GEOPOLYMER MORTAR DERIVED FROM WOOD ASH AND FLY ASH WITH SODIUM SILICATE

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GEOPOLYMER MORTAR DERIVED FROM WOOD ASH AND FLY ASH WITH SODIUM SILICATE

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PART WEI KEN

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LIST OF ABBREVIATIONS

AAS	Alkali Activated Slag
API	American Petroleum Institute
BA	Bottom Ash
BAG	Blended Ash Geopolymer
BDW	Building Demolition Waste
BFAGC	Blended Fuel Ash Geopolymer Concrete
C-A-H	Calcium Aluminate Hydrate
CSB	Calcium Silicate Bricks
C-S-H	Calcium Silicate Hydrate
CSRE	Cement Stabilized Rammed Earth
DL	Dead Load
DTG	Differential Thermogram
EDX	Energy Dispersive X-Ray
FA	Fly Ash
FBC	Fluidized Bed Combustion
FGDG	Flue Gas Desulfurization Gypsum
FTIR	Fourier Transform Infrared Spectroscopy
GBA	Ground Bottom Ash
GCS	Granulated Corex Slag
GGBS	Ground Granulated Blast Furnace Slag
HCWA	High Calcium Wood Ash
HSM	High Silica Modulus
LOI	Loss On Ignition
LSM	Low Silica Modulus
M	Melamine
MK	Metakaolin
Ms	Silica Modulus
MT	Mine Tailings
N	Naphthalene
OPC	Ordinary Portland Cement
PC	Polycarboxylate

PP	Polypropylene
PCC	Pulverized Coal Combustion
PFA	Pulverized Fuel Ash
PVA	Polyvinyl Acetate
POFA	Palm Oil Fuel Ash
RM	Red Mud
RHA	Rice Husk Ash
RCPT	Rapid Chloride Permeability Test
RHBA	Rice Husk-Bark Ash
SP	Superplasticizers
SEM	Scanning Electron Microscopy
SCMs	Supplementary Cementitious Materials
TGA	Thermogravimetry Analysis
TPOFA	Treated Palm Oil Fuel Ash
UL	Ultimate Load
UCS	Unconfined Compressive Strength
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

MORTAR GEOPOLIMER TERHASIL DARIPADA ABU KAYU DAN ABU ARANG BATU DENGAN SODIUM SILIKAT

ABSTRAK

Kajian eksperimen ini mempamerkan pembangunan mortar geopolimer beralkali rendah yang berasaskan abu kayu berkandungan kalsium tinggi (HCWA) dan abu arang batu (PFA). Kesan alam semulajadi yang diakibatkan daripada proses pembuatan simen Portland biasa (OPC) menjadikan prospek penggunaan bahan pengikat berasaskan geopolimer menarik. Tambahan pula, geopolimer konvensional dihasilkan dengan kandungan pengaktif alkali dan suhu pengawetan yang tinggi dan ini menyebabkan aplikasi industri geopolimer konvensional tidak praktikal. Kajian ini menggunakan kaedah penekanan hidraulik untuk pembuatan blok mortar geopolimer HCWA-PFA. Blok tersebut difabrikasi dengan menggunakan kandungan pengaktif alkali yang rendah iaitu 5% berat pengikat dan kaedah pengawetan suhu bilik iaitu pengawetan lembap, berbeza jika dibandingkan dengan kaedah pembuatan geopolimer konvensional. Blok mortar geopolimer HCWA-PFA diuji dari segi mekanikal, ketahanlasakan dan mikrostruktur untuk tempoh pengawetan lembap sampai 365 hari. Kinetik tindak balas sistem geopolimer HCWA-PFA dan tingkah laku struktur interlock dinding HCWA-PFA tahan beban juga telah diuji. Ciri pengerasan geoplimer HCWA-PFA didapati bergantung kepada tahap kereaktifan sistem geopolimer hibrid HCWA-PFA di mana WA30FA70-WA60FA40 (30% HCWA-60% HCWA mortar geopolimer) menunjukkan tahap pengerasan awal and akhir yang paling cepat. Penambahan HCWA meningkatkan ciri kejuruteraan blok mortar geopolimer HCWA-PFA iaitu kekuatan mampatan, kekuatan lenturan dan UPV pada tempoh pengawetan awal, di mana WA50FA50 dan WA60FA40

mempamerkan prestasi optimum. Pada tempoh pengawetan berpanjangan, campuran mortar geopolimer HCWA-PFA yang mengandungi kandungan PFA yang lebih tinggi iaitu WA30FA70 dan WA40FA60 mempamerkan prestasi optimum, disebabkan oleh kesediaan spesies aluminosilicate untuk mengambil bahagian dalam geopolimerisasi jangka masa panjang. Tahap pengecutan blok mortar geopolimer HCWA-PFA didapati meningkat berkadar langsung dengan prestasi kejuruteraan, di mana WA30FA70-WA60FA40 mempamerkan tahap pengecutan yang lebih tinggi untuk pendedahan keadaan pengeringan pada jangka masa pendek dan panjang. Ciri ketahanlasakan jangka masa panjang dan pendek seperti penyerapan kapilari, penyerapan air, tahap keliangan, kebolehtelapan udara dan rintangan sulfat telah dipertingkatkan dengan blok mortar geopolimer WA30FA70 dan WA40FA60. Pembangunan kekuatan jangka masa awal (7 dan 28 hari) geopolimer HCWA-PFA didapati bergantung kepada pembentukan (Ca)-polysialate dan (K)-polysialate manakala pembangunan kekuatan jangka masa panjang (90 sampai 365 hari) didapati bergantung kepada pembentukan rangka geopolimer poly(sialate-siloxo) dan poly(sialate-disiloxo). Dinding interlocking WA40FA60 didapati mempamerkan prestasi struktur terbaik seperti kapasiti tahap beban, beban servis, kekakuan dan kekuatan jikalau dibandingkan dengan dinding interlocking 100% OPC.

GEOPOLYMER MORTAR DERIVED FROM WOOD ASH AND FLY ASH WITH SODIUM SILICATE

ABSTRACT

The experimental investigation presented the development of low alkalinity geopolymer mortar derived from high calcium wood ash (HCWA) and pulverized fuel ash (PFA). The environmental impact resulted from the manufacturing process of ordinary Portland cement (OPC) have rendered the prospect of utilizing geopolymer-based binder materials attractive. Furthermore, conventional geopolymer was fabricated using high dosage of alkaline activator and elevated curing temperature and rendered the industrial application of conventional geopolymer impractical. The study utilized hydraulic pressed forming method for the manufacturing of HCWA-PFA geopolymer mortar blocks. The blocks were fabricated by using mild alkaline activator namely 5% binder wt. and ambient temperature curing regime namely moist curing, as opposed to the conventional geopolymer fabrication method. The manufactured HCWA-PFA geopolymer mortar blocks were assessed in terms of its mechanical, durability and microstructural properties up to 365 days of moist curing. Reaction kinetics of HCWA-PFA geopolymer paste system was derived and the structural behaviour of HCWA-PFA interlocking load bearing wall was assessed. The setting properties of HCWA-PFA geopolymer paste was found to be function of reactivity of the hybrid geopolymer system where WA30FA70-WA60FA40 (30% HCWA-60% HCWA geopolymer mortar) exhibited fastest initial and final setting time. The inclusion of HCWA enhanced the early age engineering properties namely compressive strength, flexural strength and UPV of HCWA-PFA geopolymer mortar blocks, where WA50FA50

and WA60FA40 mixes exhibited optimum performance. On prolonged curing, HCWA-PFA geopolymer mortar mixes with higher PFA content WA30FA70 and WA40FA60 consistently exhibited optimum performance, mainly due to the availability of aluminosilicate species from PFA to participate in long term geopolymerization. The shrinkage of HCWA-PFA geopolymer mortar blocks was found to be increased proportionally with the engineering performance, where WA30FA70-WA60FA40 exhibited higher degree of shrinkage for both early and long term drying exposure condition. Early and long term durability properties such as capillary absorption, water absorption, total porosity, intrinsic air permeability and sulphate resistance were enhanced with WA30FA70 and WA40FA60 geopolymer mortar blocks. The early age (7 and 28 days) strength development of HCWA-PFA geopolymer was governed by the formation of (Ca)-polysialate and (K)-polysialate while the long term strength development (90 to 365 days) was governed by the formation of poly(sialate-siloxo) and poly(sialate-disiloxo) geopolymer framework. WA40FA60 interlocking wall exhibited enhanced structural performance i.e. load bearing capacity, serviceability load, stiffness and toughness if compared with 100% OPC interlocking wall.

CHAPTER ONE

INTRODUCTION

1.1 Background

The utilization of OPC as sustainable building material has come under heavy scrutiny in the recent years due to the environmental impact by the clinker production (Ahmari and Zhang, 2012, Schneider et al., 2011). In fact, the production of Portland Cement (PC) clinker from the cement production plants worldwide emits up to 1.5 billion tons of CO_2 annually, which accounts for around 5% of the total man-made CO_2 emission and if the undesirable trend continues, the figure will rise to 6% by year 2015 (Damtoft et al., 2008, Davidovits, 1994a, Yusuf et al., 2014b). Apart from OPC, sand and aggregate are also the main constituent source materials in the production of concrete, which originated from the quarrying operations which are both energy intensive and produces high level of waste materials. Shortage of natural resources for construction materials in many developing countries has also led to long distance haulage and thus significantly increased the production cost of construction materials. All of the issues mentioned above are against the context of sustainable development in construction industry and immediate remedial actions must be taken to ensure sustainability in the construction industry (Ahmari et al., 2012).

Amidst the growing concern on the environmental and human health impact caused by the clinker production for manufacturing OPC, the emergence of geopolymer technology present a promising avenue for the total replacement of OPC as the main binder materials for construction and building materials. Conventional geopolymers were derived from aluminosilicate materials such as fly ash/ pulverized fuel ash (PFA), ground granulated blast furnace slag (GGBS), palm oil fuel ash (POFA) etc activated by external chemical activators namely alkali hydroxide and alkali silicate. In addition, it usually requires elevated temperature curing in order to attain desired properties and the current activation technique rendered the industrial application of geopolymer technology not feasible.

Demand for electricity in developing countries has increased by leaps and bounds in recent years due to the growth in world population and economic. Recent study forecasted the world energy consumption to be increased by 47% from 2007 to 2035 (Conti and Holtberg, 2011). A look at the power/electricity generation industry, many countries are starting to use renewable energy sources i.e. biomass energy instead of conventional energy sources i.e. fossil fuels to generate power for the national electric gridlines due to fossil fuels diminution and environmental concerns across the globe. However, in Malaysia, only 5.5% of total electricity was generated using renewable energy sources and 94.5% of electricity was generated using fossil fuels such as natural gas, coal and oil in the year 2009. The generation of CO_2 and greenhouse gases (CH_4, N_2O and O_3) resulted from the combustion of fossil fuels has led to some serious climate changes observed in Malaysia where in 2011, the average temperature in peninsular Malaysia increased by 0.5 ^oC to 1.5 ^oC and 0.5 ^oC to 1 ^oC in east Malaysia. The wood processing industry in Malaysia represents a great potential to be used as renewable energy source to supplement the power/electricity demand as it is considered as one of the largest untapped biomass resource in Malaysia (Shafie et al., 2012). According to Vassilev et al. (2010), wood wastes are the more preferable fuel for biomass furnaces as the incineration of wood waste yields relatively less residual and fly ash in comparison to other biomasses such as agricultural and herbaceous wastes. There are increasing numbers of timber manufacturing production plants which utilized wood waste residues generated from the production of timber products as fuel for boiler unit which resides within the manufacturing plants. The energy generated from the combustion of wood biomass in turns is used for the industrial applications such as drying of moist timber and electricity generation. Though the aforementioned practices provide a great solution to the solid waste management of wood waste residues, the use of wood wastes such as sawdust, woodchips and offcuts as fuel have resulted in a significant amount of fine wood waste ash as a by-product material in which the industry found limited practical applications for the recycling of the fine particulate ash materials (Cheah and Ramli, 2011a). In general, 70% of the total wood waste ashes generated from the wood fired co-generation power plant are landfilled, 20% are used as soil supplementary materials and the remaining 10% are used in construction materials, pollution control and metal recovery (Etiegni, 1990, Etiegni and Campbell, 1991).

PFA or more commonly known as fly ash (FA), an industrial by-products of coal burning power plant industry, makes up of 75-80% of global annual ash production (Joseph and Mathew, 2012). As 94.5% of total electricity generated in Malaysia is by the mean of fossil fuels such as natural gas, coal and oil, an enormous amount PFA is expected to be generated annually. The coal-fired power generation industry in Malaysia consumed approximately 8 million tonnes of coal annually and in 2010, the Malaysian government implemented a policy that eventually increased the national coal powered electricity by 40% due to the rapid economic growth and this has further increased the amount of PFA generated. Hence, this industrial by-product which is present in bulk volume mandates a proper disposal or recycling methods (Ahmaruzzaman, 2010).

In view of the on-going environmental impact of OPC production, waste management issue in various industries, particularly coal-fired power plant and timber manufacturing industry, coupled with the problems faced in the current geopolymer technology, the production of a new binder system which is environmental friendly, sustainable and low in embodied energy of production is crucial to both the scientific and industrial community.

1.2 Problem Statement

In the fabrication of conventional geopolymer concrete, there is a growing concern on the actual cost and embodied energy of production of the geopolymeric material due to the conventional practice of incorporating significant amount of alkaline chemical activator (sodium hydroxide, potassium hydroxide, sodium silicate etc) and elevated temperature curing in order to achieve the desired mechanical strength and durability properties (Joseph and Mathew, 2012, Salih et al., 2014, Sarker et al., 2014). Recent study conducted by Cheah and Ramli (2011b) has established that there is a significant amount of potassium oxide (K_2O) namely 12% of the total mass present in HCWA, thus it is indicative that HCWA has a high level of alkalinity. As most of the current researches in geopolymer technology are very much focused on geopolymers which are fabricated using an external source of alkaline chemical activators, the body of knowledge on leveraging one source of waste material to stabilizes another source of waste material for the production of a new sustainable geopolymeric composite remains limited or scarcely explored.

Also, it is proven that the inclusion of HCWA as a partial cement replacement material triggered continuous pozzolanic reaction between Portlandite mineral from HCWA and amorphous silica rich material (Cheah and Ramli, 2012a). Hence, HCWA could be potentially used in combination with siliceous material such as PFA for the fabrication of geopolymeric compound. Besides, Guo et al. (2010) had proven the possibility of coexistence of calcium silicate hydrate (CSH) gels together with the geopolymeric gels in the geopolymer matrix and contribute to the overall strength increment. Based on the aforementioned findings, thorough studies on the material design, engineering and durability performance of HCWA-PFA blended geopolymeric compounds is required.

As HCWA-PFA hybrid geopolymer is a relatively new sustainable construction material, the reaction kinetics of the reaction that occured in HCWA-PFA geopolymeric paste samples which solidify and stabilizes the ash materials has yet to be established. Hence, reaction kinetics derivation of the HCWA-PFA geopolymeric binder will contribute significantly to the body of knowledge in the emerging field of hybrid geopolymers.

Most of the masonry brick wall structures are made of fired-clay bricks, concrete bricks and calcium silicate bricks (CSB) which faced challenges in the context of environmental and human health concerns, high energy consumption, high production cost, dimensional stability etc. Literatures covering the masonry brick wall structural behaviour made of the aforementioned bricks can be found in abundance. On the other hand, literatures on the structural behaviour of masonry brick wall constructed using bricks made of geopolymer-based or waste material are scarce. This area of research is very much needed for the successful industrial implementations of the geopolymer masonry brick wall for structural application.

1.3 Objectives of research

The project is designed to study the feasibility of hybridization of industrial by-products i.e. high calcium wood ash (HCWA) and pulverized fuel ash (PFA) in the production of geopolymeric mortar with mild chemical activator in the form of sodium silicate. This is a full fledge research project which aimed to cover the physical and chemical properties characterization of the binder materials (HCWA and PFA), followed by a detailed studies on the mechanical properties, water sorptivity, pore volume, dimensional stability, microstructure of the binder phase and sulphate resistance characteristics of the hydraulic pressed geopolymer blocks based on the optimized mix proportions between HCWA and PFA. Besides, this study is also aimed to derive the reaction kinetics of the governing geopolymeric/hydration reaction which occurred within the hybridized binder paste samples and lead towards the solidification and stabilization of the paste matrix.

Moreover, this research is also aimed to study the structural behaviour in terms of load versus displacement characteristics, stress-strain relationship, crack development behaviour, and failure mode of the interlocking wall structures constructed using the selected optimized geopolymer mortar blocks. This is done to assess the blocks performance in the application as load bearing interlocking wall structures.

The detailed aims and objectives of the research project are as follows:

- To investigate the setting and engineering properties of HCWA-PFA geopolymer paste and mortar blocks in terms of standard consistency, setting time, workability, compressive strength, flexural strength, ultrasonic pulse velocity, drying shrinkage.
- To study the durability performance of hardened HCWA-PFA geopolymer mortar blocks in terms of intrinsic air permeability, vacuum porosity, capillary absorption, water absorption, sulphate resistance and microstructure development.
- To derive the reaction kinetics of the hydrated HCWA-PFA paste samples by the utilization of X-ray diffraction (XRD), energy dispersive X-ray (EDX), scanning electron microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and Thermogravimetry Analysis (TGA).
- To investigate the structural responses of HCWA-PFA interlocking block wall in terms of load versus displacement characteristics, stress-compressive strain relationship, ultimate load capacity, crack development behaviour, and failure mode under coaxial compression load.

1.4 Significance of research

The research project was meticulously planned with three main guiding principles i.e. environmental friendly (reduced carbon footprint), human health concern and also production cost saving. Upon successful completion of all the project's aims and objectives mentioned in the previous section, there are several major benefits that could be derived. The most significant and immediate benefit would be the large volume recycling of the waste materials generated in the timber manufacturing industry and the coal-fired power generation industry which is HCWA and PFA respectively. As wood biomass has been identified as one of the potential and emerging renewable energy source in Malaysia (Shafie et al., 2012), the initiative of conducting this research project provides a perfect solution to cater for the forecasted amount of wood ash that will be generated as a result of the utilization of wood waste in biomass power generation industry. As for the coal-fired power generation industry, this research project provides another option for the recycling of approximately 8 million tonnes of PFA generated annually in Malaysia. The aforementioned benefits in large volume recycling of wood ash and PFA in their respective industries will also indirectly contribute towards significant cost reduction and also environmental pollution reduction resulted from the disposal of the aforementioned waste materials. There is also a beneficial chain reaction in large volume recycling of wood ash and PFA. Upon successful implementation of HCWA in the production of cementless geopolymeric blocks, it will trigger an increase of biomass power plant that utilized wood biomass as a source of renewable energy across Malaysia. As a result, the amount of fossil fuel such as coal to be used as energy source in power generation can be reduced and this was in line with the international policy of utilizing renewable energy resource as a result of the depleting amount of fossil fuel sources.

The proposed testing parameters of HCWA-PFA geopolymer mortar block in the research project do not only focus on the block application, it also encompassed testing parameters for the conventional mortar and concrete. Therefore, the mechanical and durability performance data derived can be used as reference for the future development of this type of hybrid geopolymeric binder material for example in the application of high performance concrete and mortar. Also, the reaction kinetic derived from the research project can also contributes significantly to the body of knowledge in the emerging field of hybrid geopolymer.

The research project is also aimed at utilizing the HCWA-PFA blended geopolymeric blocks in the structural application of masonry brick wall. This would present the current brick manufacturing industry a whole new sustainable brick material as the proposed geopolymeric blocks are practically made of waste materials, low in cost, easy to produce, possesses low embodied energy and utilizes minimal chemical activators. This would also help in reducing the detrimental effect of manufacturing process in producing fired-clay bricks and concrete bricks in the current context of brick industry. As the current housing industry in Malaysia has suffered from the rising raw construction material price due to various reasons, the proposed HCWA-PFA blended geopolymer blocks could well be the solution to the on-going public housing problem especially in the context of developing low-medium cost or affordable housing projects. The experimental data derived will also contribute towards a better understanding on the load versus displacement characteristics, stress-compressive strain relationship, ultimate load capacity, crack development behaviour, and failure criterion under vertical compression load of masonry brick wall constructed using HCWA-PFA geopolymer mortar blocks. These data could also be useful in predicting the structural behaviour of masonry brick wall constructed using similar types of hybrid geopolymer bricks and configurations.

1.5 Scope of research

The major scope of the research project can be summarized as follows:

- Assessment of chemical and physical properties of the geopolymeric binder materials (HCWA and PFA).

- Evaluation on the properties of the HCWA-PFA geopolymer blended paste samples.
- Optimization on the important parameters such as forming pressure, water/binder ratio, curing regime and chemical activator’s content of the HCWA-PFA cementless blocks.
- Study the effect of different hybridization ratio between HCWA and PFA on the mechanical and durability properties of HCWA-PFA geopolymer mortar blocks based on the optimized parameters over a prolonged duration (up to 1 year).
- Derivation on the overall reaction kinetics of the hydrated HCWA-PFA paste samples over a prolonged curing duration.
- Investigation on the structural performance of HCWA-PFA geopolymer interlocking wall structures based on the selected optimized mix designs.

The chemical properties assessment consist of the evaluation on the chemical compositions, mineralogical phases and loss on ignition (LOI) while the physical properties investigation comprise of the determination of the particle size distribution, particle morphology, specific surface area and specific gravity of the binder materials (HCWA and PFA).

Rheological properties evaluation include the standard consistency, initial and final setting time of the blended HCWA-PFA blended paste samples based on the full scale hybridization ratios (0-100% HCWA replacement by PFA, with 10% step increment).

The three main parameters identified in the production of HCWA-PFA cementless pressed blocks are forming pressure, curing regime, water/binder ratio and the chemical activator's content. Different HCWA-PFA cementless pressed blocks series based on various forming pressure (3500-9500 psi), curing regime (lime-saturated water and moist curing), water/binder ratio (0.35 and 0.30) and chemical activator's content (0-5% based on binder weight, 1% step increment) will be fabricated in order to obtain the optimization value based on the aforementioned parameters.

The evaluation on the mechanical and durability properties of the various hybridization ratios of HCWA-PFA geopolymer mortar blocks covered the determination of compressive strength, flexural strength, intrinsic air permeability, vacuum porosity, capillary absorption, water absorption, drying shrinkage and sulphate resistance based on the optimized parameters over a prolonged curing duration (up to 1 year).

The in-depth studies on the overall reaction kinetics of the selected hydrated HCWA-PFA paste samples include the utilization of various analytical instruments and techniques such as XRD, Energy, EDX, SEM and FTIR.

The monitoring parameters of the investigation on the structural behaviour of the interlocking HCWA-PFA geopolymer block wall structure include load versus displacement characteristics, stress-strain relationship (vertical displacement), ultimate load capacity and failure mode analysis (crack pattern, yield stress) based on the selected optimized HCWA-PFA geopolymer mortar blocks.

1.6 Thesis layout

This thesis consisted of six chapters with the ultimate aim to cover the engineering, durability, microstructural and structural behaviour of hybrid HCWA-PFA geopolymer mortar block. In the first chapter, a brief background studies on the various issue currently faced in brick and cement manufacturing industry, the impact towards the sustainability of the aforementioned industry was made. Besides, the detailed problem statement, significance of research and also the scope of work were discussed.

Chapter two which is the literature review covered the critical review on the various factors which influence the physical, mechanical, durability and microstructural properties of geopolymer which derived from industrial by-products. Also include in this chapter is the properties of emerging blended geopolymer system. At the end of chapter two, a critical summary of all the reviewed literature was presented along with the identified gap of knowledge, the anticipated challenge faced and also the possible solution towards the impending issue discussed.

In chapter three, the details of the research programme and also the testing parameters employed to study the properties of HCWA-PFA geopolymer mortar block were discussed in depth.

Chapter four encompassed the detail results and discussions regarding the setting, engineering properties, structural performance and durability properties of HCWA-PFA geopolymer mortar blocks. Setting properties studied are standard consistency, initial and final setting of HCWA-PFA paste system. Engineering properties namely bulk density, compressive strength, flexural strength and ultrasonic pulse velocity of HCWA-PFA geopolymer mortar block. Besides, the shrinkage behaviour of HCWA-PFA geopolymer mortar blocks was also discussed over a prolonged curing period. The structural behaviour of HCWA-PFA interlocking block wall in terms of load versus displacement characteristics, stress-strain relationship (vertical displacement), buckling failure analysis (vertical displacement), ultimate load capacity and failure mode analysis (crack pattern, yield stress) was discussed in details. Amongst the testing parameters employed for durability assessment are water absorption, intrinsic air permeability, total porosity and sulphate resistance. Besides, the long term microstructural development of HCWA-PFA geopolymer mortar blocks was assessed in terms of Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX).

Primary objective of chapter 5 is to derive the overall reaction kinetics governing the hardening and solidification of HCWA-PFA geopolymer paste matrix. SEM, EDX, Fourier Transform Infrared Spectroscopy (FTIR) and thermogravimetry analysis (TGA) were utilized in order to obtain clearer picture of the overall reaction kinetics of hybrid HCWA-PFA geopolymer paste system.

Finally, the overall findings or conclusions made in the previous chapters were summarized in Chapter 6. Besides, the recommendations for further research purposes were also discussed in depth in this chapter.

1.7 Summary

The background, problem statement, objectives, significance of research and general thesis layout has been decribed in details in the current chapter. The environmental impact caused by the production of clinker in cement manufacturing industry has prompted the extensive research for a more sustainable binder material in the form of geopolymer. However, the transition of geopolymer technology towards industrial application faced difficulty as the need of high alkaline activator dosage and elevated curing temperature to achieve desired properties proved to be not viable for mass production.

Therefore, the ultimate aim of this study is to develop a sustainable geopolymeric binder derived from HCWA and PFA. The aforementioned binder materials will be used to fabricate mortar block sample which is catered for the application of load bearing masonry unit. The research scope encompassed the characterization of binders, long term mechanical, durability and microstructure properties, derivation of reaction kinetic and the structural performance of HCWA-PFA geopolymer mortar.

The development of HCWA-PFA geopolymer mortar will promote large volume recycling of waste materials originated from timber manufacturing and coal-fired power plant industry. Also, it will contribute significantly to the body of knowledge of geopolymer technology to derive similar sustainable geopolymeric system amongst the researchers. Finally, the reduction of OPC usage will help in terms of promoting sustainable and environmental friendly binder material in construction industry.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In this chapter, a critical review on the various factors influencing the physical, mechanical, durability and microstructural properties of geopolymer paste, mortar and concrete were discussed. The main factors identified to have major influence on the properties of geopolymers are chemical activators, curing regime, particle size distribution of binder phase, additives, aggressive environmental exposure conditions, effective water content, forming pressure etc. Besides, the physical, mechanical, durability and microstructural properties of the emerging blended geopolymers were also discussed and reviewed in detail. A dedicated section that focused on the structural performance of geopolymeric masonry brick/block wall structure is also included. Finally, a critical summary was made regarding the gap of knowledge and anticipated challenges in the future development of geopolymer technology for industrial applications.

2.2 Emergence of geopolymer technology

OPC has long been the traditional and widely used binder material in the manufacture of concrete. However, the use of OPC as primary construction material has been questioned extensively over the last decades due to the environmental impact of clinker production (Ahmari et al., 2012, Schneider et al., 2011). In fact, the production of Portland Cement clinker from the cement production plants worldwide emit up to 1.5 billion tons of CO_2 annually, which accounts for around 5% of the total man-made CO_2 emission and if the undesirable trend continues, the figure will rise to 6% by year 2015 (Damtoft et al., 2008, Davidovits, 1994a, Yusuf et al., 2014b). Apart from OPC, sand and aggregate are also the main constituent source materials in the production of concrete, which originated from the quarrying operations which are both energy intensive and produces high level of waste materials. Shortage of natural resources for construction materials in many developing countries has also led to long distance haulage and thus significantly increased the production cost of construction materials. All of the issues mentioned above are against the context of sustainable development in construction industry and immediate remedial actions must be taken to ensure sustainability in the construction industry (Ahmari et al., 2012).

The aforementioned issues prompted various researches in an attempt to reduce the global carbon footprint ranging from utilizing supplementary cementitious materials (SCMs) as partial cement replacement materials (Cheah and Ramli, 2012b, Cheah and Ramli, 2013, Cheah and Ramli, 2014, Kroehong et al., 2011, Nath and Sarker, 2011) to developing a whole new cementless binder, namely geopolymers (Hanjitsuwan et al., 2014, He et al., 2013, Mijarsh et al., 2014, Phoo-ngernkham et al., 2014). Geopolymers are alternative cementitious materials synthesized by combining source materials which are rich in silica and alumina such as FA, GGBS with strong alkali solutions such as potassium hydroxide (KOH), sodium hydroxide (NaOH) and soluble silicates (in most cases) such as sodium silicate where the dissolved Al_2O_3 and SiO_2 species undergoes geopolymerization to form a three-dimensional amorphous aluminosilicate network with strength similar to or higher than that of OPC concrete. Generally, the mechanism of geopolymerization can be divided into three main stages: (1) Dissolution of oxide minerals from the source materials (usually silica and alumina) under highly alkaline condition; (2) transportation/orientation of dissolved oxide minerals, followed by coagulation/gelation; (3) Polycondensation to form 3D network of silico-aluminates structures (Silva et al., 2007). Based on the types of resultant chemical bonding, three types of structures can be derived from the 3D aluminosilicate network: poly(sialate) (-Si-O-Al-O-), poly(sialate-siloxo) (Si-O-Al-O-Si-O) and poly(sialate-disiloxo) (Si-O-Al-O-Si-O-Si-O-) (Davidovits, 1994b).

The potential of geopolymer binders to replace the traditional OPC binders was supported by the fact that there is abundant of industrial by-products generated in various industries that was found to be suitable to use as geopolymer source materials, all of which are causing problems in term of finding an ideal solution for disposal purposes. For instance, PFA or more commonly known as fly ash (FA), an industrial by-products of coal burning power plant industry, makes up of 75-80% of global annual ash production (Joseph and Mathew, 2012), yielded geopolymer concrete with superior mechanical and durability properties as compared to OPC concrete (Giasuddin et al., 2013, Gorhan and Kurklu, 2013, Nazari et al., 2011). GGBS, by-products of pig iron manufacture from iron ore, has also found significant use in the production of high strength geopolymer concrete (Aydin and Baradan, 2012, Islam et al., 2014). The use of palm oil fuel ash (POFA), waste materials derived from the burning of empty fruit brunches, oil palm shells and oil palm clinker from the oil palm industry to generate electricity as geopolymer binder, has gathered pace in recent years. POFA is widely used as geopolymer binder especially in oil palm-rich country such as Malaysia and Thailand due to its increasing amount which rendered the disposal method in the mean of landfilling not feasible (Mijarsh et al., 2014, Ranjbar et al., 2014b, Yusuf et al., 2014b). Other industrial by products, for examples rice husk ash (RHA) from the rice milling industry, red mud (RM) from the alumina refining industry, copper and hematite mine tailings from the mining industry etc (Ahmari and Zhang, 2012, Chen et al., 2011, He et al., 2013, Nazari et al., 2011) has also find considerable interest in the fabrication of geopolymer concrete.

The ever present problem in reducing the use of OPC in the construction industry, coupled with the problems in disposing industrial by-product in various industries, geopolymer binder certainly has all the potential to replaces OPC as the binder in construction industry. Thus, the following sections aimed to review the current trends in geopolymer concrete, focusing solely on geopolymeric binders based on industrial waste materials, along with the various effects such as chemical activators, curing regime, additives, fineness of the binder materials, aggressive environment exposures etc towards the mechanical, physical, durability and microstructural properties of the geopolymer concrete as the leveraging of industrial waste in developing a whole new binder to replace OPC suited perfectly well in the context of sustainability in the cement and concrete industry.

2.3 Effect of chemical activators and curing regime on the properties of geopolymer

The presence of chemical activators such as sodium/potassium hydroxide and soluble silicates in the mix design of geopolymer has a significant effect on the properties of geopolymers. The effects of the addition of chemical activators on the mechanical, durability, shrinkage, microstructure and physical properties of geopolymers are deliberated in details as follows.

2.3.1 Mechanical properties

Chemical activator or alkali activator solution plays a vital role in the initiation of the geopolymerization process. Generally, a strong alkaline medium is necessary to increase the surface hydrolysis of the aluminosilicate particles present in the raw material while the concentration of the chemical activator has a pronounced effect on the mechanical properties of the geopolymers (de Vargas et al., 2011, Hu et al., 2009). On the other hand, the dissolution of Si and Al species during the synthesis of geopolymer is very much dependent on the concentration of NaOH, where the amount of Si and Al leaching is mostly governed by the NaOH concentration and also the leaching time (Panias et al., 2007). Gorhan and Kurklu (2013) investigated the influence of NaOH solution on the 7 days compressive strength of ASTM Class F FA geopolymer mortars subjected to different NaOH concentrations. Three different concentrations of NaOH (3, 6 and 9 M) were used throughout the laboratory work while other parameters such as sand/ash ratio and sodium silicate/NaOH (SS/SH) ratio was maintained constant. Based on the compressive strength results acquired, the optimum NaOH concentration that produced the highest 7 days compressive strength of 22.0 MPa is 6 M. In the aforementioned concentration, an ideal alkaline environment was provided for proper dissolution of FA particles and at the same time polycondensation process was not hindered. When the NaOH concentration is too low at 3 M, it is not sufficient to stimulate a strong chemical reaction while excessively high concentration of NaOH

(9 M) resulted in premature coagulation of silica which in both cases culminated in lower strength mortars.

In other study, Somna et al. (2011) studied the compressive strength of Ground FA (GFA) cured at ambient temperature by varying the NaOH concentration from 4.5-16.5 M. Results showed that by increasing NaOH concentrations from 4.5-9.5 M, significant increase in the compressive strength of paste samples can be observed. While the variation of NaOH concentrations from 9.5 to 14 M also increases the compressive strength of paste samples, but in a much lesser extent. The increase in compressive strength with the increasing NaOH concentrations is mainly due to the higher degree of silica and alumina leaching. The compressive strength of GFA hardened pastes start to decline at the NaOH concentrations of 16.5 M. This decrease in compressive strength is mainly attributed to the excess hydroxide ions which caused the precipitation of aluminosilicate gel at very early ages, thus resulting in the formation of lower strength geopolymers.

While many research papers reported enhancement in compressive strength with the increase in the concentration of chemical activators particularly NaOH (Ahmari and Zhang, 2012, Gorhan and Kurklu, 2013, Sathonsaowaphak et al., 2009, Somna et al., 2011), some research shows a total contrast in compressive strength development. For example, a study done by He et al. (2013) which focused on red mud (RM)/ rice husk ash (RHA)-based geopolymer concluded that higher concentration of NaOH had resulted in a decrease in compressive strength of geopolymer. The possible reasons for the contrasting trends could be attributed to, (i) the high viscosity of NaOH solution due to the higher concentration distrupts the leaching of Si and Al ions, (ii) excessive OH^- concentration results in premature precipitation of geopolymeric gels, (iii) the partially reacted/unreacted RHA particles