# THE UTILISATION OF WOOD ASH AS ALKALINE ACTIVATOR FOR AMBIENT CURED GEOPOLYMER CONCRETE

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# THE UTILISATION OF WOOD ASH AS ALKALINE ACTIVATOR FOR AMBIENT CURED GEOPOLYMER CONCRETE

**by**

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**PENGGUNAAN ABU KAYU SEBAGAI BAHAN PENGAKTIF ALKALI BAGI PENGHASILAN KONKRIT GEOPOLIMER YANG DIAWET PADA SUHU PERSEKITARAN**

## ABSTRAK

Konkrit geopolimer campuran hibrid yang menggunakan abu sisa buangan industri adalah satu bahan binaan alternatif untuk menggantikan konkrit simen Portland biasa (OPC). Ianya memberikan pengurangan ketara terhadap pencemaran karbon dan mempunyai kesan positif terhadap alam sekitar. Selain itu, konkrit geopolimer campuran hibrid yang dicadangkan adalah untuk mengatasi masalah pengikat geopolimer konvensional yang dikaitkan dengan penggunaan pengaktif alkali yang tinggi dan memerlukan suhu pengawetan yang tinggi dimana ianya akan menghalang penggunaan pengikat geopolimer pada peringkat perindustrian. Kajian ini dijalankan dengan matlamat utama adalah untuk menghibridkan bahan-bahan sisa industri iaitu abu arang batu (PFA), abu sangga relau bagas (GGBS), abu kayu berkalsium tinggi (HCWA) dan wasap silika (SF) dengan pengaktif alkali yang sesuai untuk menghasilkan bahan pengikat untuk konkrit. Konkrit campuran hibrid geopolimer telah dikaji berdasarkan ciri-ciri kebolehkerjaan, kekuatan mekanikal, penghantaran cecair dan prestasi keliangan. Spesimen ujikaji dinilai dari segi konsistensi piawai, masa pengerasan, kekuatan mampatan, kekuatan lenturan, modulus keanjalan, halaju denyut ultrasonik, penyerapan air, penyerapan kapilari, tahap keliangan dan pembentukan mikrostruktur. Penggunaan PFA pada kadar 20-100% daripada berat bahan pengikat pada geopolimer hibrid tiga campuran telah mengurangkan keperluan air seterusnya menambahkan jangka masa untuk pegerasan campuran geopolimer. Sebaliknya, penambahan SF sebanyak 2-16% dalam

geopolimer empat campuran memendekkan tempoh masa pengerasannya. Konkrit geopolimer hibrid tiga campuran dan empat campuran dengan kandungan PFA dalam julat 40-80% dan SF dalam jukat 2-12% daripada jumlah berat pengikat mempamerkan perkembangan pada modulus keanjalan, halaju denyut ultrasonik, keupayaan mampatan serta lenturan jika dibandingkan dengan konkrit simen Portland. Penggunaan PFA pada tahap gantian 40-80 % dan SF pada tahap 2-12% daripada berat bahan pengikat dapat mengurangkan kadar serapan air, serapan kapilari dan tahap keliangan. Selain itu, dengan merujuk kepada mikrograf SEM dan analisa EDX didapati bahawa penghasilan produk hidrat geopolimer iaitu sodium aluminosilikat hidrat, kalsium aluminosilikat hidrat dan kalsium silikat hidrat bersama-sama dengan struktur gel polimer polysialate dan polysialate disiloxo telah membantu meningkatkan kekuatan pada konkrit tiga dan empat campuran hibrid. Hasil kajian menunjukkan bahawa konkrit geopolimer tiga campuran hibrid, yang mengandungi 80% PFA (P80) dan konkrit geopolimer empat campuran hibrid, yang mengandungi 12% SF (S12) mempamerkan sifat mekanikal, pengangkutan cecair dan keliangan yang lebih baik apabila dibandingkan dengan konkrit simen Portland gred 30 dan 50. Pengetahuan yang menyeluruh yang diperolehi daripada hasil kajian ini akan membawa kepada penerimaan yang lebih besar terhadap pengaplikasian konrit geopolimer campuran hibrid dalam pelbagai kerja-kerja kejuruteraan sivil.

**THE ULTILISATION OF WOOD ASH AS ALKALINE ACTIVATOR FOR AMBIENT CURED GEOPOLYMER CONCRETE**

## ABSTRACT

The blended hybrid geopolymer concrete utilising industrial waste ash is a new option of constituent binder material to replace ordinary Portland cement (OPC) concrete. It has a significantly reduced carbon footprint and has a positive impact on the environments. Furthermore, blended hybrid geopolymer concrete proposed to resolve the conventional geopolymer binder issues associated with a high dosage of alkaline activator and elevated curing temperature that hindered the industrial application of geopolymer binder. The study was conducted with the primary aim to hybridise industrial waste ash namely pulverised fuel ash (PFA), ground granulated blast furnace slag (GGBS), high calcium wood ash (HCWA) and silica fume (SF) with suitable alkaline activators to produce binder for concrete. The properties of the blended hybrid geopolymer concrete were assessed based on the fresh properties, mechanical, fluid transport and pore performance. Test specimens were evaluated in terms of standard consistency, setting times, compressive and flexural strength, dynamic modulus of elasticity, ultrasonic pulse velocity, water absorption, capillary absorption, porosity and microstructural performance. The inclusion of PFA at the content of 20-100% by binder weight in ternary blended hybrid geopolymer paste reduced the water demand and significantly prolonged the setting times of ternary blended hybrid geopolymer paste. Meanwhile, the addition of SF by 2-16% in quaternary blended hybrid geopolymer paste shortened the setting times instead. Enhanced compressive and flexural strengths, modulus of elasticity and ultrasonic pulse velocity were observed for ternary and quaternary blended hybrid geopolymer

concrete with PFA content of 40-80% and SF of 2-12% by binder mass in comparison to Portland cement concrete, respectively. The inclusion of PFA at replacement level of 40-80 % and SF of 2-12% reduced the water absorption, capillary absorption and porosity. Besides, from SEM micrograph and EDX analysis, blended hybrid geopolymer paste matrix indicated the coexisted formation of geopolymeric hydrates of sodium aluminosilicate hydrate, calcium aluminosilicate hydrate and calcium silicate hydrate together with geopolymer framework polysialate and polysialate disiloxo that contributes to the strength development on ternary and quaternary blended hybrid geopolymer concrete. The study results indicate that ternary blended hybrid geopolymer concrete, with 80% of PFA contents (P80) and quaternary blended hybrid geopolymer concrete, with 12% of SF content (S12) exhibited significance enhanced mechanical, fluid transport and pore properties when compared with Portland cement concrete grade 30 and 50, respectively. The comprehensive body of knowledge derived from the study will lead to a broader acceptance of the blended hybrid geopolymer in various civil engineering applications.

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of research

The worldwide demand of Portland cement for development purpose is continually expanding as for the reasons of the continuous urbanisations progress and to fulfill the needs of the expanding population. Lately, there had been several issues associated with the utilisation of ordinary Portland cement (OPC) as the main constituent material used in the fabrication of building structure. It was identified that the usage of OPC brings in significant negative consequences against the environment regarding their respective demanding energy consumption together with carbon dioxide ($CO_2$) emissions during the production process (Ahmari et al., 2012; Aprianti, 2017; Schneider et al., 2011). With the growing interest regarding the environmental preservation and energy conservation, there is a rising necessity for a state-of-the-art sustainable construction material, which requires lower energy consumption and generates less $CO_2$ emissions related with the material design and production process. Therefore, one of the solution required to reduce the negative impact of OPC towards the environment is by utilising industrial waste ash to produce an alternative class of binder named geopolymer.

In the recent years, geopolymer was extensively studied and it can provide comparable performance to conventional OPC together with the additional benefits which is its ability to reduce the $CO_2$ emissions and provide an essential value of the industrial waste ash (Duxson et al., 2007). The adoption of the phrase ‘geopolymer’ is to illustrate a binder material that contains amorphous aluminosilicate activated with an alkaline source and it was discovered by a French researcher named Joseph Davidovits at the time of 1970s (Davidovits, 2011). Geopolymer could be a

prospective alternative binder for conventional concrete that utilises industrial waste ash materials. Geopolymer makes use of industrial waste ash product that possess high content of silica ($SiO_2$) and alumina ($Al_2O_3$) such as pulverised fuel ash (PFA), ground granulated blast furnace slag (GGBS) and palm oil fuel ash (POFA). Subsequently, the source materials are mixed with a strong alkaline activator such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate ($Na_2SiO_3$) or in combination with the aforementioned alkaline activators to produce the geopolymer binder (Sarker et al., 2013). With reference to the conventional synthesis path of geopolymer, it must undergo post-fabrication heat treatment curing at a temperature between 40 $^oC$ and 80$^oC$ for a minimum duration of 6 hours to achieve comparable strength to OPC concrete (Duxson et al., 2007; Palomo et al., 1999). Typically, there are three main phase in the mechanism of geopolymerisation, as stated by Silva et al., (2007).

Phase 1: Dissolution of oxide particles in the source products by the reaction with hydroxide ion.

Phase 2: Densification or condensation of precursor ions into monomers

Phase 3: Formation of polycondensation/ polymerisation of monomers into polymeric structures.

Moreover, a geopolymeric gel products can be classified from one of these three geopolymer structures, as presented in Figure 1.1. The classification is based on the elemental ratio of the silica and alumina derived from the finished product in which, Si/Al from 0-1.5 is considered as polysialate, Si/Al between 1.5-2.5 considered as polysialate-siloxo and Si/Al above 2.5 is the ratio for polysialate-disiloxo geopolymeric framework (Davidovits, 2011).

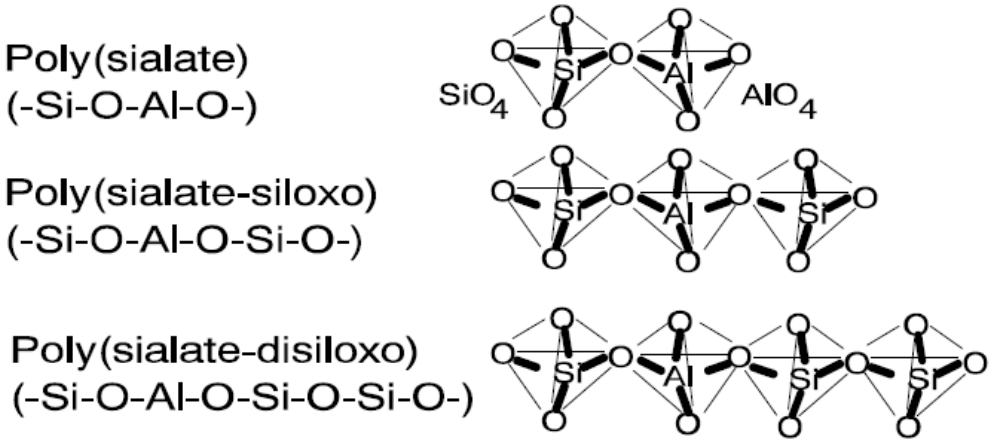


Figure 1.1 Types of geopolymer structures (Davidovits, 2011)

On the other hand, two main factors that happen to be the drawback toward the industrial application of conventional geopolymer is namely the needs of high dosage of concentrated alkaline activator and elevated temperature curing for mechanical strength development. Therefore, to reach the potential of which geopolymer binder system can be feasible to replace conventional OPC, geopolymeric binder needs to be environmentally friendly by eliminating the high alkaline activator content and elevated temperature curing. New development of geopolymeric binder needs to focus on a combination of abundant industrial waste ash products such as fly ash, GGBS and rice husk ash together with decrease content and concentration of the alkaline activator. Besides, new geopolymer system needs to utilise ambient temperature curing for improving its industrial practicability (Davidovits, 2011; Izquierdo et al., 2009).

The potential of producing hybrid geopolymer concrete as for replacing the conventional OPC concrete was substantiated by the bulk availably of industrial waste ash produced by different types of industry. Mostly all the industrial waste ash generated is containing high percentage of aluminosilicate materials which was found out to be applicable to be used as source materials for the fabrication of hybrid

geopolymer concrete. For example, power plant industry creates industrial waste ash named PFA or it is generally known as fly ash (FA). According to Joseph & Mathew (2012), the worldwide production of PFA was 75% - 80% from the entire annual industrial waste ash production which indicate the abundant availability of PFA. Meanwhile as in Malaysia, 94.5% of the entire electricity produced is still using fossil fuel, i.e. natural gas, oil and coal, which resulted to a great amount of industrial waste ash of PFA to be produced annually. In 2010, the coal power plant in Malaysia used up almost eight million tonnes of coal and this number will increase because of the execution of new government policy which will expand the Malaysia coal power sector by 40%, as a result of rapid economic growth. In such, this industrial waste ash that is produced in great volume should be managed with an innovative solution for dumping or recycling technique (Ahmaruzzaman, 2010).

Furthermore, the Department of Environment (DOE) classifies PFA and bottom ash as schedule wastes in Malaysia. DOE prohibited any form of the industrial waste ash to be discharged at sanitary landfills because of its high toxicological parametric values (Kim et al., 2017). Thus, it will open up the opportunity for many researchers to develop a new channel of utilising the industrial waste ash into various commercial application. On the other hand, it also helps to reduce the issues of shortage of dump yard at the power plant by recycling large-volume industrial waste ash into geopolymer system.

In the current years, the necessity of using environmentally friendly construction materials that support sustainable development is one of the leading environmental agenda in the construction sector. The primary concern is the continuous massive utilisation of OPC as the main constituent materials in the

fabrication of building structure that contributed significant unfavourable effect on the environment. The manufacturing process of OPC is energy consuming and produces a significant amount of greenhouse gasses to the environment. The manufacturing process of OPC is also accountable for approximately 5–7% of global anthropogenic $CO_2$ emissions (Huntzinger & Eatmon, 2009; Meyer, 2009). The factors causing the high $CO_2$ emissions from OPC production is in the process of calcination of limestone. The calcination process consist of heating of raw material inside a rotating kiln at a high temperature above 1400 °C that significantly contributed to the unfavourable release of $CO_2$ emissions associated with energy consuming process (Duxson et al., 2007).

The various industrial waste ash consists of really fine particles that can be easily suspended in the air through wind blowing can cause respiratory related disease to the community-dwelling around the disposal area of the industrial waste ash materials. Furthermore, leaching of heavy metal contents from the industrial waste ash can cause contamination of groundwater resources by seepage of rainwater. Consequently, the dumping of the industrial waste ash through landfilling needs a properly engineered landfill, which has significant impact in term of the expenditure to dispose the waste ash. In the long term, the frequent disposal of industrial waste ash could result in a shortage of landfill area that would consequently increase the cost of disposal of the industrial waste ash (Aprianti, 2017; Udoeyo et al., 2006).

Recently, there were arguments regarding the $CO_2$ emissions associated with energy-intensive production of geopolymer products that is affected by the high dosage of alkaline activator and elevated temperature curing on the geopolymer mixture. The commonly applied alkaline activators in conventional geopolymer are

sodium silicate ($Na_2SiO_3$), sodium hydroxide (NaOH), potassium hydroxide (KOH) or a mixture of sodium and potassium hydroxide with sodium silicate-potassium silicate (Ismail et al., 2014; Rashad, 2014). Nonetheless, the aforementioned alkaline activators do not present as a raw organic material but they are produced from energy consuming thermal fabrication technique, which stretches the energy required related with the production of conventional geopolymer. Furthermore, geopolymer concrete needs post-fabrication curing at an elevated temperature between 40 $^oC$ and 80$^oC$ in order to achieve comparable strength as OPC concrete (Duxson et al., 2007; Palomo et al., 1999). The thermal curing regime contributes further towards additional energy consumptions on the production of geopolymer concrete.

Turner & Collins (2013) stated the differences on the carbon dioxide equivalent ($CO_{2\text{-}e}$) emissions among FA based geopolymer and OPC, it was discovered that only approximately 9% decrement of $CO_{2\text{-}e}$ emissions were achieved by conventional geopolymer rather than approximately 26% - 80% decrement in $CO_{2\text{-}e}$ emissions claimed by Duxson et al., (2007) and Habert et al., (2011). This was concluded when considering the entire procedure involved starting from the collection of raw materials until the fabrication of geopolymer concrete. The significant factor that contributed to the low $CO_{2\text{-}e}$ emissions of geopolymer concrete is the great energy required during manufacturing of alkaline activator and the need of post fabrication heat curing on the conventional geopolymer concrete. Hence, there is a significant need for further investigation into hybrid geopolymer materials that possess lower environmental influence and improved economic advantages. This is essential to diversify the utilisation of geopolymer as the primary binder for concrete production.

This study intends to produce a new type of hybrid geopolymer concrete to widen the use of geopolymer as sustainable construction materials. With that, this study emphasises on the rheological, mechanical, fluid transport and microstructural properties of low energy hybrid geopolymer concrete.

## 1.2 Problem statement

An extensive literature review shows that, there has been little work performed to investigate the characteristic of hybrid ternary and quaternary blended geopolymer made up from PFA, GGBS, high calcium wood ash (HCWA) and silica fume (SF) activated with low content of alkaline activator that cured at ambient temperature.

The main issue that had been question lately regarding conventional geopolymer concrete is the actual cost and the embodied energy associated with the manufacturing process of conventional geopolymer. This is mainly contributed by the implementation of high dosage of alkaline activator together with the need of post fabrication heat treatment in order to reach the desired engineering properties on the proposed geopolymer products (Joseph & Mathew, 2012; Nath & Sarker, 2014).

There are emerging numbers of timber industry that utilised wood waste such as sawdust, woodchips and offcuts to be used as fuel for boiler unit for drying of moist timber and electricity generation at the manufacturing production plant. The practises resulted in abundant of fine wood waste ash as a by-product material in which have very limited recycling applications (Cheah & Ramli, 2011). According to Etiégni & Campbell (1991), 70% of total wood waste ashes are landfilled, 20% are used as soil supplementary materials and remaining 10% are used in construction materials.

Another study by Cheah & Ramli (2012) had discovered important alkaline source elements in HCWA that is potassium oxide ($K_2O$). The amount of $K_2O$ discovered in HCWA was 12%, which indicated that HCWA possess high level of alkalinity that would be an effective raw material to enhance the mechanical properties of hybrid geopolymer.

1. As much of the present research trends in geopolymer field are immensely concentrated on geopolymer manufactured by applying synthetic source of alkaline activators that lowered the $CO_{2\text{-}e}$ emissions value (Turner & Collins, 2013). With that, the understanding of using the inherent alkalinity of one source of industrial waste ash to activate the amorphous aluminosilicates minerals of another source of industrial waste ash for the production of a hybrid geopolymer binder remains rarely investigated.

2. Based on the mentioned earlier findings revealed the possibility of coexistence of calcium silicate hydrate (C-S-H) gel together with the geopolymeric gel in the same geopolymeric matrix and contributed to the improvement of engineering chracteristic (Huseien et al., 2018). With that, the study on the mix design, mechanical and fluid transport characteristic of hybrid ternary and quaternary blended geopolymeric binder is required. This is mainly driven by the limited availability of literature on the various engineering properties of hybrid ternary and quaternary blended geopolymer binder.

3. As hybrid ternary and quaternary blended geopolymer binder is a new class of sustainable construction materials invented, the reaction mechanism of the solidification and stabilisation reaction that occurs in hybrid ternary and quaternary blended geopolymer paste sample has yet to be established. Besides, the understanding of the reaction mechanism will contribute essentially to the present understanding in the emerging field of hybrid geopolymer.

## 1.3 Objectives of research

This study is designed to assess the suitability of hybrid ternary and quaternary blended geopolymer incorporating PFA, GGBS, HCWA and SF with low content of alkaline activator which is subjected to ambient temperature curing. This involves a proper mix proportioning of the hybrid geopolymer material followed by studies on the rheological, mechanical, fluid transport and microstructure properties of the fresh and hardened hybrid geopolymer mortar and concrete.

The material design and fabrication technique of hybrid ternary and quaternary blended geopolymer mortar and concrete will be establised in this study. This is to solve several human health condition, environmental issue and waste dumping problem associated to the cement and concrete industry and also the power supply sector as mentioned earlier. It is also the primary aim of the work to fill the gap of knowledge on the hybridisation of industrial waste ash as ternary and quaternary blended geopolymeric binder due to limited research and development conducted in this field.

The overall aims and objective of the research projects are summarised as follows:

- To establish the suitability of HCWA as a source of alkaline activator in hybrid geopolymer concrete.
- To develop the mix design of hybrid ternary and quaternary blended geopolymer concrete and assess the engineering performance of the material.
- To determine the reaction kinetics of the hydrated hybrid ternary and quaternary blended geopolymer binder through microstructural assessment.

## 1.4 Significance of research

This research is performed to derive the knowledge framework on material proportioning of hybrid ternary and quaternary blended geopolymer, rheological properties, mechanical and fluid transport characteristics of hybrid ternary and quaternary blended geopolymer concrete. This is done in order to support the industrial applicability of proper combinations of various industrial waste ash along with reduced alkaline activator and utilising ambient temperature curing for production of new hybrid geopolymer concrete. Several significant long-term benefits can be derived with the successful production of new hybrid geopolymer concrete. The most important being the reduction in $CO_2$ emissions from the manufacturing process of new hybrid geopolymer concrete.

Moreover, the recycling of industrial waste ash provides a long-term solution to eliminate the disposal and shortage of landfill problems. With the new body of

knowledge, geopolymer concrete could be practical to be used widely as a replacement for Portland cement concrete by producing hybrid ternary and quaternary blended geopolymer concrete with low alkaline activator content and which is cured at ambient temperature. The comprehensive body of knowledge on the properties of new hybrid ternary and quaternary blended geopolymer concrete derived from the study will lead to a broader acceptance of the materials in various civil engineering applications.

## 1.5 Scope of work

The major scopes of the research work are stated in points as follows:

- Assessment of the physical and chemical properties of industrial waste ash materials used in the study (PFA, GGBS, HCWA and SF).
- Evaluation of properties of hybrid ternary and quaternary blended geopolymer paste in term of standard consistency, initial and final setting times.
- Study on the effect of various mix proportions of hybrid ternary and quaternary blended geopolymer on mechanical properties of hardened geopolymer concrete.
- Study on the effect of various mix proportions of hybrid ternary and quaternary blended geopolymer on fluid transport and pore properties of hardened geopolymer concrete.
- Derivation on the reaction mechanism of hybrid ternary and quaternary blended geopolymer paste.

The physical properties assessment include evaluation on specific gravity of binder materials. The chemical properties assessment includes an evaluation of the chemical compositions and minerals phases of the binder materials. The binder materials used in the study are pulverised fuel ash (PFA), ground granulated blast furnace slag (GGBS), high calcium wood ash (HCWA) and silica fume (SF).

The evaluation on the settings properties of hybrid ternary and quaternary blended geopolymer includes investigation on standard consistency of hybrid ternary and quaternary blended geopolymer pastes. The initial and final setting time tests are performed for the same set of pastes composition.

On than that, the study on mechanical properties of the hybrid ternary and quaternary blended geopolymer concrete includes the determination of compressive strength and flexural strength together with ultrasonic pulse velocity and dynamic modulus of elasticity at several durations of testing ages.

The study on the fluid transport and pore properties includes the evaluation of water absorption, capillary absorption and total porosity properties of the hybrid ternary and quaternary blended geopolymer. Furthermore, scanning electron microscopy and energy dispersive x-ray analysis are performed on selected hybrid ternary and quaternary blended geopolymer paste specimens.

## 1.6 Thesis layout

This thesis consists of five chapters that covers the essential aspects of the engineering properties of the hybrid ternary and quaternary blended geopolymer concrete. In chapter one, the background to this research investigation has been briefly discussed emphasising on recent problems encountered in the cement production

industry, industrial waste ash production and deficiency of conventional geopolymer. The significance of this research study and the scope of work also covered in this chapter.

Chapter two describes a extensive literature review on the various factors which affect the mechanical, fluid transport and microstructural characteristics of geopolymer derived from industrial waste ash. A critical summary of all reviewed literature and gap of knowledge is presented at the end of chapter two.

The details of the experimental programme and relevant test methodology are described in great depth in chapter three. Other than that, the essential parameters of investigation and characteristics of materials used in the experimental programme are also discussed in this chapter.

Chapter four discusses on the rheological properties of hybrid geopolymer paste, mortar and concrete, namely standard consistency and setting times of paste. Non-destructive test and destructive assessments aspects, namely ultrasonic pulse velocity, dynamic modulus of elasticity, compressive strength and flexural strength are explained in details. There is also an extensive analysis of fluid transport and pore performance evaluation, namely water absorption, capillary absorption and total porosity. Scanning electron microscopy coupled with EDX analysis is also presented as derivation to the geopolymeric reaction kinetics on the hybrid geopolymer.

Finally, in chapter five, the overall conclusions from the experimental works are summarised. Recommendations for implementation and further research are also suggested in this chapter.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Overview

This chapter describes and discussed the critical review on the numerous factors that affect the mechanical, fluid transport properties and microstructural characteristic of geopolymer paste, mortar and concrete. The major factors identified to have a significant influence on geopolymer characteristic were investigated from current geopolymer technology in the aspects of high inclusion of alkaline activator and elevated temperature curing regime. Besides, the influence of various geopolymer constituent materials is also described in this chapter. Moreover, current blended geopolymer mechanical, fluid transport and microstructural characteristics were also reviewed and summarised in this chapter.

There has been growing concern in minimising the dependencies on Portland cement in the construction industry together with growing environmental awareness and need for sustainable disposal of industrial by-product in different industries. As such, geopolymer binder provides all the opportunities to substitute Portland cement as the binder in concrete products while addressing these concerns. Therefore, the present review is focused on current geopolymer trends along with the factors affecting geopolymer development. This covers the effects of the types of industrial by-product, alkaline activators, curing regime and constituent material towards the mechanical, fluid transport and microstructural properties of the geopolymer concrete. Finally, a critical summary was made with respect to the gap of knowledge and challenges in the future development of geopolymer technology for broader application.

## 2.2 Development of geopolymer technology

It is well known since the mid-19$^{th}$ century, OPC has been used as a binder material in the construction industry. Nonetheless, the prolonged use of OPC as the main component used in the industry has been questioned in the course of the most recent decade. This is because of the high $CO_2$ emission form clinker production and over-harvesting of limestone hills that have an unfavorable impact on the environment (Ahmari et al., 2012; Schneider et al., 2011; Vermeulen & Whitten, 1999). It is anticipated that by the year 2050, due to the expansion of construction industry in developing countries, the amount of concrete consumption will be fourfold as compared to the year of 1990 (Scrivener, 2008). As concrete is the largest material consumed in the construction industry, the exploitation of natural resources had put pressure on the industry itself to find an alternative for the main materials. Literally this led to the increasing research works all over the world on finding suitable alternative construction material for substitution of traditional materials that being continuously exploited.

It was reported that approximately 0.8 tons of $CO_2$ gas was released into the atmosphere for each ton of Portland cement manufactured and over the year it's accumulated to a total of 1.5 billion tons of $CO_2$. The main process that contributes 5-8% of total man-made anthropogenic $CO_2$ emission were the combustion of limestone and the burning of fossil fuels to generate heat (Damtoft et al., 2008; Scrivener, 2008; Yusuf et al., 2014). Other than consuming the natural resource, the natural habitat of flora and fauna were also affected by cement manufacturing process (Devi et al., 2018). There are other constituent materials needed to produce concrete besides OPC that is aggregate and sand in which originated from the quarrying activity that are both energy-intensive and generates a large amount of waste materials. Scarcity of natural

resources for the construction materials supply had led to long-distance haulage and hence automatically added on the cost of production of construction materials. As for now, the construction industry is moving towards sustainable construction. As such, the altogether problems mentioned earlier need to be tackled to strengthen sustainability in the construction industry (Ahmari et al., 2012).

Supplementary cementitious materials (SCMs) was introduced in order to solve the previous issues by numerous researchers to cut down carbon emission from construction industry by utilising industrial by-product, for example fly ash, blast-furnace slag and wood ash which is the by-product from coal-burning power plant, steel manufacturing industry and lumber mill (Cheah & Ramli, 2013; Kroehong et al., 2011a; Lothenbach et al., 2011). By an effort of introducing SCMs to substitute cement, the amount of Portland cement needed in the year 2020 is estimated to be threefold of the amount consumed in the year 1990 (Sharp et al., 2010). Even after taking into accounts the efforts made by the cement industry to lower their carbon footprints by implementing the SCMs, the $CO_2$ emission will still be substantial unless the cement percentage is reduced drastically. In order to overcome this, the volume of SCMs needs to be increased as substitution material for cement. However, increasing SCMs material to a large proportion of binder led to a significant fraction of the SCMs materials that cannot be activated through cement hydration product only. Thus the addition of an external source of alkali activation is needed (Sharp et al., 2010). This opens up the opportunity for a new class of binder that eliminates the need of cement that is called geopolymer (He et al., 2013; Mijarsh et al., 2014; Pangdaeng et al., 2014).

Geopolymer is defined as an amorphous, three-dimensional short-range inorganic polymer that is formed when a highly concentrated aqueous alkali

hydroxide-silicate solution (e.g. sodium/potassium hydroxide and sodium/potassium silicate) is added to an aluminosilicate rich raw materials such as slag, fly ash (PFA) and metakaolin (Davidovits, 2011). The presence of a highly alkaline solution or chemical activator is crucial for the initiation of geopolymerisation reaction during the dissolution stage of silica and alumina species and catalysis of the poly-condensation reaction. Calcined clay and low calcium fly ash are the most prevalent precursors in geopolymer binder synthesis. Generally, geopolymer binder formed by using fly ash is usually cured at a temperature between 60 to 90$^{o}$C for a particular duration and activated with an alkaline solution of $SiO_2$: $Na_2O$ (molar ratio)<1.2 and high alkalinity level (8-14M) (Davidovits, 2011).

The emergence of geopolymer study among researchers is substantiated by the abundance of industrial waste ash produced by different industries. Heidrich et al., (2013) reported, the global production of coal combustion products, together with fly ash was 780 million tonnes in the year 2010, and its utilisation percentage was around 50%. The materials were discovered to have aluminosilicate properties that can be used as geopolymer based materials. Geopolymer also helps the industry to find a solution for the needs of large disposal of industrial waste ash and provide economic value to the industrial waste ash. There were also another source of industrial waste ash used for geopolymer synthesis i.e. slag (Hasnaoui et al., 2019; Samantasinghar & Singh, 2018; Sun & Vollpracht, 2018), red mud (Hu et al., 2018a; Nie et al., 2019) and biomass fly ash (De Rossi et al., 2019).

Zhang et al., (2018) claimed that geopolymer products exhibited high chemical and fire resistance together with high mechanical performance. For this reason, geopolymer was suitable to be used as construction and building materials as a

prospect of being a sustainable and environmental friendly Portland cement replacement. Geopolymer also can be integrated into the flexible pavement as stabilising agents which had been studied by Hu et al., (2018b) who invented geopolymer-stabilised aggregate bases. Other than that, geopolymer had also been proven to be cost-effective, eco-friendly and high efficiency when used as adsorption agent of heavy metal and dyes because of their porous structure and the presence of negative charges located on aluminium tetrahedra (Siyal et al., 2018). Together with the aforementioned trends and advantages of geopolymer, it can be said that geopolymer can be the next sustainable and eco-friendly binder to replace Portland cement.

## 2.3 Fundamental of the reaction mechanism of geopolymeric binder

Geopolymeric binders can be fabricated by polymerising the aluminosilicate rich sources such as PFA, GGBS, metakaolin and palm oil fuel ash by activation using alkaline solutions. Geopolymer is considered as one of the inorganic polymers in which it is amorphous rather than crystalline when compared to other natural zeolites material (Davidovits, 2011; Palomo et al., 1999). The polymerisation process needs a significantly rapid response of silica (Si)-alumina (Al) under the alkaline conditions that subsequently produces a three-dimensional polymeric chain of Si-O-Al-O bonds. Unlike OPC or other pozzolanic cement, geopolymer utilised the polycondensation of silica and alumina together with a strong alkali content to achieve compressive strength gains (Davidovits, 2011). The geopolymer phase is based on one of this three mixture of poly (ferro-sialate-siloxo), poly (ferro-sialate-disiloxo) and poly (ferro-sialate-multisiloxo) binder category with $Ca^{2+}$, $Mg^{2+,}$ and $Na^{+}$ will act as charge-balancing

cations (Djobo et al., 2016a; Djobo et al., 2016b). Besides, the mechanism of geopolymerisation propose by Król et al., (2018) involves three steps as follows:

1. Dissolution of aluminosilicate raw material
2. The decrease in the content of polymeric aluminosilicate species with an increase in orthosilicate phases
3. Condensation of tetrahedra and disappearance of polarised forms

The speed of the first step increase in order $Li < Na < K$ depending on the alkaline activators used in the geopolymer synthesis. The geopolymeric gel is usually expressed as zeolites like phase, zeolite precursors or metastable amorphous zeolites in which unable to crystallise due to unfavourable conditions (Sturm et al., 2016). Rees et al., (2008) come out with The Ostwald Law of Successive Transformations, which states that a phase does not constantly transform straight into the most stable state, but often changes into a metastable state of greater likeness to itself.

There is also another contributing reaction towards the enhancement of geopolymer properties which is the hydrated phase. Sodium or potassium aluminosilicate gel (K-A-S-H, N-A-S-H) constituted the hydrates phase. As for geopolymer mixture with the presence of CaO in waste ash and when additional calcium source is added, it will form various types of hydrates phase, i.e. sodium calcium aluminosilicate hydrate (N, C-A-S-H), calcium aluminosilicate hydrate (C-A-S-H) and calcium silicate hydrate (C-S-H). These hydrates can coexist i.e. N-A-S-H and C–S–H (calcium silicate hydrate) or it's Al-substituted C-A-S-H form when there is a raw material with CaO content is used for the synthesis of geopolymer (Khalid et al., 2018). Furthermore, Zhang et al., (2010) suggested that at high alkalinity N-A-S-

H is a predominant phase with a few precipitates of a calcium compound, while at low alkalinity both N-A-S-H and C-S-H gel coexisted.

Meanwhile, there was also geopolymeric binder that makes use of OPC as an activator, which produces calcium silicate hydrates (C-S-H) in conjunction with polycondensation of silica and alumina together with high alkali content to attain compressive strength. During the beginning of geopolymerisation process, the following reaction occurs as in Equation 2.1 and Equation 2.2, respectively (Komnitsas, 2011).

$$(Si_2O_5,Al_2O_2)_n + H_2O + OH^- \Rightarrow Si(OH)_4 + Al(OH)^{4-} \quad (2.1)$$

$$Si_2(OH)_4 + Al(OH)^{4-} \Rightarrow (Si - O - Al - O)_n + 4H_2O \quad (2.2)$$

Geopolymer concrete can be fabricated by either natural mineral or industrial waste ash that mostly contains highly amorphous aluminosilicate. It was discovered that the hydration products of FA and metakaolin are sodium aluminosilicate hydrates gel and hydration products of GGBS are calcium silicate hydrate gels (Singh et al., 2015). As indicated by Duxson et al., (2007) Metakaolin based geopolymer is better if compared with other hydrates because it can be as its properties are more persistence, but unfortunately metakaolin based geopolymer required high water hence resulted in severe rheological problems. As for other hydrates, FA based geopolymer showed better durability while GGBS based geopolymer presented higher early strength and more excellent acid resistance.

## 2.4 Constituents of geopolymer concrete

Other than fine aggregate, coarse aggregate and additional water used in geopolymer concrete, the two main constituents of geopolymer concrete are the raw source materials and the alkaline activators. The final geopolymeric products of geopolymer mostly depend on the aluminosilicate source materials and the alkaline activators. Characteristic of the source aluminosilicate will directly affect the dissolution process and the subsequent reaction, meanwhile for the alkaline activator it will partially or entirely dissolve the source aluminosilicate by splitting and recombination of the aluminosilicate structure, polycondensation and charge balance in the reaction system (Duxson et al., 2007).

Geopolymeric source materials can be formed by natural raw materials or industrial waste ash that have a rich aluminosilicate composition (Villa et al., 2010). Potential source material for the fabrication of geopolymer products is made up by any pozzolanic compound or material that contains alumina and silica predominantly in amorphous form and is readily dissolved in the alkaline solution (Ismail et al., 2014). The source material used for geopolymerisation can be an individual material or a binary and ternary mixture which in a combination of various types of raw materials. The selection of the source materials for fabrication of geopolymer however depends on several factors such as availability, cost, type of application, and specific requirement of the end products. Among the most widely used aluminosilicate based materials for fabrication of geopolymeric binder are fly ash, ground granulated blast furnace slag, metakaolin, rice husk ash and silica fume (Duan et al., 2017; Hasnaoui et al., 2019; He et al., 2013; Mijarsh et al., 2014; Onoue & Bier, 2017; Rostami & Behfarnia, 2017; Wan et al., 2017). In the following sub-section, a description of FA, GGBS, HCWA and SF are given as these materials were utilized in the present study.

### 2.4.1 Pulverised fuel ash (PFA)

Generally, PFA or commonly known as fly ash are divided into two categories by the combination of their $SiO_2$, $Al_2O_3$ and $Fe_2O_3$ content, whether high calcium PFA (class C) or low calcium PFA (class F). Mostly the available PFA is a class F, an industrial by-product obtained from the burning of anthracite and bituminous coal. It is considered one of the most abundant and essential source materials for geopolymer (Khale & Chaudhary, 2007; Lloyd & Rangan, 2010). Typically, PFA contains acidic oxides such as $Al_2O_3$, $SiO_2$ and $Fe_2O_3$, which provide the potential for alkali reaction (Williams et al., 2002). Most PFA from the combustion of coal is made up of an inhomogeneous mix of aluminosilicate and silica glasses with small amounts of crystalline materials including mullite, quartz, hematite and magnetite (Song et al., 2000). This degree of inhomogeneity means that additional precaution is required to ensure an optimal mix design and the consistent of geopolymer final product produced (Lloyd & Rangan, 2010).

Physical characteristics of PFA which includes particle size distribution and particle fineness have a significant impact on their reactivity, whereas relative silica content is most influential from a chemical perspective (Chen & Brouwers, 2007). The presence of highly reactive silica in the ash increases the potential formation of the aluminosilicate gel which provides strength development to geopolymer mixes. Duxson et al., (2007) found that PFA with a highly reactive $SiO_2$ and $Al_2O_3$ content with Si/Al ratios below 2.0 perform best with the addition of alkaline solution. The Si/Al ratios are the proportion of Si and Al mass of atoms in the binder materials. Potential geopolymer applications based on their inherent Si/Al ratios are presented in Table 2.1

Table 2.1 Application of geopolymer materials as related to atomic Si/Al ratio (Duxson et al., 2007)

| Si: Al Ratio | Applications |
|---|---|
| 1 | Bricks Ceramics<br>Ceramics<br>Fire protection |
| 2 | Low $CO_2$ cements and concretes<br>Radioactive and toxic waste encapsulation |
| 3 | Fire protection fibreglass composites<br>Foundry equipment<br>Heat resistant composites, 200°C to 1000°C<br>Tooling for aeronautics titanium process |
| >3 | Sealants for industry, 200°C to 600°C<br>Tooling for aeronautics SPF aluminium |
| 20-35 | Fire-resistant and heat resistant fibre composites |

The final reaction product of PFA geopolymer is an amorphous to semi-crystalline structure similar to a zeolite precursor. The activation process and rate of reaction within the geopolymer paste are directly related to the glass content of the ash material (Chen & Brouwers, 2007). The critical factor for a PFA based geopolymer product for optimum binding properties should be considered with the following properties: less than 5 % of unburned material; less than 10 % $Fe_2O_3$; a high content of CaO; 40–50 % relative silica; 80–90 % of particles with diameter equal to or less than 45 μm; and a high vitreous phase (Chen & Brouwers, 2007).

The aluminium content of a PFA is critical to the hardening properties of a geopolymer binder. In the presence of alkali aluminosilicate solution, the aluminium content is believed to be the chemical trigger for irreversible cement hardening (Lloyd & Rangan, 2010). The dissolution of solid $Al_2O_3$ regions by the activating solution controls the rate, stoichiometry and extent of solution-phase reactions is dependent upon several variables including pH level, binder temperature, Si/Al ratio and alkali concentration (Lloyd & Rangan, 2010). For this reason, the composition and

mineralogy of raw industrial waste ash are critical in the formulation of hybrid geopolymer concrete.

The utilisation of PFA in hybrid geopolymer is considered as environmental friendly in several aspects. Namely, it reduces the amount of raw material that needs to be extracted when producing OPC, fewer greenhouse emissions are emitted into the environment and less energy is used during the production process of the geopolymer constituents. Furthermore, PFA does not have a calcination process unlike OPC and therefore utilisation of PFA on hybrid geopolymer concrete should have lower embodied energy, consuming approximately 70% less energy compared to OPC concrete with the same strength (Sakulich, 2011).

### 2.4.2 Ground granulated blast furnace slag (GGBS)

Ground granulated blast furnace slag (GGBS) is another industrial by-product resulting from rapid water-cooling of molten slag. It is well known to have advantageous properties for the concrete industry as it is relatively inexpensive to obtain, highly resistant to chemical attack and maintains excellent thermal properties. Major components of the slag product include amorphous CaO, $SiO_2$, MgO and $Al_2O_3$ are commonly found in commercial silicate glasses. Typical slag based binder products are formed by combining GGBS with 3.5–5.5 % (by mass) sodium hydroxide or sodium silicate. Alkali-activation of GGBS yields a low-basic, highly amorphous calcium silicate hydrate (C-S-H) gel product possessing high aluminium content (Pacheco-Torgal et al., 2008). Some researchers refer to this product as alkali-activated slag (AAS).

Chemical shrinkage and porosity volumes in saturated Ground Granulated Blast Furnace Slag (GGBFS) pastes are significantly higher than in Portland cement