STUDY ON CITRIC ACID AS ALTERNATIVE ADMIXTURES FOR ORDINARY PORTLAND CEMENT BASED BINDER

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ABSTRACT

In this study, Citric Acid can be used as the alternative admixture in Ordinary Potland Cement, OPC based binder. Experiments were carried out to determine the effect of Citric Acid on the setting time and workability of fresh binder cement paste and the effect of Citric Acid on the compressive strength and porosity of hardened cement paste. Analysis is to identify the optimum inclusion of citric acid that contributes to the improvement of OPC based binder performance. The different concentration of citric acid in 0.5, 0.75, 1.0, 1.25 and 1.5milimole/L were mixed together with OPC paste. Fresh binder of cement pastes were test for Vicat Setting time according ASTM C191 and flow table according C230 for their workability. The another fresh binder of cement pastes also were cast into 50mm x 50mm x 50mm cube molds for hardening test purpose such as compressive strength test and porosity test according ASTM C109 and C642. The specimens were demolded after 24 hours. The mold cured for day 1, day 7 and day 28. Based on vicat setting time result, citric acid tends to be a retarder in 0.5 milimole/L dosages. In addition increases concentration of citric acid, the porosity and compressive strength not constantly was increasing in day 1, 7 and 28 compare to control specimen. There was the optimum dosages 1.5 milimole/L of citric acid that will increase the performance of OPC based binder.

Keywords: Ordinary Portland Cements, Citric Acid, Admixture

ABSTRAK

Dalam kajian ini, asid sitrik boleh digunakan sebagai campuran alternatif dalam simen Portland biasa, pengikat asas OPC. Eksperimen ini dijalankan untuk menentukan kesan asid sitrik di penetapan masa dan kebolehkerjaan adunan simen asas pengikat yang masih basah dan kesan asid sitrik pada kekuatan mampatan dan keporosan adunan simen yang sudah keras. Analisis ini adalah untuk mengenal pasti kepekatan asid sitrik yang optimum memberi kesan kepada peningkatan prestasi pengikat asas OPC. Kepekatan asid sitrik yang berbeza dalam 0.5, 0.75, 1.0, 1.25 dan 1.5 milimole /L diadunkan bersama dengan pengikat asas OPC. Pengikat asas simen yang melekatkan akan diuji bagi menentukan penetapan masa dengan menggunakan ujian Vicat berdasarkan ASTM C191 dan ujian aliran simen basah berdasarkan C230 untuk kebolehkerjaan mereka. Simen yang telah keras dalam acuan kiub 50mm x 50mm x 50mm akan di uji untuk ujian seperti kekuatan mampatan dan ujian keporosan berpandukan ASTM C109 and C642. Spesimen akan dibuka dari acuan kiub selepas 24 jam. Spesimen simen akan diuji untuk hari pertama, hari ke 7 dan hari ke 28. Berdasarkan penetapan masa, asid sitrik cenderung untuk menjadi satu perencat simen pada kepekatan asid sitrik 0.5 milimole/L. Selain itu, peningkatan kepekatan asid sitrik juga memberi kesan kepada keporosan dan kekuatan mampatan tetapi penambahannya tidak menentu pada hari 1, 7 dan 28 berbandingan specimen yang di kawal. Oleh itu, kepekatan yang optimum adalah dalam sukatan 1.5 milimole/L asid sitrik yang akan meningkatkan prestasi asas pengikat OPC.

Kata kunci: Simen Portland biasa, asid sitrik, bahan campuran

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°C	Degree Celsius
m^2/kg	Meter square per kilogram
MPa	Megapascals
%	Percentage
pH	Power of hydration
g/mol	Gram per mole
milimole/L	Milimole per litre
g	Gram
mm	Milimetre
kg	Kilogram
min.	Minute
in.	Inci
kPa	Kilopascals
CaO	Calcium oxide
SiO_2	Silicon dioxide
Al_2O_3	Aluminium oxide
Fe_2O_3	Iron oxide
MnO	Manganese oxide
K_2O	Potassium oxide
TiO_2	Titanium dioxide
SO_3	Sulphur trioxide
CO_2	Carbon dioxide
Cl	Chlorine

LIST OF ABBREVIATIONS

OPC	Ordinary Portland Cement
ASTM	American Society for Testing and Materials
ACI	America Concrete Institute
ATS	Admixture Technical Sheet
MS	Malaysian Standard
CAA	Cement Admixture Association
HERA	Human and Environmental Risk Assessment
ASSHTO	American Association of State highway and Transportation Official
BS	British Standard

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Nowadays, Ordinary Portland Cement (OPC) is the main material as a binder that most widely used in the construction. The mixture of Ordinary Portland cement with water and aggregate will form the ubiquitous concrete that use in construction. According to Brandit (2009), the OPC binder will provide a good bond with the other components. Their role is to bind together fine and course aggregate grain and eventual fibre when mix together with water. The OPC basd binder also applied to cement paste that the OPC mixed together with water only.

To improving the properties of the OPC based binder in fresh and hardened state, the OPC based binder are added the special chemical compounds, natural minerals or other substance (Brandit, 2009) that called as concrete admixture. Normally, the admixture will be added in the small amount or quantities into the cement paste while mixing or manufacturing of OPC. The small amount of admixture will be added such as the small percentage from the mass of OPC or based on concentration of admixture from the mass of water.

The inclusion of admixture in OPC can give several effects. The effect of chemical admixture in OPC based binder is to improve the ability to control work time, workability, compressive strength and durability of OPC (David, n.d). Each type of chemical admixtures have their different function in performance of OPC, some been develop as retarder to slow down the hydration and some as accelerator to initiate the hydration in the lower temperature. The usage of admixture can reduce the cost of

performance of OPC. Although citric acid we know as retarder in concrete, but in certain dosage of citric acid will be as accelerator. Then, the several concentration of citric acid will mix together with OPC based binder to know the optimum concentration of citric acid can be used to give positive effect in OPC based binder.

Moreover, the present price of the additive commercial is higher than other concrete component. The usage of citric acid as alternative admixture will help to reduce the cost in construction. Between the types of additives at this time should be reviewed to identify the factors that contribute to the strength of concrete with previous studies. Therefore, this study aimed to investigate the effect chemical composition of citric acid which can easily be used as an alternative admixture in OPC based binder.

1.3 OBJECTIVES OF STUDY

In this research, there are three objectives that involve achieving the aim of the research on to study Citric Acid as Alternative Admixture for OPC based binder.

1.3.1 To determine the effect of Citric Acid on the workability of fresh binder cement paste.

1.3.2 To determine the effect of Citric Acid on the compressive strength and porosity of hardened cement paste.

1.3.3 To determine the optimum inclusion of citric acid that contributes to the improvement of OPC based binder performance.

1.4 SCOPE OF STUDY

The experiment will carry out to achieve the objective of study by using OPC type 1 that several use for general purpose. The OPC based binder are made by the mixing the OPC and water. Analytical reagent of citric acid ($C_6H_8O_7$) used as the proposed alternative admixtures in OPC based binder. The citric acid will prepared in different concentration which 0.5, 0.75, 1.0, 1.25 and 1.5 milimole/L of citric acid from the mass of water. The specimens will be compared with the control specimen which does not contain any admixture.

Performance of OPC based binder will be based on fresh and harden state of OPC based binder. In fresh OPC based binder, the workability performance will be conducted based on vicat setting time and flow table test. Afterwards, in hardened state of OPC based binder will be test by compressive strength test and porosity test. The specimens will be tested in Compressive Strength Test conducted on 1, 7, and 28 days. Then, porosity test will be conducted at 1, and 28 days of each specimen. Performance of these admixtures will be based on: Compressive Strength & Porosity Test and Workability Test.

1.5 RESEARCH SIGNIFICANCE

The aim of this research is to determine the suitability and the effectiveness of the citric acid as alternative binder for OPC based binder. There are many type of admixture that can be uses but in this research will prove the suitability concentration of citric acid as alternative admixture in OPC based binder. The optimum inclusions of citric acid that contribute the improvement of OPC based binder are analysed. To produce alternative admixture that can impact OPC based binder's workability of fresh OPC based binder. Finally, the OPC based binder are analyse inclusion of the citric acid indicates whether it is suitable as an admixture in hardened cement paste. Compressive strength and porosity test has been used as a basic indicator for evaluating the performance of this admixture in hardened OPC based binder.

CHAPTER 2

LITERATURE REVIEW

2.0 INTRODUCTION

Literature review is several studies which related to the project. Literature review was discussed the relevant materials and experiments which involves in OPC binder based. Besides that, the characteristics of OPC based binder and citric acids as an alternative admixture were discussed too. The experiments involve workability, compressive strength and porosity also discussed in this chapter. In addition, the past researches on alternative and the commercial admixture in OPC based binder will be discuss in this chapter. This chapter was a significant study for this project.

2.1 ORDINARY PORTLAND CEMENT (OPC)

2.1.1 Introduction of Ordinary Portland Cement (OPC)

Nowadays, for developing country like Malaysia, industrialization was the most activity in high demands to uplift the nation's economy growth. The construction sectors are the most important industry that helps in economy growth. The most important material that mostly use in construction is ordinary Portland cement in concreting stage. The OPC is the basic ingredient of concrete. The OPC is the fine powders have properties hardening when react with water and form a rigid chemical structure (Zhiang, 2011). When OPC combine with water, it will create a paste that will binds with sand and rock to harden as a concrete that called binder.

In 1824 Joseph Aspidin in England is the first person that made Portland cement by burning the powdered limestone and clay in his kitchen stove. By this method, he laid the based for the industry that annually processes literally mountains of limestone, cement rock and clay into a fine powder that can pass through a sieve (PCA, 2014). Then, Portland cement given name after the cement gives a colour and strength likely to the stone from the island of Portland in Southern England. There were some of the histories of OPC.

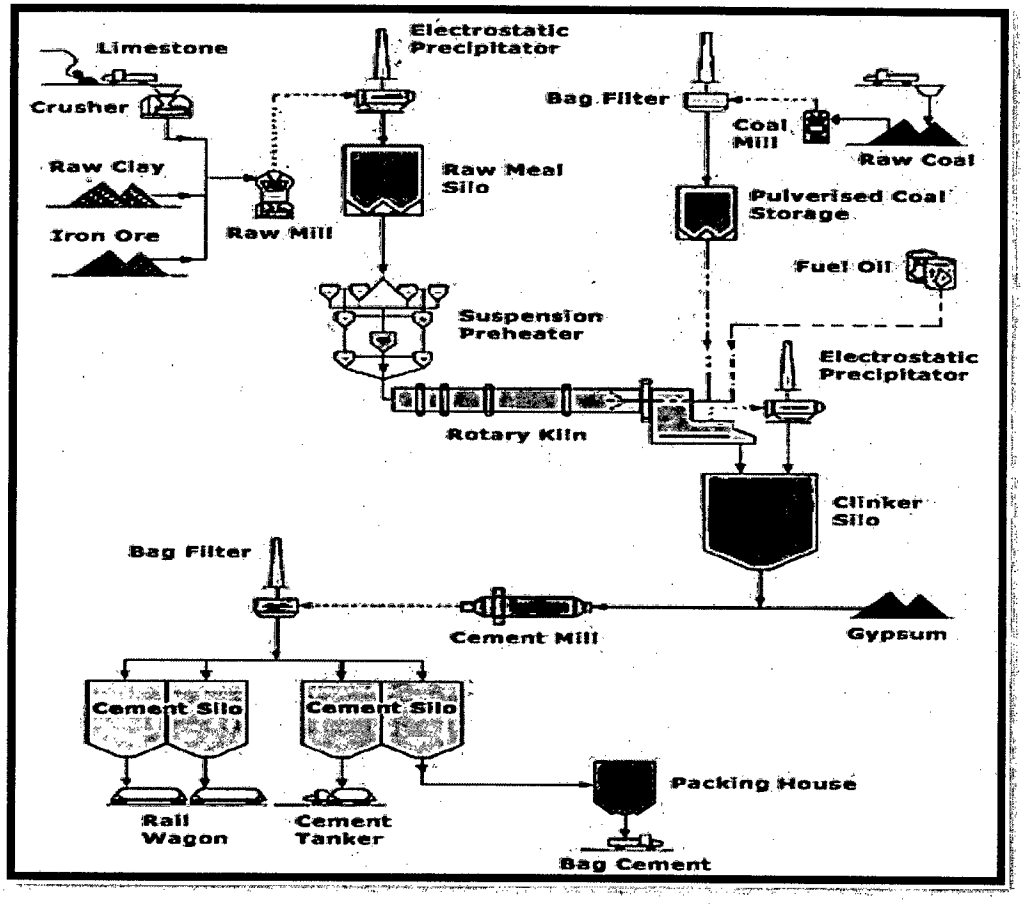

Figure 2.1: Process of production cement (www.tasekcement.com)

Figure 2.1 above showed the cement production process from the raw material until as Portland cement. There are the several ways to manufacture of cement through a dry or wet method. The commonly way in cement production is dry method. According to Lafarge (2014), the manufacture of OPC is required by several raw materials such as calcareous and argillaceous material. Limestone or chalk is the one of the calcareous

material and argillaceous material is such as shale or clay. All the materials are mixed together then burnt at the high temperature in 1400 °C into a rotary kiln to form clinker. Then, the clinker is cooled and grounded with a requisite amount of gypsum into the fine powder known as Portland cement.

The manufactured of OPC must be achieved the quality requirements specification of Malaysian Standard MS 522: Part 1: 1989, which likely based on British Standard BS 12. However, in European Union standard use the specify test for the cement to control their quality such as blaine method to test the fineness, vicat method to test their setting time, mortar cube to test the strength and Le'Chatelier method to test their soundness.

There is the standard that uses for classified the type of OPC. The OPC in the U.S are appropriate to the American Society for testing and Material (ASTM) C 150. In this standard describe several type of OPC in their specification and usage in Table 2.1 below. In this specification, the cement shall only contain the portland cement clinker, water or calcium sulphate, or both, limestone, processing additions, and air-entraining addition for air entering OPC (ASTM 105).

Table 2.1: Classification of Ordinary Portland Cement (OPC)

Cement Type	**Description**
Type I	Normal purpose
Type II	Moderate Sulphate resistance
Type III	High early strength
Type IV	Low heat hydration
Type V	High Sulphate Resistance
White	White colour

2.1.2 The Properties of OPC

Generally, OPC are characterized by their properties that contain in OPC that showed their physical and chemical properties of OPC. The physical property characterization may develop by physical test such as compressive test, vicat test, and many more. The physical properties of OPC are important to control the quality of OPC such as setting time, soundness, fineness and strength.

According to VTU learning, the setting time are used to characterizes how particular of cement paste. Then, the soundness is refers to ability of a hardened cement to retain its volume after setting without delay. Moreover, the fineness is to know the particle size of OPC that effect the rate of hydration and rate of strength. Finally, strength test to define the ability of OPC tend to the external load by compressive, tensile and flexural

Table 2.2: Physical Properties of OPC type 1

Physical properties of OPC		**Type I**
Fineness : minimum (m^2/kg)		280
Soundness: maximum, autoclay expansion (%)		0.8
Time of setting, minute	Initial set (min)	45
	Final set (max)	375
Compressive strength , MPa	1 day in moist air	None
	1 day moist air + 2 days water	12.4
	1 day moist air + 6 days water	19.3

Table 2.2 showed the physical properties requirement of OPC specified by ASTM C150. The explanation more about the test will be in experimental detail. The chemical properties of OPC also the most important to identify the chemical contain in OPC. But the way according to Camp (n. d.), even though the different of chemical composition of OPC may similar with the physical behaviour of OPC. The procedure to determine the chemical compound in OPC will be very complex and not very strict. The

test that required identify the chemical properties is chemical analysis by Bogue method or XRD method.

Based on research done by Sajedi and Razak (2011), the compositions cementitious materials in OPC are shown in table 2.3. The chemical compositions of OPC used in this their research by the X-ray fluorescence spectrometer (XRF) test. The Chemical compound that contain in OPC are calcium oxide (CaO), silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3), Manganese oxide (MnO), potassium oxide (K_2O), titanium dioxide (TiO_2), Sulfur trioxide (SO_3), Carbon dioxide (CO_2) and chlorine (cl). These proportion of oxide determine the proportions of the compound which affect the performance of the OPC.

Table 2.3: Compositions of cementitious materials

Oxide formula	**Percentage by mass**
CaO	64.09
SiO_2	18.47
Al_2O_3	4.27
Fe_2O_3	2.06
MnO	0.05
K_2O	0.28
TiO_2	0.22
SO_3	4.25
CO_2	4.20
Cl	0.02

According to Thomas and Jennings (2010), the OPC type 1 contains the fairly high tricalcium silicate, C_3S that gives good for early strength development of OPC based binder. There are the most high contain mineral that occupying between 40 % until 70 % in OPC. C_3S is highly reactive composite that can form in three different crystals structure in different temperature such as triclinic, monoclinic and rhombohedral. However, all these elements are similar in their reactivity. The C_3S in cement will forms clinker that contains 3% until 4% of oxide other than CaO and SiO_2.

Therefore, almost OPC contains one of the monoclinin polymorphs of C_3S. There are the most composite mineral in OPC type 1.

2.1.3 The Effect Usage of OPC Based Binder

As we know, the OPC is the traditional binders that use in the constructions. According Prabir et al, (2012) about 1 ton of carbon dioxide is emitted into the atmosphere in the production process of 1 ton of OPC. Therefore, we must to reduce the usage of OPC by increase the physical properties of OPC. By addition of some substances likely addictive that can improve the physical properties of OPC. That can cause of decreasing quantity of OPC as a binder in concreting but the similar performance with high quantity of OPC while concreting.

According to Oldcastle Material, there are common problems of concreting using OPC. One of them is discoloration cause by the variations in the concrete placing operation, finishing concrete too soon or too late and excessive or hard troweling. These problems can be prevents by addition of substance than can be accelerate the set time of concrete such as calcium chloride. Liquid calcium chloride does not cause discoloration. Each problem has their way to solve it. To improve the physical properties of OPC by addition of chemical solution that react to the chemical properties in OPC.

OPC based binder are form from the mixture of OPC and water. Ouellet et al (n. d.) studied that the cement paste mixtures were prepared to cementitious effect to isolate interaction between water and binder. Depending on contain of water in the hydration process of binder can precipitate in the paste and possibility generate cracks and loss of strength. So, the mineral that contain in water are important because can effected the chemical properties of OPC. To improve the performance of cement paste is by changing the chemical properties of water.

2.2 THE ADMIXTURE IN OPC

2.2.1 Introduction of Admixture in OPC

Admixture is the addition ingredient in the form powder and liquid in the concrete other than OPC, water and aggregate that will mix immediately before or during mixing (PCA, 2014). The advantage of usage admixture in concrete are to reduce the cost of construction, to ensure the quality of concrete during mixing, transporting, placing and curing and to overcome certain emergencies during concreting phase. The admixture that successful depends on the use of appropriate methods of batching and concreting. But the effectiveness of an admixture depends on several factors such as type and amount of OPC, water content, mixing time, slump, and temperature. Therefore, the admixture will give the benefit effect on OPC performance depend on several factors.

The function of each admixture is different between them depend on their needs. According to Whitney, (n. d.), some of admixture already have chemistry that effect physical and chemical properties of OPC and some have simple been combined for ease of addition while mixing process. The definition and specification of admixture are discussed in the ASTM C494 and America Concrete Institute (ACI). There classified into several type including retarder, accelerators, air entraining agent, water reducer, and superplastizers.

Each of them have their function such as retarder that allow for longer working time with minimal effect on final strength and accelerator develop as initiate the cement hydration process faster in lower temperature. Then, air entraining agent observes that air entrainment improved the resistance of concrete to freezing and thawing and water reducer allowed the concrete with much less water that produce higher strength and more durable. Finally, the superplasticizers adjust the plasticity of low water concrete to consistency that easily to pump up to higher elevation.

2.2.2 The Retarder Admixture

The retarding admixtures are used to delay the rate of setting of concrete. The combination of cement and water can produce a high temperature of fresh concrete that will cause the increasing the rate of hardening that can reduce the workability while placing and finishing. The solution for this effect is to reduce the temperature of OPC based binder by cooling the mixing water. Retarding admixture will delay the setting time of concrete and decrease the slump loss and increase the workability. According to Whiting and Dziedzic (1992), the addition of retarder resulted in an increased rate of slump loss compare to control mixtures.

The retarder admixture gives the benefit in fresh OPC based binder. But in harden state, admixture retarder reduce the early strength of OPC based binder. Therefore, there is some disadvantage of usage retarder admixture. But some of difference than mention in ATS 3 that the strength of concrete with water reducing admixtures, ultimate strength gains is increased by increasing water reduction. Previous studied by Ramachandran (1981), the presence of retarder effect the early strength of cement mortar are lower than control specimen. In the day 1 of compressive strength reduced from 11.8 Mpa down to 1.2 Mpa at addition rate 2% of phosphoric acid retarder, but in day 28 strength increase from 45 Mpa to 65 Mpa.

According to ATS 3, the level of retardation achieved is related to the level of dosage. Any increasing of dosage will effect an increasing of setting time. But, in the large overdoes of retarder can produce very long setting time that may not recover its strength. If the strength is still not found in a reasonable time, then it may not gain useful mechanical strength. They also will affect the time schedule working on site. Dias et al (2010) studied that the concrete with retarder overdose will eventually reach or exceed their corresponding 28 day strength. Hence, the overdose of retarder not appreciably affected the concrete strength gain.

2.2.3 The Accelerator Admixture

The accelerator admixture is used to accelerate the rate of hydration in OPC such as their setting time and harden OPC in early age. Accelerators are designated as Type C admixtures under ASTM C 494. According to Whitney, the chemical accelerator that commonly uses in industry is Calcium chloride ($CaCl_2$) especially for non-reinforcement concrete. The usage of calcium chloride as an accelerator admixture has been proved and provided much data about the effect of this chemical admixture. Calcium chloride can gain of strength in concrete. But the way, calcium chloride can causes the shrinkage in concrete and potential reinforcement corrosion and potential for scaling. It also can cause the discoloration in concrete. There are many negative effect usage calcium chlorides as an accelerator admixture in concrete.

According to CAA (2012), the rate of hydration of cement increase by accelerating admixture because they provide the earlier heat evaluation and strength development such as calcium nitrate and calcium nitrite. Both of them are the effective set accelerator that widely used commercially in construction. Nitrite gives some strength of acceleration in cement. Calcium nitrate provides corrosion protection against chloride against in concrete that will increase the service life of reinforced concrete structures because this chemical can provide basic protection for steel in concrete.

Accelerator admixture is suitable in many conditions such as in cold weather concreting, precast concrete, concreting under water, concrete highway and bridge construction. Accelerator admixture is formulated to reduce the setting time and produce high early strength in certain application concrete. Based on study by BRIENS (2014), Set accelerators are also known as quick set is normally used for urgent repair work especially in particular condition in tunnelling, mining and undersea concreting works. The chemical that commercially use are aluminium chloride, potassium carbonate, sodium fluoride, sodium aluminate and ferric salts.

2.3 THE CITRIC ACID AS ADMIXTURE

2.3.1 Introduction of Citric Acid

An acid is a chemical substance which aqueous solution was characterized by a sour taste, changed the blue litmus red and can react with the bases and certain metals to form salts. Acid solutions normally have pH value less than 7. If the value lower than 7 that's meaning the solution have the higher acidity and higher concentration of hydrogen ions in the solution. Reinhardt (1979) said that the substance or solutions that have the properties of an acid is considered as acidic substance.

There are many type of acid that used as an admixture in concrete, the commercially admixture that wisely use are fatty acids, sulfonic acid, organic acid salts, rosin acids and many more. There chemical acids are used as air-entraining admixture in concrete by ASTM C260. Therefore, in this study will inclusion the citric acid as admixture in OPC based binder that will test in fresh and hardened specimen. According from the test we will know the characteristic of citric acid that as retarder or accelerator in cement based binder.

Citric acid is the one of the most widely distributed plant acids and occurs in high concentration in lemon juices. This substance was found in variety of plants and fruits such as citrus fruit. Citric acid has been produced for many years with high volume and added to processed food and beverages as flavour or stabilizer. Then, in this study we apply acid citric as addictive in OPC based binder because it more affordable and available compare with other chemical. The usage of citric acid is very favourable ecology profile and wide dispersive use of citric acid does not give bad affect to the environmental. (HERA, 2005)

Citric acid with formula $C_6H_8O_7$ is the one of a weak organic acid that was produced as a white crystalline powder form in room temperature. Citric acid also have the molecular weight 192.12 g/mol. According from Wikispace (2014) Citric acid can exist as an anhydrous (water-free) form that crystallizes from hot water or as a monohydrate form when citric acid from cold water. Citric acid will decomposes when

heated above 175°C through the loss of carbon dioxide and water then citric acid will leaves a white crystalline precipitate. The citric acid is soluble in water. Therefore, citric acid is suitable to dissolve with water to mix together with OPC.

2.3.2 The Characteristic of Citric Acid as Admixture

The inclusion of admixture in concrete widely uses to increase the physical and mechanical properties of concrete. There are many chemical or organic compounds that suitable as admixture in concrete. Based on studied by Khalil (2009), the concrete that containing citric acid has good performance after 1980 day exposure to salt solution compare to control specimen. Therefore, citric acid are affected the chemical and physical properties of cement because the citric acid will reduce the pH and remove the calcium when drilling cement and reduce the crosslinking polymer ion. He also observed that the optimum dosage of citric acid is 0.02% by weight of cement. These results are conforming to ASTM C494 requirements for setting time that the delay in initial and final setting time must not less than 1 hour and not more than 3 and half hour relative to reference mix. Therefore, he concludes that citric acid can be categorized as retarder. But, it difference than this study because the dosage of the citric acid is depend on concentration (milimole/L) of citric acid from the mass of water.

The previous study by Mochner et al (2009) observed that citric acid can be used to retard the hydration of cement. Analysis of the solid phases showed that dissolution of alite and aluminate slowed down while analyses of the pore solution showed that citric acid was removed almost completely from the pore solution within the first hour of hydration. Thus, the citric acid retards the cement hydration not by complex formation, but by slowing down the dissolution of the clinker grain. That are the reason how citric acid can be a retard admixture in cement based binder.

Singh (1986) also observed the effect of the citric acid on the hydration of Portland cement. The results showed that the presence of citric acid indicate that 0.1 % citric acid accelerates but too high dose of citric acid retard the hydration of cement paste more than 0.1% citric acid. That was because the presence of 0.1% of citric acid causes the increasing of rate of heat evolution. But while increase the dosage of citric