THE DURABILITY PROPERTIES AND MECHANICAL STRENGTH PERFORMANCE OF COAL ASH HYBRID GEOPOLYMERIC COMPOSITE

CHUNG KOK YAW

UNIVERSITI SAINS MALAYSIA

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by

CHUNG KOK YAW

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C_3A	Tricalcium Aluminate
$Ca(OH)_2$	Calcium Hydroxide
CO_2	Carbon dioxide
C_3S	Alite or Tricalcium Silicate
C_2S	Belite or Dicalcium Silicate
C-S-H	Calcium Silicate Hydrate
EDX	Energy-Dispersive X-Ray Spectroscopy
GGBS	Ground Granulated Blast Furnace Slag
HVFA	High Volume Fly Ash
PLC	Portland Limestone Cement
PFA	Pulverised Fuel Ash
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction
OPC	Ordinary Portland Cement

CIRI-CIRI KETAHANAN DAN PRESTASI KEKUATAN MEKANIK KOMPOSIT ABU ARANG BATU HIBRID BERGEOPOLIMER

ABSTRAK

Pengunaan Portland simen dalam penghasilan konkrit semakin meningkat dalam industri pembinaan. Pada masa yang sama, prestasi simen juga menghadapi pelbagai cabaran seperti memerlukan kekuatan yang tinggi, ketahanan yang baik dan sebagainya. Oleh itu, bahan binaan geopolimer telah digunakan untuk mengatasi caraban-cabaran teknikal ini. Kajian eksperimen ini dijalankan untuk mengaji sifat-sifat fizikal dan kimia seperti prestasi ketahanlasakan dan kekuatan mekanikal mortar yang mengandungi Bahan binaan seperti sanga daripada penghasilan besi iaitu GGBS dan sisa habuk daripada pembakaran arang batu iaitu PFA bersamaan aktivasi beralkali daripada simen Portland yang mengandungi batu kapur yang tinggi. Dengan proses aktivasi penggilingan selama 2 jam di antara PFA dan GGBS dalam pengisar bola besi selama dua jam, keputusan kajian ini menunjukan sebanyak 50-60% kandungan simen Portland batu kapur dicampurkan dalam penghasilan mortar, prestasi mortar dari segi mekanikal and ketahanan dapat dipertingkatkan sekiranya berbanding dengan sampel mortar kawalan iaitu mortar yang mengandungi 100% simen Portland dan mortar yang mengandungi 100% bahan hibridan sanga dan abu arang batu. Penyelidikan ini menunjukkan bahawa mortar yang mengandungi 60% simen Portland batu kapur, 32% GGBS dan 8% PFA dapat menunjukkan kekuatan sebanyak 19% pada 7 hari and 34% pada 90 hari lebih tinggi dalam kekuatan mekanik sekiranya berbanding dengan sampel mortar kawalan 100% simen Portland batu kapur.

THE DURABILITY PROPERTIES AND MECHANICAL STRENGTH PERFORMANCE OF COAL ASH HYBRID GEOPOLYMERIC COMPOSITE

ABSTRACT

The utilization of Portland cement in concrete production is increasing. At the same time, the performance of Portland cement poses different kind of challenges such as high mechanical strength and good durability performance. Thus, geopolymeric material has been incorporated to overcome these technical challenges. The experimental investigation was conducted to characterize physical and chemical properties of hybrid geopolymer binder material which consist of ground granulated blast furnace slag (GGBS) and pulverised fuel ash (PFA) with the activation of Portland limestone cement (PLC) in different aspect such mechanical strength, durability performance and dimensional stability. By the process inter-grinding of 2 hours duration, it shows that with the inclusion of 50-60% of PLC in the production of mortar, the mechanical and durability performance of mortar mix was found to be exceptionally better as compared to both control mortar mixes produced using 100% PLC and 100% of geopolymeric binder material. The hybrid matrix of cement and geopolymer with the ratio of 60% PLC, 32% of GGBS and 8% of PFA shows improvement of 19% at 7 days and up to 34% at 90 days of increment in compressive strength as compared to control mix with only PLC.

CHAPTER 1

INTRODUCTION

1.1 Background of Research

Global demand of cement is consistently increasing annually. One of the most common types of cement used in the construction industry is ordinary Portland cement. Ordinary Portland cement (OPC) is used as the main binder material in concrete, mortar, paste and other cement based material. At the same time, cement is also facing different challenges such as resistance to sulphate attack, chloride penetration, carbonation, heat resistance and others which cause barriers and limitations to the application of conventional mortar with OPC as primary binder especially for the usage in aggressive exposure environment.

Geopolymer has been recommended as a new construction material with the revolutionary and outstanding performance as compared to OPC in concrete with some advance properties such as high early strength, better thermal and chemical resistance. There are several type of material which are commonly used as the binder material in geopolyemer mortar such as pulverized fuel ash (PFA), ground granulated blast-furnace slag (GGBS), palm oil fuel ash (POFA), rice husk ash (RHA), kaolin, metakaolin and so on. The potential of geopolymer is not only proven by its extraordinary performance and yet it is also supported by the construction practices from the industry which provide assurance on sustainable supply for the production of concrete in both ready mix and pre-cast concrete manufacturing sector. One of the good examples is the pulverized fuel ash (PFA). PFA is commonly known as fly ash is one of the geopolymeric material in the production of geopolymer mortar. It is an industrial by-product from coal burning power plant which generated up to 75% to 80% of global annual waste ash production (Joseph and Mathew, 2012). Besides the production of mortar material, it also provides a solution towards the disposal of these industrial waste materials through recycling.

1.2 Problem Statement

Although geopolymer mortar performs better as compared to conventional mortar with ordinary Portland cement, it faces some difficulty in total replacement of OPC in actual construction practices. One of the significant drawback factors of geopolymer mortar is the requirement of heat treatment in the early stage in order to achieve the desired mechanical strength performance and form (Davidovits, 2008; Rangan, 2007; Bakharev, 2005a). Heat treatment causes geopolymer mortar to require higher activation energy which increases the complexity of the manufacturing process and most important is affecting the economic feasibility of this new construction material.

Besides, geopolymer mortar requires high dosage of alkali activating solution in order to stimulate the geopolymerisation process and achieve the required mechanical strength properties. The most common geopolymer alkaline activator is the mixture of sodium or potassium hydroxide with sodium or potassium silicate (Kong and Sanjayan, 2008). However, high alkalinity of geopolymer mortar is corrosive in nature and there is a safety risk in the manufacturing process.

Thus, in order to solve the aforementioned issues of geopolymer mortar, a new alternative method in activating the geopolymeric material for the usage as part of the primary binder system in concrete production need to be explored and further studied. One of the alternatives in activating geopolymeric material is through inter-grinding process which able to ensure two or more of the aluminosilicate source materials are blended homogeneously. The duration and hybridization ratio of GGBS and PFA were determined in this research. Besides, utilization of Portland limestone cement (PLC) as the source of calcium hydroxide to be alkaline activator in the geopolymer system was also studied in this research.

1.3 Research Questions

There are several research questions which can be revealed as the followings:

1) Through mechanical activation of inter-grinding, how much is the improvement in reactivity of GGBS and PFA?
2) Based on various aspects covering mechanical strength, durability performance and dimensional stability, is the use of PLC as alkaline activator feasible?
3) As a replacement material to PLC, how many percent of replacement level can be achieved by using the mechanically activated GGBS and PFA to produce cementitious composites with similar performance as 100% PLC?

1.4 Aim and Objectives of the Research

This research is designed to determine the reactivity enhancement of the geopolymeric material GGBS and PFA through inter-grinding process and utilization of PLC as alkaline activator with curing at ambient temperature.

The overall objectives of this research study can be defined as follows:

1) To determine the optimum inter-grinding duration, hybridization ratio and improvement in mechanical strength of mortar consisting of binder material GGBS and PFA only.
2) To assess the mechanical strength, durability performance, dimensional stability, and microstructural development of the hybrid geopolymeric composite mortar with utilizing PLC as alkaline activator.
3) To determine the replacement level of the PLC by using mechanically activated geopolymeric material with similar or better performance in the aspect of mechanical, durability and dimensional stability.

1.5 Significance of the Research

This research is conducted mainly to derive the experimental data on the physical and chemical properties of hybrid geopolymeric composite formed by GGBS and PFA with the use of PLC as alkali activator. The interpretation and analysis of the experimental results on mechanical strength, durability performance, dimensional stability and microstructural development provides useful information on the properties of the material for use in mortar and concrete as the primary binder material.

The output of the study is able to justify the feasibility of inter-grinding towards reactivity enhancement of GGBS and PFA without the elevated curing regime and to eliminate the need for the use of alkali activators for stabilization of the aluminosilicate materials as a primary binder phase in the production of cementitious composites. Besides, utilization of PLC as alkaline activator able to mitigate the handling issue on highly alkaline geopolymer mortar. With the hybrid system between cement and geopolymer system, the performance of the mortar material able to be further improved. At the same time, recycling the industrial waste ash provides a solution towards waste management of ground granulated blast furnace slag and pulverized fuel ash by recycling these materials as major binder material in structural mortar and concrete. Hence, the possibility of recycling of ground granulated blast furnace slag and pulverized fuel ash as binder material will produce environmental friendly and low carbon footprint construction material for building and infrastructure development projects.

1.6 Scope of Study

In this research, there are four major scope of research are given as follows:

1) Material design development for the inter-grinding of hybridized material between GGBS and PFA as a primary binder phase in geopolymeric composite through evaluation in term of mechanical strength.
2) Mechanical strength evaluation on the hybrid geopolymeric composite with PLC as alkaline activator.
3) Durability performance assessment on hybrid geopolymeric composite with PLC as alkaline activator.
4) Dimensional stability study for establishing the time based shrinkage behaviour of hybrid geopolymeric composite with PLC as alkaline activator.
5) Studies on the microstructural development in the hybrid geopolymeric composite with PLC as alkaline activator.

Through these 5 main aspects of assessment, the potential of the GGBS and PFA to be used as the primary binder in mortar with the presence of PLC as alkali activator can be evaluated effectively.

1.7 Layout of Thesis

This thesis mainly consists of 5 chapters to cover the major aspect of the engineering properties and all investigation research in this research.

In chapter one, the background studies of the research has been discussed briefly with due regard on the contemporary problems encountered in the cement production industry, the significance of this research study and also the scope of work covered in this research.

In chapter two, a critical review of literature on the past and present studies of geopolymer mortar technology have been presented. It involves the chemical characteristic, reaction kinetics, related research on geopolymer and so on had been further discussed in this chapter. Moreover, the discussion also included the background knowledge of ground granulated blast furnace slag, pulverized fuel ash and Portland composite cement in different applications.

Chapter Three is a chapter whereby the details of the experimental programme and relevant testing methodology are presented. Besides, the important parameters of the investigation and characteristics of materials used in the experimental programme are also discussed.

The major content in chapter four is regarding the result of laboratory testing to the hybrid geopolymeric composite. At the same time, the analysis and interpretation of the results is also presented in this chapter.

In chapter five, the overall conclusions from the experimental works are summarized. The framework for further investigation on the subject matter is also proposed.

CHAPTER 2

LERATURE REVIEW

2.1 Introduction

An overview to the previous studies regarding geopolymer material such as physical and chemical properties of geopolymer, reaction kinetics and application of geopolymer would be further discussed in this chapter. Moreover, background studies toward the material used in this research would be further interpreted in different section of this chapter. Besides, the discussions of relevant researches were also reviewed and summarised.

2.2 Definition of Geopolymer

“Geopolymer” was first coined by a French scientist Joseph Davidovits (2008) in reference to alumina-silicate polymers with an amorphous chemical microstructure which formed under alkaline environment. According to latest definition by the Geopolymer Institution, geopolymer defined as the ambient X-ray amorphous material that are composed of mineral molecule chains or 3-D networks linked with covalent bonds (Geopolymer Institution, 2012). Besides, Davidovits (2008) states that geopolymer is generally formed through a reaction of alumina-silicate material such as fly ash, kaolin, metakaolin and so on. It is mainly being activated by an alkaline solution under ambient room condition (Davidovits et al., 2008). Pozzolanic materials such as fly ash and metakaolin which rich in silica (Si) and alumina (Al) are able to produce good mechanical performance and physical properties when react with an alkali activator (Davidovits et al., 2008).

Geopolymer has diverse advantages such as high in mechanical strength of 62-66 MPa after curing at 60-75 ^{o}C for 24 hours (Rowle et. al, 2003). As compared to concrete with ordinary Portland cement (OPC) as main binder material, geopolymer possess a good resistant towards high temperature (Kong et. al, 2008). Moreover, geopolymer also have better chemical resistant as compared to concrete with ordinary Portland cement (OPC) as main binder material such as resistant to sulphates (Bakharev, 2005). This aluminosilicate-based geopolymer material causes much less CO_2 emission and effective way in recycling industrial by product. These advantages of geopolymer provide a possibility to replace the ordinary Portland cement (OPC) in future for a sustainable concrete manufacturing industry (Duxson et al, 2007).

2.3 Reaction Kinetics of Geopolymer

Geopolymer is dominantly composed of silica (SiO_2) and alumina (AlO_2) in the shape of tetrahedral order. According to Davidovits (2008), the term poly(sialate) for the chemical designation of geopolymers is based on silico-aluminates. Sialate is an abbreviation form for alkali silicon-oxo-aluminate in which the alkalis being sodium-potassioum-lithium-calcium and the term poly(sialate) covers all geopolymers containin at least one (Na, K, Li, Ca)(Si-O-Al), (Na, K, Li, Ca)-sialate unit (Davidovits, 1976).

The sialate molecular structures involve at least four elementary units classified according to the Si:Al ratio (Davidovits, 2008):

Si: Al = 1, sialate

Si: Al = 2, sialate-siloxo

Si: Al = 3, sialate-disiloxo

Si:Al > 3, sialate link

These molecular structures of polysialates are chain and ring polymers with Si^+ and Al^{3+} in IV-fold coordination with oxygen and range from amorphous to semi-crystalline. The empirical formula of polysialate is:

$$\mathbf{M_n\,(\text{-}(SiO_2)z\text{–}AlO_2)_n.wH_2O}$$

In this formula, n is the degree of poly-condensation whereas M is the monovalent cation like K^+ or Na^+. “z” is the ratio of Si/Al and can be 1, 2 or 3. This geopolymer can be synthesized from fly ash and alkali activating solution. Davidovits (2008) also stated that the silica-aluminates structures can exist in one of the three basic forms as shown in the figure below:

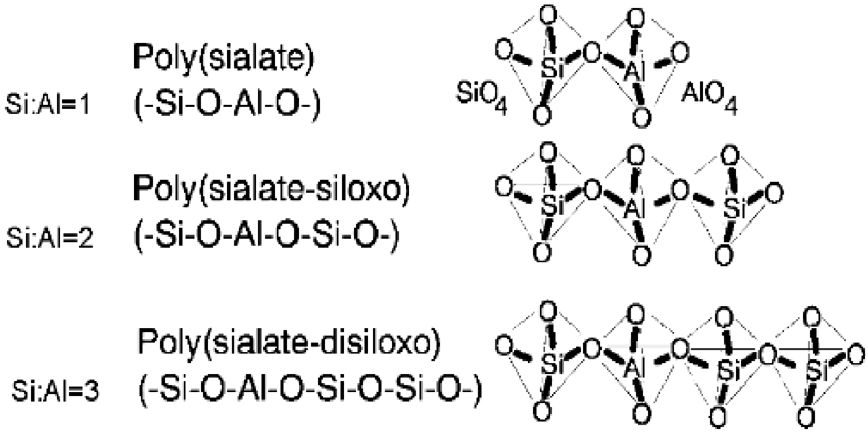

Figure 2.1: Chemical structures of polysialate (Davidovits, 2008)

The chemical composition of geopolymer is similar to zeolite. However, the amorphous microstructure is different from the crystalline alumina-silicate with a cage structure which is found in zeolitic materials (Grzeszezyk & Lipowski, 1997).

Although the chemical compositions of the geopolymer material have been studied extensively, there is still a lot of uncertainty in the understanding of the reaction kinetic involved in the geopolymerisation process. Glukhovsky (1959) proposed a general reacting mechanism to the primary components of silica and reactive alumina with the inclusion of alkali activator.

The mechanism that he proposed to the geopolemerisation can be divided into three stages:

- Destruction - coagulation stage
- Coagulation – condensation stage
- Condensation – crystallization stage

In the recent years, other researchers such as Duxson et al. (2007) had proposed a distinct theory of the geopolymerisation and the hardening process based on Glukhovsky's model. This conceptual model is shown in Figure 2.2 below:

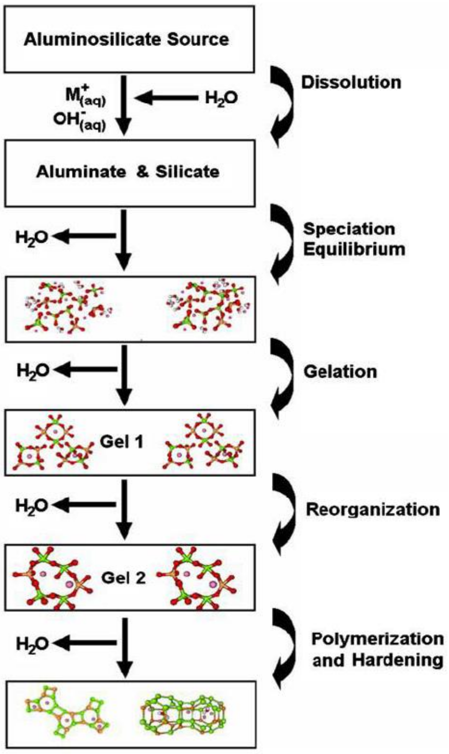

Figure 2.2: Conceptual model for geopolymerisation (Fernandez-Jimenez et al., 2006)

Meanwhile, Davidovits (2008) also proposed the conceptual model of setting and hardening process in phases as below:

1) Dissolution of Si ion and Al ion from the source material through the action of hydroxide ions.
2) Transportation or orientation and condensation of precursor ions into monomers.
3) Solidification or polycondensation/polymerisation of monomers into polymeric structures.

However, Palomo et al. (1999) mentioned that these stages occurred in parallel and simultaneously which make it difficult to differentiate them in specific phases.

Davidovits (2008) proposed the possible application of the geopolymer material depending on the molar ratio of silicate (Si) to aluminate (Al) as shown in Table 2.1:

Table 2.1: Application of Geopolymer Material (Davidovits, 2008)

Si/Al Ratio	Application
1	Brick, ceramics, fire protection
2	Low CO_2 cements, concrete, radioactive & toxic waste encapsulation.
3	Heat resistance composites, foundry equipments, fibre glass composites
>3	Sealants for industry
20<Si/Al<35	Fire resistance and heat resistance fibre composites

Davidovits (2008) summarised the synthetic reaction and hardening process into two series of equation as follows:

Series 1:

$$(Si_2O_5, Al_2O_2)_n + 3nH_2O \xrightarrow{\text{NaOH/KOH}} n(OH)_3\text{-Si-O-Al}^-(OH)_3$$

$$n(OH)_3\text{-Si-O-Al}^-(OH)_3 \xrightarrow{\text{NaOH/KOH}} \text{-}(\text{SiO-O-Al-O-O})\text{-}_n \quad + \quad 3nH_2O$$

Series 2:

$$(Si_2O_5, Al_2O_2)_n + 2nSiO_2 + 4nH_2O$$

$$\Big\downarrow \text{NaOH/KOH}$$

$$n(OH)_3\text{-Si-O-Al}^{-}(OH)_2\text{-O-Al}^{-}(OH)_2\text{-O-Si}(OH)_3$$

$$\Big\downarrow \text{NaOH/KOH}$$

$$\left(\text{SiO-O-Al-O-O-SiO-O}\right)_n + 4nH_2O$$

Under highly alkaline environment, the silicon and aluminium oxides from fly ash are dissolved and become aluminosilicate ions which show in the first equation of the series above. Meanwhile, the mixture appears to be a gel or dough-like phase. The aluminosilicate ions accumulate and form into polycondensed products and water as shown in the second equation of each series. These polycondensed products could precipitate from the original gel or dough-like phase and turn into hardened 3-D molecule networks which provide the required strength and durability for geopolymer products (Davidovits, 2008).

Rangan (2007) provide an explanation on the second part of both equations that water is released during the chemical reaction in the formation of geopolymers. The water which expelled from the geopolymer matrix during the curing will leave behind discontinuous nano-pore in the matrix after drying period (Rangan, 2007).

2.4 Properties of Geopolymeric Material

In the development of geopolymer, various aspects and performances need to be further explored namely physical, chemical properties, as well as long-term durability in order to determine the suitability as a construction material in the building or structure.

2.4.1 Physical Properties

Researcher Davidovits (2008) carried out various testing in different aspects such as physical and chemical testing on mechanical properties of geopolymer and the result shows that this material possess exceptional properties such as high early strength, low degree of shrinkage, high resistance towards freezing and thawing, sulphate attack and corrosion. They reported that geopolymer which act as a binder material in mortar could harden quickly at room temperature with the compressive strength of 20 MPa after only 4 hours of curing and about 70-100 MPa after 28 days from fabrication. Comrie et al (1988) also conducted physical tests on unconfined cubes which consist of sand and geopolymer. The result shows that the compressive strength could obtain 30 MPa with only 2 days of curing and 40 MPa after 28 days from fabrication. As compared to the mortar made of ordinary Portland cement with geopolymer mortars it appeared that strengths were acquired more quickly with the later.

2.4.2 Heat and Fire Resistance

Davidovits (2008) conducted tests to determine the heat and fire resistance of geopolymeric binder compared to Portland cement, geopolymer materials were found to have a better behaviour. He found that the concrete which was made from ordinary Portland cement exhibited rapid deterioration in terms of compressive strength when exposed to the environment of 300^oC. Meanwhile, the concrete with geopolymer material as a binder remained stable at 600^oC and exhibit low shrinkage as compared to Portland cement (Rangan & Wallah, 2006)

2.4.3 Chemical Properties

Fernandez-Jimenez et al. (2006) stated that geopolymer pastes and mortar have been proven to exhibit exceptional performance in terms of chemical resistance when exposed to different chemical such as sulphates, seawater attack, acidic media, and alkali-silica reaction.

Comrie et al. (1988) stated that Portland cement and lime do no perform as good as geopolymers in terms of chemical resistance mainly due to the absent of lattice structure. Generally, the common factors which causes the deterioration in ordinary Portland cement is the reaction between aggregates and alkalis such as alkali-silica reaction or alkali-carbonate reaction. These reactions might cause expansion and cracking to happen in the microstructure of mortar. On the other hand, for geopolymeric material, due to the absence of alkalis from cement, the calcium rich phases can diminish the deterioration and prevent the chemical process from happening.

Davidovits (2008) used the standard of Accelerated Mortar Bar Test to determine the alkali-aggregate resistance of geopolymer and ordinary Portland cement. The result shows that the geopolymer specimens remain unaffected whereas ordinary Portland cement specimens did generate alkali-aggregate reaction.

Garcia-Lodeiro et al. (2007) also studied the same issue. The research outcome shows that alkali-activated fly ash mortar which made with sodium hydroxide or sodium silicate solution expanded less than 0.1% which is the maximum value recommended by the ASTM standard C1260-94 after 16 days (Provis & Van Deventer, 2009).

Rangan et al. (2006) conducted the research on the resistance of geopolymeric material towards acid attack. The research outcome shows that almost all of the geopolymeric specimens with alkali-activated binders exhibit better performance compared to ordinary Portland cement when exposed to chemical aggression by acid. This was attributed to the present of high calcium content in ordinary Portland cement.

Bakharev (2005a) studied the comparison on the durability of geopolymer materials and ordinary Portland cement. The geopolymer material used is made of class F fly ash and alkaline activators and the specimens were exposed to 5% solutions of acetic and sulphuric acids. The research outcome shows that the geopolymeric specimens exhibited exceptional performance as compared to ordinary Portland cement when it is fabricated with sodium hydroxide and cured at elevated temperature.

Fernandez-Jimenez et al. (2007) conducted a research to determine the reaction of alkali-activated fly ash and ordinary Portland cement when the specimens were fully submerged in hydrochloride acid (HCl) solution. The research outcome shows that the geopolymeric specimens remained unaffected from physical appearance after 90 days of exposure to the acid solution whereas the specimens fabricated by using ordinary Portland cement were seriously deteriorated after only 56 days of submergence.

In the aspect of seawater attack, it involves several types of chemical reaction such as sulphates, chlorides, and magnesium ions by mechanisms of crystallization of expansive salts, precipitation of insoluble compounds, ionic attacks and so on. Chlorides usually do not cause significant deterioration on the microstructure of the concrete but the intrusion of chloride ions into concrete would promote the corrosion of embedded steel reinforcement through a localized de-passivation process which leads to reduction of load carrying capacity of a reinforced concrete structural element. Eventually it could lead to structural failure or even collapse. Bakharev (2005), Fernandez-Jimenez et al. (2007), had concluded that alkaline activated fly ash pastes and mortars shows exceptional performance with the exposure to sulphates and seawater.

2.5 Factors Affecting the Properties of Geopolymeric Material

There are several factors which have been identified as vital parameters which affect the properties of geopolymers. The first important parameter is the curing temperature of geopolymer products. Palomo et al. (1999) stated that the curing temperature, curing time and type of alkaline activator could accelerate the reaction of fly ash based geopolymers and it significantly affects the mechanical strength. Higher curing temperature with longer curing time has been proven to enhance the compressive strength performance of fly ash based geopolymer. Alkaline activator that contained soluble silicates has also been proven to enhance the rate of reaction as compared to alkaline solutions that contained only hydroxide.

Van Jaarsveld et al. (2002) stated that the water content could affect the properties of geopolymers. However, they also stated that there is an optimum curing temperature for geopolymer based products. The curing temperature above the optimum level will cause adverse effect on the properties of the material and induced cracks. Subsequently, they suggested that the use of mild curing temperature could improve the physical properties of the material. In another report, Van Jaarsveld et al (2003) states that the content of the material determine the properties of geopolymers such as calcium oxide (CaO) content and the water-to-fly ash ratio.

Xu and van Deventer (2000) stated that other parameters which could significantly affect the mechanical performance of geopolymers products such as the percentage of calcium oxide (CaO), percentage of potassium oxide (K_2O), the molar Si-to-Al ratio in the source material, the types of alkali activator, the extent of dissolution of Si and the molar Si-to-Al ratio in solution.

2.6 Background Study of Geopolymer Source Material

2.6.1 Ground Granulated Blast Furnace Slag (GGBS)

Production

Blast furnace slag is an industrial by-product from the manufacturing plant of iron in a blast furnace. It mainly results from the fusion of a limestone flux with ash from coke and the siliceous and aluminous residue remaining after reduction and separation of iron from ore. The operation of blast furnace and the production of both iron and slag is a continuous process rather than batch process. The molten slag is cooled down rapidly either by high pressure water jets or to cold air/water jets. Subsequently, the slag turns into a glassy granulate with a consistent particle size range and chemical composition. After the slag has been dried, it appears to be light brown in colour. However, after further milling until the fineness similar with cement powder, it becomes pale and white in colour which shown in Figure 2.3.

Figure 2.3: Physical appearance of Ground Granulated Blast Furnace Slag (GGBS) used in this research.

GGBS concrete appears bluish tint in the internal section and it is due to the formation of complex iron sulphides. However, this phenomenon fades rapidly as the sulphides are oxidised when exposed to the air (Concrete Society, 1991).

Physical Properties

One of the important physical properties of GGBS is the fineness. It is because fineness will area influences the properties of GGBS in different aspect such as workability, bleeding, heat, evolution and strength development (Harrison and Spooner, 1986). In normal practice, GGBS will be ground until minimum fineness of 275 m^2/kg which have been specified in standard BS 6699 (1992). In Australia and the USA, the common practice of the fineness is 500-600 m^2/kg and much higher than that in the UK. In USA, the common practice of incorporating this material in production of concrete is adding it before or during mixing in order to improve the plastic or hardened properties of the concrete (ASTM C989, 1999). It is referred to as a cementitious constituent in concrete (ACI 226-IR 1987).

Besides, the specific gravity of GGBS is 2.86 whereas Portland cement is 3.02. The different of specific gravity cause the GGBS to use as cement replacement material able to produce more volume of slurry mix with the similar weight of material (Concrete Society, 1991).

Chemical Compositions

The chemical compositions of GGBS may vary from work to work which depends on the nature of the limestone flux and also the blast furnace conditions. The major oxide components of slag are lime, magnesia, silica and alumina. If slowly hardened in air, these chemical components would form an assemblage of crystalline minerals.

However, the rapid quenching in water to produce granulated slag results in the formation of slag glass consisting of a network of calcium, silicon, aluminium and magnesium ions in disordered combination with oxygen. Minor components such as sodium, potassium and titanium are also integral parts of this structure and further modify or disorder the glass network. GGBS also contains small quantities of sulphides which present usually as calcium sulphide. However, calcium sulphide decompose to form hydrogen sulphide when expose to air (Concrete Society, 1991).

Chemistry in Concrete

During the reaction between GGBS and water, pH of the slurry mix would increases, generating heat and developing a particle-to-particle cementitious bond similar to Portland cement. This intrinsic hydraulic distinguishes GGBS from other pozzolans. The intrinsic reaction of GGBS with water is relatively slow as compared to Portland cement. Hence, for the practical purposes, the hydraulicity is activated by the hydroxides and sulphate present in Portland cement. These activators react with the GGBS disturbing the structure of glass; releasing reaction products for hydrate formation and continuation of hydration process (Concrete Society, 1991). Besides the primary reaction between OPC and water, GGBS and water, the secondary pozzolanic reaction also occurs in between OPC and GGBS by the reaction product from both materials. The hydrates formed in these combinations are similar to those produced during the hydration of Portland cement such as calcium silicate and aluminate hydrates (Neville, 2012).

In short, the hydration of C_3S and C_2S phases in cement is shown in following reactions:

$$\mathbf{2Ca_3SiO_5 + 6H_2O \rightarrow 3CaO\ .\ 2SiO_2\ .\ 3H_2O + 3Ca(OH)_2}$$

(C_3S, Alite) (C-S-H) (CH, Portlandite)

$$\mathbf{2Ca_2SiO_4 + 3H_2O \rightarrow 3CaO\ .\ 2SiO_2\ .\ 3H_2O + Ca(OH)_2}$$

(C_2S, Belite) (C-S-H) (CH, Portlandite)

The portlandite (CH) is also carrying a primary advantage in increasing the reserved alkalinity (pH) of cement. However, this material is somewhat leachable in water and it would leave behind voids after leaching which result in increasing in porosity of the cement pastes. Furthermore, CH is known to enhance the gypsum type of sulphate attack upon exposure to sulphate-bearing media. Moreover, ettringite formation is reported to be more expansive with the increase in alkalinity provided by the portlandite produced by cement hydration. Thus, in order to prevent these disadvantages, it is judicious to consume this portlandite through the pozzolanic reaction.

The pozzolanic reaction between the glass phase in the pozzolan such as GGBS and PFA with portlandite produced during the hydration of OPC would form more binding calcium silicate hydrate (C-S-H) as simplified in the following equation:

$$\mathbf{Ca(OH)_2 + H_4SiO_4 \rightarrow CaO\ .\ SiO_2\ .\ 3H_2O}$$

Calcium hydroxide + dissolved reactive silica → Calcium Silicate Hydrate

The pozzolanic reaction brings certain changes in the chemical environment of mortar and cause a significant change in physical structure of the hardened cement paste (Algahtani et al. 1994).

It is interesting to note that blended cement have often been observed to increase the measure Cl^-/OH^- ratio in mortar with a given in chloride ion content making them potentially at risk of reinforcement corrosion. However, the increase of Cl-/OH- ratio is always offset by the distinct improvement in the physical characteristics of the cement paste matrix and the substantial reduction in permeability of blended cement mortar to chloride ingress, thereby reducing the risk of corrosion (Rasheeduzzafar et al. 1992a and 1992b).

2.6.2 Pulverised Fuel Ash (PFA)

Pulverised Fuel Ash (PFA) which is also commonly known as fly ash is one of the waste product from the burning of finely ground coal in the boiler of electricity generator (USEPA, 2012). It is physically fine, powdery material which particle size ranges from silt to clay which is 1.0 μm to 150 μm glassy spherical in shape (Malhotra, 2008). PFA consists of high content of silica (SiO_2) which is semi-amorphous and semi-crystalline in nature. Amorphous silica exists in round shape and smooth in surface texture whereas crystalline silica is sharp in shape and mostly unreactive. Figure 2.4 shows the physical appearance of PFA.