EFFECTS OF BY-PRODUCTS AS CEMENT REPLACEMENT MATERIALS TOWARDS CONCRETE CARBONATION DEPTH

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Thesis submitted in fulfillment of the
requirements for the award of the degree of
Bachelor of Civil Engineering

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JUNE 2013

ABSTRACT

Carbonation is a common threat to reinforced concrete structures. Carbonation causes deterioration by the corrosion of the reinforcement bars as it allows moisture to penetrate to the depth of the steel and also leads to concrete spalling. Although the causes, mechanisms and factors that promote concrete carbonation have been widely studied, there is very little data relating carbonation with industrial by-products such as palm oil fuel ash (POFA), pulverized fly ash (PFA) and whatsoever. Thus, the aim of this research is to study the effects of POFA and PFA towards concrete carbonation depth as POFA and PFA have been used extensively as cement replacement materials to improve concrete characteristics. Three different samples at 3 years of age were used, each for control concrete, POFA concrete and PFA concrete where POFA and PFA are added up to 30% cement replacement, starting with 10% and 20%. Water absorption test, alkalinity test and carbonation test were all carried out to achieve the objectives of this research. From the results, reduction of alkalinity and permeability occurs in concrete containing POFA and PFA and is decreasing as the amount of POFA and PFA is increased. Though permeability of concrete is improved due to introduction of POFA and PFA, carbonation depth is found to be higher in those concrete compared to control concrete.

ABSTRAK

Pengkarbonan adalah ancaman biasa untuk struktur konkrit bertetulang. Pengkarbonan menyebabkan kemerosotan oleh kakisan bar tetulang kerana ia membolehkan kelembapan untuk menembusi kedalaman keluli dan juga membawa kepada konkrit spalling. Walaupun punca, mekanisme dan faktor-faktor yang menggalakkan pengkarbonan konkrit telah dikaji secara meluas, terdapat data yang sangat sedikit yang berkaitan dengan pengkarbonan industri oleh-produk seperti minyak kelapa sawit abu (POFA), serbuk abu terbang (PFA) dan sekalipun. Oleh itu, tujuan kajian ini adalah untuk mengkaji kesan POFA dan PFA ke arah kedalaman pengkarbonatan konkrit POFA dan PFA telah digunakan secara meluas sebagai bahan pengganti simen untuk meningkatkan ciri-ciri konkrit. Tiga sampel yang berbeza dan berusia 3 tahun telah digunakan, masing-masing untuk konkrit kawalan, POFA konkrit dan konkrit PFA di mana POFA dan PFA ditambah sehingga 30% penggantian simen, bermula dengan 10% dan 20%. Ujian penyerapan air, ujian kealkalian dan ujian pengkarbonan telah dijalankan untuk mencapai objektif kajian ini. Daripada keputusan, pengurangan kealkalian dan kebolehtelapan yang berlaku di dalam konkrit yang mengandungi POFA dan PFA, didapati kadar kealkalian dan kebolehtelapan semakin berkurangan kerana jumlah POFA dan PFA bertambah. Walaupun kebolehtelapan konkrit bertambah baik berikutan pengenalan POFA dan PFA, kedalaman pengkarbonatan didapati lebih tinggi pada konkrit yang mengandungi POFA dan PFA berbanding dengan kawalan konkrit.

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LIST OF ABBREVIATIONS

C-S-H	calcium silicate hydrate
$Ca(OH)_2$	calcium hydroxide
CO_2	carbon dioxide
MPOB	Malaysian Palm Oil Board
NOx	mono-nitrogen oxides
OPC	Ordinary Portland Cement
PFA	Pulverised Fly Ash
POFA	Palm Oil Fuel Ash
SO_2	Sulphur dioxide

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Concrete is the most common material used in construction industry nowadays. A major factor that makes concrete been chosen to be used widely is its properties which comprises of strength and durability, versatility, low maintenance, affordability, fire resistance, thermal mass, locally produced and used, albedo effect and low life-cycle carbon dioxide (CO_2) emissions (Properties of Concrete, n.d). Concrete strength has always been the center of attention as many recommendations in selection of concrete are made based on its strength. Concerns on durability problem have skyrocketed as concrete is not an inert material that immune to environmental conditions to which it is exposed. Structural deterioration often occurs before the stipulated time, causing lots of economic damage and public inconvenience (Chandra, 2000). The durability problems may occur due to inadequate quality control, along with heterogeneity of the materials which increase due to the use of chemical and mineral admixtures in concrete (Chandra, 2000). Among concrete deterioration that usually occurs is carbonation which takes place after calcium carbonate is formed in the cement matrix and reduces its alkalinity. Reinforcement bars in concrete are exposed to corrosion when alkalinity in concrete dropped to pH lesser than 9 and breaks the passive layer that protects the bars (Carbonation of concrete, n.d)

Pulverised fuel ash (PFA) and palm oil fuel ash (POFA) are among two most common pozzolanic materials used as cement replacement. PFA is a by-product from the burning of powdered coals in electric generating power plants while on the other hands; POFA is obtained from burning of pressed fiber and shell which are used as fuel to generate steam and energy required for the operation of mill (Muthusamy, 2013). Using pozzolanic materials as cement replacement will reduce the production cost of Portland cement as these materials are usually industry by-products and thus much cheaper. Concrete mixed with pozzolanic materials are also found to have higher ultimate strength and workability and more durable compared to normal concrete.

1.2 PROBLEM STATEMENT

Healthy concrete has high alkalinity, around pH 12-13 that provides good protection against corrosion for embedded reinforcement bars. High pH environment in concrete causes a passive and non-corroding protective oxide film to form on the steel bars. Chemical reaction between carbon dioxide in air and calcium hydroxide in cement paste will produce calcium carbonate that will reduce the alkalinity of concrete and soon destroy the layer that protects the steel bars hence causing corrosion (Muthusamy, 2013).

PFA, POFA and other pozzolanic materials are widely used in producing durable concrete nowadays. Pozzolanic reactions in concrete result in the partial conversion of non-cementitious and leachable calcium hydroxide into cementitious secondary calcium silicate hydrates. Al-Amoudi et al (1989) states that pozzolanic reactions in concrete may result in reduction of the pH which would lower the level of protection provided by concrete to the embedded reinforcement bars against corrosion. As comparison, Hamada (1969) and Ho et al (1984) have reports that concrete with fly ash carbonate faster than concrete without fly ash.

1.3 OBJECTIVES

I. To investigate the relationship of carbonation depth with POFA & PFA as cement replacement materials.
II. To study the relationship between carbonation depth with concrete water absorption.
III. To investigate the effect of byproduct as cement replacement material towards concrete pH.

1.4 SCOPE OF STUDY

I. Carbonation depth is measured for different types of concrete; normal concrete, concrete mixed with POFA and concrete mixed with PFA.

II. POFA and PFA are used as cement replacement materials and are added at amount of 10%, 20% and 30%.

III. A total of 18 samples are used, consists of 9 concrete cubes and cylinders each and all samples are approximately 3 years of age.

IV. 9 cubes are used for water absorption test and the cylinders are used for carbonation depth measurement.

1.5 EXPECTED OUTCOMES

At the end of the study, there are some outcomes to be achieved, such as:

I. Alkalinity is lower in concrete with POFA and PFA.

II. Concrete with POFA and PFA have higher carbonation depth compared to normal concrete.

III. Concrete permeability is reduced by the addition of POFA and PFA.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Nowadays, concrete has been selected and used as the most common construction material in industry. Concrete basically possessed high compressive strength, but weak in tension as concrete cannot be stronger than the bond between the cured cement and the surfaces of aggregate. However, concrete has suffers from durability problem since ages ago and is getting worse nowadays. According to Mishra (2012), durability refers to the concrete resistance against weathering action, chemical attack, abrasion or any process of deterioration while maintaining its desired properties.

There are several factors that contribute to durability problem of concretes and one of them is carbonation. Carbon dioxide from atmosphere penetrates the concrete surface and interacts with water, yielding carbonic acid which then will react with the alkalis produced from the hydration process. The depth of carbonation increases with time, and thus neutralizes the concrete paste. Calcium hydroxide for instance, can form leachable salts with NOx and reducing the concrete strength while SO_2 can form expansive salts which lead to cracks.

Pozzolanic materials such as palm oil fuel ash (POFA), pulverized fuel ash (PFA), silica fume, ground granulated blast furnace slag and whatsoever have been used widely in the industry as an admixture and cement replacement materials. Utilization of these materials has managed to improve durability of concrete, increase strength of concrete, reduce permeability and in some cases may increase concrete workability. Plus, utilization of pozzolanic materials will help in reducing cost for raw materials, as amount of cement used will be lesser and these materials are basically industrial wastes.

2.2 CONCRETE

2.2.1 Introduction

Li (2011) states that concrete is a composite material composed of coarse granular material embedded in a hard matrix of a material that fills the space among the aggregate particles and glues them together. Concrete has been used in construction since centuries ago and concrete technology was known by the Romans and widely used in Roman Empire. According to Lancaster (2005), concrete in Roman Empire was made from quicklime, pozzolana and aggregate of pumice and widely used in the structures such as in shape of vaults, arches and domes.

Application of concrete by the Romans has trigger to the improvement and broader use in industry. Utilization of concrete, worldly, is twice as much as steel, plastics, woods and aluminum combined (Christensen, n.d). Additives in concrete have been used ever since Romans and Egyptians times, when it was discovered that addition of volcanic ash to the concrete mix allows it to set underwater (Brief history of concrete, n.d).

2.2.2 Application of concrete

Concrete has a broad range of application starting from dams, bridges, buildings, patios, basements, pavement blocks, kerbs, drain cover and so on so forth. Each year, around six billion tons of concrete is produced and is regarded as second mostly used in the world, only exceeded by the usage of natural water. Concrete has wide applications, such as rebuilding, mending and construction and usually are made into different sizes and shapes of several components such as slab, beam, column, wall panels and so on.

Concrete is used in construction not only because it is durable, but also due to other advantages. Among advantages of concrete are fire-resistance, low maintenance compared to steel, energy efficiency in production, excellent thermal mass, albedo effect and whatsoever.

2.2.3 Durability of concrete

American Concrete Institute has define concrete durability as it's resistant to weathering action, chemical attack, abrasion and other degradation process. A durable material helps the environment by preserving resources and reducing wastes and environmental impacts in terms of repair and replacement. Most buildings have service life around 30 years, though buildings often last to 50 to 100 years or even longer. Concrete and masonry buildings are often demolished due to obsolescence rather than deterioration as concrete the ability to withstand deterioration mechanisms caused by nature, as well as natural disaster.

Durability of concrete depends on type of concrete, properties desired and exposure environment. For instance, concrete exposed to seawater will have different requirements compared to indoor concrete floor. Durability of concrete can be increased by using low cement-ratio to reduce permeability, increase concrete cover and also by the application of pozzolanic materials such as POFA and PFA.

2.2.4 Permeability

According to American Concrete Institute, permeability is defined as the coefficient that represents rate at which water is transmitted through a saturated specimen of concrete under an externally maintained hydraulic gradient. Permeability is often linked to durability, where the lower the permeability, the higher durability of concrete and vice versa. Decreased permeability improves concrete's resistance to resaturation, sulfate and other chemical attack and chloride ion penetration (Kosmatka and Panarese, 1988).

2.2.4.1 Permeability Test

Permeability test measured the flow of a liquid or gas into concrete under the action of a pressure gradient.

2.2.4.1.1 Air Permeability

There are several tests that can be conducted to measure air permeability of concrete, for instance, Figg air permeability test, Schönlin air permeability test, surface airflow test and whatsoever. Figg air permeability test is among the most common method used. Figg test measures water permeability in a 5.5mm diameter hole drilled 30mm into the concrete. A vacuum pump is used to reduce the pressure in the hole to 15 kPa and a manometer is used in the place of a capillary tube. Time is measured when pressure in the hole is rise to 5 kPa after the valve to the vacuum pump is closed (Figg test, n.d).

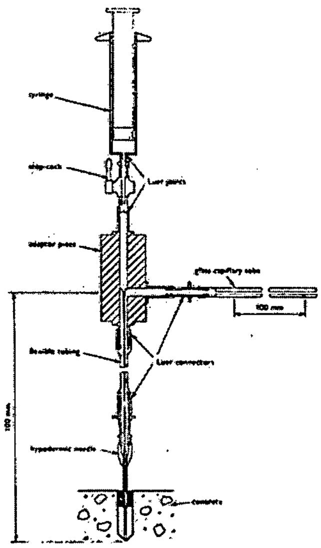

Figure 2.1: Figg Air Permeability Test

Source: http://www.concrete.org.uk/fingertips_nuggets.asp?cmd=display&id=572

2.2.4.1.2 Water Permeability

Water permeability test is almost similar to air permeability test. The only difference is that water is introduced on the top of the cell and pressure is applied to force water to penetrate through the sample. Permeability is measured by a method based on penetration depth, where a color indicator is applied that helps in determining the border of penetration depth (Castro-Gomes et. al., 2002). However, for this study, permeability is measured by water absorption test where difference in weight in dry and saturated condition resembles the concrete absorption in percentage.

2.2.5 Alkalinity

Alkalinity indicates the strength of alkaline in concrete. Longo (2007) states that alkalinity is generally generated by alkalis in solution such as sodium hydroxide and potassium hydroxide. Alkalinity often measured by pH tests, where higher reading indicates higher amount of alkaline and vice versa. Addition of pozzolanic materials has been used extensively nowadays to improve concrete properties such as strength and durability. However, some previous studies claimed that addition of pozzolanic materials decreased the alkalinity of concrete. Kothandaraman (2010) claims that alkalinity of PFA concrete is found to be lower than the reference concrete, and is decreasing with the increase of PFA content. This statement is supported by Al-Amoudi et. al. (1989) which states that addition of pozzolanic materials may have adverse effects in terms of corrosion kinetics, as it may result in the reduction of pH which would lower the level of protection by concrete to the reinforcement bars against corrosion.

2.3 POZZOLANIC MATERIALS

Pozzolanic materials are usually industrial byproducts that used widely in concrete industry nowadays, as cement replacement material. According to ASTM C618 (2008), pozzolanic materials are siliceous or siliceous and aluminous materials which possess little or no cementitious property, but in a fine form, and in the presence of moisture, these materials can react with calcium hydroxide in concrete at ordinary temperatures to form compounds of cementitious properties.

2.3.1 Pozzolanic Reaction

Karim et. al., (2011) claim that POFA contained high amount of silicon dioxide in amorphous form that can react with calcium hydroxide produced from the hydration process to produce more calcium silicate hydrate, C-S-H gel compound.

$$2S + 3CH \rightarrow C_3S_2H_3$$

Products of pozzolanic reaction cannot be distinguished from those of the primary cement hydration and therefore make their own contribution to the strength and other properties of the hardened cement paste and concrete (Eldagal, 2008).

Pozzolanic reaction can only take place soon after calcium hydroxide is produced during the hydration process. Water is essential for pozzolanic reaction to occur and form secondary C-S-H gel. Thus, initial water curing is vital in ensuring faster hydration process in order to create large amount of lime for the occurrence of pozzolanic reaction as well (Muthusamy, 2012).

2.3.2 Palm Oil Fuel Ash (POFA)

Malaysia is known as main palm oil producer and exporter in the world. In 2010, Malaysian Palm Oil Board (MPOB) estimated that total palm oil planter is around 4.85 million hectares around Malaysia. The total amount of fresh fruit bunches processed by over four hundred palm oil mills are estimated to be 87.5 million tons. Around 61.1 million tons of solid waste by-products in the form of fibers, kernels and empty fruit bunch are produced, where about 70% of fresh fruit processed (MPOB, 2010). Combustion process of palm oil husk and palm kernel shell in the steam boiler produces POFA, which is around 5% of solid waste by-product and equals to 3.1 million tons in Malaysia for 2010 (Tangchirapat et. al., 2006).

Albeit production of POFA increase annually, allocation of transportation cost and landfills for the disposal of POFA become ineffective way to manage the waste as POFA has no commercial return value and hence will lead to environmental problems in the future (Tangchirapat et. al., 2006). Previous studies from Tay (1990), Hussin and Awal (1997) and Tangchirapat et. al., (2006) have proved that POFA can be used as cement replacement material or as an aggregate in concrete due to its pozzolanic properties.

POFA has low pozzolanic property due to its large particle size and porous structure and hence, need to be grounded into finer particles to increase pozzolanic reaction. POFA has high amount of silica content but less amount of lime compared to Ordinary Portland Cement (OPC). High amount of silica content increase the degree of pozzolanic reaction when it reacts with free lime available thus, create extra C-S-H gel that can increase concrete strength. Quality of POFA depends on type of material and the burning efficiency. A proper and complete combustion process will produce a whitish grey POFA and it will become darker as amount of carbon increases.

2.3.2.1 Chemical Properties of POFA

Chemical properties of POFA vary as it depends on the combustion process and efficiency and state of the mill. Chemical composition of POFA is shown in Table 2.1 below:

Table 2.1: Chemical composition of POFA

Chemical Composition	**Percentage (%)**
Silicon dioxide (SiO_2)	43.6
Aluminum oxide (Al_2O_3)	11.4
Ferric oxide (FE_2O_3)	4.7
Calcium oxide (CaO)	8.4
Magnesium oxide (MgO)	4.8
Sulphur trioxide (SO_3)	2.8
Sodium oxide (Na_2O)	0.39
Potassium oxide (K_2O)	3.5
Phosphorus oxide (P_2O_2)	3.5
Loss of ignition (LOI)	18.0

Source: Muthusamy (2013)

2.3.3 Pulverised Fuel Ash (PFA)

PFA or sometimes called as fly ash, is a by-product from the burning of powdered coal in electric generating power plants and comprises fine particles that rise with flue gases. Fly ash is collected in the dust-collection system (electronic or mechanical precipitators) that removes particles from the exhaust gases. Components of fly ash varies, depend on the source and makeup of the coal being burned but all fly ash contains large amount of silicon dioxide (SiO_2) and calcium oxide (CaO).

According to ASTM C 618, PFA can be divided into two categories; Class C and Class F based on their chemical composition. Class C or high-calcium fly ash, is produced from burning subbituminous coal or lignite. Class C fly ash contains about more than 10% CaO and this amount can be high up to 30%. On the other hand, Class F fly ash is also called as low-calcium fly ash as it contains less than 10% CaO. Class F fly ash is obtained from burning of bituminous coal and possess only slight amount of cementing properties, but in a finely divided form and in the presence of water, it can react with calcium hydroxide ($Ca(OH)_2$) produced in the hydration process.

2.3.3.1 Chemical Properties of PFA

Chemical composition of POFA varies for Class C and Class F. Table 2.2 below shows the comparison.

Table 2.2: Chemical composition for Class C and Class F fly ash

Chemical Compound	**Class C**	**Class F**
Silicon dioxide (SiO2)	39.90	54.90
Aluminum oxide (Al2O3)	16.70	25.80
Ferric oxide (Fe2O3)	5.80	6.90
Calcium oxide (CaO)	24.30	8.70
Magnesium oxide (MgO)	4.60	1.80
Sulphur trioxide (SO3)	3.30	0.60
Sodium oxide & potassium oxide (Na_2O & K_2O)	1.30	0.60

Source: Chemical Comparison of Fly Ash and Portland Cement (2005)

2.4 CARBONATION

Carbonation is a slow process and always associated with loss of alkalinity of the pore solution. Muthusamy (2013) states that carbonation is a process by which carbon dioxide in the air penetrates the concrete and reacts with the hydroxides such as calcium hydroxides to produce carbonates. Formation of calcium carbonate requires three important substances; carbon dioxide, calcium and water. First reaction occurs in the pores when carbon dioxide and water reacts to produce carbonic acid. Equations below show the chemical reaction in the pores (Carbonation of Concrete, n.d).

$$CO_2 + H_2O \longrightarrow H_2CO_3 \quad (2.1)$$

Carbonic acid will then reacts with calcium phases

$$H_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2H_2O \quad (2.2)$$

Soon after $Ca(OH)_2$ is converted, hydrated CSH (Calcium Silicate Hydrate - $CaO•SiO_2•H_2O$) will release CaO which then will also carbonate.

$$H_2CO_3 + CaO \longrightarrow CaCO_3 + H_2O \quad (2.3)$$

pH value will start decreasing once these reactions take place as alkalinity in the cement paste is being neutralized by carbonic acid. Healthy concrete usually have pH around 12.5 to 13.8 (Concrete Alkalinity-pH Introduction, n.d). In carbonated concrete, alkalinity is decreases and as pH value drops to below 9, the passive film that protects the reinforcement concrete will be totally gone.

Pozzolanic materials such as POFA and PFA have been used extensively in producing durable concrete. However, some previous studies have claimed that these pozzolanic materials may contribute to carbonation process. Al-Amoudi et al. (1989) in their study has found that carbonation depth is higher in fly ash concrete compared to OPC concrete both in chloride free and chloride contaminated concretes. This statement is supported by previous studies by Ho et al.(1984) and Hamada (1969) that reports concrete with fly ash carbonates faster than concrete without fly ash (OPC concrete).

2.5 SUMMARY

Addition of pozzolanic materials in concrete is without a doubt helps improving concrete properties most likely in terms of durability and strength. However, introduction of pozzolanic materials in concrete results in lower alkalinity compared to normal concrete. Consumption of calcium hydroxide due to pozzolanic reactions in concrete reduces the alkalinity and is decreasing with pozzolanic materials content and would lower the protection towards reinforcement bars against corrosion.

Carbonation usually occurs when concrete pH is reduced to below 9. Concrete added with pozzolanic materials have lower alkalinity and tends to drop faster than normal concrete. Hence, carbonation will occur faster in concrete added with pozzolanic materials compared to normal concrete. As carbonation is occurring faster in concrete with pozzolanic materials, it is expected that carbonation depth will be higher compared to in normal concrete. Some previous studies also found that carbonation occur faster in concrete containing pozzolanic materials than normal concrete as reported by Hamada (1969), Ho et. al. (1984) and Al-Amoudi et. al.(1989).

CHAPTER 3

METHODOLOGY

3.1 GENERAL

This chapter will discuss briefly the procedures involved in carrying out the experimental works and laboratory tests to achieve the objectives of the study. There are several tests need to be carried out such as water absorption test, alkalinity test and carbonation test.

3.2 MATERIALS AND PREPARATION

18 samples consist of 9 concrete cubes and 9 concrete cylinders are used for laboratory testing. 3 concrete cubes and 3 cylinders are used for each different type of concrete mix; control mix, POFA concrete and PFA concrete. Concrete cubes are used for water absorption test while the cylinders are subjected to carbonation test. All samples are approximately 3 years of age and are according to standard practice; 150mm x 150mm for concrete cubes and 150mm x 30mm for cylinders.

3.3 LABORATORY TESTING

This section will describe the procedures for all tests involved in this study.

3.3.1 Water Absorption Test

Water absorption test is one of the tests related to permeability. In general, concrete with low permeability is considered as good as it resists the entrance of water into cement paste and aggregates.

Procedures for testing are described as below (ASTM C 140 Water Absorption):

I. Weight all the samples and record their initial weight.
II. Immerse all the samples in a curing tank for approximately 24 hours.
III. After 24 hours, samples are taken out from the curing tank, and their weight is measured.
IV. Increase in weight as a percentage of the original weight is expressed as its absorption (in percentage).

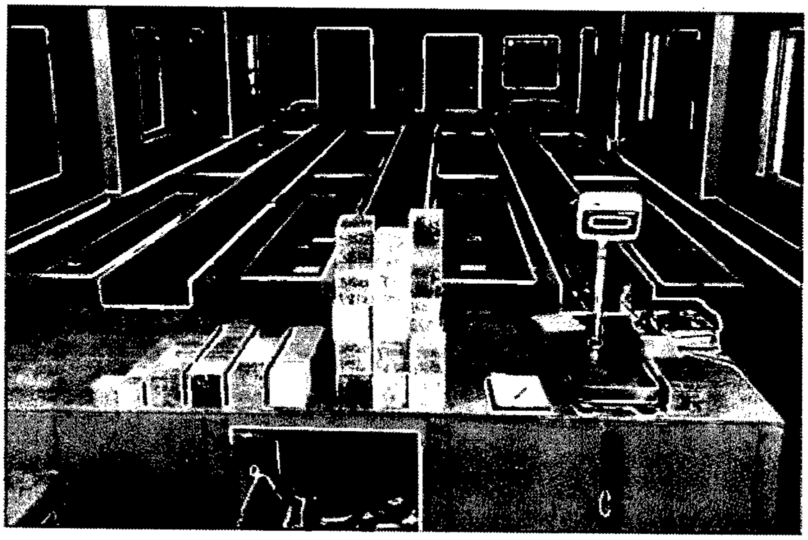

Figure 3.1: Water absorption test

Source: http://interlabbh.com/pg/view/87

3.3.2 Alkalinity Test

Alkalinity test is carried out basically to measure the alkaline value in concrete. Concrete with high alkalinity will have high pH value and vice versa. This test is carried out for all three different cement mixes; control mix, cement with POFA and cement with PFA.

Testing procedures:

I. For control mix, cement is mixed with adequate amount of water and stir until cement paste is formed.
II. Then, measure the alkalinity by using a digital pH meter.
III. Test is repeated by mixing cement with POFA, starting with 10%, 20% and 30% with water is adequate amount of water and stirred thoroughly.
IV. Alkalinity is measured using the pH meter and test is again repeated for PFA with 10%, 20% and 30%.

Figure 3.2: Measuring alkalinity with pH meter

3.3.3 Carbonation Test

Carbonation test is conducted to measure carbonation depth by time. Carbonation usually occurs below the exposed surface of concrete and is known as time-consuming