

**STUDY ON POZZOLANIC REACTION AND FLUIDITY OF
BLENDED CEMENT CONTAINING TREATED PALM OIL
FUEL ASH AS MINERAL ADMIXTURE**

by

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LIST OF ABBREVIATIONS

AFt	:	Ettringite
AFm	:	Monosulfate
C	:	Cristobalite
C-A-H	:	Calcium aluminates hydrates
C-S-H	:	Calcium silicate hydrates
C ₃ A	:	Tricalcium aluminate, aluminate
C ₄ AF	:	Tetracalcium aluminoferrite, ferrite
C ₃ S	:	Tricalcium silicate, alite
C ₂ S	:	Dicalcium silicate, belite
CH	:	Calcium hydroxide (Ca(OH) ₂)
GPOFA	:	Ground palm oil fuel ash
K	:	Potassium aluminum phosphate
LOI	:	Loss on ignition
POFA	:	Palm oil fuel ash
Q	:	Quartz
SP	:	Superplasticizer
TGPOFA	:	Treated ground palm oil fuel ash
S _{BET}	:	BET (Brunauer, Emmett and Teller) surface area

**KAJIAN TINDAKBALAS DAN KEBENDALIRAN POZZALANA SIMEN
TERADUN YANG MENGANDUNGI ABU BAHAN API KELAPA SAWIT
SEBAGAI BAHAN TAMBAH MINERAL**

ABSTRAK

Tujuan kajian ini ialah untuk mengkaji tindakbalas pozzolana dan kebendaliran simen teradun yang mengandungi abu bahan api kelapa sawit sebagai bahan tambah mineral. Abu bahan api kelapa sawit (POFA) telah dikisar di dalam kempa bebola untuk menghasilkan abu bahan api kelapa sawit terkisar (GPOFA) dan dirawat pada suhu 500°C selama satu jam untuk mengeluarkan karbon tak terbakar untuk membentuk abu bahan api kelapa sawit terkisar terawat (TGPOFA). Bahan-bahan mentah telah dicirikan berdasarkan komposisi kimia, kandungan karbon, komposisi mineral, morfologi and sifat fizikalnya. Kebendaliran, haba penghidratan dan kereaktivitian pozzolana untuk simen teradun yang mengandungi GPOFA and TGPOFA serta dalam sistem GPOFA/TGPOFA telah dikaji. Sifat-sifat mekanikal simen teradun tersebut seperti kosistensi piawai, tempoh pensetan dan kekuatan mortar juga dikaji. Keputusan menunjukkan bahawa rawatan haba telah mengurangkan kandungan karbon tak terbakar dari 6.01% ke 0.07% yang meningkatkan fasa kekaca dari 67.22% ke 73.89% tanpa menyebabkan pengaglomeratan partikel. Hasil dari penurunan kandungan karbon ter terbakar dan peningkatan fasa kekaca ini telah meningkatkan kebendaliran dan kereaktivitian pozzolana TGPOFA dalam simen teradun. Kebendaliran pasta simen teradun yang mengandungi TGPOFA (10% - 40%) adalah menghampiri kebendaliran pasta OPC tanpa *superplasticizer* (SP) apabila 0.2% SP ditambah ke dalam pasta simen teradun.

TGPOFA mempunyai reaktiviti pozzolana rendah pada tahap awal penghidratan dengan jumlah haba penghidratan rendah pada hari ketujuh. Untuk mencapai kekuatan mampatan mortar melebihi 75% mortar OPC pada hari ke 28 dan 91 (jangka panjang) seperti yang ditetapkan oleh ASTM C 618, TGPOFA boleh digunakan sebagai bahan tambah mineral di dalam simen teradun masing-masing sehingga 20% dan 40% nisbah penggantian. Oleh itu, dapat disimpulkan bahawa penyahan karbon tak terbakar menyebabkan peningkatan dalam kebendaliran dan tindakbalas pozzolana untuk simen teradun yang mengandungi TGPOFA sebagai bahan tambah mineral.

**STUDY ON POZZOLANIC REACTION AND FLUIDITY OF BLENDED
CEMENT CONTAINING TREATED PALM OIL FUEL ASH AS MINERAL
ADMIXTURE**

ABSTRACT

The aim of this work is to study on pozzolanic reaction and fluidity of blended cement containing treated palm oil fuel ash as mineral admixture. Palm oil fuel ash (POFA) was ground in a ball mill to produce ground palm oil fuel ash (GPOFA), and further treated at 500 °C for 1 hour to remove the unburned carbon, namely treated ground palm oil fuel ash (TGPOFA). Raw materials have been characterized in terms of chemical composition, carbon content, mineral composition, morphology and physical properties. The fluidity, heat of hydration and pozzolanic reactivity of blended cement containing GPOFA and TGPOFA as well as pozzolanic reactivity in GPOFA/TGPOFA lime system were investigated, while the mechanical properties of blended cement such as standard consistency, setting time and mortar's strength were also studied. The results show that the heat treatment has reduced unburned carbon content from 6.01% to 0.07% with the increase in glassy phases from 67.22% to 73.89%, without causing the agglomeration of particles, improving the fluidity and pozzolanic reactivity of TGPOFA in blended cement. The fluidity of blended cement pastes containing TGPOFA (10%-40%) are approaching the fluidity of OPC paste without superplasticizer (SP), when SP at dosage of 0.2% is added to blended cement pastes. TGPOFA has low pozzolanic reactivity at the early stage of hydration with low total heat of hydration at 7 days. To achieve compressive strength of mortar higher than 75% of OPC mortar at the age of 28 and 91 days (long

term), as specified by ASTM C 618, TGPOFA can be used as mineral admixture in blended cement up to the replacement ratio of 20% and 40%, respectively. It can be concluded that the removal of unburned carbon results in the improvement of fluidity and pozzolanic reaction of blended cement containing TGPOFA as mineral admixture.

CHAPTER 1

INTRODUCTION

1.1 Introduction

In the manufacture of Portland cement clinker, the raw materials, typically a limestone and a clay or shale, are intimately mixed and heated, ultimately to a temperature of about 1450 °C (Taylor, 1997), and then grinding the product with approximately 5% of gypsum to produce cement (Bye, 1999). Cement production process is energy intensive as well as raw materials demanding and emits large amount of CO₂ which is responsible for the greenhouse effect that leads to climate change and increase in the earth temperature (Pipilikaki and Beazi-Katsioti, 2009). In order to reduce these impacts (CO₂ emission and raw materials demand), many cement producers are promoting the use of blended cement which results in lower CO₂ emission and lower energy consumption compared to ordinary Portland cement production (Pipilikaki and Beazi-Katsioti, 2009). Blended cement is a mixture of Portland cement with other mineral admixtures such as blast furnace slag, natural pozzolans, silica fume, metakaolin, fly ash and limestone added either during or after the finish grinding of cement in the ball mill (Aitcin, 2008). These mineral admixtures are generally called pozzolanic materials or pozzolans.

A pozzolanic material or pozzolan has been described as a siliceous or siliceous and aluminous material (Malhotra and Mehta, 2004). In the presence of moisture, amorphous SiO₂ and Al₂O₃ in pozzolanic material chemically react with calcium hydroxide which is released from the hydration of Portland cement to form

calcium silicate hydrates or calcium aluminates hydrates. This chemical reaction is known as pozzolanic reaction (Neville, 2002). The use of mineral admixtures in blended cement can improve the quality of cement paste or concrete by physical effect associated with the presence of very fine particle size and by chemical effects which are associated with pozzolanic reaction (FHWA, 1999). Strength and durability (such as resistance to thermal cracking, alkali-aggregate expansion, permeability, acid penetration and sulfate attack) are the main effects associated with the pozzolanic reaction. Mix proportion, fluidity and degree of hydration are caused by the physical effects associated with the particle size and morphology of mineral admixtures (Ramezaniapour, 1987).

The finely divided mineral admixtures have a physical effect in that they behave as fillers. This is particularly significant in the interfacial zone regions where they produce more efficient packing at the cement paste-aggregate particle interface which will reduce the amount of bleeding and produce a denser, more homogeneous, initial transition zone microstructure and also a narrower transition zone. Thus, relative to no cement replacement, partial replacement by ultra-fine solids results in a reduction in the strength of pastes (due to the dilution effect) but an increase in the strength of concrete (due to an improved transition zone) (Wild et al., 1996).

In addition, some mineral admixtures with spherical and smooth particles, i.e. good quality fly ash, enhance the fluidity of blended cement paste or concrete (Taylor, 1997); but some mineral admixtures such as rice husk ash, fly ash with high content of unburned carbon and palm oil fuel ash, would decrease the fluidity and increase the water demand of blended cement paste or concrete due to their angular

shape of particles and high surface area (fineness, porous particle and unburned carbon particle) (Lee et al., 2003a; Bui et al., 2005; Rukzon and Chindaprasirt, 2009a). In this respect, chemical admixture, especially superplasticizer (SP) (high range water reducer), need to be added into cement paste or concrete to improve the fluidity or workability rather than to increase the water-cement ratio which caused the decrease of strength and durability. The use of SP has become a common practice and was originally developed in Japan and Germany in the early 1960s and the United States in the mid of 1970s (FHWA, 1999). By adding SP, the fluidity or workability of blended cement paste or concrete can be enhanced; while the strength and durability can be improved due to the pozzolanic reaction. However, superplasticizer (P-34) effects only the early hydration of cement paste. The late stage of cement hydration is not influenced by adding SP (Sakai et al., 2006).

The use of well-known mineral admixtures such as fly ash, silica fume and blast furnace slag in the production of concrete and blended cement has been widely quoted (De Schutter, 1999; Mazloom et al., 2004; Sakai et al., 2005). On the contrary, the potential of using mineral admixtures from agro-waste ashes such as rice husk ash, saw dust ash, bagasse ash and especially palm oil fuel ash in production of concrete or blended cement have not been fully understood (Elinwa and Mahmood, 2002; Tangchirapat et al., 2007; Ganesan et al., 2008; Cordeiro et al., 2009). Palm oil fuel ash has attracted the attention of many researchers recently, because of its high silica content and good pozzolanic reactivity. The incorporation of palm oil fuel ash into blended cement or concrete as mineral admixture tends to improve the strength and durability due to its pozzolanic reactivity, but the fluidity is decrease because its particles are angular shape and have pore on the surface

(Jaturapitakkul et al., 2007; Sata et al., 2007; Chindaprasirt et al., 2008a; Tangchirapat et al., 2009b). Further studies on palm oil fuel ash as mineral admixture in blended cement are required to push for future application in concrete production.

1.2 Source and Production of Palm Oil Fuel Ash

Palm oil is an important product in tropical countries, especially in Malaysia, due to its wide spectrum of acknowledged usability such as precursors of food products and bio-fuel. The oil extraction process from fresh oil palm fruit requires the separation of the fresh fruit bunches (FFB) prior to further process, and produces more than 70% of fresh palm oil fruit to solid waste by-products in the form of fibers, nutshells, and empty fruit bunches. The shell and fiber are used extensively as fuel (biomass) for the production of steam in the palm oil mills, which provides a means of waste disposal and energy recovery (Tonnyopas et al., 2009) while the empty fruit bunch is sent to the incinerator, producing the ash which is being used widely as fertilizer in oil palm plantation area because of its potassium content which is a good nutrient for the soil.

There is approximately 5% of ash, known as palm oil fuel ash (POFA), being produced after combustion in the steam boiler. Due to the limitation of POFA's utilization, it has to be disposed as landfill materials, leading to potential future environmental problem (Sata et al., 2004). Figure 1.1 shows the estimated amount of solid waste by-product and POFA in Malaysia recorded by Malaysian Palm Oil Board (MPOB) (MPOB, 2010a; MPOB, 2010b). The shape of POFA is generally like rough grainy sand. The particle size is between 60 μ m to 2000 μ m with high porosity. The large particle sizes mostly are due to incomplete burning of fiber and

shell. Some particles are dark grey in color while others are white grey in color, depending on the content of unburned carbon. The major constituents of POFA are silica, calcium oxide, aluminum oxide, ferrite and potassium. The particle sizes and chemical composition of POFA are different in every palm oil mill because of the different ratios of fiber and shell used, as well as boiler operation condition.

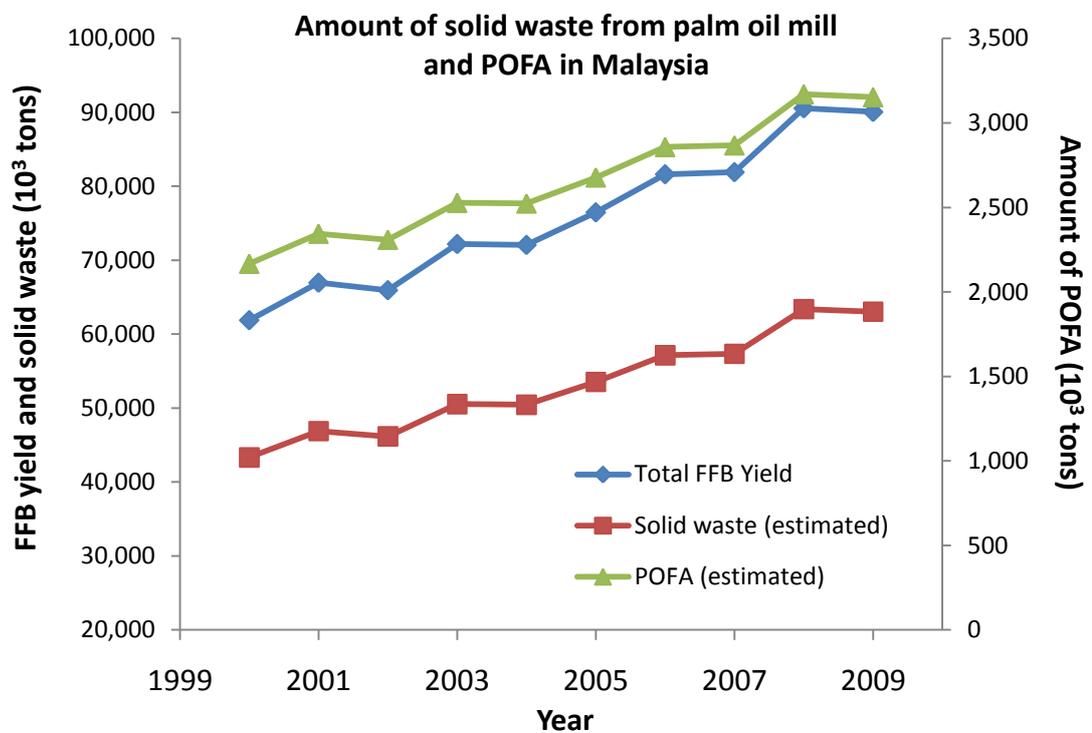


Figure 1.1: Amount of solid waste from palm oil mill and POFA in Malaysia (MPOB, 2010a; MPOB, 2010b)

1.3 Problem Statement

In recent years, many researchers have studied the use of agro-waste ashes as constituents in concrete, including rice-husk ash, saw dust ash and bagasse ash. These results revealed that these agro-waste ashes contained a high amount of amorphous silica and could be used as pozzolanic materials. The amorphous silica in these ashes reacts at ambient temperature with lime produced by the hydration of C₃S

and C_2S to form C-S-H similar to that produced by the direct hydration of C_3S and C_2S (Aitcin, 2008). POFA is also an agro-waste ash that contains large amount of silica and has high potential to be used as pozzolanic materials. In 2009, the MPOB estimated the amount of POFA produced in Malaysia is approximately 3 million tons (MPOB, 2010b). Because of the limited uses of POFA, it is currently disposed of as landfill which could lead to environmental problems in the future (Sata et al., 2004).

To solve this potential environmental problem, many researchers have studied the use of POFA as concrete admixtures. It has been reported that POFA has low pozzolanic properties and should not be used as a cement replacement in quantities greater than 10% by mass of binder (Tay, 1990). In order to improve the pozzolanic reactivity of POFA, ground POFA (GPOFA) has been investigated and it showed that GPOFA is a good pozzolanic material and can be used as a replacement in Portland cement up to levels of 20% and 30% for medium particle size (15.9 μm) and small particle size (7.4 μm), respectively (Tangchirapat et al., 2007). GPOFA also has good potential for preventing the expansion caused by alkali—silica reactions (Awal and Hussin, 1997). In addition, the sulfate resistance of concrete can be improved by adding GPOFA (Jaturapitakkul et al., 2007). The incorporation of GPOFA into concrete or mortar could improve the permeability as well as resistance to chloride penetration, but its irregular shape particle and pores on surface of particle causes the decrease of fluidity of cement paste or concrete. The dosage of SP also needs to be increased to maintain the same fluidity of concrete without GPOFA (Chindaprasirt et al., 2007a; Chindaprasirt et al., 2008a; Rukzon and Chindaprasirt, 2009a).

However, most of researches done previously were on the physical properties of concrete or mortar containing POFA and GPOFA (Jaturapitakkul et al., 2007; Rukzon and Chindaprasirt, 2009a; Chindaprasirt et al., 2007a). But the study on the chemical effects associated with its capability of providing siliceous and aluminous compounds from chemical reaction (pozzolanic reaction) with calcium hydroxide in the presence of water is not yet fully understood. The pozzolanic reactivity of POFA is supposed to be mainly influenced by the amorphous SiO_2 content and its composition, but there has not been much study on the quantitative data for the reaction ratio of POFA and the hydration of blended cement containing POFA yet. The reaction ratio of POFA in blended cement can be determined by using selective dissolution method as it has been used on blended cement containing fly ash and blast furnace slag (Ohsawa et al., 1985).

Moreover, the pozzolanic activity is due to the presence of SiO_2 and Al_2O_3 in the glassy phase (amorphous), thus it is necessary to determine the content of crystalline phase and glassy phase in POFA. The mineralogical compounds which determine how a mineral admixture influences the important engineering properties of concrete or cement paste such as workability, strength and durability, but it is not so much about the chemical composition of mineral admixture (Malhotra and Mehta, 2004). Semi-quantitative XRD analysis can be used to determine mineralogical compounds (such as crystalline phase and glassy phase) in POFA as it already has been applied to quantify those in fly ashes by using CaF_2 as internal standard (Lee et al., 2003b).

In addition, when SP is added to cement paste or concrete to improve the fluidity, the unburned carbon in POFA is the most important factor to consider. Lee et al., (2003a) reported that unburned carbon in fly ash adsorbed a lot of SP compared with the other particles in cement paste, and it can be removed by treatment at 500 °C for 3 hours which neither glassy phase crystallization nor particle agglomeration occurred (crystallization and particle agglomeration are prohibited to prevent the changing of pozzolanic properties). In this consideration, treated ground palm oil fuel ash (TGPOFA) without unburned carbon needs to be studied in order to improve the fluidity of blended cement paste, especially the study on the effect of unburned carbon with SP on the fluidity and early hydration of blended cement paste such as fluidity, adsorption of SP and heat of hydration.

1.4 Objective

- To study the properties of ground palm oil fuel ash after the heat treatment (TGPOFA), in terms of carbon content, crystallization and agglomeration of particles.
- To study the fluidity and heat of hydration of blended cement pastes containing GPOFA and TGPOFA.
- To study the pozzolanic reaction of blended cement containing GPOFA and TGPOFA using several chemical quantitative methods (calcium hydroxide content and reaction ratio of GPOFA & TGPOFA), qualitative methods (phase analysis by XRD) as well as its mechanical properties (standard consistency, setting time and compressive/flexural strength). The pozzolanic reactivity of GPOFA and TGPOFA in GPOFA/TGPOFA-lime system will also be investigated.

A good understanding on pozzolanic reaction and fluidity of blended cements containing GPOFA and TGPOFA are the key factors to produce good quality blended cement.

1.5 Scope of Research

The scope of research is designed to cover the four essential elements such as characterization of raw materials, fluidity and heat of hydration of blended cement paste with and without SP (fluidity, SP adsorption and heat of hydration), pozzolanic reactivity of GPOFA and TGPOFA (GPOFA/TGPOFA-lime system and blended cement hardened pastes) and mechanical properties of blended cement (setting time and strength).

The scope of investigations in this work is as follows:

- ❖ Characterization of raw materials in terms of their chemical composition, mineral phase composition, unburned carbon content, morphology, particle shapes, specific gravity, particles size distribution, Blaine surface area and BET specific surface area.
- ❖ Fluidity and heat of hydration of blended cement paste: Fluidity, SP adsorption and heat of hydration of blended cement paste.
- ❖ Pozzolanic reactivity (GPOFA/TGPOFA-lime system): Calcium hydroxide (lime) content and phase analysis of hydrated products after hydration.
- ❖ Pozzolanic reactivity of GPOFA and TGPOFA in hardened paste: Hydration products, calcium hydroxide content and reaction ratio of GPOFA and TGPOFA.

- ❖ Mechanical properties of blended cement paste such as its standard consistency and setting time as well as compressive strength and flexural strength of blended cement mortar.

CHAPTER 2

LITERATURE REVIEWS

2.1 Introduction

The cement industry has made great progress over the past 100 years, going from a process adapted from the manufacturing of lime to an entirely automated process in modern cement kilns that can produce up to 10,000 tons of Portland cement clinker per day. However, the first petroleum crisis has forced cement producers to start looking for more energy-efficient ways of producing Portland cement as early as the 1970s whereby the industry is urged to decrease its CO₂ emission significantly. In order to further decrease its CO₂ emission from the raw materials (lime stone); the industry has further moved forward to promote the use of blended cement.

Blended cement is a combination of Portland cement with mineral admixtures (pozzolanic material) such as fly ash, slag, metakaolin and silica fume added either during or after finish grinding of cement (Bouzoubaâ et al., 2000; Singh et al., 2002; Aitcin, 2008). Mineral admixture is commonly used to improve the performance of blended cement paste or concrete in terms of fluidity, strength and durability; hence could reduce the costs, the environmental impact and demand for raw materials for cement production.

However, some mineral admixtures such as rice husk ash, fly ash with high content of unburned carbon and palm oil fuel ash decrease the fluidity of blended

cement paste. Superplasticizer, which is high range water reducer, is commonly added to improve the fluidity or workability of blended cement containing these mineral admixtures (Lee et al., 2003a; Bui et al., 2005; Rukzon and Chindapasirt, 2009a).

2.2 Components of Blended Cement

Blended cement is a mixture of Portland cement with mineral admixture. In the past, mineral admixtures were added to Portland cement without considering the potential interaction, but today blended cement is manufactured to meet a performance specification which is normally set to improve the strength and durability. Blended cements can help in controlling some problems in concrete such as corrosion of steel, salt scaling, cracking, external sulfate attack, chloride-ion penetration, failure due to freezing and carbonation. In addition, blended cement can reduce the permeability of concrete which prevents easy diffusion of water and salt into concrete.

Mineral admixture in blended cement is a pozzolanic material that can produce the important cementing material needed in concrete through a chemical reaction, called pozzolanic reaction. These additions will reduce the large pores and amount of calcium hydroxide, which is a product of the hydration of Portland cement but its effect does not contribute to strength development, in concrete. In contrary, the addition of mineral admixture will increase the amount of calcium silicate hydrates (C-S-H) which contributes to strength development and durability of concrete (Tay and Show, 1994; Bouzoubaâ et al., 2001; Hossain, 2003; Uzal and Turanli, 2003; Chindapasirt et al., 2005; Pane and Hansen, 2005; Hossain, 2008).

However, some mineral admixtures reduce the fluidity of blended cement paste. Thus, superplasticizer is added to improve the fluidity (Lee et al., 2003a).

2.2.1 Ordinary Portland Cement (OPC)

The manufacture of ordinary Portland cement requires raw materials which contain lime, silica, alumina and iron. The sources of these elements vary from one manufacturing location to another, but once these materials are obtained, the process is rather uniform (Marotta and Herubin, 1997). The process of manufacturing Portland cement consists essentially of grinding the raw materials, mixing them intimately in certain proportions and burning in a large rotary kiln at a temperature of up to about 1450 °C, and the clinker is formed when the material sinters and partially fuses into balls. The clinker is cooled and ground into a fine powder, with some gypsum added, and the resulting product is the commercial Portland cement, which is Ordinary Portland cement (OPC), which is widely used throughout the world (Neville, 2002).

Ordinary Portland cement is composed of four basic chemical compounds such as alite (tricalcium silicate, C_3S), belite (dicalcium silicate, C_2S), aluminate (tricalcium aluminate, C_3A) and ferrite (tetracalcium aluminoferrite, C_4AF). These mineral compounds can be calculated by Bogue's equations based on the chemical composition results.

Each compound of OPC has a different behavior and effect on the properties of OPC such as rate of hardening, strength development and evolution of heat of hydration (Eglinton, 1987). Taylor (1997) reported that C_3S is the most important of

the constituent phases for strength development at the age up to 28 days because it reacts relatively quickly with water. C_2S reacts slowly with water and contributes little to the strength during the 28 days, but substantially to further increase the strength that occurs at later ages. By one year, the strengths obtainable from pure alite and pure belite are about the same under comparable conditions. C_3A reacts rapidly with water and cause undesirably rapid setting unless a set-controlling agent, usually gypsum, is added. For C_4AF , the rate at which it reacts with water appears to be somewhat variable, perhaps due to differences in composition or other characteristics, but in general is high initially and low or very low at later ages.

In addition to the compound composition, the fineness of cement also affects its reactivity with water. Generally, the finer the cement, the more rapidly it will react. The strength development can be enhanced by finer grinding of cement as shown in Figure 2.1 (Neville, 2002); however, the cost of grinding and the heat evolved on hydration set some limits on the fineness. The fineness of cement can be determined by either particle size distribution or surface area analysis (Blaine Air Permeability Method) (Mehta and Monteiro, 2006).

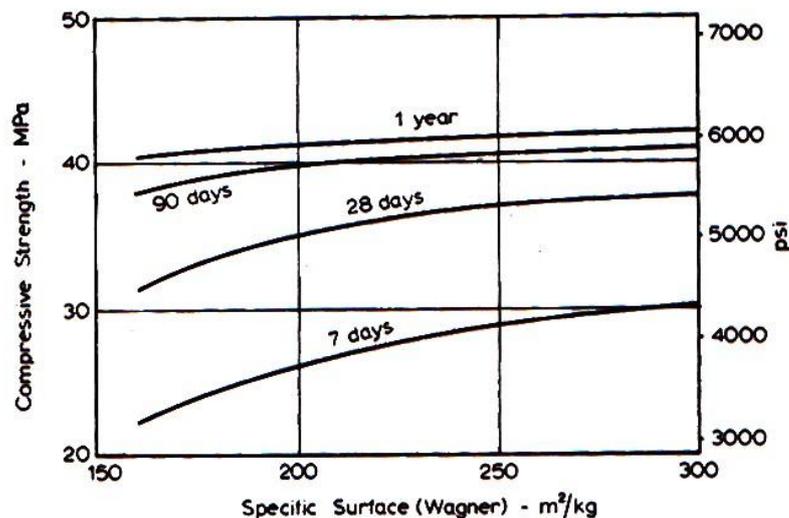


Figure 2.1: Relation between strength with surface area of cement (Neville, 2002)

2.2.2 Mineral Admixture

Pozzolanic materials or pozzolans are generally classified as mineral admixture in blended cement production (Malhotra and Mehta, 2004). Pozzolanic material has been found in lime-pozzolan composite as construction material during the Roman Empire. One source of pozzolan was an ash produced by the volcanic eruption of Mount Vesuvius in 79 A.D., which destroyed Pompei, Herculaneum and several towns along the Bay of Naples. In fact, it was in Italy that the term, “Pozzolan” was first used to describe the volcanic ash mined at Pozzuoli, a village near Naples. It should be noted that a similar natural ash which is a result of volcanic eruption in Santorini Island around 1500 B.C., had been in use for making lime-pozzolan mortar in Greece, much before the word Pozzolan was coined or expressed.

Mineral admixture which can either be natural or by-product pozzolanic material (Table 2.1) has been described as a siliceous or siliceous and aluminous material (Mindess et al., 2003).

Table 2.1: The common pozzolanic materials (Mindess et al., 2003)

Category	Typical materials	Active components
Natural materials	Unaltered volcanic ash	Aluminosilicate glass
	Weathered volcanic ash (tuff, trass, etc.)	Aluminosilicate glass; zeolites
	Pumice	Aluminosilicate glass
	Diatomaceous earth	Amorphous hydrated silica
	Opaline cherts and shales	Hydrated silica gel
By-product materials	Fly ash – Class F	Aluminosilicate glass
	Fly ash – Class C	Calcium aluminosilicate glass
	Silica fume	Amorphous silica
	Rice husk ash	Amorphous silica
	Calcined clays	Amorphous aluminosilicate

In the presence of moisture, it chemically reacts with calcium hydroxide (Ca(OH)_2) (pozzolanic reaction) to produce cementitious products such as calcium silicate hydrate, calcium aluminum hydrate, and sulfoaluminate (ASTM C 595, 1975; Neville, 2002).

2.2.2.1 Natural Pozzolans

All natural pozzolanic materials are derived from volcanic rocks. Volcanic eruptions launch into the atmosphere large quantities of molten lava, which is composed mainly of aluminosilicates. Quick cooling of lava results in the formation of vitreous phases (glass) with disordered structure or poorly crystalline minerals. Also, the escaping gases and water vapor impart to the volcanic material a porous texture with a high surface area. A combination of glassy or poorly crystalline structure and high surface area is the cause for the reactivity of aluminosilicate phases present in volcanic ash as mineral admixture with calcium hydroxide at normal temperature in blended cement (Rodríguez-Camacho and Uribe-Afif, 2002; Çolak, 2003; Malhotra and Mehta, 2004; Turanli et al., 2004). Some natural pozzolans may cause problems because of their physical properties (angular and porous form) but it can be improved by calcination in the range of 550–1100 °C, depending on the material itself (Davraz and Gunduz, 2005).

2.2.2.2 By-product Pozzolans

Calcined clay and shale are by-product pozzolanic materials which come from the calcinations of clay minerals at temperatures between 600–900 °C where the crystalline structure of aluminosilicate minerals present in clay can be destroyed. In fact, before the arrival of fly ash, calcined clay and shale have been frequently

employed as a mineral admixture for construction of many mass concrete structures (Malhotra and Mehta, 2004; Toledo Filho et al., 2007; Fernandez et al., 2011).

Metakaolin is essentially a poorly anhydrous crystallized aluminosilicate by product produced by calcining kaolin, a naturally occurring clay basically containing kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), at temperatures between 500 °C to 800 °C (Moulin et al., 2001; Souza and Dal Molin, 2005; Al-Akhras, 2006). It is a silica-based product that reacts with $\text{Ca}(\text{OH})_2$ producing CSH gel at ambient temperature. Metakaolin also contains alumina that reacts with $\text{Ca}(\text{OH})_2$ to produce additional alumina-containing phases, including C_4AH_{13} , C_2ASH_8 and C_3AH_6 (Ambroise et al., 1994; He et al., 1995; Zhang and Malhotra, 1995)

Fly ash is a by-product during the coal power generation and consists mainly of SiO_2 , Al_2O_3 , Fe_2O_3 and CaO . The molten ash particles which passed the combustion zone are cooled rapidly from 1500 °C to 200 °C in a few seconds and they form spherical particles in amorphous glass with small amount of crystalline minerals such as quartz and mullite (Qian et al., 2001; Fu et al., 2002; Malhotra and Mehta, 2004). Fly ash is removed by the dust collection systems from the exhaust gases of fossil fuel power plant as very fine, predominantly spherical glassy particles from the combustion gases before they are discharged into the atmosphere. The size of particles is largely dependent on the type of dust collection equipment. Diameter of fly ash particles ranges from 1–150 μm . It is generally finer than Portland cement (Siddique, 2008). Because of high fineness and pozzolanic reactivity, fly ash is widely used as mineral admixture in blended cement to improve properties of

concrete (Bouzoubaâ et al., 2000; Bouzoubaâ et al., 2001; Fu et al., 2002; Chindapasirt et al., 2004; Chindapasirt et al., 2005).

Granulated Blast Furnace Slag is a by-product of the manufacturing of iron in a blast furnace where iron ore, limestone and coke are heated up to 1500 °C (Pal et al., 2003; Bellmann and Stark, 2009). When materials in the blast furnace melt, molten iron and molten slag are produced, where molten slag which is lighter floats on top of the molten iron. Molten slag is rapidly cooled through high-pressure water jets forming granular slag comprising 95% of non-crystalline calcium-aluminosilicates. The granulated slag is further processed by drying and then ground to a very fine powder, which is ground granulated blast furnace slag (Malhotra and Mehta, 2004; Siddique, 2008). The main constituents of ground granulated blast furnace slag are CaO, SiO₂, and Al₂O₃. It also contains small amount of MgO, FeO, and sulphide such as CaS, MnS, and FeS (Kumar et al., 2008). Ground granulated blast furnace slag has been widely used as a successful mineral admixture in blended cement to improve some properties in concrete and to bring environmental as well as economic benefits, due to its pozzolanic reactivity which is determined by the quantities and the properties of amorphous glass, as well as the chemical compositions (Osborne, 1999; Escalante et al., 2001; Sobolev, 2005; Binici et al., 2007).

Silica fume is a by-product of the manufacture of silicon or of various silicon alloys. It contains more than 80–85% SiO₂ in amorphous form, which is suitable to use as mineral admixture in blended cement to improve the qualities of concrete or mortar (Langan et al., 2002; Rao, 2003; Yajun and Cahyadi, 2003; Song et al., 2010),

because silica fume acts both as a chemical inert filler, improving the physical structure, and as a pozzolanic material, reacting chemically with $\text{Ca}(\text{OH})_2$ which is formed during hydration of cement (Zhang and Gjrv, 1991; Zelic et al., 2000; Song et al., 2010). Before the mid-1970s, nearly all silica fumes were discharged into the atmosphere. After environmental concerns necessitated the collection and landfilling of silica fume, it became economically justified to use silica fume in various applications (FHWA, 1999). In the process, SiO_2 vapors are produced which oxidize and condense in the form of very tiny spheres of non-crystalline silica (0.1 μm average diameter) which is high pozzolanic material (El Sökkary et al., 2004). Silica fume is light and has a low bulk density, which may cause difficulty in transporting and handling. Thus, the processing of silica fume is generally carried out in the form of slurry or a pelletized product to increase its bulk density (Boddy et al., 2000; Malhotra and Mehta, 2004).

Rice husk is an agricultural by-product material. It constitutes about 20% of the weight of rice. It contains about 50% cellulose, 25–30% lignin, and 15–20% of silica (Siddique, 2008). When rice husk is converted to ash by uncontrolled burning below 500 °C, the ignition is not complete burning resulting in a considerable amount of unburnt carbon containing in the rice husk ash (Al-Khalaf and Yousif, 1984). The content of carbon in rice husk ash, which has an adverse effect, should not be in excess of 30%. The ash which is produced by controlled burning of the rice husk between 550 °C and 700 °C for 1 h contains high amount of silica in amorphous phase. The produced ash need to be ground to a required fineness before been used as mineral admixture in blended cement to improve the strength and durability of

concrete (Bui et al., 2005; Saraswathy and Song, 2007; Chindaprasirt et al., 2007b; Ganesan et al., 2008; Chatveera and Lertwattanaruk, 2011).

Palm oil fuel ash is the by-product pozzolanic material from the boiler in palm oil mill (Tonayopas et al., 2009). Due to the limitation of palm oil fuel ash's utilization, it has to be disposed as land fill materials, leading to potential future environmental problem (Sata et al., 2004). The major constituents of palm oil fuel ash are silica, calcium oxide, aluminum oxide, ferrite and potassium. The high silica content in palm oil fuel ash, the high potential of using it as mineral admixture in blended cement to improve the strength and durability of concrete (Abdullah et al., 2006; Tangchirapat et al., 2009a).

2.2.3 Superplasticizer as Water Reducer

The water-reducing admixtures are group of products which possess the ability to produce concrete or cement paste of a given workability at a lower water-cement ratio than that of a control concrete or cement paste without admixture (Rixom and Mailvaganam, 1999).

Superplasticizer, which is known as high range water reducer, was originally developed in Japan and Germany in the early of 1960s and were introduced in the United States in the mid-1970s (FHWA, 1999). Currently, six different types of superplasticizers are used (Siddique, 2008):

- Sulphonated salts of polycondensates of naphthalene and formaldehyde known as “naphthalene polysulphonates” or, more simply, “polynaphthalene”.

- Sulphonated salts of polycondensates of melamine and formaldehyde known as “melamine polysulphonates” or, more simply, “polymelamine”.
- Lignosulphonates having a very low content of surface active agents and sugar.
- Polycarboxylates
- Polyacrylates
- Poly-phosphonates and different copolymers.

When using a superplasticizer, it is possible to make cement paste with a water-binder ratio lower than 0.30 having a high fluidity. It is even possible to make fluid reactive powder cement paste having a water-binder ratio lower than 0.20. When superplasticizer which is commonly used to disperse cement particles is added, the yield value of the paste decreases close to zero, but the plasticity does not decrease significantly. Thus, the cement paste will obtain good flow ability without ingredient segregation (Termkhajornkit and Nawa, 2004).

During grinding of clinker and gypsum results in the development of a great number of electrical charges on the surface of cement particles: essentially, negative charges on C_3S and C_2S particles and positive charges on C_3A and C_4AF particles. When these cement particles come into contact with a liquid such as polar as water, they have a strong tendency to flocculate as can be seen schematically in Figure 2.2 (a). With the presence of superplasticizer, the adsorption of the superplasticizer molecules is possible on negative sites due to the presence of Ca^{2+} ions that bridge the cement particle and the superplasticizer molecule (Figure 2.2 (b)). When these two cement particles are covered with superplasticizer molecules, they repel each

other as shown in Figure 2.2 (c). It is well accepted that polynaphthalene and polymelamine sulphonate molecules work essentially under this mode of repulsion. Figure 2.2 (d) represents a case of steric repulsion between two molecules of superplasticizer that are adsorbed on two cement particles. The adsorption of superplasticizer molecules on hydrated phases creates an electrostatically charged germ which participates to the electrostatic repulsion and avoids flocculation (Prince et al., 2002; Siddique, 2008; Hallal et al., 2010).

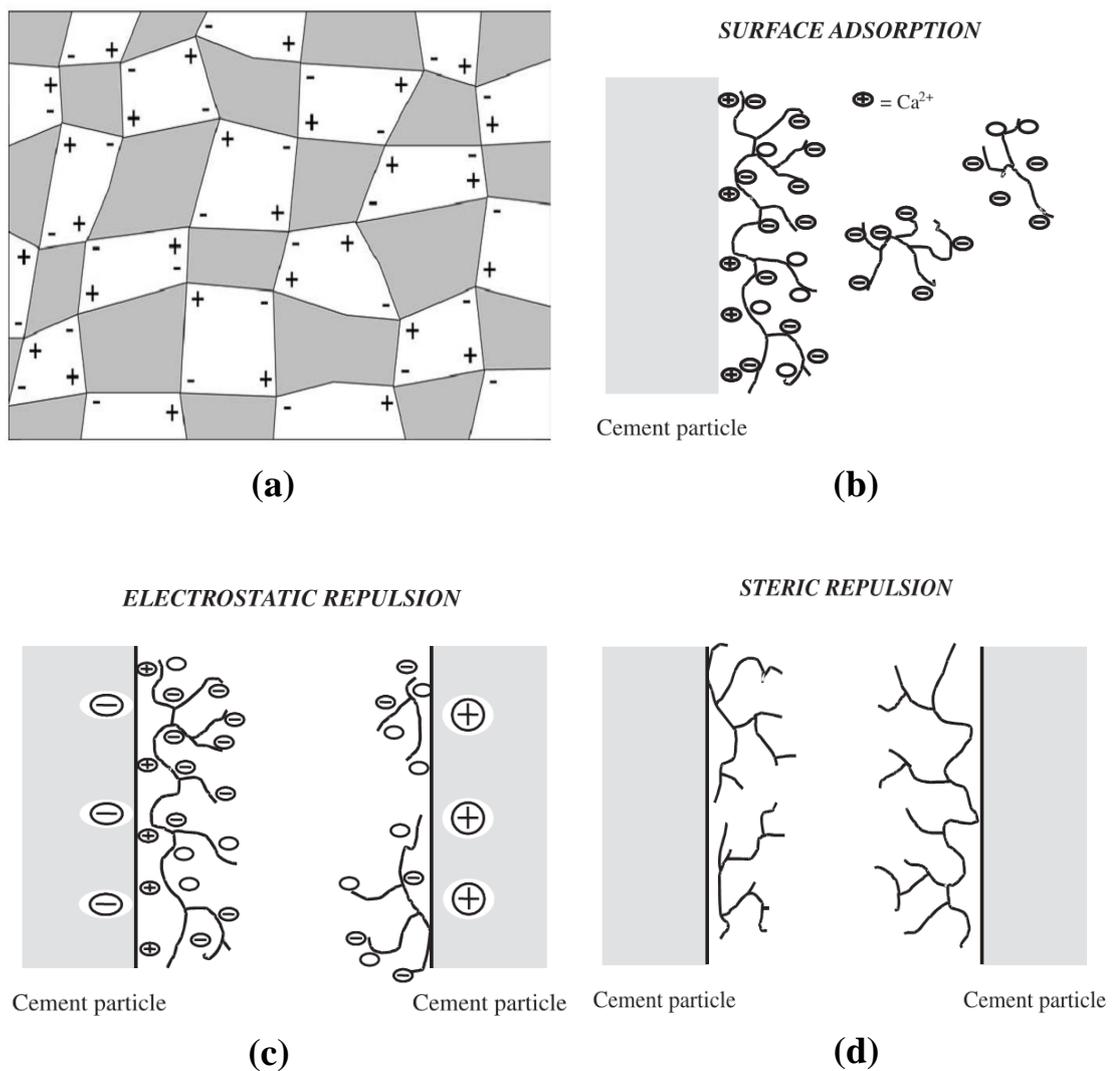


Figure 2.2: (a) Flocks of cement particles, (b) Adsorption of superplasticizer molecules on a cement particle, (c) Electrostatic repulsion and (d) Steric repulsion (Siddique, 2008)

The double physico-chemical action of the molecules of a superplasticizer can be very easily seen by adiabatic calorimetry: the use of a superplasticizer moves the maximum of the heat flux. When a small amount of superplasticizer is added, the peak of heat of hydration appears sooner than in a water/cement system without superplasticizer. The peak of heat of hydration is delayed when the superplasticizer dosage increases. This initial accelerating effect is explained by a better deflocculation of the cement particles which results in a more homogeneous dispersion of the cement particles within the suspension. However, as the superplasticizer dosage increases, this accelerating effect disappears, because the adsorption of the superplasticizer molecules on the surface of the cement particles prevents them from reacting with water. Not only the peak is delayed, but the heat of evolution rate is also not as high. This simple experiment shows that the action of superplasticizer molecules is not simply physical but that there is a chemical action taking place simultaneously (Aitcin, 2008).

In addition, when superplasticizer is added to blended cement paste to improve the fluidity, the unburned carbon in POFA is the most important factor to consider. It is reported that unburned carbon in fly ash adsorbs a lot of superplasticizer compared with the other particles in cement paste due to its large surface area (Lee et al., 2003a). It means that the higher the surface area of blended cement, the more the adsorption of superplasticizer. On the other hand, superplasticizer effects only on the early hydration of cement paste. The late stage of cement hydration is not influenced by adding superplasticizer (Sakai et al., 2006).

2.3 Palm Oil Fuel Ash as Mineral Admixture in Blended Cement

2.3.1 Palm Oil Production in the World

Malaysia and Indonesia are the world's largest producers of palm oil production according to U.S Department of Agriculture. Malaysia was the world leader of palm oil production for a few decades, but a significant change in the palm oil industry has taken place during the past few years, as Indonesia surpassed Malaysia in production of palm oil and now is the world leader as shown in Figures 2.3 and 2.4.

World production 2008-2009 (43.49 million metric tons)

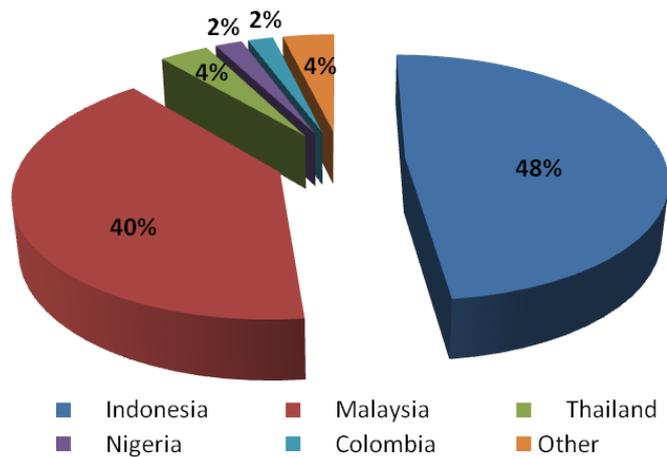


Figure 2.3: World palm oil production 2008-2009 (U.S Department of Agriculture, 2010)

World production 2009-2010 (44.82 million metric tons)

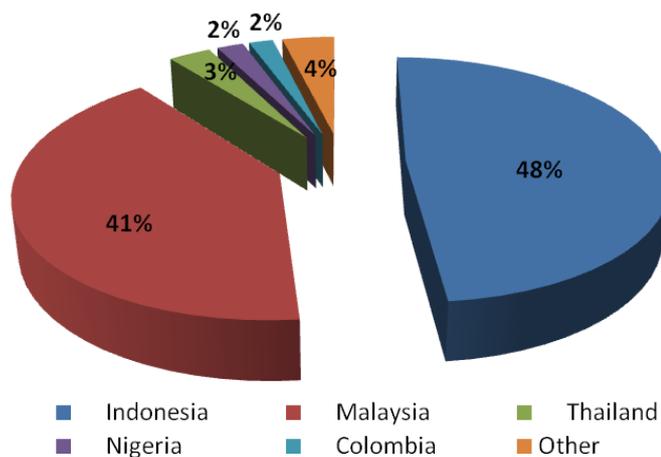


Figure 2.4: World palm oil production 2009-2010 (U.S Department of Agriculture, 2010)

Malaysia was the second largest producer of palm oil with around 40% and 41% of the total world supply in years 2008-2009 and 2009-2010, respectively. Indonesia is the world largest producer with 48% of the total world production of palm oil in both years 2008-2009 and 2009-2010. Another 12% of world palm oil production in 2008-2009 comes from Thailand (4%), Colombia (2%), Nigeria (2%) and others (4%) (U.S Department of Agriculture, 2010).

Based on the statistics of Malaysian Palm Oil Board (MPOB), the fresh fruit bunch (FFB) yield is around 20.18 and 19.2 tons per hectare in the year 2008 and 2009 respectively as shown in Table 2.2 with the total production of fresh fruit bunch around 90,566,972 tons and 90,070,272 tons in the year 2008 and 2009, respectively (MPOB, 2010a; MPOB, 2010b).

Table 2.2: Fresh fruit bunch (FFB) yield in Malaysia (MPOB, 2010a; MPOB, 2010b)

Year	FFB Yield (Tons/ Hectares)	Oil Palm Area (Hectares)	Total FFB Yield (Tons)
2000	18.33	3,376,664	61,894,251
2001	19.14	3,499,012	66,971,090
2002	17.97	3,670,243	65,954,267
2003	18.99	3,802,040	72,200,740
2004	18.60	3,875,327	72,081,082
2005	18.88	4,051,374	76,489,941
2006	19.60	4,165,215	81,638,214
2007	19.03	4,304,913	81,922,494
2008	20.18	4,487,957	90,566,972
2009	19.20	4,691,160	90,070,272