company named MJM Palm Oil Mill for this research. However, this material collected was known as the raw POFA. The actual material to be used in this research was known as treated POFA. Using the treated POFA instead of the raw POFA could dramatically improve the quality of the POFA in HPC mixes (Sofri et al. 2015). In addition, POFA was ground into micro and nano-size so that POFA could react in a more effective way during casting (Lim et al. 2015). The procedures to produce the treated POFA are stated below. Fortunately, all the required machines and facilities were accessible in another Curtin University campus situated in Miri, Sarawak.

1) The raw POFA was placed into the oven and dried for 24 h at 105 ± 5 °C. The oven is shown in Figure 9.
2) After drying, POFA was sieved through 150 μm sieve to remove coarser particles.
3) The POFA was ground up until 90% passing 45 μm size. The grinder is shown in Figure 10. At this stage, this POFA was known as grounded POFA.
4) The grounded POFA was then heated to 500 °C for 1 h in a furnace. This furnace is shown in Figure 7. At this stage, it was known as "treated micro POFA."

Figure 7 Grinder & Furnace

5) The treated micro POFA was subjected to further grinding using ball mill until it reached the median size of less than 1 μm. The ball mill is shown in Figure 8. At this final stage, the "treated nano POFA" is produced.

Figure 8 Ball Mill

3.1.4.1 Ball mill

The model of the high energy ball mill used in this research was Ball Mill Model 3VS (Model Code: 1144-VS-A) from Capco Test Equipment Company in UK. The volume of the ceramic jar was $0.032 \ m^3$ and the total weight of the stainless steel ball was 30kg. There were three different sizes of stainless steel ball 12.7 mm diameter, 19.0 mm diameter and 25.4 mm diameter with 9.0 kg, 9.0 kg and 25.4 kg weight respectively. A total of 1.8 kg of mPOFA was loaded into the ball mill placing on top of the stainless steel balls, which produced 1.5kg of nPOFA. Masses were lost due to the particles flew as dust as the nPOFA was very light weight. The production of nano size particles had also been done by Zulkhairi and Othman. (Zulkhairi Rizlan and Othman Mamat, 2014)

3.1.5 Custom Built Concrete Prism Mould

The samples of concrete prism moulds are shown in Figure 9. The materials and tools required to construct concrete prism mould were plywood, brush, hammer, screwdriver, nails and silicon. Two prism moulds were constructed. Each mould produced 4 concrete prism samples; hence, two concrete prism moulds produced 8 concrete prism samples with the dimension of 70mm x 70mm x 280mm during each casting. This concrete prism size was in accordance to British Standard for testing of carbonation.

Figure 9 Custom Built Concrete Mould

The procedures of constructing concrete prism moulds are:

1) Cut the 12 mm thickness of plywood into three different sizes

    a.   100 mm x 70 mm   - 26 pieces

    b.   100 mm x 1720 mm   - 4 pieces

    c.   430 mm x 1720 mm   - 1 piece

2) The above dimensions of plywoods were used to attach together to create 70 mm x 70 mm x 280 mm concrete prism mould shown.

3) Prepared four pieces of 75 mm x 1720 mm aluminium. This was to attach 100 mm x 1720 mm plywood onto 430 mm x 1720 mm plywood.

4) Applied silicon using silicon gun on every corner of the wood to prevent leakage of water during casting concrete.

5) Applied frictionless oil on every surface of plywood before casting so that de-moulding would be easier.

3.1.6 Concrete Mixing Proportions

The concrete mixing proportions with varying contents of OPC and micro and nano POFA is shown in Table 10.

Table 10. Concrete Mixing Proportions

SPECIMEN	OPC	MICRO POFA	NANO POFA	COARSE AGGREGATE (KG/m^3)	FINE AGGREGATE (KG/m^3)	SP (%)	SLUMP (MM)
S1	100%	0%	0%	1093	268	0.2	140
S2	89.5%	10%	0.5%	1093	268	0.2	125
S3	79.5%	20%	0.5%	1093	268	0.2	50
S4	69.5%	30%	0.5%	1093	268	0.2	40

S5	89.0%	10%	1.0%	1093	268	0.2	140
S6	79.0%	20%	1.0%	1093	268	0.2	65
S7	69.0%	30%	1.0%	1093	268	0.2	45
S8	88.5%	10%	1.5%	1093	268	0.2	145
S9	78.5%	20%	1.5%	1093	268	0.2	80
S10	68.5%	30%	1.5%	1093	268	0.2	65

The mixing proportions were determined accordingly to "Section 2.9 Previous Cases of Incorporating Palm Oil Fuel Ash". It had shown that with the inclusion of 10% to 30% micro POFA (mPOFA) would eventually increase the mechanical properties of concrete such as the compressive strength, flexural strength and tensile strength. Furthermore, it was also reported that nano POFA (nPOFA) has the potential to improve the porosity of the concretes, as a result, 1% to 3% of nPOFA was used in this research.

There were several research done in proving the advantage of mPOFA and nPOFA individually in both durability and mechanical properties. However, this research was combining both mPOFA and nPOFA to investigate the change in the characteristics of concretes. Therefore, there were 10 different concrete mixtures containing 10% to 30% of mPOFA and 1% to 3% of nPOFA. With these mixtures, by conducting X-Ray Diffraction, X-Ray Fluoresces, Scanning Electron Microscopy, Sorptivity Testing, Slump Test and lastly, Carbonation testing would show and prove the resistivity of concretes to carbonation effect with justifications.

Chapter 3   Methodology

3.1.7 Weight of Materials Preparation

The weight of each material used in casting specimens according to the proportions is shown in Table 11.

Table 11. Weight of Materials Preparation

Weight (kg) with inclusion of 20% wastage

Specimen	Cement	POFA		Coarse Aggregate	Quarry Dust	Sand		Water	SP Dosage (0.2%)
		Micro	Nano			Wet	Dry		
S1	2.9	0	0	5.40	1.33	0.266	1.06	0.90	0.0058
S2	2.6	0.288	0.0144	5.40	1.33	0.266	1.06	0.90	0.0058
S3	2.31	0.58	0.0144	5.40	1.33	0.266	1.06	0.90	0.0058
S4	2.02	0.871	0.0144	5.40	1.33	0.266	1.06	0.90	0.0058
S5	2.58	0.288	0.0288	5.40	1.33	0.266	1.06	0.90	0.0058
S6	2.3	0.58	0.0288	5.40	1.33	0.266	1.06	0.90	0.0058
S7	2	0.871	0.0288	5.40	1.33	0.266	1.06	0.90	0.0058
S8	2.57	0.288	0.0432	5.40	1.33	0.266	1.06	0.90	0.0058
S9	2.28	0.58	0.0432	5.40	1.33	0.266	1.06	0.90	0.0058
S10	1.99	0.871	0.0432	5.40	1.33	0.266	1.06	0.90	0.0058
Total	**23.55**	**5.217**	**0.2592**	**54.00**	**13.3**	**2.66**	**10.6**	**9.00**	**0.058**

3.1.7.1 Wastage

The inclusion of wastage weight was crucial for every material. Practically, there was always wastage produced during casting concrete especially during mixing or conducting slump test. To prevent any insufficiency of materials, the most efficient way was to add at least 20% of additional weight into each of the materials.

Chapter 3   Methodology

3.1.7.2 Design of the mixing proportions
In accordance to ACI 211-4R, the design mix in this research used as control mix is stated below:

1) Cement content $= 588$ kg/m^3
2) Coarse aggregates $= 1093$ kg/m^3
3) River sand $= 268$ kg/m^3
4) Quarry Dust $= 268$ kg/m^3
5) Water content $= 208$ kg/m^3 (w/c: 0.35)
6) Superplasticizer $= 0.2\%$ dosage of cementitious materials

3.1.7.3 Sample Calculation
The sample calculation for specimen **"S2"** is shown below.

Volume of one specimen $= 0.07$ x 0.07 x 0.28

                                    $= \mathbf{0.001372\ m^3}$

Number of specimen required $= \mathbf{3\ specimens}$

Total Volume $= 0.001372$ x 3

                                    $= \mathbf{0.004116\ m^3}$

Density of Cement $= 588$ kg/m^3

Weight of the cement (89.5%) $= \frac{89.5}{100}$ x 588 x $0.004116 + 20\%$ wastage

                                    $= 2.166 + 20\%$ wastage

                                    $= 2.166 + \frac{20}{100}$ x 2.166

                                    $= \mathbf{2.599\ kg}$

Weight of the Micro POFA (10%) $= \frac{10}{100}$ x 588 x $0.004116 + 20\%$ wastage

                                    $= 0.242 + 20\%$ wastage

                                    $= 0.242 + \frac{20}{100}$ x 0.242

                                    $= 0.290425$ kg

                                    $= \mathbf{290.425\ g}$

Weight of the Nano POFA (0.5%) $= \frac{0.5}{100}$ x 588 x $0.004116 + 20\%$ wastage

                                    $= 0.0121 + 20\%$ wastage

                                    $= 0.0121 + \frac{20}{100}$ x 0.0121

                                    $= 0.014521$ kg

                                    $= \mathbf{14.521\ g}$

Density of Coarse Aggregate $= 1093$ kg/m^3

Weight of Coarse Aggregate

= 1093 x 0.004116 + 20% wastage

= 4.499 + $\frac{20}{100}$ x 4.499

= **5.399 kg**

Density of Fine Aggregate = 268 kg/m^3

Weight of Quarry Dust

= 268 x 0.004116 + 20% wastage

= 1.103 + $\frac{20}{100}$ x 1.103

= **1.324 kg**

Weight of Wet Sand (20%)

= 268 x 0.004116 x $\frac{20}{100}$ + 20% wastage

= 0.221 + $\frac{20}{100}$ x 0.221

= **0.266 kg**

Weight of Dry Sand (80%)

= 268 x 0.004116 x $\frac{80}{100}$ + 20% wastage

= 0.882 + $\frac{20}{100}$ x 0.882

= **1.06 kg**

Density of water = 183 kg/m^3

Weight of Water

= 183 x 0.004116 + 20% wastage

= 0.753 + $\frac{20}{100}$ x 0.753

= **0.904 kg**

Weight of SP Dosage (0.2%)

= Summation weight of cement and POFA x $\frac{0.2}{100}$

= 2.599 + 0.290425 + 0.014521 x $\frac{0.2}{100}$

= 0.005808 kg

= **5.8 g**

3.2 CASTING OF CONCRETE SPECIMENS

Once the first phase of the preparation of the materials was completed, the second phase of the experiment can proceed which was to cast the concrete prism specimens with the size of 70 mm x 70 mm x 280 mm and slump test. The additional materials required in the second phase were weight measurement, concrete mixer, slump cone, rod and tray, hammer, screwdriver and brush, trowel, scooper and bucket, PPE equipment: safety boots and safety gloves. The total duration of the casting period for both carbonation and sorptivity testing was five days. The slump test was done immediately before each specimen was cast.

The total duration of the casting period for carbonation testing's specimens was three days. There would be three specimens in each mix. The size of the specimens for carbonation testing was 280mm x 70mm x 70mm. The casting sequence was:

1st day: Specimens S1, S2 & S3   Total specimens = **9** concrete prism specimens

2nd day: Specimens S4, S5 & S6   Total specimens = **9** concrete prism specimens

3rd day: Specimens S7, S8, S9 & S10   Total specimens = **12** concrete prism specimens

The total duration of the casting period for sorptivity testing's specimens was two days. There would be two specimens in each mix. The size of the specimens for sorptivity testing was 50mm height x 100 mm diameter. The casting sequence was:

4th day: Specimens S1, S2, S3, S4 & S5 Total specimens = 10 concrete cylinder specimens

5th day: Specimens S6, S7, S8, S9 & S10Total specimens = 10 concrete cylinder specimens

3.2.1 Weight measurement

Table 9 listed the total weight used for each material. It showed that the materials in each specimen were different, thus, a weight measurement was required in this case.

3.2.2 Concrete mixer

As for this research, there were many concrete prism specimens required to be cast. It would be too much to manually mix the concrete with high volume. The alternative method was to get the concrete mixer. The concrete mixer could mix the materials completely and thoroughly without doubts.

The correct practice sequence was to mix the coarse aggregates and fine aggregates inside the concrete mixer first. On the other hand, premixed the cementitious materials by combining cement, micro POFA and nano POFA in a bucket. After mixing, poured the cementitious materials inside the concrete mixer and mixed well with the aggregates. Once it had been evenly mixed, slowly added water with superplasticizer into the concrete mixer.

Summary of the correct practice for mixing concrete is shown below:

First Step: Mixed coarse aggregates and fine aggregates (stone + river sand & quarry dust).

Mixed all the cementitious materials together (cement + micro and nano POFA).

Mixed the water with superplasticizer.

Second Step: Mixed the aggregates with cementitious materials in the concrete mixer.

Third Step: Lastly, poured the water with superplasticizer into the concrete mixer and mix well.

3.2.3 Slump cone, rod and tray

The slump test shall be done in accordance with the standards ASTM C143. The tools for conducting slump test were slump cone, rod and a rectangle tray. After mixing the concretes, it should be immediately transferred into the slump cone to do slump test. Every delay would affect the slump result.

As stated in the standard, the slump cone should be first filled with the cement paste up to one-third of the cone's height. Once the cement paste had filled till one-third of the cone, dropped the rod 20 times freely for compaction purpose. The process was repeated three times until the cone was completely filled. Clear the excessive cement paste on top of the cone. The next step was slowly to remove the cone vertically and place the cone next to the cement paste. Use a measuring tape to measure the slump loss. In order to meet the HPC requirement, the slump result should be within 150 mm to 200 mm.

3.2.4 Hammer, screwdriver and brush

Hammer, screwdriver and brush were used for de-moulding and cleaning the concrete prism mould. The concretes were cast in the custom built concrete prism mould with the size of 70 mm x 70 mm x 280 mm. After 24hr, the concrete were de-moulded to prepare for the next casting as the casting period had been spread into three days. Hammer was to remove the nails from the plywood. Screwdriver was to remove the screw connecting the aluminium to the plywood. After removing all the connecting parts, concretes could be freely removed from the concrete prism mould. Cleaned all the moulds and reattached all the parts for further casting.

3.2.5 Trowel, scooper and bucket

Trowel, scooper and bucket were used during casting of the concrete. Trowel was used to flat the concrete surface. Scooper was to scoop the cement paste into the custom built concrete prism mould. While the bucket was to fill the materials for casting such as aggregates, cementitious materials and water.

3.2.6 PPE equipment: safety boots and safety gloves

The PPE equipment such as safety boots and safety gloves were important during the casting. Wear it at all times to prevent injuries from any accidents. There was a lot hazardous objects and heavy materials that could cause major injuries. Using PPE equipment was to increase safeness during casting.

3.3 CURING STAGE AND AIR DRYING CONDITIONING

Curing stage and air drying conditioning were considered as the third phase of the experiment. This stage would proceed once the concrete prism specimens of 70 mm x 70 mm x 280 mm and concrete cylinder of 50 mm height x 100 mm diameter had been cast. A total of 30 concrete prism specimens plus 20 concrete cylinder specimens were cast and cured at a room temperature in a curing room. In accordance with BS EN 12390-2:2009 the total number of curing days was 28 days by completely immersing all the specimens into the water curing tank and leave them for 28 days.

Only the 30 concrete prism specimens would undergo the air drying condition. Following BS 1881-210:2013, air drying conditioning of concrete specimens was required after 28 days of curing. The method to conduct this conditioning was to place all the concrete prism specimens in a room with RH of between 50% and 60% and temperature between 18°C and 25°C. The duration of this phase was 14 days. Applied paraffin wax on the concrete surfaces leaving only two surfaces of the concrete exposed to the environment. Then, sealed the top and bottom longitudinal faces and the two end faces of prisms. The aim of this paraffin wax was to prevent the ingression of carbon dioxide in multi-directional, otherwise, the results would be unreliable and confusing.

After completing the above curing and conditioning including applying paraffin wax, the specimens were ready to be transported to Perth for further testing at the Bentley campus of Curtin University. Due to this, it was important to ensure that the specimens were well-protected. During the transportation, there would be many unknown factors such as random impact from random objects or dropping the specimens.

The best method to protect the specimens was to wrap all the specimens with polystyrene and two layers of bubble wrap. After that, placed all the specimens into a thick box and once again wrap the box with two layers of bubble wrap. The bubble wrap was the most reliable material to reduce huge impact and prevent water contacting. The total duration for the third phase was 42 days.

3.4 TESTING OF CARBONATION

The procedures for testing the carbonation of reinforced concrete was following the standards BS 1881-210:2013. It was considered the fourth phase which was the main phase for this research. On the arrival at the test laboratory, unwrap and ensure that the concrete specimens have not been damaged.

Instead of letting the carbonation effect occurs naturally, the most efficient method to test for carbonation was by using an accelerated carbonation method, which could be performed using a carbonation chamber. The carbonation chamber allowed the carbonation effect to speed up dramatically. The carbon dioxide content in this chamber was 4.2% by volume while in the natural environment was 0.45%. By comparing the difference, it was almost 10 times higher concentration, as a result, accelerating the carbonation effect.

Three parameters should be controlled known as the carbon dioxide concentration, relative humidity and the temperature. The carbon dioxide concentration was controlled by using the valve monitoring the carbon dioxide content in the chamber. The relative humidity was controlled by using the sodium nitrite. This sodium nitrite is a salt solution used to decrease or increase the relative humidity. Lastly, the temperature parameter was controlled by using a 250W lamp. Two things were used to monitor the parameters known as CO_2 meter and temperature data-logger. The CO_2 meter was used to monitor the concentration level of carbon dioxide while the temperature data-logger was used to monitor both relative humidity and temperature in the carbonation chamber.

Once all the specimens had been unwrapped, placed all the specimens into the carbonation chamber. Put all the specimens at the low height of the chamber. This was because the carbon dioxide was heavy which would sink to the bottom of the chamber. Hence, to ensure the concrete specimens were fully exposed to carbon dioxide, it was important to place all the specimens at the bottom. It was also required to leave at least a 25-mm gap between each sample for better diffusion of carbon dioxide. In accordance with the standards BS 1881-210:2013, the total duration for the specimens to be exposed to carbon dioxide was 70 days.

3.5 SORPTIVITY TESTING

The sorptivity testing was following the standard ASTM C 1585-13. The purpose of this standards was to measure the rate of absorption of water by hydraulic cement concretes.

The apparatus required for this standards were a pan, support device (rod, pins or other devices), timing device, paper towel and callipers. Two specimens for each mixture proportion of concrete specimens with the size of 100 mm diameter x 50 mm height were cast and prepared. The procedure of the sorptivity test is stated below:

1) After 28 days of curing concrete, placed all the specimens into an oven with the temperature of 50°C for 3 days.

2) Removed all the concrete specimens and sealed the side surface of each specimen with a suitable sealing material.

3) Measured each of the initial weight of concrete specimens including the sealing material attached.

4) Measured the diameter of each concrete specimens.

5) Placed the support device at the bottom of the pan and filled the pan with tap water so that the water level is 1 to 3 mm.

6) Placed all the concrete specimens on top of the support device.

7) Start the timing device immediately after completing step 4.

8) Measure the weight of each concrete specimens and recorded at 60sec, 5min, 10min, 20min, 30min and 60 min.

9) Using the formula $\frac{\Delta mass}{exposed\ area\ x\ density}$ of water to obtain the rate of absorption of water.

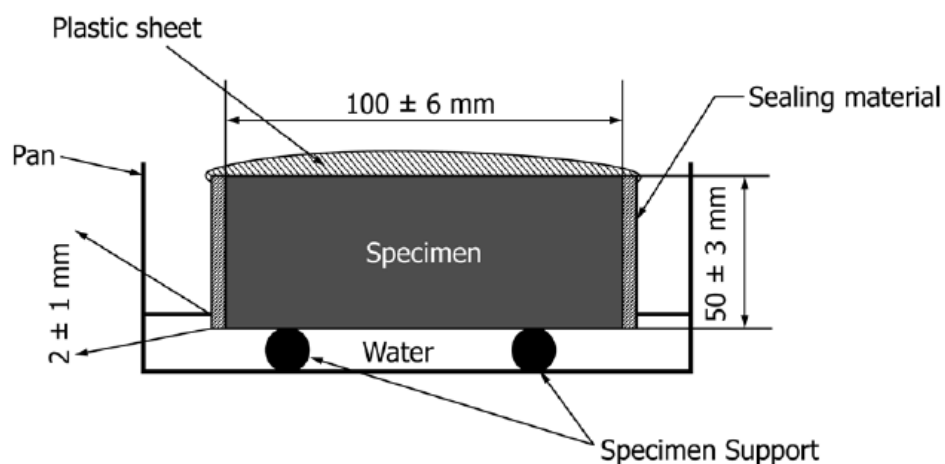The overview of the setup procedure is shown in Figure 10.

Figure 10. Schematic of Sorptivity Procedure

3.6 OTHER TESTINGS

Further testings were required in this research to further explain and justify the obtained experimental results. The specimens were tested using X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM).

3.6.1 X-Ray Diffraction (XRD)

This testing was primarily used to identify a crystalline material and different polymorphic forms. It was also able to quantify the amount percentage of crystallinity of a sample to justify the suitability of POFA in terms of the glassy material. The crystallinity glassy material was responsible for the concrete's properties. Therefore, this testing was performed on the micro and nano POFA powder. The result of XRD for micro POFA and nano POFA is shown in "Section 4.2 X-Ray Diffraction".

3.6.2 X-Ray Fluorescence (XRF)

This testing was ideally used for a qualitative analytical tool for elemental analysis of materials. This testing was used to prove the advantage of the conversion from raw POFA to treated POFA.

Summary of conversion product of POFA:

Raw POFA -> Grounded POFA -> Treated POFA -> Micro treated POFA -> Nano treated POFA

The most significant elements in cementitious materials were silicon, calcium, iron and aluminium. These elements were responsible for building up the mechanical and durability properties. Using XRF shows that there were higher contents of those four elements in nano treated POFA than in the raw POFA. The result of XRF for raw, micro and nano POFA is shown in "Section 4.1 X-Ray Fluoresces".

3.6.3 Scanning Electron Microscopy (SEM)

This testing was conducted to familiarise the samples in term of topographical, morphological and compositional information. It could detect and analyse the microstructure of the POFA and concrete samples. The SEM machine used was known as the Neon 40EsB FESEM and operated at 15kV.

The purpose of doing SEM on the POFA powder was to determine the shape of the particles. The shape of the particle is significant as it influences the workability of concrete. The shape of the particle can determine the effectiveness of the filling ability of concretes. The results are shown in "Section 4.3 Scanning Electron Microscopy".

Next, the purpose of doing SEM on the concrete samples was to determine the microstructure of the concrete. The results could be used to explain the rate of penetration of carbon dioxide into the concrete. The formation of calcium hydroxide, ettringite and calcium silicate hydroxide affect the porosity of the concrete as these particles have different sizes. The formation of the particles differed from different mix proportion of OPC and POFA. Therefore, the SEM was conducted on the concrete samples to justify the results of the carbonation depth. The results are shown at "Section 4.6 Morphology of Concrete Samples with and without POFA".

CHAPTER 4   RESULTS AND DISCUSSIONS
4.1 X-RAY FLUORESCES

Table 12. Chemical Composition of Different Binders

CHEMICAL COMPOSITION (%)	OPC	RAW POFA	MICRO POFA (MPOFA)	NANO POFA (NPOFA)
SiO_2	16.40	59.1	72.89	71.77
Al_2O_3	4.24	4.5	4.34	4.69
Fe_2O_3	3.53	6.5	4.29	4.54
CaO	68.30	8.6	8.50	9.11
MgO	2.39	2.6	5.65	6.10
SO_3	4.39	2.7	0.605	0.626
K_2O	0.39	8.25	1.08	1.32
Na_2O	0.03	0.35	0.35	0.35
$SiO_2 + Al_2O_3 + Fe_2O_3$	24.17	70.1	81.52	81.00
LOI	2.40	10.5	1.71	1.60

The purpose of doing X-Ray Fluoresces (XRF) was to do the comparison of all binders used in this research such as Ordinary Portland Cement (OPC), raw Palm Oil Fuel Ash, treated Palm Oil Fuel Ash (mPOFA and nPOFA). The results are shown in Table 12. The binders were chosen accordingly to the highest percentage of SiO_2 or CaO. These elements contributed to the concrete's properties such as the strength and durability. Furthermore, these results show similar trend to the results reported by other researchers (Belal Alsubari et al. 2016 & Nor Hasanah Abdul Shukor Lim et al. 2015)

The OPC, mPOFA and nPOFA were used in this research. In general, the concrete specimens did not contain any other admixture, only OPC was used. In this research, POFA was incorporated inside the concrete instead of using OPC only. This was because, if OPC alone was used, the CaO reacted with water to form calcium hydroxide ($CaOH$) and only some would react with SiO_2 to form Calcium Silicate Hydrate gel (C-S-H). This C-S-H gel was nano size particle, which in fact, was very good to concrete as it could fill in the tiny pores or voids present. However, using OPC only would form a very little amount of C-S-H gel due to the limited amount of SiO_2 present in OPC. Therefore, POFA was used in this research to compensate for the lower percentage of SiO_2 in OPC.

The raw POFA was not used but, it had been treated to convert it into mPOFA and nPOFA. At the final conversion of raw POFA, it had caused the element of SiO_2 to increase from 59.1% to 69.19% (mPOFA) and 68.07% (nPOFA) shown in Table 10. The reason of this decrement was due to the removal of unburnt carbon and other unnecessary elements present at the raw POFA during the burning process using a blast furnace. In addition, treated POFA

was used instead of raw POFA was due to the lower LOI percentage. Lower LOI percentage could minimize the chance of internal cracking due to high heat during the casting. With the increment of SiO_2 and decrement of LOI value, it leads the treated POFA to be more suited to act as supplementary cementitious material.

As mentioned above, both OPC and POFA should be used in this research so that the concretes can have better performance. To have better concrete, it was important to produce more C-S-H gel in the concrete. In order to achieve this, it was crucial to balance both OPC and POFA at the optimum point to produce essential amount of C-S-H gel. This was because OPC and POFA each had higher content either in calcium ions or silica ions. As there was a higher volume of C-S-H gel, it would fill in the voids and reduce the porosity. In addition, this would cause the concrete to be denser and compacted, hence; higher mechanical strength. Since the concrete was more compacted, the rate of penetration of any substances or gases into the concrete was decreased. Therefore, concretes contained POFA would have better durability properties.

As for this research, the main purpose was to obtain the highest carbonation resistance concrete, hence; concrete containing POFA was good to be investigated. Different mixture proportion of OPC and POFA was investigated and examined so that how much OPC should be replaced by POFA to produce the highest carbonation resistance.

4.2 X-RAY DIFFRACTION

Figure 11. Mineralogy Phase of Micro POFA

Figure 12. Mineralogy Phase of Nano POFA
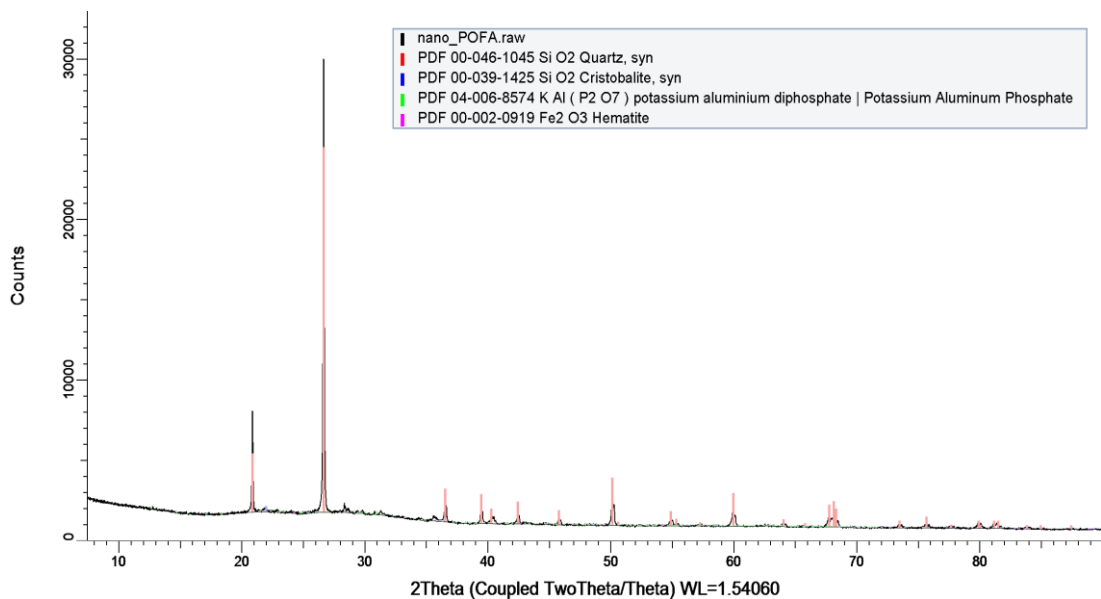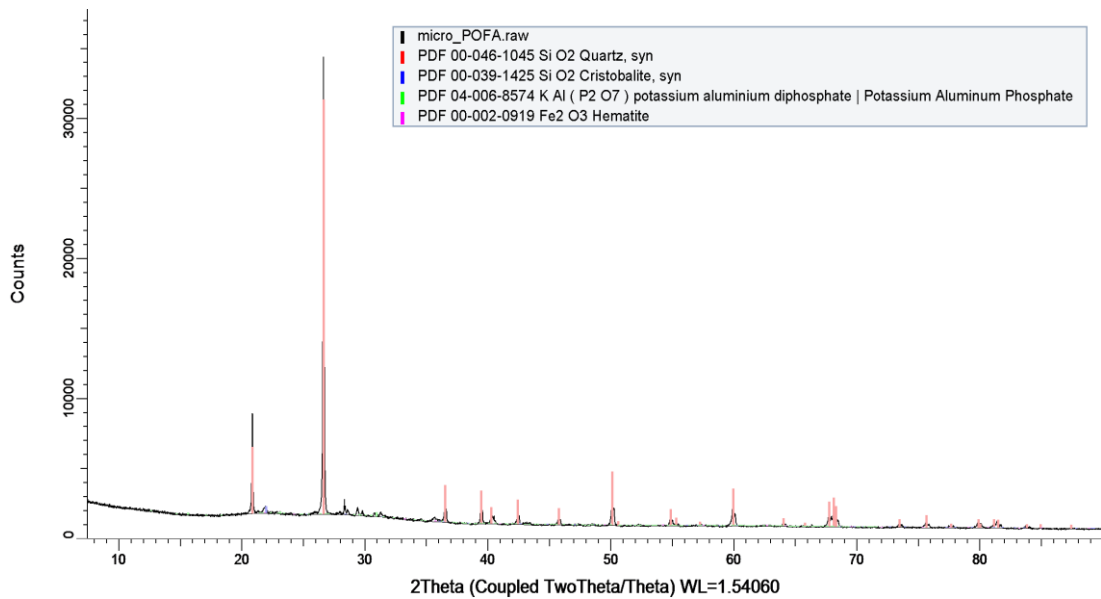
The X-Ray Diffraction (XRD) patterns of mPOFA and nPOFA in Figure 11 and 12, obviously shows that the amorphous and crystalline phases of both materials were very identical and consistent. The amorphous phase both mPOFA and nPOFA was represented by the flaw halo of silica at 20° to 30° of XRD diffract grams, while the crystalline phases were referring to the existence of α-Quartz (α-SiO_2), Cristobalite, Potassium Aluminium Diphosphate ($K_3Al_2(PO_4)_3$) and Hematite (α-Fe_2O_3).

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The similarity of diffract grams and diffractive halos structure between 20° to 30°, it signified the region of low crystallinity (glassy phase) of the material. It was similarly reported at the previous finding of Zeyad (Zeyad et al. 2017). During the heat treatment of POFA, it did not affect the material glassy phase, unlike the material fineness. However, this treatment removed the un-carbon elements present in the POFA which caused changes in terms of carbon content. The carbon content did not affect the POFA strength development but the rate of pozzolanic reaction. Furthermore, this assertion was strengthen by the glassy phase as this would remain unchanged even after treatment. Therefore, going through the heat treatment process was significant in the sense of improving the POFA compounds. The POFA reactivity to produce calcium hydroxide and calcium silicate hydrate would be unhindered in the long run, regardless of removing carbon content.

The diffractive grams were identified at different angles. A peak of 26.5° (2θ) was observed which corresponds to α-Quartz as the major phase for both mPOFA and nPOFA. There were few other phases acted as the minor phases at different angles. The highest peak of other crystalline phases such as the Cristobalite, Potassium Aluminium Diphosphate and Hematite were detected at a 2θ of angle of 22.1°, 31° and 33.3° respectively.

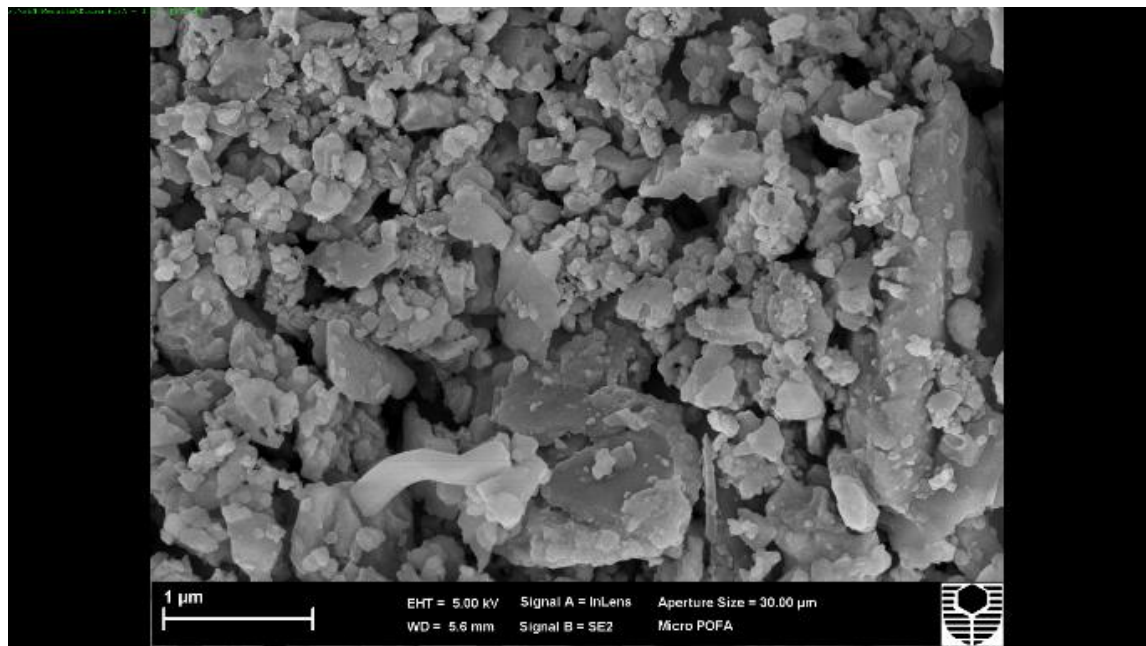## 4.3 SCANNING ELECTRON MICROSCOPY OF POFA POWDER
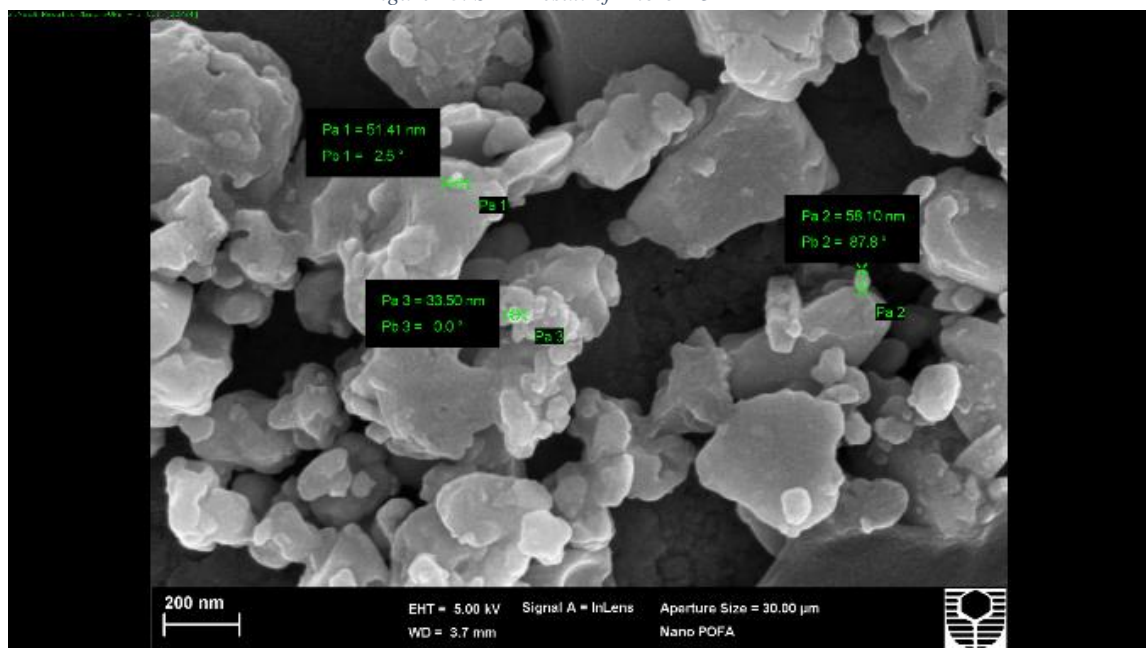

Figure 13. SEM Result of Micro POFA

Figure 14. SEM Result of Nano POFA

The surface morphology was carried out by using Scanning Electron Microscope (40EsB FESEM) operated at 15kV. The result of the morphology of mPOFA and nPOFA are shown in Figure 13 and Figure 14 respectively. Figure 13 shows the mPOFA had crushed and irregularly shaped particles. The nPOFA had almost similar characteristics, however; it seemed to be more porous and smaller particles size. In Figure 14, nPOFA had a size range from 33.50 nm to 58.10 nm. Due to its tiny size particles, a higher magnification was required to measure the nano size. Most importantly, this nano size and spherical shape, could eventually bring huge benefit to the concrete by improving the filling ability of concrete. As

the filling ability had been improved, this may bring benefits to durability properties of concrete as this nano and spherical particles could help to fill in tiny pores and reduce the pore size diameter.

4.4 ACCELERATED CARBONATION TESTING

4.4.1   Overview of Carbonation Testing

Figure 15 shows the overview set-up of a carbonation chamber used to conduct the accelerated carbonation testing.

Figure 15. Overview of Carbonation Chamber

The accelerated method was chosen over the natural occurrence of carbonation was due to more efficient and feasible ways to produce the carbonation results. Generally, in the atmospheric concentration of CO_2 by volume was about 0.04%, but at certain areas may vary such as in industrial areas or along the roads maybe 0.3% or higher and somewhere close to the coastal area may be even higher. For this research experiment, the carbonation chamber had 4.5% of CO_2 concentration by volume. By doing the simple mathematical calculation, this caused the carbonation effect to occur roughly 10 times more than the natural conditions, hence; it was considered as the accelerated method.

In terms of accelerated carbonation method, there were three parameters that had to be controlled known as the temperature, relative humidity and concentration of CO_2. In order to have constant carbonation effect occurred at the concrete specimens placed inside the chamber, the relative humidity had to be in the range of 50% to 70% (López-Arce et al. 2011). Regarding the temperature and the concentration of CO_2, the carbonation would definitely occur at different rate correspond to different points. However, the theory of this was that rate of carbonation was higher at higher temperature and concentration of CO_2 as the molecular activity increased. This carbonation testing was in accordance with standards BS 1800-210-

2013, therefore; the temperature was 20 ±2 °C, relative humidity of 55 ±5 % and storage chamber with CO_2 level of 4.0 ±0.5 %.

There were certain ways to control the parameters. The relative humidity was controlled by using the sodium nitrite. This sodium nitrite acted as salt substances. Once this substance was placed inside the chamber, the relative humidity would decrease. On the other hand, removed the sodium nitrite in the chamber if the relative humidity was too low. By doing that, the chamber was able to maintain at 55 ±5 % of relative humidity. During the period of conducting that experiment, the temperature was constant at 20 ±2 °C and only a few days of slightly over a temperature of 24 °C and below 22°C, therefore; there was no need to adjust the temperature. Lastly, the concentration of CO_2 was controlled by pumping CO_2 from the carbonation cylinder connected to the chamber. It could be used to decrease or increase by controlling the valve at the pipe.

As mentioned above, the parameters were able to be controlled in some certain ways. It was also important to measure those parameters. There were two equipment used to measure the parameters known as CO_2 meter and temperature data-logger. These equipment are shown in Figure 20. Obviously, the CO_2 meter was used to measure the CO_2 concentration of chamber by volume while the temperature data-logger was used to measure the relative humidity and temperature of the chamber.

Figure 2. Co2 meter & Temperature data-logger

The data measured by using the CO_2 meter and temperature data-logger are shown on graphs in appendix A, appendix B and appendix C. The data of the temperature and relative humidity were quite constant from the beginning until the end of the experiment. However, for the data of CO_2 meter, it fluctuated at some different points. This was due to limited equipment provided and repeating opening and closing the lids of the chamber. Even though the data

fluctuated, the average of the CO_2 concentration by volume was still remained at 4.2%. This may only slightly affect the final result.

4.4.2   Examination of Carbonation Results

The simple understanding of chemical reaction of carbonation process was the formation of calcium carbonate ($CaCO_3$) with the depletion of calcium hydroxide ($CaOH$) and calcium silicate hydrate (C-S-H). This chemical equation of carbonation process can be found in equation 1 shown in the section "2.1.2 INTRODUCTION OF CARBONATION". By depleting the $CaOH$, this caused the pH of the concrete dropped from approximately 13 to 8 (J. Collado et al. 2015). Therefore, it concluded that carbonated concrete had lower pH while un-carbonated concrete had higher pH. Since there was a difference value of pH in concrete, phenolphthalein solution may be used.

Phenolphthalein solution was produced by using 1 gram of phenolphthalein powder dissolved in a 100 ml solution of 70 ml ethanol and 30 ml of deionized water. This solution reacted differently to the different value of pH, thus; could be used to differentiate between carbonated and un-carbonated concrete. The un-carbonated concrete turned into purple while carbonated concrete remained colourless. The Figure 16 showed the concrete specimen sprayed with phenolphthalein solution showing different colours.

The arrow showing in Figure 16 was the carbonation depth of concrete. It showed the carbonation occurred during the exposure period of carbon dioxide in the chamber. The carbonation depth was measured using Vernier calliper.

Figure 16. Samples of Carbonated Concrete

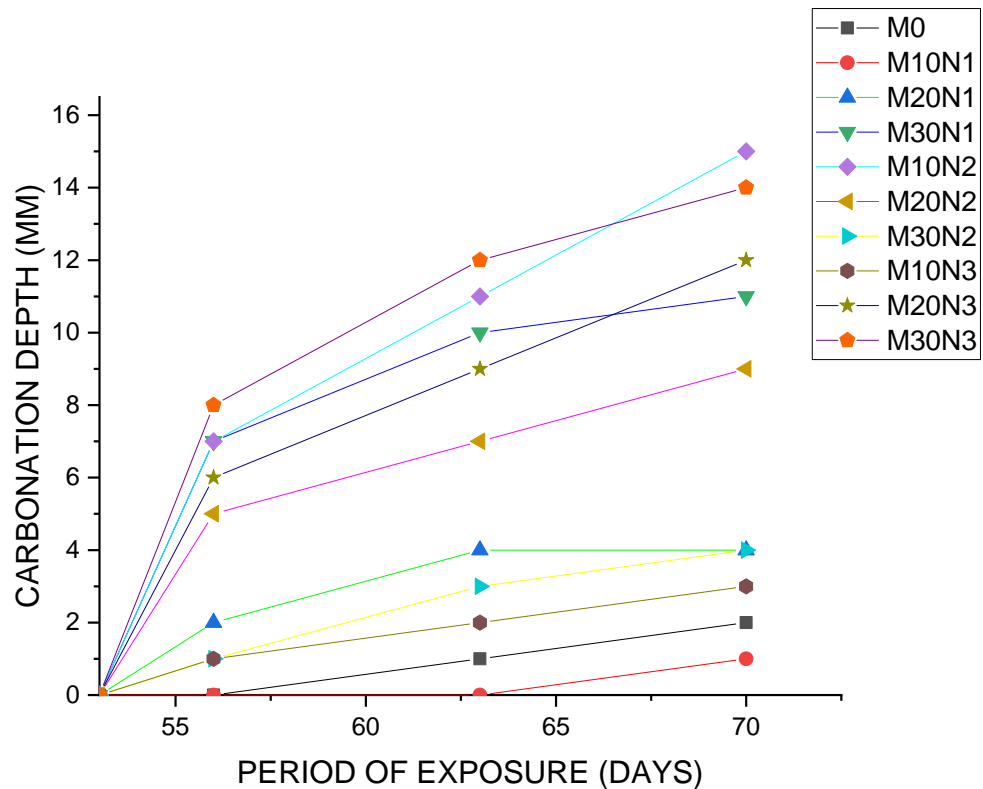### 4.4.3   Carbonation Depth of Concrete Samples

Figure 17. Result of Carbonation Depth of different concretes

Figure 17 shows the results of the carbonation depth of different mixture proportions of OPC and POFA by using the carbonation chamber with the exposure period of 56 days, 63 days and 70 days. The trend of the carbonation depth result shows similarity to the equation 8 in the section "2.5 THEORETICAL FOUNDATIONS OF CARBONATION MODELLING". Almost every concrete had the rate of carbonation effect with a square root of time.

The carbonation depth increased as the time elapsed. Theoretically, the carbonation effect would not inhibit if there was constant CO_2 gases supplied into the chamber using the carbonation rig. That was why the carbonation depth at 56 days was lower than 70 days for every mixture proportions of concretes. Taking note that some of the carbonation depth remained constant from 63 days to 70 days. That did not mean that the carbonation effect stopped, but only the rate of carbonation was too small. Where the carbonation depth was constant, there was only slightly carbonation effect occurred as the resistance of carbonation was increasing as time passed. As time passed the rate of carbonation effect decreased for every different mixture. This could be explained by relating to the carbonation mechanism shown in Figure 18.
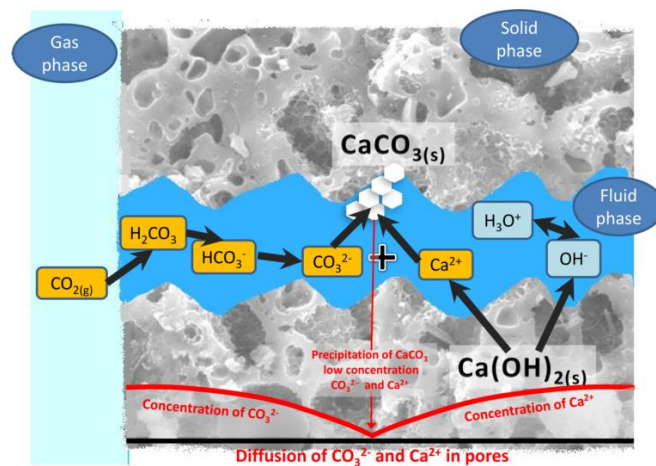
Figure 18. Mechanism of Carbonation Effect

Due to the formation of $CaCO_3$ in the concrete during carbonation effect, this increased the density of the concrete. As the densification of concrete occurred, it created difficulties for the penetration of carbon dioxide gases into the concrete, therefore; decreasing the rate of carbonation. The formation of $CaCO_3$ could reduce the porosity and pore diameter size as $CaCO_3$ was nano size particle. The small size particles brought advantage to the filling ability or particles into tiny pores and caused the concrete to be more compacted. The densification and compactness of concrete maybe varied with different proportions of OPC and POFA incorporated as well. Therefore, this research experiment was conducted to deduce which proportion had the best and weakest carbonation resistance.

Table 13. Comparison of Carbonation Depth of Control Mix and Low POFA

	DAYS OF EXPOSURE		
SPECIMENS	**56 Days**	**63 Days**	**70 Days**
M0	0 mm	0 mm	2 mm
M10N1	0 mm	0 mm	1 mm

From the Table 13 shows the comparison of carbonation depth between the M0 and M10N1. At the exposure at 70 days, the carbonation depth without POFA was 2mm while with POFA was 1mm. It had shown that the concrete had better carbonation resistance if POFA was incorporated into the concrete. POFA contained higher silicon ions than the OPC but lower in calcium ions. Since POFA had a higher percentage of silicon ions, there would be more formation of Calcium Silicate Hydrate (C-S-H) than Calcium Hydroxide (CaOH). As there was a higher C-S-H formation in the concrete, this would cause the concrete to be more compacted because the C-S-H is smaller size particle than CaOH.

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Table 14. Comparison of Carbonation Depth of Control Mix and High POFA

	DAYS OF EXPOSURE		
SPECIMENS	56 Days	63 Days	70 Days
M0	0 mm	0 mm	2 mm
M30N3	8 mm	12 mm	14 mm

By referring to Table 14, it shows the concrete contained very high POFA would cause detrimental. At the 70 days of the exposure period, M0 had 2 mm of carbonation depth while M30N3 had 14 mm. This showed a huge difference of carbonation depth between these specimens. There were two main reasons caused this result. Firstly, the POFA had low calcium ions but high silicon ions. Due to this circumstance, there was a low volume of C-S-H formed as there was a limited amount of calcium ions. Secondly, the POFA had slower pozzolanic reactivity compared to OPC. Since the high volume of POFA was used, therefore; it required more time to develop more C-S-H or CaOH. Take note that the rate of carbonation effect on M30N3 decreased enormously as the time elapsed. In other words, the M30N3 would eventually be better than the control mix as the time passed. In conclusion, the concrete containing high POFA has weak carbonation resistance at the early stage but as the time goes on, it will have better carbonation resistance. This could be explained by using Figure 19.
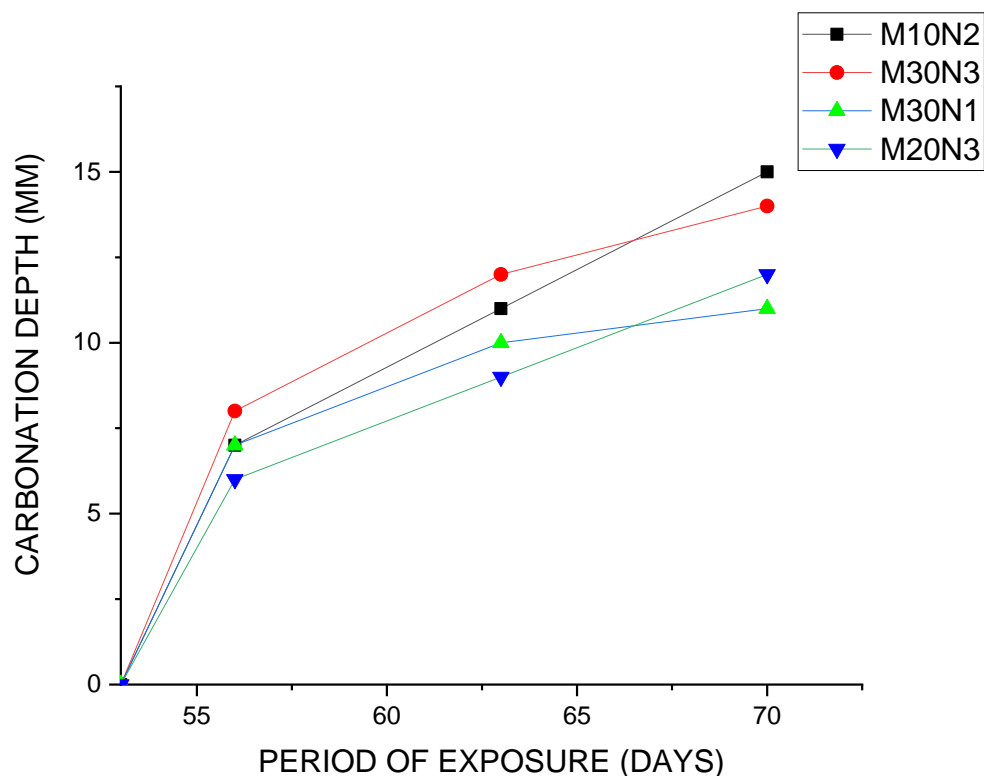

Figure 19. Interception of two lines of carbonation depth between High POFA and Low POFA

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Figure 27 shows the interception of different mixture proportions of POFA, M30N3 (contained 30% mPOFA and 1.5% nPOFA) intercepted M10N2 (contained 10% mPOFA and 1% nPOFA while M30N1 (contained 30% mPOFA and 0.5% nPOFA) intercepted M20N3 (contained 20% mPOFA and 1.5% nPOFA). This indicated that higher POFA had higher carbonation rate at the exposure period of 56 days but lower carbonation depth at 70 days. This was due to the development of better densification by the hydration products of binders and water. From the Table 15, the increment of carbonation depth from the exposure period of 63 days to 70 days for 30% mPOFA was 2 mm while for 10% mPOFA was 4 mm. In summary, the rate of carbonation decreased faster at higher POFA than lower POFA.

Table 15. Result of Differences of Carbonation Depth between High POFA and Low POFA

SPECIMENS	CARBONATION DEPTH AT (MM)		INCREASING DEPTH (MM)
	63 Days	**70 Days**	
M30N3 (30% MPOFA)	12 mm	14 mm	2 mm
M10N2 (10% MPOFA)	11 mm	15 mm	4 mm

By using the M10N1 as the reference to compare the effectiveness of mPOFA and nPOFA, could show which could produce better carbonation resistance shown at Table 16 and Table 17.

Table 16. Results of differences of Carbonation Depth between different amounts of mPOFA

SPECIMENS	CARBONATION DEPTH AT 70 DAYS	INCREMENT OF DEPTH (MM)
M10N1 (10% MPOFA)	1 mm	10 mm
M30N1 (30% MPOFA)	11 mm	

Table 17. Results of differences of Carbonation Depth between different amounts of nPOFA

SPECIMENS	CARBONATION DEPTH AT 70 DAYS	INCREMENT OF DEPTH (MM)
M10N1 (0.5% NPOFA)	1 mm	2 mm
M10N3 (1.5% NPOFA)	3 mm	

From Tables 16 and 17 show the comparison of carbonation depth between micro and nano POFA. By increasing mPOFA from 10% to 30% had increased the carbonation depth from 1 mm to 11 mm while increasing nPOFA from 0.5% to 1.5% had increased the carbonation depth from 1 m to 3 mm. These suggested that using nPOFA was better than mPOFA. Obviously, since the nPOFA had smaller particles size, therefore; it acted better in filling the voids. Furthermore, mPOFA can be used to fill in the void created by OPC, in addition, nPOFA can fill in the voids created by mPOFA. Due to this, the nPOFA reduced the porosity of concrete and pore diameter size better than mPOFA. This theory could be proven by

referring to the slump test results shown in Table 18. It shows by using mPOFA alone would bring detrimental to the workability, but with using both mPOFA and nPOFA would increase the workability of concrete. The control mix gave 140 mm for the slump test while M10N1, M10N2 and M10N3 gave 135 mm, 140 mm and 145 mm respectively.

Table 18. Results of Slump Test

Specimens	Slump Test	Specimens	Slump Test
M0	140 mm	M20N2	65 mm
M10N1	135 mm	M30N2	45 mm
M20N1	50 mm	M10N3	145 mm
M30N1	40 mm	M20N3	80 mm
M10N2	140 mm	M30N3	65 mm

Theoretically, the mPOFA did not contribute much in improving the workability but nPOFA did. It was reported that fine particles of treated POFA were absorbed on the oppositely charged surfaces of cement particles which would prevent them from flocculation. This effect would cause the cement particles to be more dispersed, hence; would not trap large amounts of water. As a result, with the inclusion of nPOFA had greatly increased the workability of concretes.
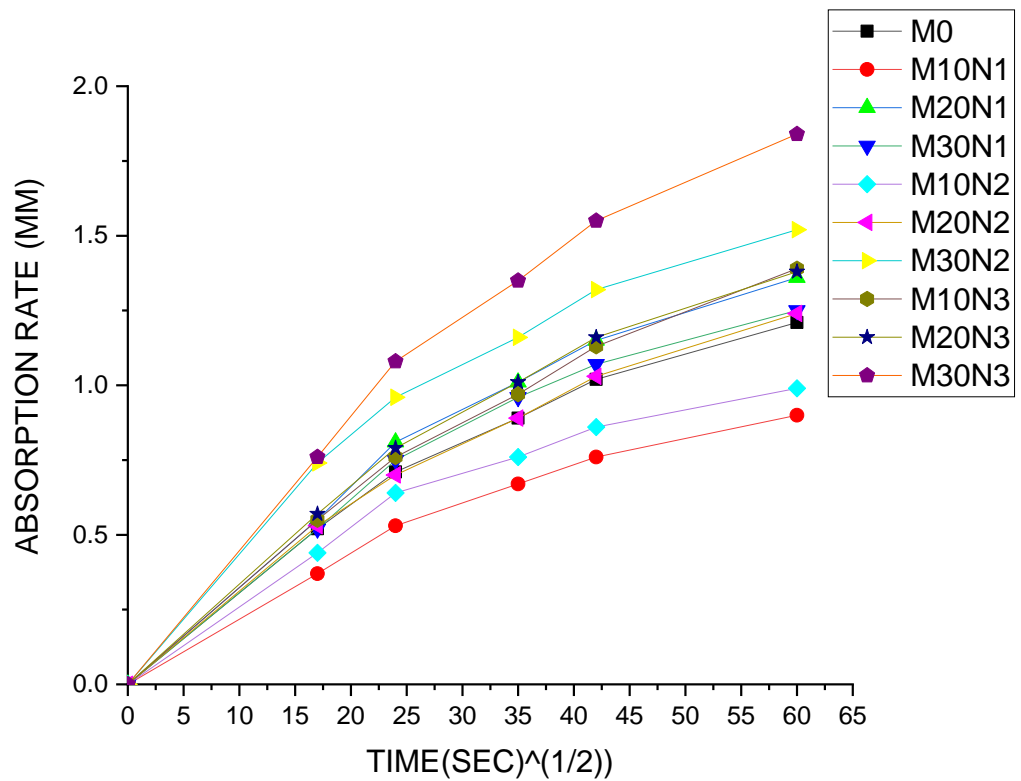
4.5 SORPTIVITY TESTING ON CONCRETE SPECIMENS

*Figure 20. Results of Sorptivity Test of Different Concrete Specimens*

As previous results from the section 4.4.3 showed that the best carbonation resistance was M10N1 while the weakest was M30N3. Figure 20 shows M10N1 had low absorption rate while M30N3 had high absorption rate which matched with the carbonation results. A concrete had different absorption rate than another was simply defined by different sizes of porosity of concretes. If a concrete was defined to have low absorption rate, the concrete could be assumed to have low porosity and smaller pores diameter sizes. On the other hand, if a concrete was defined to have high absorption rate, this would mean that the concrete had large porosity. The M10N1 had low absorption rate which this concrete could be assumed to have low porosity, therefore, causing difficulties penetration of carbon dioxide into the concrete, hence; high carbonation resistance. While for the M30N3, it had high absorption rate which could conclude that of having a high porosity which in fact causing low carbonation resistance.

The M10N1 was showing a better result that M30N3 was due to the number of curing days done for the concrete specimens. The curing days of concrete done for this research experiment was 28 days. With a low amount of POFA incorporated into the concrete by doing 28 days of curing would be suitable, however; with the high volume of POFA such as M30N3 would require a longer time to produce more C-S-H and CaOH. This was because the POFA has slower reactivity of hydration products compared to OPC. There is a potential that
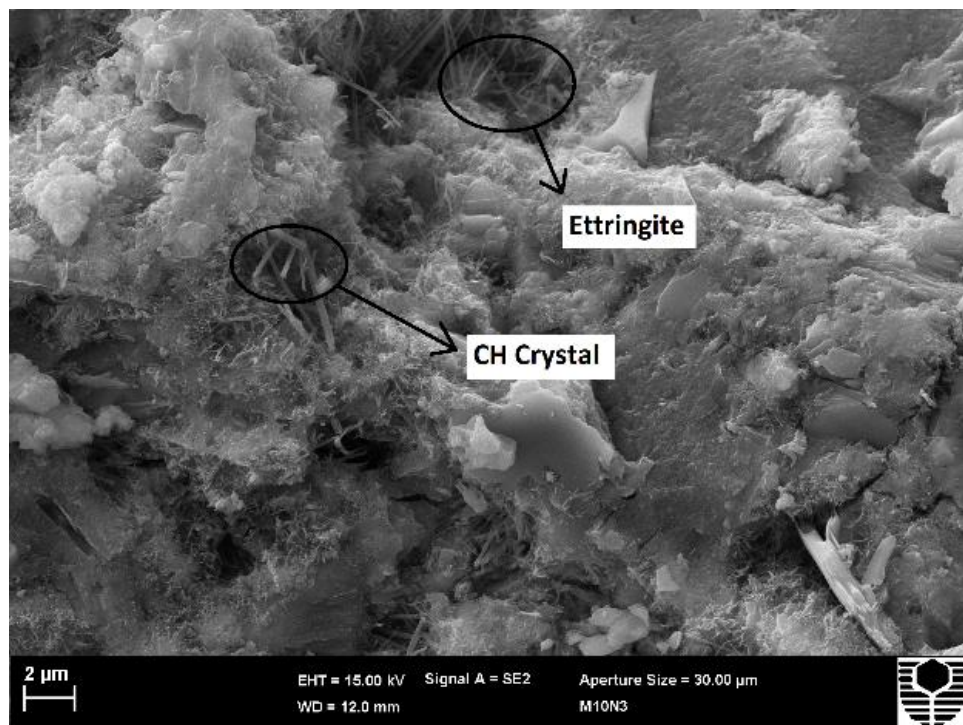
incorporating high volume of POFA would produce better concrete than a low volume of POFA by increasing the number of curing days.
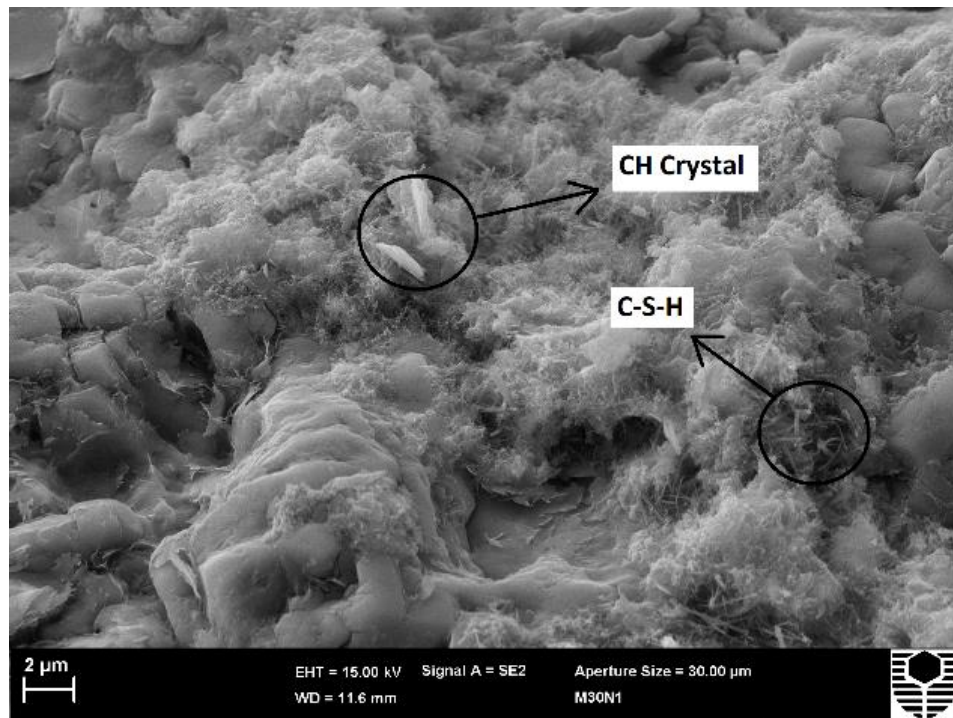
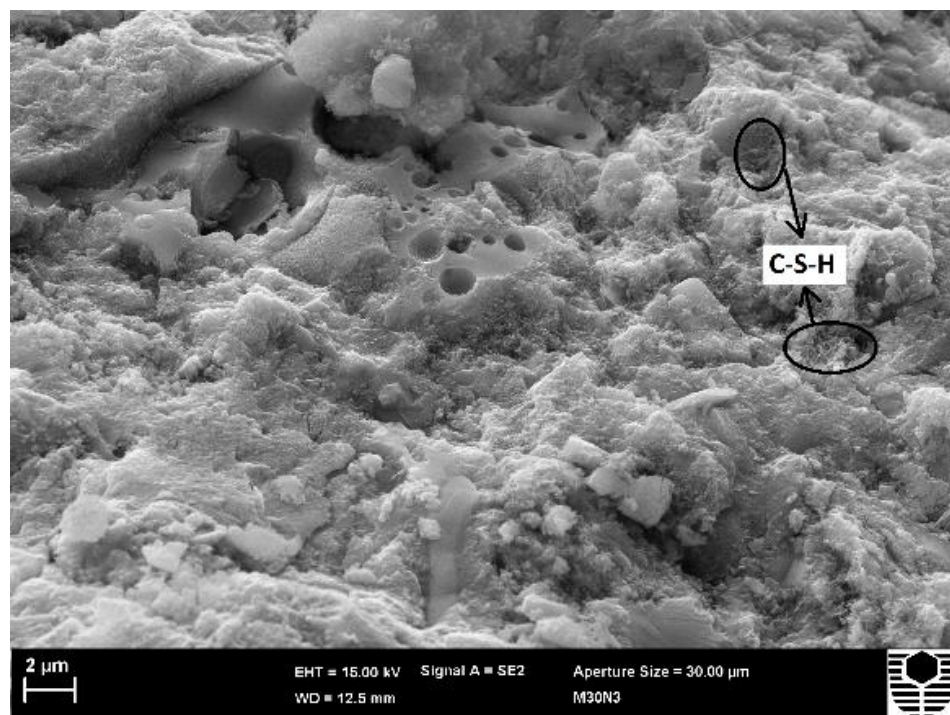## 4.6 MORPHOLOGY OF CONCRETE SAMPLES WITH AND WITHOUT POFA
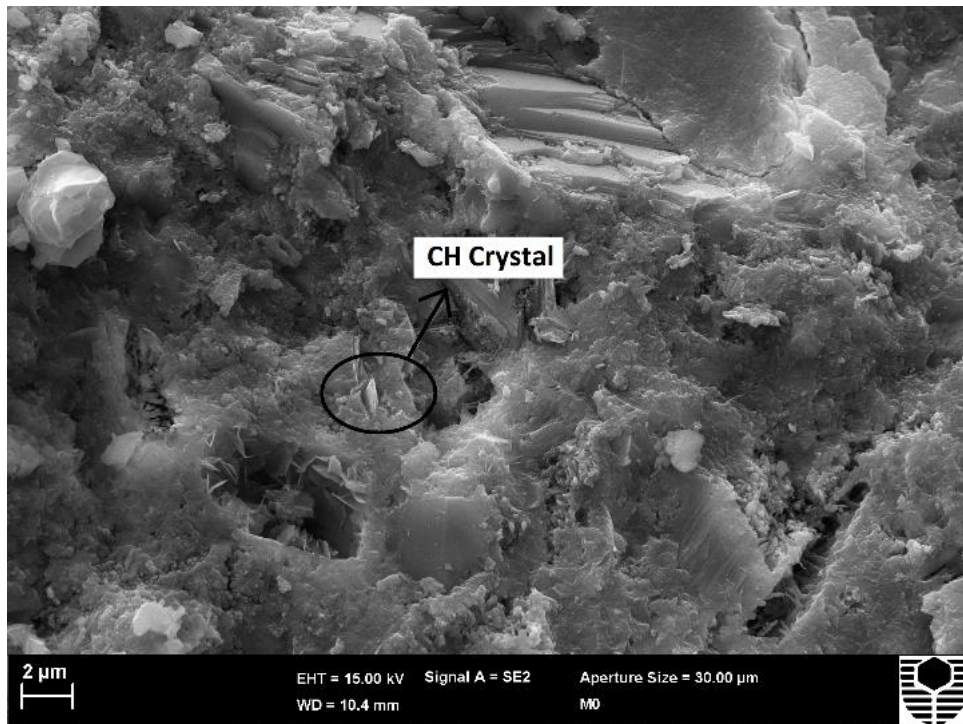
(a)

(b)

(c)

(d)

Figure 21. Morphology of (a) M0 (b) M10N3 (c) M30N1 (d) M30N3 at 28 days of curing age

Figure 21 shows the microstructure of concrete with and without POFA. There was obvious densification of concrete by incorporating mPOFA and nPOFA. This was able to explain which M10N1 had better carbonation resistance and sorptivity compared to M0.

Figure 21a refers to the morphology of concrete without POFA while Figure 21, Figure 21c and Figure 21d are referring to the morphology of concrete with POFA but different amount incorporated. From Figure 21a, it was difficult to find C-S-H particles but Figure 21b, Figure 21c and Figure 21d, the C-S-H particles can be found at many places (it is labelled on these Figures). This concluded that POFA improved the concrete's microstructure. Moreover, by comparing Figure 21c and Figure 21d, the morphology of lower nPOFA had a larger average diameter size of pores and voids compared to higher nPOFA. This suggested that POFA improved the workability of concrete.

As nPOFA had a better specific surface area of the particles than mPOFa, as a result, nPOFA was better than mPOFA. With this characteristics, it induced better stimulated the precipitation of hydration products. In summary, both mPOFA and nPOFA gave better results but nPOFA can achieve better than mPOFA. In addition, POFA acted as nucleation sites and accelerated the precipitation of hydration products such as C-S-H gels and CaOH in the cementitious matrix.

Even though POFA gave better results, but POFA alone cannot produce good performance concrete. This was because POFA had a high amount of silicon ions but with a limited amount of calcium ions. Due to this, OPC is used to compensate for the amount of calcium ions. It was important to have both calcium and silicon ions to achieve high durable concretes. The equation 10 was shown in the section "2.8 SUPPLEMENTARY CEMENTITOUS MATERIALS AND POZZOLANIC REACTION" to show the reaction of these two components.

Calcium and silicon ions were used to produce more C-S-H gels. As previously mentioned, C-S-H was able to densify the concrete due to its properties. Therefore OPC and POFA should be balanced to develop early and later strength of concrete. With the formation of C-S-H, it can create a highly compacted and dense cementitious matrix.

4.7 COMPARISON BETWEEN POFA AND OTHER SCMs

In general perspective of concrete, the most important character is the strength of its material, therefore, it has become famous as a building construction material. But from the engineering point of view, the concrete has to meet almost any desired specification, adaptable, quite incombustible, affordable and easily obtained. Achieving all these requirements would only be satisfied by engineers. Therefore, the concretes have to be properly designed and manufactured by using the supplementary cementitious material such as rice husk ash, fly ash, slag, silica fume and palm oil fuel ash.

Global produces a high amount of different wastes as by-products from the different region like industrial, agricultural and wastes from urban and rural society. These wastes did not deposit safely would create hazardous to human beings and disposing into the landfill is not a viable solution. One of the satisfactory solutions to this crisis is recycling the wastes as it can solve the environmental issues from the pollution and problems associated with waste management. The only requirement to consider the wastes as supplementary cementitious materials is to be pozzolanic materials (high silica content).

Some commonly agricultural and industrial wastes to act as pozzolanic materials are rice husk ash (RHA), fly ash (FA), slag, silica fume (SF) and palm oil fuel ash (POFA). RHA is an agricultural solid waste material and enormously available in rice-producing countries which are formed on rice grains during their growth. FA is formed during the burning of coal in the thermal power plants. Slag is iron dust which is produced during the refining process. POFA is formed when the palm oil residue, palm fiber and shells are burnt at temperatures of about 800°C to 1000°C in biomass thermal power plants.

The waste is considered as super-good pozzolanic materials in the production of concrete only when it contains high silica content. It constitutes a highly reactive pozzolanic. The utilization of SCM affects the concrete properties such as hydraulic factors, permeability, strength and durability. The concrete properties can be improved because the presence of high silica content caused the increment of pore refinement. Furthermore, all these wastes usually go through treatment such as heating or grinding processes so that the fineness and silica contents can be increased. The fineness influenced the rate of reaction and rate of gain in the early strength. In addition, fineness also influenced water-cement ratio demand, creep, shrinkage and workability of concrete.

4.7.1 Comparison of performance between POFA and other SCMs

For this research experiment, POFA was used instead of any other wastes. POFA is usually specifically used to produce "High-Performance Concrete" (HPC) because the pozzolanic reaction of POFA is small at the early stage and increased significantly at the later stage. Since the objective is to obtain the desired carbonation resistance of concretes, thus; durability is more priority to mechanical properties. This material is well-known pozzolanic materials as it contributes to durability in two ways: as the filler effect and the pozzolanic reaction. A pozzolanic is siliceous material, when combined with CaOH, it produces C-S-H. The equation is shown to verify the reaction of silica and calcium. As the density of C-S-H is lower than Portlandite and pure silica, hence; it provides densification of concrete.

4.7.2 Comparison of environmental and economic impacts between POFA and other SCMs

POFA was preferred in this research because the environmental and economic impacts are greater than other SCMs. POFA disposed into the landfill have caused great impact to the environment compared to other SCMs. As the urban population density is increasing, the demand of oil dramatically increased too. Hence, this problem leads to the increasing of oil palm plantation, thus, increasing the wastes produced by the oil palm. These wastes are eventually disposed into the landfill causing hazardous to human beings and animals. From this point of view, the wastes produced by POFA may overwhelm the wastes produced by other SCMs, therefore, it is important to introduce POFA for industrial use.

Secondly, the comparison of economic factor between POFA and SCMs is also crucial. The cost to produce POFA and other SCMs are almost same. As these materials are wastes, hence the cost is zero. However, the cost starts when grinding and treating process are conducted. As mentioned in Chapter 3, the method to produce the mPOFA and nPOFA is not complicated and expensive. Overall, the cost of producing mPOFA and nPOFA is cheaper compared to the cost of using 100% of OPC in concrete.

In conclusion, the POFA was used in this research due to two main reasons. Firstly, it is to reduce the environmental impacts, and secondly, it is to produce better performance concrete by using cheaper products.

4.8 CONTRIBUTION OF POFA TO DURABILITY PROPERTIES

Numbers of research have been done on the contribution of POFA to mechanical properties. All of the researches have shown POFA improves the mechanical properties of concrete such as the compressive strength, splitting tensile strength and flexural strength. In 2013, Sooraj showed the strength decreased as more POFA was used at the early stage but increased at the later stage when compared to OPC (Sooraj V.M. et al. 2013). The most recent case had been done by Wan Nur Firdaus Wan Hassan, showed slightly different results (Wan et al, 2017). The POFA improved the early strength of the concrete and might have the potential to increase more in the later stage. The reason that the early strength was increasing because nano POFA and micro POFA were used. The addition of 1-3% of nano POFA with 10% micro POFA increased the compressive, tensile and flexural strength by 3%, 10% and 47% respectively at the age of 7 days. Therefore, it concludes that POFA brings benefits only to the concretes.

Since many researchers have been done to investigate the mechanical properties of concrete by incorporating POFA, hence; only durability properties was investigated in this research, more specifically the carbonation effect only. Other durability properties such as water absorption, sulfate attack and chloride penetration were previously done but not for carbonation effect. There are certain few cases that carbonation effect was investigated but with different SCM such as fly ash or slag but not POFA. All of the above durability properties mentioned shown positive result except for the carbonation effect is still unknown.

In this research, the results shown using 10% of micro POFA and 0.5% of nano POFA with curing age of 28days will increase the carbonation resistance of concrete. Further increment usage of POFA would decrease the carbonation resistance. In summary, POFA contributes to carbonation resistance by using a small amount of POFA only.

CHAPTER 5   CONCLUSIONS

- XRF results show that using treated POFA instead of raw POFA can produce a better performance of concretes as the silica ions have increased and LOI has reduced. Due to these, there will be more formation of C-S-H particles in concrete and provide better workability as the LOI reduced.

- XRD results show the similarity of diffract grams and diffractive halos structure for both mPOFA and nPOFA. Both of these POFA contained α-Quartz (α-SiO_2), Cristobalite, Potassium Aluminium Diphosphate ($K_3Al_2(PO_4)_3$) and Hematite (α-Fe_2O_3) which are good for the rate of pozzolanic reaction and strength development.

- SEM results of the POFA particle shows the spherical and irregular shape and more importantly, more porous. Due to these characteristics, it has a better filling effect and pozzolanic reactivity.

- The carbonation results show the best carbonation resistance with the curing age of 28 days is by using 10% mPOFA with 0.5% nPOFA (M10N1). This has been done by evaluating and comparing the carbonation depth with different specimens. Further increasing the amount of POFA would bring detrimental effect to the carbonation resistance.

- The sorptivity results show the lowest absorption rate with the curing age of 28 days is by using 10% mPOFA with 0.5% nPOFA (M10N1). Further increasing the amount of POFA would increase the rate of absorption. Since M10N1 has the lowest absorption rate, therefore; it has the low porosity and small size pores.

- The slump test results show that using nPOFA bring huge benefits in terms of workability. Due to its small size particles, it is very effective in filling in the voids created inside the concrete.

- The SEM results of concretes show the microstructure of concrete. It shows more formation of C-S-H particles formed with a higher amount of POFA used. In addition, it is important to balance both the usage of OPC and POFA as the formation of C-S-H required both calcium and silicon.

- According to the results of carbonation and sorptivity, the overall result shows that M10N1 which contained 10% mPOFA and 0.5% nPOFA can produce the desired carbonation resistance.

CHAPTER 6   RECOMMENDATIONS

One of the ways to improve this research project is to control the concentration of CO_2 more accurately by changing the design of the carbonation chamber. Two main important specifications of the carbonation chamber should be changed which are the controlling valve of CO_2 and installed a power socket in the chamber. "Section 4.4.1 Overview of Carbonation Testing" showed a graph representing the concentration of CO_2 at the exposure period of 70 days. The line graph fluctuated throughout the whole process. This may affect the carbonation depth's result. In order to prevent this matter, the valve controlling the CO_2 gas should change to so-called "needle valve". Needle valve can control the valve more accurately, hence; an accurate amount of CO_2 can be pumped into the chamber. Another reason causing the fluctuation of the CO_2 gas was the constant opening the chamber's lid. The lid was opened several times because the CO_2 meter needed to change the battery. Therefore, to avoid this unnecessary matter, installed the power socket at the chamber so that CO_2 meter's battery can never go flat.

There are two recommendations for future research. Firstly, increasing the curing age of the concrete specimens to be more than 28 days. As the Palm Oil Fuel Ash is slower pozzolanic reaction compared with any other admixtures or cement, increasing the curing age may increase the rate of pozzolanic reactivity. As a result, causing different carbonation resistance. Secondly, since the curing age increased, incorporating more Palm Oil Fuel Ash may change the results as well. Therefore, increase the amount of Palm Oil Fuel Ash to at least 3% of nano POFA. In this research, the author had only used 1.5% of nano POFA as the curing age of the concrete was 28 days only. Since the curing age has increased to be more than 28 days, therefore, additional POFA can be used so that it can achieve higher carbonation resistance.

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CHAPTER 8 APPENDIX

Appendix A - Data of CO2 Concentration over the exposure period of 70 Days
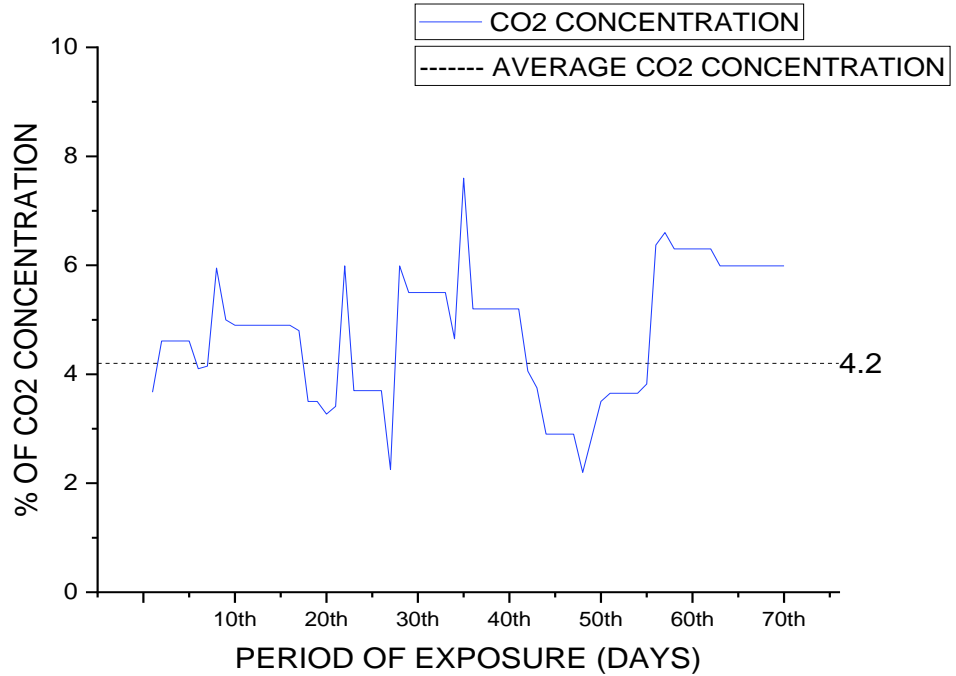
Appendix B - Data of Temperature over the exposure period of 70 Days
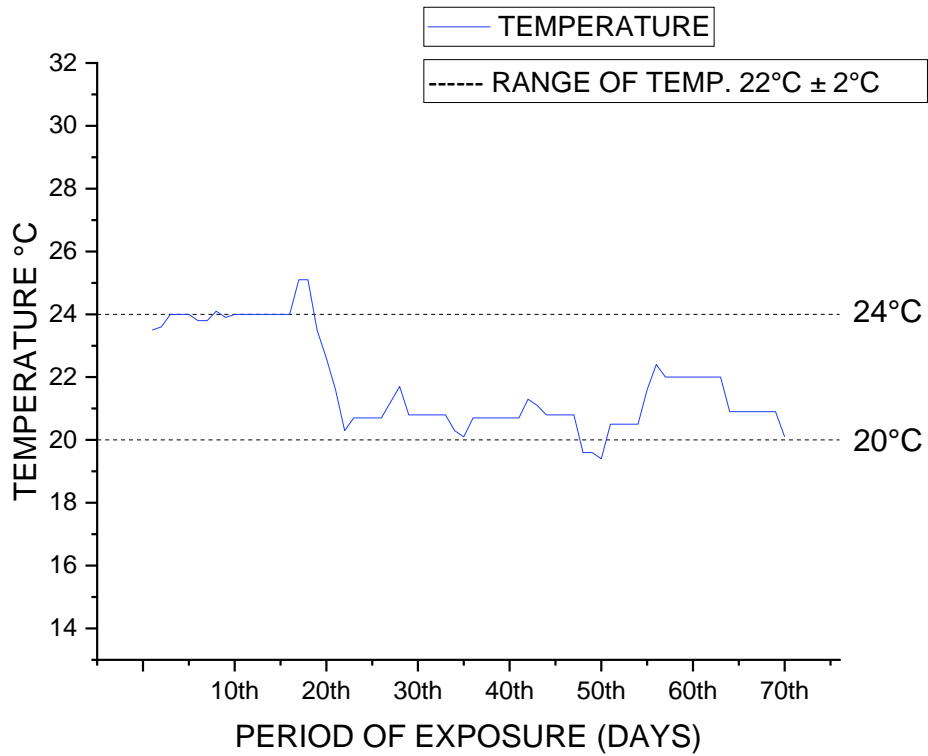
Appendix C - Data of Relative Humidity over the exposure period of 70 Days