DEVELOPMENT OF SUPERSULFATED SELF-CONSOLIDATING CONCRETE INCORPORATING HIGH-VOLUME OF INDUSTRIAL BY-PRODUCTS

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by

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LIST OF ABBREVIATIONS

ASTM	American Society of Testing Materials
BS	British Standard
BET	Brunauer, Emmett and Teller Surface Analysis
BOF	Basic Oxygen Furnace Slag
CDW	Construction and Demolition Waste
CH	Calcium Hydroxide
C-S-H	Calcium Silicate Hydrate
EAF	Electric Arc Furnace
EDX	Energy Dispersive X-Ray Analysis
GGBS	Ground Granulated Blast Furnace Slag
GQW	Granite Quarry Waste
HRWA	High Range Water Reducer
LOI	Loss of Ignition
LQW	Limestone Quarry Waste
OPC	Ordinary Portland Cement
RH	Relative humidity
SCC	Self-Consolidating Concrete
SCM	Supplementary Cementitious Materials
SEM	Scanning Electron Microscopy
SF	Silica Fume
SP	Superplasticizer
TGA	Thermogravimetric Analysis
UPV	Ultrasonic Pulse Velocity
VMA	Viscosity Modifying Admixture
w/b	Water to binder Ratio
XRD	X-Ray Diffractometry
XRF	X-Ray Fluorescence

PEMBANGUNAN KONKRIT MEMADAT SENDIRI SUPERSULFATED DENGAN MENGANDUNGI PRODUK SAMPINGAN PERINDUSTRIAN YANG TINGGI

ABSTRAK

Produk sampingan industri ialah salah satu bahan simen alternatif yang menarik dan berupaya mengurangkan penggunaan sumber asli serta menggalakkan aktiviti kitar semula. Salah satu cara penggunaan bahan ini dalam komposisi yang tinggi adalah dengan menggunakannyya di dalam sistem pengikat *supersulfated*. Walau bagaimanapun, pengetahuan rangka kerja terkini mengenai sifat-sifat pengikat *supersulfated* adalah terhad dan perlu diberi perhatian. Oleh itu, penyelidikan ini bertujuan untuk menilai sifat-sifat konkrit memadat sendiri (SCC) *supersulfated* dengan menggabungkan produk sampingan industri dalam komposisi yang tinggi iaitu serbuk sanga relau bagas tergiling (GGBS), abu terbang dengan sebahagian kecil gipsum dan simen. Selain itu, sisa kuari granit (GQW) digunakan sebagai agregat halus dan sanga relau arka elektrik (EAF) dan batu granit sebagai agregat kasar dalam pembangunan SCC. Komposisi pengikat terdiri daripada 80% GGBS dan 20% abu terbang dicatatkan sebagai kandungan optimal untuk digunakan sebagai pengikat primer dalam pengikat *supersulfated.* Kombinasi ini diaktifkan dengan menambahan campuran 0-10% OPC-gipsum. SCC supersulfat telah dibiarkan di bawah keadaan pengawetan lembap sehingga 270 hari. Pemeriksaan sifat-sifat segar, kejuruteraan, pengecutan pengeringan, ketahanan dan struktur mikro kemudiannya dijalankan untuk membangunkan pengetahuan rangka kerja komprehensif SCC *supersulfated*. Semua SCC *supersulfated* hanya memerlukan nisbah air (w/b) sebanyak 0.27-0.33 untuk pengikat dengan kandungan tetap bahan pemplastikan polikarboksil (SP) sebanyak

0.6% untuk mencapai keperluan sifat segar SCC yang diinginkan. SCC *Supersulfated* yang mengandungi 4% OPC and 6% GGBS mempamerkan sifat-sifat kejuruteraan dan ketahanan optimal sepanjang proses pengawetan yang berpanjangan. Semua SCC supersulfated menunjukkan ketahanan yang lebih baik di bawah persekitaran yang agresif berbanding SCC yang mengandungi 100% simen. Walau bagaimanapun, SCC rosak pada kadar yang lebih tinggi apabila terdedah kepada 5% asid sulfurik untuk SCC yang mengandungi sanga EAF. Pengembangan kekuatan bahan berdasarkan kajian struktur mikro pada pengikat *supersulfated* ditentukan oleh pembungkusan zarah padat pada matrik pengikat dengan kehadiran produk hidrasi yang kurang. Sebagai kesimpulan, pengikat *supersulfat* diperbuat daripada GGBS dan abu terbang dalam komposisi yang tinggi adalah bahan pengikat yang bernilai untuk pembuatan SCC disamping menyediakan saluran untuk kitar semula bahan buangan dalam jumlah yang besar.

DEVELOPMENT OF SUPERSULFATED SELF-CONSOLIDATING CONCRETE INCORPORATING HIGH VOLUME OF INDUSTRIAL BY-PRODUCT

ABSTRACT

An industrial by-product is one of the attractive alternatives to cement materials that can reduce the consumption of natural resources as well as encouraging recycling activity. One of the high-volume utilisations is by using it in supersulfated binder system. However, current limited knowledge framework established about the properties of supersulfated binder need to be addressed. Thus, this research was aims to evaluate the properties of supersulfated self-consolidating concrete (SCC) containing combination of high-volume industrial by-products namely ground granulated blast furnace slag (GGBS), fly ash with small portion of gypsum and cement. Apart from that, the granite quarry waste (GQW) was used as fine aggregate, and electric arc furnace (EAF) slag and granite stone were used as the coarse aggregates in the development of SCC. The binder composition consists of 80% GGBS and 20% fly ash was recorded as optimum percentage to be used as primary binder phase in supersulfated binder. The combination was activated with the addition of 0-10% blended OPC-gypsum. The supersulfated SCC was cured under moist curing condition and tested up to 270 curing ages. The examination of fresh, engineering, drying shrinkage, durability and microstructure properties was later conducted to develop a comprehensive knowledge framework on the properties of the supersulfated SCC. All supersulfated SCC only required water to binder (w/b) ratio of 0.27-0.33 with a fixed 0.6% of the polycarboxylate superplasticiser (SP) to achieve the desired SCC fresh properties requirement. Supersulfated SCC containing 4% OPC and 6%

GGBS exhibited the optimum engineering and durability properties over prolong curing. All supersulfated SCC regardless type of coarse aggregate exhibited better resistance under aggressive environment compared to the 100% cement SCC. However, the concrete deteriorates at a higher rate upon exposure to 5% sulfuric acid for SCC containing EAF slag. The microstructure study on supersulfated paste shows that the strength development of the material was governed by the dense particle packing of the binder matrix that resulted in a rigid interlocking particle in the presence of a scarce amount of hydration products. In conclusion, the supersulfated binder made with a large volume of GGBS and fly ash is a valuable binder material for making SCC while providing a channel for extensive volumes recycling of the waste materials.

CHAPTER 1

INTRODUCTION

1.1 Background

The construction industry is one of the critical drivers in boosting Malaysian's economic development and the civil engineering subsector is the lead contributor in this industry followed by non-residential, residential, and specialised construction subsectors as of 2016 (Ministry of Finance, 2017). The construction industry provided socio-economic infrastructure towards providing essential amenities and subsequently facilitates economic development. However, the growth of the construction industry also contributed to the high of carbon dioxide (CO_2) emission to the environment. The increasing trend of CO_2 emission in Malaysia indicated that it is higher than the neighbouring countries such as Thailand and Indonesia (The World Bank, 2014).

According to Malaysia's biennial update report (BUR) to the United Nations Framework Convention on Climate Change (NFCCC) in 2016, the manufacturing and construction industry was the third-largest contributor of CO_2 emission in Malaysia. These industries had contributed to 11% of CO_2 emission with a total of 208,258 Gg being CO_2 emitted. The largest contributor was the energy industry, followed by the transportation industry. Cement production, limestone and dolomite use, and iron and steel production contributed to 4, 3 and 1% CO_2 emission respectively. Currently, the cement industry is the third-largest industrial energy consumer and represents 7% of the total world's CO_2 emission. The arising of global population and urbanisation will eventually increase the demands on for cement and concrete (IEA, 2018).

According to the International Energy Agency's (IEA) Reference Technology Scenario, direct carbon emission from the cement industry is expected to increase a further 4% from the expected growth of cement production and this translates into 12-23% globally by 2050, due to increasing urban population. According to Davidovits (2013), the production of one tonne of Portland cement could generate 0.95 tonnes of CO_2. From that value, 0.55 tonnes come from releasing the CO_2 chemical using the clinkering process and another 0.40 tonnes from the combustion of coal. At the same time, the making of OPC needs an abundant amount of natural resources and this indirectly caused the depletion of the natural resources.

Carbon captures, energy-efficient technology, waste heat recovery, alternative fuels and the alternative binder production are among the initiatives that had been applied in cement plants to mitigate the CO_2 emission (Ishak and Hashim, 2015). As an ambitious target to limit the global temperature rises to 2 °C by 2100, lowering the clinker content with an alternative binder is one of the mitigation measures that yield the most substantial cumulative CO_2 emission. It is because clinkering is the most energy-intensive process that involves the calcination of calcium carbonate and also heating of raw materials up to 1450 °C. The alternative binder can be the usage of well-known industrial by-products. Such industrial by-products are ground granulated blast furnace slag (GGBS), fly ash, silica fume (SF), rice husk ash (RHA) and palm oil fuel ash (POFA) as supplementary cementitious materials (SCMs). However, it only reduces CO_2 released by not more than 15%. This contributed to the emergence of geopolymer and alkali-activated technologies to fully utilise the use of industrial by-products materials. However, it still required high temperature curing and the need for chemical activators that may not be feasible in large-scale construction application.

Nevertheless, Malaysia's efforts to reduce up to 45% of greenhouse gas emission intensity of Malaysian Gross Domestic Product (GDP) by 2030 lead to the establishment of the Green Technology Master Plan (2017-2030). The master framework which supports the National Green Technology Policy towards directions of Eleventh Malaysian Plan is one of the government initiatives to move forward with sustainable development. Greening the building sector is one of the critical factors on its life cycle approach and this includes sustainable construction practice together with the increase of the number of green building materials as well as making policy amendments to allow for the usage of recycled materials in construction (KeTTHA, 2017).

On the other hand, GGBS is one of the famously known recycled materials or interchangeably known as industrial by-product material that is widely used in the construction industry. It is also one of the by-products of the iron production industry that comes from the iron blast furnace. It is distinctively different from the electric arc furnace (EAF) slag that originates from the electric arc furnace used in the steel making process. These by-products had been proven to have excellent properties to be used as a binder and aggregate substitution in concrete (Horii *et al.*, 2015, Faleschini *et al.*, 2015) and the utilisation of slag can contribute to zero waste in the steel and iron making industry. World crude steel production showed an increasing trend each year with 1689 million tonnes of crude steel produced in 2017 and EAF slag is expected to increase due to the growing rate of recycling of scrap steel in the future.

Likewise, the flue gas produced in pulverised coal-fired furnace also releases a pozzolanic, by-product material namely fly ash from its separation of dust particles from the flue gas in the electrostatic precipitator. In 2016, Malaysia produced 1,332,600 tonnes of coal with the face value of RM159,950 million from 5 of the local coal mines. The coal is mainly consumed by the cement production plants, power generation and iron and steel making industry (Malaysian Minerals, 2016). Even though currently natural gas is the primary source of power generation, it is expected that in the coming years; the coal demand will continuously increase and it could become the number one fuel sources of power generation in Southeast Asia. This is due to the addition of power generation capacity, taking advantages of the abundance of young coal fleets across this region (Burnard *et al.*, 2016). It will also subsequently increase the generation of fly ash which will in turn obligate appropriate disposal and recycling measures to be put in place for sustainable management of the waste.

The present study has attempted to develop a new formulation of innovative binder materials by incorporating a high volume of industrial by-products in the making of self-consolidating concrete. This contributed to the reduction of CO_2 emission from the construction industry and shifting the continuous dependence on natural materials towards recycling of industrial by-products which will subsequently eliminate the land area required for landfills.

1.2 Statement of Problem

Concrete is one of the widely use composite material in the world. Even though we already moving forward from lime based, clay bake binder, the modern and industrialised Portland cement do not always give positive contribution towards the environment. Carbon captures, energy-efficient technology, waste heat recovery, alternative fuels and the alternative binder production are among the initiatives that had been applied in cement plants to mitigate the CO_2 emission. Alternatives binder is one of the initiatives that not only can reduce the CO_2 emission, but also capable of reducing the continuous need for natural raw materials in the making of OPC that cause the depletion of natural resources. Not only that, it also allowed the utilisation industrial by-products as a binder instead of dumping in landfills. However, the incorporation of industrial by-products as alternative binder often use as SCMs in low volume and can only reduce the CO_2 released by not more than 15% (Bonavetti *et al.*, 2014, Vijayagowri *et al.*, 2015). The slow strength development of most of the industrial by-product makes them only suitable to be used in high volume for specific application such as in mass concrete application or with high early strength cement (Gholampour and Ozbakkaloglu, 2017). The elimination of OPC and fully utilised industrial by-products as a binder can be accomplished by executing alkali-activated or geopolymer technologies to increased strength development. Nevertheless, these binder existing binder technologies required chemical ingredients with high alkalinity or high temperature curing that might not be reliable and could pose a handling hazard if implemented in big-scale construction.

Existing alternative binder named supersulfated cement used to have a reputation in Europe in the early 1900s as its capabilities to incorporate high-volume industrial by-products up to 85% without affecting its strength performance. However, the change in the pig iron manufacturing process had altered the chemical compositions of its by-products, namely GGBS that subsequently made it less reactive to be used as a primary binder in supersulfated cement. Few researchers have conducted studies on improvement in supersulfated cement to make it practical to be used as a binder for concrete production. Such improvement to initiate sufficient reactivity was again included chemical activator thus makes it no different than an alkali-activated binder. Moreover, the existing studies also more focused on the hardening mechanism of low alumina GGBS as primary binder materials without an in-depth analysis of its durability and engineering performance. Therefore, a new formulation of binder materials that can activate the GGBS without chemical activator and elevated curing temperature needs to be developed.

On the other hand, the making of self-consolidating concrete (SCC) requires a high volume of binder to achieve its desired fresh properties. Thus, incorporating supersulfated binder is one of the ways to cater to this need since incorporating OPC in high volume may not be sustainable. However, there is limited knowledge framework on the properties of the supersulfated SCC that has been established compared to conventional concrete. The limited knowledge was not only in terms of rheological properties but also in term of engineering, durability, and shrinkage performance. Such gap of knowledge is especially critical for supersulfated SCC material containing high volume GGBS and fly ash where there is a distinct absence of knowledge framework on the properties of such materials in the present body of literature.

1.3 Research aims and objective

This research is designed to evaluate the suitability and performance of the combination of high-volume low reactivity GGBS, fly ash and the small inclusion of gypsum and/or OPC (supersulfated binder) in the production of self-consolidating concrete for implementation in structural load-bearing applications. The inclusion of these high-volume industrial by-products in concrete not only reduce the amount of waste to be landfilled but also promoting the sustainable way of recycling. Moreover, SCC made with high-volume GGBS-fly ash with various gypsum/OPC combinations was assessed in terms of rheological, engineering, durability and microstructure development. The overall objectives of this research are listed as follow:

a) To develop a suitable SCC mix composition which enables large volume reuse of industrial by-products to be used and low alkalinity level for ease of handling for construction.
b) To establishing the knowledge framework on the rheological properties and engineering performance of supersulfated SCC.
c) To study the durability and drying shrinkage of supersulfated SCC with GGBS and fly ash as the primary binder phase.

1.4 Significance of the research

The evolution of manufacturing process of pig-iron iron produced slag output with different chemical composition compared than when they first been introduced, thus its manifest low in early strength. The significant of this research of not only can solve the problems that discussed prior, but also to bridge the gap of knowledge of currently available literature of supersulfated and slag-activated binder. The new formulation will reshape on how the supersulfated binder being made, with combination of multiple supplementary cementitious materials (SCMs). The usage of SCMs from by-products of coal and ironmaking industries can improved the quality of the environment by eliminating the large disposal site needed over time. At the same time, it also avoiding cost for landfill disposals. Not only that, the use of industrial by-products will reduce the demand of OPC and subsequently alleviate the carbon dioxide emission associate with its production.

Moreover, also intended to encourage concrete producers on effectively use industrial by-products in concrete with valuable economic and environmental benefits without limiting their applications. This research also aiming to develop a supersulfated binder that are adaptable and versatile. The comprehensive body of knowledge derived from this research can be applied not only into SCC production but also for conventional concrete even when exposure to aggressive environment. The supersulfated SCC in this research was designed to eliminate the need of viscosity modifying admixture (VMA) and making it suitable to be used in SCC with normal or high-density aggregates.

1.5 Scope of the research

In order to achieve the objective of the research, the scopes of this research are:

a) Assessment physical and chemical properties of material used in this research (GGBS, fly ash, gypsum and OPC)
b) Establishing the optimum hybridisation matrix for mortar containing GGBS and fly ash binder.
c) Choosing the suitable type of gypsum sources to be add into GGBS-fly ash binder to create supersulfated binder.
d) Establishing the suitable fine to coarse aggregate ratio for supersulfated SCC containing WQD as fine aggregate together with granite stone or EAF slag as coarse aggregate.
e) Study on the rheological properties of various mix proportion on supersulfated SCC
f) Investigating the influences of supersulfated binder with various gypsum and OPC content in term of engineering, drying shrinkage and durability of SCC.

Hence, the limitations of this study are:

a) The amount of gypsum and OPC used are limited to not more than 10% of the total binder content.

b) The superplasticizer used was fixed for all mix design and water content was added to get the desired flow diameter including for fully OPC mix.

c) The industrial by-product used in this study for coarse and fine aggregates were fixed to 100%.

d) With exception of drying shrinkage, the study does not consider a curing exposure under normal air as only curing by plastic wrapping were considered.

1.6 Thesis layout

The thesis consists of six chapters to cover the significant aspect of engineering properties and structural behaviour of supersulfated self-consolidating concrete. In Chapter One, the background of this research investigation was briefly discussed particularly concerning the increasing trend of CO_2 admission in a relationship with the world's cement production industry and the sustainable use of industrial by-product. In addition to that, this chapter also discussed the problems of the current trend in innovative binder technology and the significance of this research, and the scope of work covered throughout this research.

In Chapter Two, the use of industrial by-product mainly GGBS and fly ash in concrete were discussed thoroughly. The implementation of GGBS in innovative binder technology such supersulfated cement, sulfate-based cement and sulfate-activated cement very review in depth. Not only that, the incorporation of industrial by-products as binder or as aggregate replacement in SCC application were critically reviewed. The influence of these materials such as GGBS, fly ash, GQW, and EAF slag in terms of fresh, durability, engineering and hardening mechanism were reviewed and discussed.

Chapter Three thoroughly discussed the experimental programme and relevant test methodology applied to investigate the essential parameters of the characteristics and performance of the materials used in this research program. Chapter Four discussed the fresh properties of supersulfated paste and SCC including the standard consistency, setting time. There was also a detailed assessment on the engineering properties of the supersulfated self-consolidating concrete, namely the ultrasonic pulse velocity test (UPV) and drying shrinkage for non-destructive test and compressive and flexural test for a destructive test of hardened concrete.

A detailed analysis of the durability of supersulfated self-consolidating concrete was thoroughly discussed in Chapter Five. The durability analysis, for supersulfated pastes were X-Ray Diffraction (XRD) analysis, surface area analysis via Brunauer-Emmett-Teller (BET), material characterisation via Thermogravimetric and analysis (TGA). For supersulfated SCC, water absorption, porosity, intrinsic air permeability, resistance to sulfate attack, chloride permeability, and resistant under sulfuric acid were sufficiently elaborated. Apart from that, microstructure analysis binder of supersulfated pastes by Scanning Electron Microscopy (SCM) also presented to further justify the hardening mechanism and relationship with the durability performance in an earlier subsection.

To conclude, Chapter Six presented the overall conclusion and summary from the experimental works mentioned the preceding chapter. Recommendation for future research was also suggested in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, the background of past studies on the properties of concrete fabricated using industrial by-product had been intensively discussed either in conventional or self-consolidating concrete. Factors influencing the rheological, engineering properties, durability properties and hardening mechanism of the industrial by-products by implementing them as innovative binder or aggregates replacement in concrete or mortar had also been discussed and reviewed in detail.

2.2 The recycling of industrial by-product as a concrete constituent

Civil engineering works undeniably cause the depletion of natural resources and growing demands for building materials, making the efforts of various researchers to contribute towards the creation of more sustainable materials imperative. These lead to investigations that were primarily aimed at lessening the dependence on the extraction of natural resources. Also, due to its decreasing availability and also the concern about creating a better environment. Innovative and new materials have been developed and studied to solve the increasing demands for new and sustainable construction materials. Such materials are based on waste materials or also known as an industrial by-product or recycle materials. Table 2.1 shows various categories and nature of solid waste and their recycling application potentials compiled by Grubeša *et al.* (2016). Concrete, the well-known composite material widely used in various structural areas of civil engineering consists of ordinary Portland cement (OPC), coarse and fine aggregate and water is the most used man-made material in the world. However, cement, as the traditional binder material with excellent binding properties in concrete, contributed to

CO_2 emission during the production process. On the other hand, the aggregate is an unreactive particle in concrete that contributed to the concrete strength and occupied a substantial portion of the concrete’s volume such as rock, gravel, sand and crushed stone. It is also typically derived and dependent on depleting natural resources. Currently, the high demand of natural aggregate causes exhaustion of aggregate quarry which can contribute to the new quarry opening which can increase the transportation distance and costs as the sources become scarce (Qasrawi, 2014). A sustainable approach to replace natural aggregate in concrete with industrial by-product can reduce the depletion of the available land for landfill, stockpiles or illegal dumping activities. Such approach would be able to respond to the impending crisis due to the exhaustion of natural aggregate.

2.3 The utilisation of industrial by-product as binder materials in concrete

The most common reactive industrial by-product materials that show cementitious properties include ground granulated blast furnace slag (GGBS), cement kiln dust (CKD) and waste gypsum while materials with pozzolanic properties such as fuel ash, calcined clay (metakaolin), silica fume, risk husk ash (RHA), palm oil fuel ash (POFA), wood ash, volcanic ash, waste glass, or sewerage sludge incineration ash. Cementitious and pozzolanic materials have widely been used as SCMs to replace OPC as a binder in concrete partially due to the existence of reactive component such SiO_2, Al_2O_3 and CaO in their chemical compositions as shown in Figure 2.1. The emergence of binary, ternary or quaternary blends of these materials also attracted researchers’ interests not only to achieve excellent properties but also to accommodate and maximise the use of these materials depending on their availability in various regions across the world. These contributed to the development of innovative binder technology such as blast furnace slag cement, pozzolanic cement, supersulfated cement, alkali-activated cement, sulfate activated cement and geopolymer. Other than that, these binder materials have also been used as mineral admixtures to improve the properties of concrete, mortar or paste.

Table 2.1 Categories and nature of solid waste and their recycling application potential (Grubeša *et al.*, 2016)

Categories of solid waste	**Source details**	**Recycling and application in building application**
Agro organic	Bagasse, rice and wheat straw and husk, cotton stalks, sawmill waste, ground nut shells, banana stalks, and jute, sisal, vegetable residue	Plasterboard, insulation boards, wall panel, printing paper and corrugating media, roofing sheets, fuel, binders, fibrous building panels, brick, acid-proof cement, coir fibre, reinforced composites, cement board
Industrial waste (inorganic)	Coal combustion residue, slag, bauxite red mud, waste glass, rubber tires, construction debris	Cement, bricks, blocks, tiles, paint, aggregate, cement, concrete, wood substitute products, ceramic products, subbase pavement materials
Mining/mineral waste	Coal washery waste, mining overburden waste, quarry dust, tailing from the iron, copper, zinc, gold, aluminium industries	Bricks, tiles aggregate, concrete surface finishing materials, fuel
Non-hazardous other process waste	Waste gypsum, lime sludge, limestone waste, marble processing residue, broken glass and ceramics, kiln dust	Gypsum plaster, fibrous gypsum board, bricks, blocks, cement clinkers, supersulfated cement, hydraulic binders
Hazardous waste	Metallurgical residue, galvanising waste, tannery waste	Cement, bricks, tiles, ceramics and boards

Currently, an emergence of geopolymer technology enables the elimination of OPC by activating the unary or more amorphous to semi-crystalline three-dimensional aluminosilicate materials as precursors with alkali activator (Davidovits, 2011). The general types of alkali-activator are sodium hydroxide (NaOH) and sodium silicate

(Na_2SiO_3) to form similar or better properties as conventional OPC concrete. Geopolymer technology should not be mistaken for the well-known alkali-activated materials (AAMs) technology as the same terminology. Aluminosilicate rich materials with a high content of silica (Si) and alumina (Al) are essentials for geopolymer formation with co-existence of calcium aluminosilicate hydrate (C-A-S-H) and sodium aluminosilicate hydrate (N-A-S-H). The terminology is still being debated as a recent study by Liu *et al.* (2016) had proven that the geopolymerisation product of fly ash-based geopolymer is unlikely to contain hydrates. Regardless, both technologies had proven to be beneficial especially towards a better environment but introducing relatively high alkali content into the mix design can be unpractical especially in mass production. Geopolymeric alkaline elements might be dangerous as they are classified as corrosive and irritant products thus appropriate safety procedures for handling are necessary (Davidovits, 2011).

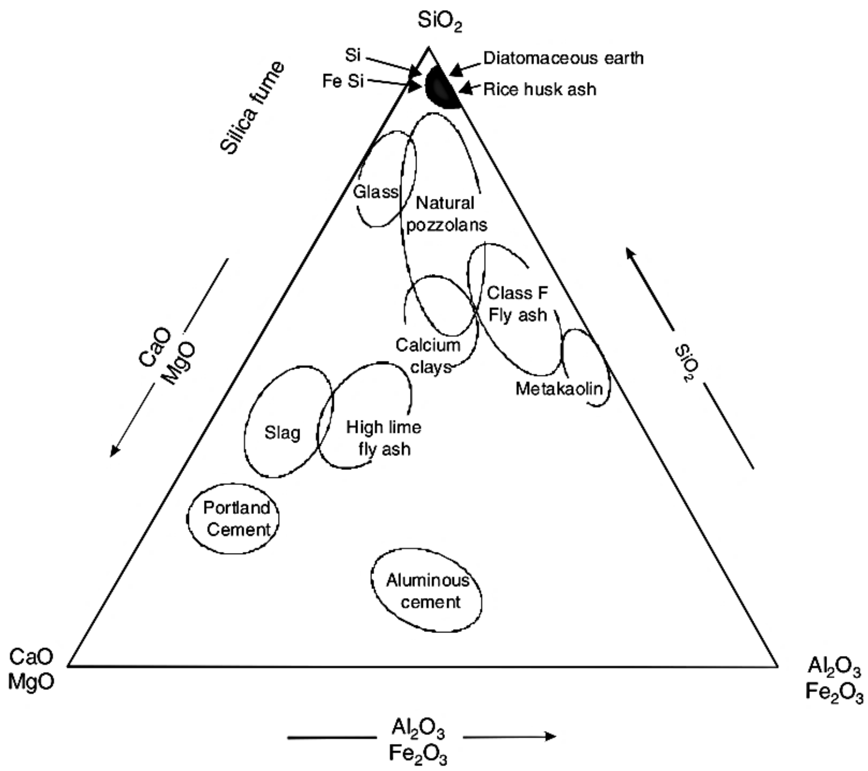

Figure 2.1 The chemical composition of primary cementitious materials (Aitcin, 2008)

2.3.1 Fly ash

Long before the discovery of artificial pozzolan, the Greeks used Santorine earth, which was volcanic ash from Santorine's volcanic explosion that covered the surface Thera island as a binding material or also known as a natural pozzolan. Later, the ancient Romans found the non-hydraulic cement made of natural pozzolan, namely volcanic ash and pumice (Li, 2011). Roman architect, Marcus Vitruvius has described in his book *De Architectura,* the principals of the formation of foundation and marine concrete based on the combination of volcanic ash and hydrated lime mortar which was capable of binding volcanic rock fragments under self-reinforcing framework (Jackson *et al.*, 2018). Later, in 1756, John Smeaton begins experimenting with the combination of slaked lime and pulverised pozzolans in order to rebuild Eddystone Lighthouse, off the coast of Cronwell, England, which could withstand the severe marine environment. However, not until 19th century, the now famously known artificial pozzolanic material, fly ash or also known as pulverised fuel ash was found extensively used as a binder material in concrete due to its pozzolanic behaviour. Fly ash, a by-product of combustion of coal for the generation of energy, accounts for approximately 70-85% of all coal ash produced from around the world.

The laboratory study on fly ash for use in concrete was started in the United States by Raymond E. Davis and his associates as the availability of fly ash from coal-burning fired plant in 1930s growing (Davis *et al.*, 1937, ACI, 2003). Soon after, the Bureau of Reclamation begins to use fly ash for the repair of tunnel spillway at Hover Dam in 1942. Fly ash was subsequently started to be used in large scale when 110,000 tons of fly ash or approximately 30% of total cement weight used during the construction of Hungry Horse Dam on the Flathead River, Montana in 1948 (Bensted and Barnes, 2002). It was the only known fly ash specification written by Bureau for that construction project before the specification covering the used of fly ash in concrete established by ASTM in 1953. Later, a new cement that consist of fly ash as blended cement material was first patented in the early 1950s by M. Fouilloux in France (Jarrige, 1967). During this period, fly ash was extensively used in cement plant by blended with finish cement product, interground with cement clinker or blended with other materials in cement raw batch to achieved certain chemical composition in kiln feed. Furthermore, in the 1980s, French researcher, Joseph Davidovits had proposed that the magnificent ancient Egypt structure; the Great Pyramid of Giza was made from the granular limestone aggregate bound with alkali aluminosilicate-based binder which was cast in situ. The binder resemblance chemistry of aluminosilicate materials of pozzolan, namely fly ash and metakaolin called geopolymeric reaction had contributed to the invention of geopolymer cement. Since then, fly ash had been widely used as construction materials, not only limited as a binder in concrete but also as a soil stabilisation material, road or sub-base and structural fill.

In Malaysia, fly ash is still abundant and this resulted from the combustion of coal to generate electricity. Based on Malaysian Energy Commission (2017), the power sector utilises 23 million tons of coal annually in Peninsular Malaysia. As of December 2016, Malaysia had 1938.37 million tonnes of coal reserves which comprised mainly of bituminous, sub-bituminous, anthracite, lignite and coking coal types. For the fly ash to be used as construction materials, a few countries have their own standards of reference to understand their reactivity based on its chemical composition. Table 2.2 shows the most relevant standards used around the world and the type of fly ash available was grouped in different categories. For example, the reactivity of fly ash as described in American Standard, ASTM C618 (ASTM, 2019) reference standard can be classified as Class C or F. The fly ash classification is customarily based on its lime (CaO) content which often belongs to Class F fly ash for low CaO content and Class C fly ash for high silicon dioxide (SiO_2). However, some Class C fly ash may possess some cementitious properties if it contains higher than 10% of CaO. In Malaysia, the Malaysian standard MS EN 450 (Standards Malaysia, 2014) for fly ash is adopted from the European (EN) Standard, EN 450 (BSI, 2012).

Fly ash also contains some carbonaceous matter that is taken as equivalent to its loss on ignition (LOI). For a technical and aesthetical reason, it is essential for the LOI values to be maintained at the maximum of 7% according to MS EN 450: Part 1 (Standards Malaysia, 2014) or 10% as recommended by ASTM C618 (ASTM, 2019) The high carbon content in fly ash may reduce the effectiveness of air-entraining admixtures or unsatisfactory water reduction of the water reducers when in used with chemical admixtures due to the highly absorptive nature from the interaction of fly ash and variability of carbon content (Cheah *et al.*, 2014).

The reactivity of fly ash is also different based on its geographical location. For instance, the fly ash sourced from 4 different power plant in USA based on the study by Cross *et al.* (2008) were produced by burning on same type of sub-bituminous coal and same combustion process. Such coal and combustion process produce high calcium fly ash that competent to produced cementless, 100% fly ash concrete. Similarly, fly ash sourced from Lampang, Thailand based on research by Chindaprasirt *et al.* (2011) was derived from lignite coal which also contained high in calcium. Table 2.3 shows the chemical composition of fly ash that comes from different locations around the world in the making of various types of binder for concrete or mortar applications. Fly ash from different coal origins would expect to have differences in term of chemical, physical and mineralogy. Thus, it will affect their ability and reactivity when used as a binder. Fly ash produced from anthracite or bituminous coal predominantly contains crystalline phases that are inert which are composed of aluminosilicate glasses with varying amount of quartz, magnetite, mullite and hematite. This type of fly ash needs support from an alkaline activator to react actively and to form cementitious hydrates. In contrast, fly ash from lignite and sub-bituminous coals contain calcium-alumino-silicate glasses with a variety of crystalline phases including the phases found in anthracite and bituminous. Calcium bearing glass and some of these phases, when reacted with water, will react rapidly and exhibit their pozzolanic and hydraulic nature (Thomas, 2007).

Table 2.2 Fly ash requirement to be used in concrete by various relevant standards.

Standard	Type/ Categories	Loss of ignition (%)	Moisture (max %)	Silicon Trioxide, SO_3 (max %)	SiO_2 (min %)	SiO_2 + Al_2O_3 + Fe_2O (min %)	Total Chloride (max %)	Fineness at 45 µm retained (max %)
Europe EN 450 – 1 : 2012	A	5	-	3	-	70	0.1	40[a], 12[b]
	B	7	-		-			
	C	9	-		-			
USA ASTM C618 : 2019	Class N	10	3	-	-	7	-	34
	Class F	6		-	-	70	-	
	Class C	6		-	-	50	-	
Japan JIS A 6201 :2015	I	3	1	-	> 45	-	-	10
	II	5		-		-	-	40
	III	8		-		-	-	40
	IV	5		-		-	-	70
China GB/T 1596: 2017	I	5	1	3	-	-	-	12
	II	8			-	-	-	25
	III	15				-	-	45
India IS 3812 – 1 : 2013	Siliceous	5	2	3	35	70	0.05	34
	Calcareous				25	50		
Australia AS 3582 – 1: 1998	Fine (Special)	4	1	3	-	-	-	25
	Fine	4			-	-	-	
	Medium	5			-	-	-	
	Coarse	6			-	-	-	45
Canada CSA A3001 : 2013	F	8	5	-	-	-	-	34
	CI	6		-	-	-	-	
	CH			-	-	-	-	

[a] For category S cement
[b] For category N cement

All cementitious materials, including fly ash and GGBS, consisted of alkali metal ions. However, instead of being present as water-soluble sulfate just like OPC, they are concentrated in the glassy structure of their particles with low content of soluble alkali metal ions. The reaction of this glass particles liberates the alkali metal ions but does not affect the alkalinity of the concrete compared to OPC since the lower ratio of CaO: SiO_2 in calcium silicate hydrate (C-S-H) caused higher alkali metal ions to be removed from the solution (Jackson and Dhir, 1996). Fly ash has been widely used as binary or ternary binder materials in various types of concrete not only in conventional (Cheah *et al.*, 2019b) but also geopolymer (Ken, 2017) and alkali-activated concrete. Besides, for the use of fly ash in concrete, it is essential for the ash to exhibit consistency in the overall composition rather than small scale variations.

Table 2.3 The main chemical composition of fly ash used by various researchers from a different geographical location

Authors	Fly ash sources location	Composition (%)				
		CaO	SiO_2	Al_2O_3	Fe_2O_3	LOI
Cementless binder (no cement and alkali-activator)						
Cross *et al.* (2008)	USA*	28.89	32.37	17.52	5.43	0.23
		27.00	35.05	18.63	6.46	0.19
		27.60	35.10	18.40	4.90	0.80
		26.88	33.99	21.39	5.86	0.40
Zhong *et al.* (2012)	China	6.49	48.90	33.80	5.08	-
Binary blended						
Guo *et al.* (2010)	USA	20.00	38.00	19.00	9.00	3.50
Siddique *et al.* (2012)	India	2.23	58.55	28.20	3.44	4.17
Arezoumandi and Volz (2013)	USA	26.28	33.46	19.53	6.28	0.34
Darmawan *et al.* (2015)	Indonesia	25.50	26.20	9.20	31.0	-
Zhao *et al.* (2015)	China	< 3.00	56.79	28.21	5.31	3.90
Nežerka *et al.* (2019)	Czech Republic	4.20	48.80	24.20	12.50	5.53
Triple blended						
Barbhuiya (2011)	Thailand	13.78	42.54	23.59	12.36	-
Yu and Leung (2017)	Hong Kong*	4.99	51.40	30.84	4.98	1.69
		7.29	49.05	25.93	7.58	0.77
Matos *et al.* (2019)	Brazil*	1.10	69.30	18.90	6.20	0.20
		2.07	56.03	29.41	6.16	0.50
Alkali – activated						
Ismail *et al.* (2014)	Australia	< 0.1	62.93	24.91	5.22	2.64
Marjanović *et al.* (2015)	Serbia	7.98	55.23	21.43	7.42	1.66
Karim *et al.* (2015)	Malaysia	3.04	58.95	20.24	5.18	3.16
Luga *et al.* (2017)	Turkey	1.77	61.81	19.54	0.98	2.20
Wang and Ma (2018)	China	4.9	49.1	34.8	4.5	-
Geopolymer						
Xie *et al.* (2009)	China	1.88	70.4	30.9	5.38	-
Chindaprasirt *et al.* (2011)	Thailand	13.34	45.03	23.98	10.68	0.58
Kumar and Kumar (2011)	India	1.71	60.48	28.15	4.52	1.59
Ryu *et al.* (2013)	Korea	2.90	55.30	25.80	5.50	3.20
Xie and Kayali (2016)	Australia*	4.67	58.60	20.20	9.25	-
		25.77	43.03	14.90	8.94	-
Kalaw *et al.* (2016)	Philippine	5.30	66.50	28.80	2.5	2.18
Hung *et al.* (2017)	Vietnam	2.56	54.42	23.90	8.14	4.31

* Research consists of two types of fly ash with different composition

2.3.2 Ground granulated blast furnace slag (GGBS)

Blast furnace process is one of the famous steelmaking routes for worldwide steel production. The method uses coke and coal as the primary source of fuel and reductant materials, flux materials such as dolomite or limestone. At the same time, sinter, pellet and lump ore act as iron-bearing components blasted with a high-temperature flame of 1500 °C. It is later transformed into two separate products, namely pig iron or liquid hot metal and molten slag formed from the gangue materials such as the coke and coal ash and the ore burden. The hot liquid metal was collected from the bottom of the furnace and transported in liquid before the refinement process to become steel can take place by removing other elements such as silicon, carbon, sulphur, phosphorus and manganese (Geerdes *et al.*, 2009). On the other hand, the low-density molten slag that floats on hot liquid metal is later quenched rapidly with water to a form glassy and granulated slag. It was then ground into a fine powder known as the ground granulated blast furnace slag (GGBS) which will be reviewed thoughtfully in this section.

GGBS, the by-products of iron and steel making industry was first used in Germany as a binder constituent back in 1862 after its latent hydraulic potential in the granulated form, or vitrified form which was discovered by Emil Langen (Papadakis and Venuat, 1968, Bensted and Barnes, 2002). Three years later, the first commercial production as slag-lime cement began in the same country. However, the first standard on the usage of slag cement was only issued after almost half a century later in 1903. Following that, Hans Kühl discovered the possibility of sulfate activation of GGBS using calcium sulfate (Keil, 1952) then was known as the supersulfated cement. SiO_2, CaO, MgO and Al_2O_3 are four primary compounds in GGBS and resembled a mineral whose compositions correspond to the melilite phase, a solid solution phase between gehlenite (C_2AS) and akermanite (C_3MS_2) as well as a standard component in commercial silicate glasses (Song and Jennings, 1999, Li *et al.*, 2010). Except for SiO_2 that decreases its reactivity if the content is increased, other primary compound increases the reactivity if the content increases (Pal *et al.*, 2003). These primary compounds in GGBS can also generate C-A-S-H colloid as their hydration product (Wu *et al.*, 2015) and can make up about 95% of the GGBS. The balance is typically made up of other components such as manganese (MnO_2), sulphur (S), potassium (K_2O), phosphorus (P) and titanium (TiO_2). Based on MS EN 15167: Part 1 (Standards Malaysia, 2010) for GGBS to be used in concrete, mortar or grout, the ratio by mass of CaO + MgO / SiO_2 should exceed 1 to ensure the high alkalinity, without which the GGBS can be hydraulically unreactive.

According to Haha *et al.* (2011), GGBS with higher MnO_2 content had shown faster hydration kinetics regardless of the activator used to activate it. The main factors that govern the cementitious properties of GGBS are the chemical composition, fineness, glass content and the concentration of alkali in the reacting system (Siddique and Bennacer, 2012). The cementing properties of GGBS are typically observed after three days, but some hydration might occur immediately after it comes in contact with water, and the protective layer is formed on the surface of GGBS particles. It was usually used in conjunction with alkalis, gypsum or lime that act as accelerators or activators to promote GGBS hydration with different hydration products as shown in Table 2.4 (Ramachandran *et al.*, 2002, Mozgawa and Deja, 2009). However, according to Li (2011), the strength contribution may also become apparent as early as 7 days after hydration.

Table 2.4 The hydration products of GGBS activated with various activators (Ramachandran *et al.*, 2002, Mozgawa and Deja, 2009)

Activators	**Crystalline Phases**	**Comments**
NaOH, Na_2CO_3, Na Silicate	C-S-H, C_4AH_{13}, C_2AH_8, $Mg(OH)_2$, C-A-S-H	Some Si is included in C_4AH1_3; Ca/Si ratio of C-S-H is less than in OPC paste
$Ca(OH)_2$	C-S-H, C_4AH_{13}	C_2AH_8 is not present
Gypsum, Hemihydrate, Phosphogypsum	C-S-H, AFt, $Al(OH)_3$	SO_4 in slag may act as an internal activator
OPC	C-S-H, AFm, Aft, Hydrogarnet, Hydrocalcite-like phase, Vicatite (C_3-S_2-H_3)	Any one paste may not have all these phases

GGBS generally has fineness around 4500 to 4800 cm^2/g. According to Mun *et al.* (2007), the high fineness only contributed to the early strength development since the high surface area of GGBS accelerates the hydration and filling action once it comes in contact with water. The strength performance of high fineness GGBS is comparable to low fineness GGBS at 28 days, as shown in Figure 2.2. GGBS with particle size less than 10 μm can contribute to the early-age strength up to 28 days, while 10 to 45 μm contribute to later age strength and particles with size higher than 45 μm are challenging to hydrate (Li, 2011). Likewise, high temperature curing for concrete containing GGBS also only affect the early age and similar strength could be achieved at 14 days of curing regardless any curing temperature up to 50 °C (Turuallo and Soutsos, 2015). However, it was suggested by Neville (2011) that proper curing such as moist curing for concrete containing high volume GGBS is necessary since poor curing can lead to the evaporation of the capillary pore water which can prevent further hydration process.

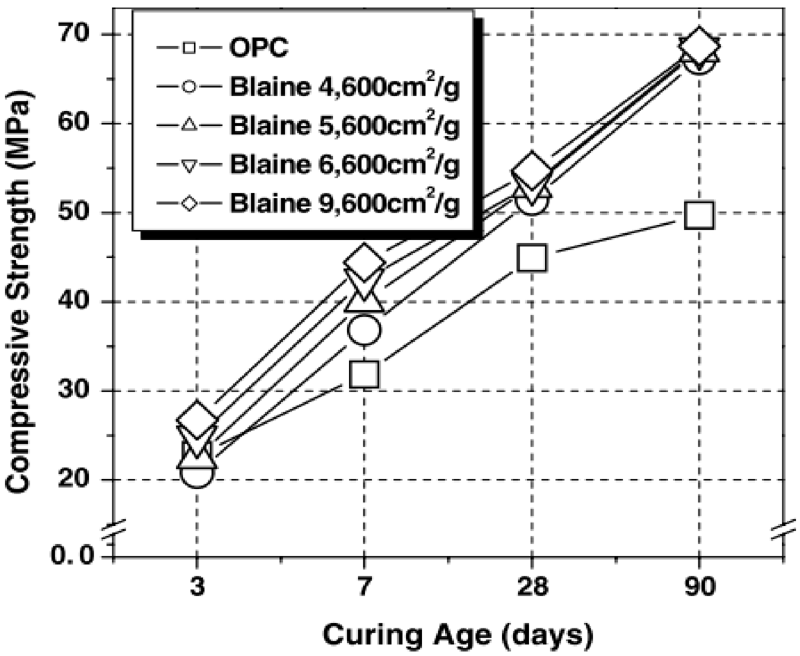

Figure 2.2 Compressive strength development of GGBS and OPC mortar with different fineness
(Mun *et al.*, 2007)

The usage of a high volume of GGBS favours the heat of hydration compared to standard OPC concrete which makes it a suitable material for the mass concrete application. According to Lee *et al.* (2015), the decrease in reaction degree when increasing the GGBS content in GGBS-OPC blended concrete was due to the shortage of $Ca(OH)_2$ sources from the OPC. When compared to other industrial by-products, it was proven in the study by Han *et al.* (2017) that the reaction degree is higher in GGBS compared to fly ash as shown in Table 2.5. When the hydration degree of GGBS and fly ash achieved 100%, the heat of hydration of per gram of GGBS is 530 J and 285 J for fly ash. The amount of hydration heat of GGBS was considered high compared to OPC which is only 468 J/g when calculated based on mineral composition and the heat of hydration of each mineral composition of the OPC itself. Other than that, by increasing the OPC replacement with GGBS shows a reduction in water demand to