PROPERTIES AND CHARACTERIZATION OF GROUND GRANULATED BLAST FURNACE SLAG GEOPOLYMER AT HIGH TEMPERATURE EXPOSURES

by

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“In the name of Allah, the Most Gracious, the Most Compassionate"

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Material
ANOVA	Analysis of Variance
CASH	Calcium Aluminate Silicate Hydrate
$CaCO_3$	Calcite
$Ca(OH)_2$	Calcium Hydroxide
CO_2	Carbon Dioxide
CSH	Calcium Silicate Hydrate
DOE	Design of Experiment
FTIR	Fourier Transform Infrared Spectroscopy
K	Potassium
KOH	Potassium Hydroxide
LOI	Loss of Ignition
Na	Sodium
Na_2SiO_3	Sodium Silicate
NaOH	Sodium Hydroxide
SEM	Scanning Electrn Microscopy
SL	Solid-to-Liquid ratios
SN	Sodium Silicate-to-Sodium Hydroxide
XRD	X-ray Diffraction
XRF	X-ray Fluoresence

LIST OF SYMBOLS

A	Area
F	Force
n	Number of moles
M	Concentration
M_w	Molecular Weight
σ	Compressive Strength
°C	Degree Celsius
Θ	Theta
kV	Kilovolt

Sifat dan Pencirian Geopolimer Relau Letupan Sanga Tanah Pada Pendedehan Suhu Tinggi

ABSTRAK

Proses pengeopolimeran menggunakan geopolimer relau letupan sanga tanah (GGBFS) sebagai sumber aluminosilikat telah dijalankan. GGBFS adalah bahan alternatif yang boleh diperbaharui bagi menggantikan Portland biasa. Ia berkembang mengikut kesedaran global isu-isu alam sekitar yang sohor kini. Kajian terhadap GGBFS sebagai pengikat dalam penghasilan geopolimer adalah terlalu kurang di serata dunia. Oleh yang demikian, kajian ini sangat penting bagi menilai pencirian fizikal dan mekanikal GGBFS yang berpotensi digunakan dalam bidang pembinaan. Pes geopolimer dihasilkan daripada pencampuran serbuk GGBFS, larutan natrium hidroksida dan natrium silikat. Pes buburan dipadatkan dalam plastik akrilik dan diawetkan pada suhu bilik selama 28 hari. Masa pengerasan yang lebih singkat akan menyebabkan kereaktifan GGBFS lebih tinggi dan ia merupakan kekangan utama kajian ini. Tujuan kajian ini adalah untuk mengkaji kesan kepekatan natrium hidroksida, nisbah pepejal kepada cecair dan nisbah natrium silikat kepada natrium hidroksida terhadap kekuatan mampatan geopolimer GGBFS. Hasil keputusan menunjukkan bahawa kepekatan natrium hidroksida sebanyak 10M, nisbah pepejal kepada cecair sebanyak 3.0, dan natrium silikat kepada natrium hidroksida sebanyak 2.5 pada suhu bilik dan diawetkan sehingga 28 hari adalah pencampuran yang optimum untuk sintesis geopolimer GGBFS. Kekuatan mampatan tertinggi geopolimer GGBFS dicapai pada 168.71 MPa. Kalsit ($CaCO_3$) dan Kalsit Silikat Hidrat (C-S-H) muncul dalam geopolimer GGBFS selepas tindak balas pengeopolimeran seperti yang ditentukan oleh analisis fasa. Pengenalpastian kumpulan berfungsi menunjukkan pembetukkan lebih banyak ikatan geopolimer dalam geopolimer GGBFS pada reka bentuk pencampuran optimum tersebut. Bagi menentukan perkaitan parameter pemprosesan dalam pembetukan geopolimer GGBFS, statistik reka bentuk eksperimen telah dijalankan. Analisis varians (ANOVA) menunjukkan pembolehubah nisbah pepejal kepada cecair adalah factor yang paling tinggi pemprosesan geopolimer GGBFS dengan bacaan 0.00 berbanding variabel kepekatan natrium hidroksida dan variabel nisbah natrium silikat kepada natrium hidroksida. Pes geopolumer GGBFS didedahkan pada suhu tinggi sehingga 1000 ºC. Sampel geopolimer GGBFS yang terdedah menunjukkan kemerosotan kekuatan mampatan sebanyak 8.9 MPa. Sebaliknya sampel geopolumer GGBFS mengalami peningkatan kekuatan mampatan sehingga 19.8 MPa selepas terdedah pada 1000 ºC iaitu pada pembentukkan fasa pengkristalan. Selain peningkatan kekuatan mampatan, sampel geopolimer GGBFS mengekalkan bentuk kiubnya tanpa berlakunya kerapuhan struktur apabila terdedah pada suhu tinggi. Tambahan pula, pembetukkan fasa gehlenit, mayenit, dan larnit mempamerkan permukaan geopolimer yang kasar dan kemunculan gua. Tuntasnya, kajian ini memberikan pemahaman yang lebih baik mengenai sifat-sifat dan ciri-ciri geopolimer GGBFS. Bagi penyelidikan masa depan, adalah dicadangkan untuk mengunakan bahan GGBFS mortar, konkrit ringan dan geopolimer busa untuk analisis prestasi pada persekitaran suhu yang tinggi.

Properties and Characterization of Ground Granulated Blast Furnace Slag Geopolymer at High Temperature Exposure

ABSTRACT

Geopolymerization process using ground granulated blast furnace slag (GGBFS) as aluminosilicate sources was performed. The utilization of GGBFS as an alternative and renewable material for Portland cement is growing due to global awareness towards environmental issues. Research on ground granulated blast furnace slag as a sole binder in geopolymer production is limited throughout the world. Hence, this study is essential to evaluate the physical and mechanical characterizations of GGBFS for the potential use in construction fields. The geopolymers paste was produced from the mixing of GGBFS powder, sodium hydroxide and sodium silicate solution. The slurry pastes were compacted in acrylic plastic and cure at room temperature for 28 days. Shortened setting times leads to higher reactivity of GGBFS, thus becomes the major limitation in this study. The aim of this study is to investigate the effect of NaOH concentration, solid-to-liquid ratio and Na_2SiO_3/NaOH ratio on GGBFS geopolymer compressive strength. The results exhibited that 10 M of NaOH concentration, solid-to-liquid ratio of 3.0, and sodium silicate-to-sodium hydroxide ratio of 2.5 at room temperature and cured until 28 days were the optimum mixing conditions for GGBFS geopolymers synthesis.The highest compressive strength of GGBFS geopolymer was achieved at 168.71 MPa. Calcite ($CaCO_3$) and calcium silicate hydrate (C-S-H) appeared in GGBFS geopolymers after the geopolymerization reaction as determined by phase analysis. Functional group indentification shows the formation of more geopolymer bonding in GGBFS geopolymer at optimal mixing designs. In order to determine the correlation of the processing parameters in the formation of GGBFS geopolymer, a statistical design of experiment (DOE) was approach. The analysis of the experiment results through ANOVA revealed that solid-to-liquid ratios was the highest influenced with the result of 0.00 compared to NaOH concentration and sodium silicate-to-sodium hdyroxide ratios. The GGBFS geopolymer paste was exposed to elevated temperatures up to 1000 °C. The exposed GGBFS geopolymers samples indicated a compressive strength degradation of 8.9 MPa. In contrast, the GGBFS geopolymers samples had an increasing of compressive strength up to 19.8 MPa after being exposed at 1000 °C with the formation of crystallization phases. Despite strength increment, GGBFS geopolymer samples remained in cubic shape with no spalling occurred when exposed at high temperature. Furthermore, the formation of gehlenite, mayenite, and larnite phases exhibited rugged geopolymer surface with cavern appearance. As a conclusion, this study provides a better understanding of the properties and characteristic of GGBFS geopolymers. Hence, for future research, it is suggested to apply the GGBFS material in mortar, lightweight concrete and geopolymer foam in order to analyze the performance at high temperature environments.

CHAPTER 1: INTRODUCTION

1.1 Research Background

Steel is the vital raw material used in the engineering and machinery industries, automotive equipment, manufacturing sectors, and as major component for infrastructure works. Steel production has a huge boost effect in the economy through increased activities in other related fields. The level per capita of steel consumption is considered as one of the most valuable indicators of socio-economic development and living standards of the consumer. In 2017, Malaysia became the world's eighteenth-largest steel importer. Malaysia imported 7.6 million metric tons of steel in 2017, a 15 % lower than 8.9 million metric tons in 2016 (Iron & Federation, 2017). Otherwise, based on the Malaysia Iron and Steel Industry Federation, Malaysia has over 100 steel manufacturing and processing companies which are the total steel-making capacity of 10.7 million metric tons produced in 2016. The structure of Malaysia's iron and steel industries leads to 2.9% of Gross Domestic Product (GDP) in 2016 and has the promising potential to develop up to 6.5% of GDP growth in 2020. However, the production of iron and steel generated a huge solid waste during the processing steps in steel plants. The solid wastes caused a crucial environmental pollution that must be discarded.

Over the last decade, the slag and sludge produced by integrated steel plants were known as "waste" but in present are classified as a "by-product" due to the intensive re-utilization and managing of the solid wastes (Pappu, Saxena, & Asolekar, 2007). The "4 Rs" (reduce, reuse, recycle and restore) was proposed as the viable solution for solid waste management in the steel industry. Recycling and reusing the by-product management during the steel making process were applied in targeting a green, clean and zero waste technology pertaining to the sustainable development of the steel industry (Sarkar & Mazumder, 2015). Sources of solid wastes generated in steel industries are such as coke oven by product plants, refractory materials, basic oxygen furnace, rolling mill and blast furnace. An enormous amount of solid wastes in the steel industry were namely coal dust, mill scrap, refractory waste and blast furnace slag (Das, Prakash, Reddy et al., 2007).

One of the solid wastes in the steel industry, blast furnace slag was applied for the manufacturing of road base, lightweight concrete blocks, high performance concretes, admixtures and the manufacturing of Portland cement (Chaurand, Rose, Briois et al., 2007). Hence, there is an expanding interest on the beneficial use of alternative materials with pozzolanic activity for comparable properties to Portland cement in order to produce valuable products from economical and technical point of view for the profitability of the recycling process (Angulo-Ramírez, de Gutiérrez, & Puertas, 2017). The utilizing of alternative materials and renewable materials for Portland cement is growing due to global awareness towards the environmental issues (da Luz Garcia & Sousa-Coutinho, 2013).

Geopolymer have attracted spotlight over from various researches with its performance (chemical, and fire resistance, fast setting, and long term durability) and potentially build up market demands comparable with Portland cement (Davidovits, 2002). Theoretically, geopolymer technology can be applied in numerous fields such as aerospace, automobile, foundry, and metallurgy, plastic industries and construction. Geopolymer chemistry consists of aluminosilicate sources material, mostly are naturally existing, industrial wastes or by-product of those that require relatively less energy to manufacture (Sabir, Wild, & Bai, 2001). Geopolymer are well-known as having great volume stability, high mechanical properties, and good thermal characteristics. The production of geopolymer releases no greenhouse gases and with low energy consumption and production cost (Davidovits, 1994a).

In current studies, various research works have been performed on the performance of environmental friendly construction materials at elevated temperature exposure. Instead of utilizing conventional cement as binding component, geopolymer technology was proposed as an alternative to cement binder due to the excellent thermal behaviour. Kong et al. (2007) found that fly ash geopolymer developed 6% of strength after being exposed at 800 °C attributed by highly dispersed pores in the geopolymer matrix. Otherwise, the blended geopolymer (50/50 of slag/metakaolin) obtained 86% strength degradation when exposed above 1000 °C. This was caused by some partial melting of the geopolymer binders that suffered the structural changes at high temperature exposure (Sarker, Kelly, & Yao, 2014).

As Portland cement, most of the calcium oxide (CaO) obtained in GGBFS was tied up as calcium aluminate, calcium silicate, and calcium aluminosilicate (Rabbani, Daghigh, Atrechian et al., 2012). Research on geopolymer using ground granulated blast furnace as main aluminosilicate sources was very limited. Moreover, most of the studies focused on thermal performance of fly ash, metakaolin and/or slag incorporated geopolymers (Bernal, Rodríguez, De Gutiérrez et al., 2011; Guerrieri & Sanjayan, 2010; Rashad, Bai, Basheer et al., 2012). Hence, this research is focused on investigating the physical and mechanical properties of ground granulated blast furnace slag geopolymer at high temperature exposure.

1.2 Problem Statement

There has been an increasing trend on recycling waste materials worldwide. The incorporation of ground granulated blast furnace slag in the manufacturing of geopolymer concrete has been applied since the last century (Deb, Nath, & Sarker, 2014; Kim, Jun, Lee et al., 2013; Kumar, Kumar, & Mehrotra, 2010). However, the use of ground granulated blast furnace slag as the sole binder in the production of geopolymer is not common throughout the world. Ground granulated blast furnace slag attracts less attention among researches due to the shortened setting times during the curing period (Lachemi, Şahmaran, Hossain et al., 2010; Mounanga, Khokhar, El Hachem et al., 2011; Xu, Gong, Syltebo et al., 2014). This shortened setting times contributes to the higher reactivity of ground granulated blast furnace slag and becomes the major limitation in the study.

The possibility of ground granulated blast furnace slag is used as cement replacement material contributing several advantages such as reducing the natural resources exploration, decreasing environment burdens of waste accumulation and recycle for profitable materials (Dos Anjos, Sales, & Andrade, 2017). Ground granulated blast furnace slag has the potential to attain satisfactory mechanical performance by replacing the Portland cement in order to develop new economic and green environmental low cost materials. Accordingly, it is necessary to characterize the physical and mechanical properties of ground granulated blast furnace slag for its potential use in the construction fields.

In earlier studies, the incorporation of slag in geopolymers exhibited strength deterioration towards to elevated temperature exposure. The increasing of large pores and decomposition induced to the strength loss due to cracking after exposed up to 1000 ºC (Ye, Zhang, & Shi, 2014). The performance of alkali activated slag concrete (AASC) in the range of 400 C to 800 C similar to ordinary Portland cement (OPC) contributes to the strength deterioration at elevated temperatures. The remaining strength of AASC was 10 % after exposed up to 800 ºC and was believed due to the absence of $Ca(OH)_2$ (Guerrieri, Sanjayan, & Collins, 2009). Nevertheless, the use of solely GGBFS in geopolymer as aluminosilicate source at high temperature exposure has not been studied. It is substantial to study on the fundamental material to address the GGBFS applied alone in the production of geopolymers.

As less literature has been reported on the mechanical and material characterization of ground granulated blast furnace slag based geopolymer, it is necessary to improve the fundamental theory in the geopolymer field. The chemical composition, such as sodium concentration, solid-to-liquid ratio, and alkali activator ratio was also investigated in order to achieve the possibility to enhance the manufacturing of ground granulated blast furnace slag towards geopolymerization reaction. Hence, this research is being escalated to produce economic ground granulated blast furnace slag geopolymer with possibly greater engineering application bases.

1.3 Objective of Study

This research proposed to study the utilization of ground granulated blast furnace slag in geopolymer synthesis. The properties and characteristic of ground granulated blast furnace slag at various mixing compositions were developed. The objectives of study are:

1) To formulate the optimum mixing composition based on compressive strength and analyze the correlation of the processing parameter in the formation of ground granulated blast furnace slag geopolymers.

2) To validate the physical and characterization of ground granulated blast furnace slag geopolymers.

3) To evaluate the performance of ground granulated blast furnace slag geopolymers towards high temperature exposure.

1.4 Research Scope

Scope of this research is to consolidate on the study of the characterization, mechanical properties, and the performance of ground granulated blast furnace slag determined through the compressive strength, density, and the durability at high temperature environment. Additionally, materials characteristic will be evaluated based to the mass ratio of NaOH concentration, solid-to-liquid ratios, and sodium silicate-to-sodium hydroxide ratios by morphology and mineralogical analysis at laboratory UniMAP.

A number of specimens were prepared in the laboratory to determine the optimum mixing ratio according to mixing variations of parameters and mechanical properties of ground granulated blast furnace slag geopolymer. There are three main series of GGBFS geopolymer mix designs that were casted. Each series was designed based on the parameters (NaOH concentration, solid-to-liquid ratios, and sodium silicate-to-sodium hydroxide ratio) affected on the compressive strength of GGBFS geopolymers. The ratios of NaOH concentration was 6 M, 8 M, 10 M, 12 M, and 14 M. The solid-to-liquid ratios and sodium silicate-to-sodium hydroxide ratios were 1.0 to 3.0 and 1.5 to 2.5, respectively.

The hardened paste was taken out from the mould after 24 hours of casting and cured at ambient temperature with the fixed curing period of 28 days for all samples. The weight measurement and compressive strength test were conducted after 28 days of curing period followed by materials characterizations. Compressive strength of Ground granulated blast furnace slag geopolymer was tested using Instron machine to assess the success of the geopolymerization reaction. X-ray powder diffraction (XRD) and fourier transform infrared (FTIR) spectroscopy were used to determine the phase identification and functional group of Ground granulated blast furnace slag geopolymer. Moreover, scanning electron microscope (SEM) was performed to evaluate the microstructural changes and to observe the different degrees of the geopolymerization reaction. The data collection for the proper investigation into strength characteristics of GGBFS geopolymer is obtained and discussed in the following chapter. Meanwhile, high temperature exposure will be studied and discussed after the tests are completed by obtaining the optimum mixing ratios.