

**MECHANICAL PROPERTIES AND DURABILITY
PERFORMANCE OF POFA-BASED ENGINEERED
ALKALI-ACTIVATED CEMENTITIOUS
COMPOSITES**

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POFA-BASED ENGINEERED ALKALI-ACTIVATED CEMENTITIOUS
COMPOSITES**

by

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LIST OF ABBREVIATIONS

AAB	Alkali-Activated Binder
ASM	Alumino-Silicate Material
ASTM	American Society for Testing and Materials
BS EN	British Standard European Norm
C-A-S-H	Calcium Aluminate Silicate Hydrate
CAS No.	Chemical Abstracts Service Number
COP21	Conference of the Parties (21 st Conference)
COP23	Conference of the Parties (23 rd Conference)
C-S-H	Calcium Silicate Hydrate
EACC	Engineered Alkali-activated Cementitious Composite
FTIR	Fourier Transform Infra-Red
GGBFS	Ground Granulated Blast Furnace Slag
GHG	Green House Gas
IEA	International Energy Agency
ICSD	Inorganic Crystal Structure Database
IPCC	Intergovernmental Panel for Climate Change
LEED	Leadership in Energy Certification and Environmental Design
LOI	Loss on Ignition
MOR	Modulus of Rupture
Ms	Silica Modulus
N-A-S-H	Sodium Aluminate Silicate Hydrate

NH	Sodium Hydroxide (NaOH)
NMR	Nuclear Magnetic Resonance
NS	Sodium Silicate (Na ₂ SiO ₃)
OPC	Ordinary Portland Cement
PDF	Pair Distribution Functions
POFA	Palm Oil Fuel Ash
PSA	Particle Size Analysis
PVA	Polyvinyl Alcohol
RH	Relative Humidity
SCM	Supplementary Cementitious Material
SEM	Scanning Electron Microscope
SENB	Single Edge Notched Bend
SP	Superplasticizer
SSD	Saturated and Surface Dry
UN	United Nations
WBCSD	World Business Council for Sustainable Development
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

LIST OF SYMBOLS

Gt	Gigatonne
Mt	Megatonne
°C	Degree Celcius
mm/yr	Millimeter per year
kg/m ³	Kilogram per cubic meter
mins	Minutes
kN/sec	Kilo Newton per second
M	Molarity
h	Hour
mm	Millimeter
MPa	Mega Pascal
mA	Milliampere
kV	Kilovolt
kN	Kilo Newton
MPa/min	Mega Pascal per minute
g/mol	Gram per mole
v/v	Volume per volume
w/v	Weight per volume
w/w	Weight per weight
mL	Milliliter
cm ³	Cubic centimeter

g	Gram
cm ⁻¹	Per centimeter
°	Degree
°/min	Degree/minute
Å	Angstrom

**SIFAT-SIFAT MEKANIKAL DAN PRESTASI KETAHANLASAKAN
KOMPOSIT BERSIMEN TERJURUTERA TERAKTIF ALKALI BERASASKAN
POFA**

ABSTRAK

Abu sisa kelapa sawit (POFA) telah digunakan sebagai bahan penyimenan tambahan untuk menggantikan sebahagian simen Portland beberapa tahun kebelakangan ini dalam menghasilkan konkrit dan mortar. Walau bagaimanapun, untuk menyelamatkan alam sekitar daripada sisa buangan POFA dari tapak pelupusan yang boleh menyebabkan masalah kesihatan dan mengurangkan penggunaan simen Portland, 100% POFA telah digunakan dalam kajian ini. Ciri-ciri mekanikal dan prestasi ketahananlasakan mortar POFA teraktif alkali dan komposit bersimen terjurutera teraktif alkali POFA (POFA-EACC) telah dikaji. Tujuan penyelidikan adalah untuk membangunkan POFA-EACC dengan kekuatan mekanikal dan sifat-sifat ketahananlasakan matriks yang baik. Matlamat ini telah dicapai melalui penggunaan POFA sebagai satu-satunya bahan asas untuk POFA-EACC. Kajian ini merangkumi penilaian kesesuaian matriks mortar POFA teraktif alkali (tanpa gentian polyvinyl alcohol (PVA)) untuk POFA-EACC, prestasi ketahananlasakan matriks mortar POFA teraktif alkali dan prestasi mekanikal komposit POFA-EACC (dengan gentian PVA). Campuran mortar teraktif alkali telah disediakan dengan kemolaran NaOH yang berbeza (10, 12 dan 14M), nisbah $(\text{Na}_2\text{SiO}_3 + \text{NaOH})/\text{POFA}$ ((NS+NH)/POFA) 0.4, 0.5 dan 0.6, nisbah NS/NH 2.5, 2, 1 dan 0.5, nisbah pasir/POFA 1.5 dan 2% pecahan isipadu gentian PVA (untuk POFA-EACC). Keputusan menunjukkan potensi yang besar dalam penggunaan POFA sebagai bahan asas bagi pengaktifan alkali. Campuran optimum

terdiri daripada parameter rekabentuk: $NS / NH = 2.5$, $(NS + NH) / POFA = 0.4$ dan kemolaran $NaOH = 10M$. Kekuatan mampatan tertinggi 23.47 MPa dan kira-kira 25 MPa masing-masing dicatatkan selepas hanya 3 dan 28 hari pengawetan. Pengikat POFA teraktif alkali mempunyai produk utamanya, gel N-A-S-H dengan sedikit gel C-(A)-S-H yang terbentuk seiring dalam mikrostruktur mortar teraktif alkali. Usaha juga telah dibuat untuk meningkatkan kekuatan mampatan pengikat POFA rendah alumina teraktif alkali dengan penambahan peratusan $Al(OH)_3$ yang berbeza, tetapi keputusan menunjukkan kehilangan kekuatan pengikat. Kekuatan mampatan campuran optimum menurun daripada kira-kira 25 MPa hingga 18 MPa, yang paling rendah dengan tambahan $Al(OH)_3$. Di samping itu, mortar POFA teraktif alkali mempamerkan prestasi ketahanan lasakan yang cemerlang dalam pendedahan terhadap H_2SO_4 dan $MgSO_4$ berbanding dengan pendedahan terhadap Na_2SO_4 , HCl dan HNO_3 . Hasil yang diperoleh adalah bersetujuan dengan analisis SEM/EDS, XRD dan FTIR. Selain itu, sifat tegangan dan lenturan POFA-EACC sangat bergantung kepada sifat mortar POFA teraktif alkali dan ikatan antara muka matriks mortar POFA dan gentian PVA. Kekuatan mampatan ekapaksi POFA-EACC berkurangan berbanding dengan mortar tanpa gentian PVA disebabkan oleh kelemahan antara muka gentian-matriks POFA. Walaupun POFA-EACC menunjukkan kemuluran yang ketara seperti yang dipamerkan dalam keputusan kapasiti terikan tegangan, kekuatan tegangan muktamad dan kekuatan retak pertama adalah rendah. Secara amnya, parameter campuran terutamanya kemolaran $NaOH$ dan kandungan air sangat mempengaruhi semua sifat POFA-EACC.

MECHANICAL PROPERTIES AND DURABILITY PERFORMANCE OF POFA-BASED ENGINEERED ALKALI-ACTIVATED CEMENTITIOUS COMPOSITES

ABSTRACT

Palm oil fuel ash (POFA) has been partially used over the years in developing concrete and mortar. However, to save the environment of POFA waste from dumpsites causing health issues and to reduce the consumption of Portland cement, 100% POFA was used in this study. The properties and performance of POFA alkali-activated mortar and POFA engineered alkali-activated cementitious composite (POFA-EACC) have been studied. The aim of the research is to develop POFA-EACC with good mechanical strength and better matrix durability properties. This aim was achieved through the utilization of POFA as the only base material for the POFA-EACC. The study encompasses the suitability evaluation of POFA alkali-activated mortar matrix (without polyvinyl alcohol (PVA) fibers) for POFA-EACC, the durability performance of the alkali-activated mortar matrix and the composite mechanical performance of the POFA-EACC (with PVA fibers). The alkali-activated mortar mixtures were prepared with different NaOH molarities (10, 12 and 14M), $\text{Na}_2\text{SiO}_3(\text{NS})+\text{NaOH}(\text{NH})/\text{POFA}$ ratios of 0.4, 0.5 and 0.6, NS/NH ratios of 2.5, 2, 1 and 0.5, constant sand/POFA ratio of 1.5 and 2% volume fraction for PVA fibres (for POFA-EACC) were used. The results revealed a huge potential in the use of POFA as base material for alkaline activation. The optimum mixture consists of design parameters: NS/NH = 2.5, (NS+NH)/POFA = 0.4 and NaOH molarity = 10M. The highest compressive strength of 23.47 MPa and approximately 25 MPa were recorded after just

three days and 28 days of curing respectively. The developed POFA alkali-activated binder has as its main products, N-A-S-H gel with some C-(A)-S-H gel forming in tandem within the alkali-activated mortar microstructure. Attempts were also made to improve the compressive strength of low-alumina POFA alkali-activated binder through the addition of different percentages of $\text{Al}(\text{OH})_3$, but results showed some losses in strength. The compressive strength of the optimum mixture reduced from approximately 25 MPa to 18 MPa, the lowest with the $\text{Al}(\text{OH})_3$ addition. In addition, the POFA alkali-activated mortar performed excellently in durability with H_2SO_4 and MgSO_4 exposures in comparison to Na_2SO_4 , HCl and HNO_3 . The obtained results were in agreement with the SEM/EDS, XRD and FTIR analyses. In addition, the tensile and flexural properties of POFA-EACC is very much dependent on the properties of POFA alkali-activated mortar and the interfacial bond between the POFA mortar matrix and PVA fibres. The uniaxial compressive strength of POFA-EACC reduced in comparison with those without PVA fibers due to the fibre-POFA matrix interface weakness. Although the POFA-EACC showed appreciable ductility as revealed in the tensile strain capacity results, the ultimate tensile and first cracking strength is generally low. Generally, the mixture parameters especially the NaOH molarity and water content greatly influenced all the properties of the POFA-EACC.

CHAPTER ONE

INTRODUCTION

1.1 Background

The recent UN COP21 climate change conference in Paris focuses on low carbon innovations in energy, transport, and food, which is crucial to creating pathways to tackle climate change (Jayaraman 2015). In the adoption document published by the United Nations Office at Geneva, Switzerland, serious concerns were raised on the urgency in mitigating the increase in the global average temperature to well below 2 °C above pre-industrial levels and pursue efforts to limit the temperature increase by 1.5 °C (Sutharssan et al. 2015). During the UN COP23 held at Bonn, Germany, discussions on the climate change had reached the preparations stage geared towards the implementations of the Paris agreements (Carrington 2017). One of the viable and sustainable means to achieve the set temperature limit is for the cement industry to lower the production of the ordinary Portland cement (OPC) and come up with an economically and environmentally friendly substitute. Without this, there will be a terrific strain on the natural resources due to the carefree attitude and unsustainable use of this material. The far-reaching consequences of this will be; depletion of these natural resources, pollution of the environment, increase in global warming, the rise in sea level and biodiversity endangerment. As was reported in the United Nations Intergovernmental Panel for Climate Change (IPCC) publication (Change 2007), the global sea level has risen at an average rate of 1.8 mm/year since 1960 and at 3.1 mm/year since 1993. The IPCC and the International Energy Agency (IEA) estimate that the annual mitigation potential of GHG emissions in the cement industry will vary between 480 and 1700 million metric tons in 2030 (Change 2007; International

Energy Agency 2007). The scary forecast made the industry reaffirm at COP21 its commitment to tackling climate change, releasing a set of action plans aimed at reducing carbon emissions by 1 Gt by 2030 compared to business as usual.

With the growing importance of green business and sustainable industry through Leadership in Energy Certification and Environmental Design (LEED) certification for buildings and reduction of greenhouse gases emissions, there is a strong focus on minimizing the use of ordinary Portland cement (OPC). It is simply not possible to achieve robust and sustainable growth without taking consistent action in the promotion of sustainable development. According to the 2015 edition of *Reporting matters* (WBCSD 2015), a key publication developed by the World Business Council for Sustainable Development (WBCSD), the annual growth rate of cement production is 4% due to the rapidly increasing construction in developing countries. Global cement production grew by over 73% between 2005 and 2013 from 2310 Mt to 4000 Mt. Buildings and infrastructure are one of the heaviest consumers of natural resources and account for a significant proportion of the energy consumption and greenhouse gas (GHG) emissions. As one of the largest sources of emissions, the building and construction industries contribute to increasing the GHG emissions through the manufacture of raw materials and transportation of finished products. The industry faces immense pressure to reduce these emissions as the importance and understanding of sustainable development and construction grow. One of those viable strategies to reduce emission is to cut down the use of OPC.

OPC concrete after water is the single most used and predominant materials for all the developmental activities on earth. It is arguably the largest consumer of the natural resources (sand, stones and water). The importance and dominance of concrete are due to

its low cost of production, easy access to its ingredients, ability to sustain heavy loads and its ability to be molded into different shapes and sizes. Despite all these advantages, OPC concrete has been criticized for many reasons chiefly due to the enormity of energy used in its production and the release of CO₂ gases into the atmosphere. For concrete production, one solution is the reduction of the cement content in concrete by using supplementary cementitious materials such as fly ash, blast-furnace slag, silica fume, metakaolin, natural pozzolans, and biomass ash to replace cement (Golizadeh and Banihashemi 2015).

Since early civilization, the use of pozzolanic and supplementary cementitious materials (SCM), both naturally occurring and artificially produced have been in existence. They are used either as a replacement for cement or as an enhancement for concrete. The pozzolanic ability of a material is revealed in its physical and chemical properties. Fly ash retains the position of the most used artificial pozzolanic material globally according to reports (Bouzoubaâ and Lachemi 2001; Aponte et al. 2012; Boğa and Topçu 2012; Abdulkareem et al. 2014; Baščarević et al. 2014) among other ones such as silica fume, rice husk ash etc. SCMs include high-calcium fly ash and ground granulated blast furnace slag (GGBFS). SCMs utilization has proven their effectiveness in producing not only strong concrete but also a durable one (Awal and Hussin 1999). The last two decades had undoubtedly witnessed the unprecedented development of huge innovative cementitious composite materials that provide excellent mechanical properties and high durability properties. With more and more diversification in the use of these waste materials having pozzolanic behavior, more materials are likely to surface to substitute cement in the production of concrete. One of such materials is palm oil fuel ash (POFA), an agro-waste material resulting from the burning of palm fibers, empty fruits bunches and kernel shells.

The burning of these materials is to heat the boiler to produce steam used in the generation of electricity and to power palm oil extraction process at the mill. The ash produced after this burning is termed POFA and is indiscriminately disposed of without any economic value, posing environmental and social problems at the mill sites and its surrounding. An enormous amount of POFA are produced in Malaysia, Thailand and Indonesia and the annual increment is expected (Altwair, Johari, et al. 2012). According to the factsheet of the European Palm Oil Alliance®, global palm oil production has increased from 15.2 million tons in 1995 to 54 million tons in 2012 and expected to grow by more than 25% by 2020 to a global level of more than 68 million tons (European Palm Oil Alliance 2014). The implication of this is that POFA, a major palm oil waste will increase massively as the production and consumption of palm oil continue to grow in line with the increasing demand globally. Normally, POFA is dumped on the bare soil close to the factory or large areas of land, which is suitable for infrastructural development like roads, pedestrian walkway, residential, commercial etc. This trend calls for the immediate and beneficial use of this waste to avert health hazards, which can lead to diseases affecting the bronchi and lungs (Tay and Show 1995) and other environmental problems. These kinds of materials have found beneficial use in the production of all types of concrete from high strength to the fibre reinforced concrete, which engineered cementitious composite (ECC) is part of its family.

ECC is a special class of high-performance fiber reinforced cementitious composites (HPFRCCs) which utilizes a small amount of discontinues fibers (typically 2% or less by volume) and exhibits very high tensile strain capacity of up to 6%. ECC is cement mortar-based with superior ductility (about 600 times the ductility of normal concrete in tension) (Li 1998; Kong et al. 2003; Dhawale and Joshi 2013). According to past researchers

(Maalej, Hashida and Victor C. Li 1995; Li 2002; Li et al. 2004; Altwair, Johari, et al. 2012), ECC mixture design can be replaced partially by supplementary cementitious materials such as slag, fly ash and POFA to reduce the use of OPC thereby reducing the emission of CO₂ from OPC production. However, a more sustainable approach to develop green ECC is by replacing completely the cementitious binder with alternative cement-free binder such as alkali-activated binder in order to achieve engineered alkali-activated cementitious composites (EACC). Researches have started and in progress in the development of EACC using different base materials and with different types fibers to achieve deflection hardening and multi-crack criteria. Nematollahi et al. (2014) evaluated the behavior of ductile fiber reinforced geopolymer concrete in exhibiting deflection hardening and multiple cracking employing four different activators (two Na-based, one K-based and 2 Ca-based activators). Polyvinyl alcohol (PVA) short random fibers (2% v/v) were used to reinforce the brittle low calcium class F fly ash. In another work by Yunsheng et al. (2008), short fibers in metakaolin-based geopolymer was also used to study the ductility properties of the developed composite.

1.2 Problem statement

Sustainable development is a holistic concept, which carries with it the environmental, economical, engineering and social requirements. For these requirements to be satisfied there is a need for the problems that come with it to be clearly defined and solved.

1.2.1 Environmental problems

Undoubtedly, there are quite a number of studies that have assessed the suitability of different base materials to replace partly the OPC binder like fly ash, metakaolin, ground granulated blast-furnace slag (GGBFS) in the development of alkali-activated binders.

The critical problem facing the Portland cement industry is how to trade the industry-generated and indiscriminately-emitted CO₂ into the atmosphere. CO₂ emission trading refers to the economic tools and techniques required to help countries worldwide meet the emission target set, for instance at the 2015 Paris agreement (ICAP 2016). The climate change is not only attributed to global warming; a phenomenon caused by the absorption of sunlight by CO₂ and other gases, but also attributed to global dimming. Global dimming is the reduction in the sunlight radiation due to the obstruction caused by particulate matters, which absorbs the sunlight and reflects it back into space. These particles are believed to be caused by human actions which cement particles from industries are part of. In the simplest term, the global contribution of Portland cement production stands at an estimated value of 1.3 billion tons or 8% of the global CO₂ emitted on the surface of the earth (Olivier et al. 2015). Due to sporadic growth in global inhabitants and high demand for concrete, cement production is expected to increase by 0.8 - 1.2% reaching 3.7 – 4.4 billion tons by 2050 (Breisinger et al. 2010). However, through the application of appropriate strategies like energy efficiency, utilization of alternative fuels, cement substitution and carbon capture and storage, these emissions may be reduced and finally reach to 1.55 billion tons in 2050 (IEA 2009). Based on this scope of this study, as a way to contribute to reducing global CO₂, the Portland cement responsible for the CO₂ emission is fully substituted by POFA, a green and sustainable material. As mentioned above, POFA is a waste from palm oil processing mill, since the palm oil production continues, the generation of POFA continues. The POFA waste is dumped indiscriminately in wastelands, which could easily be carried by wind, cause smog on humid days leading to impaired visibility for traffic users and equally lead to bronchi and lung diseases (Tay and Show 1995). Alkali-activated binder presents a better mechanical

performance and poses some environmental challenges due to high utilization of ordinary Portland cement (OPC), hence the need for replacement with POFA. In order to improve on alkali-activated mortar mechanical properties from the quasi-brittle to ductile, it is reinforced with fiber to produce the fiber-reinforced alkali-activated cementitious composite (FRACC). When the volume fraction of the fiber is 2% and less, the FRACC will be otherwise known as engineered alkali-activated cementitious composite (EACC). The high amount of OPC required in the production of EACC makes it environmentally “ungreen” and calls for the need for a green and sustainable replacement, hence the utilization of 100% POFA.

1.2.2 Economic problems

Cement is arguably the most important and most used construction material until date. By 2020, as estimated by market research analysts, the global cement industry will grow more than 9% (GCIO 2016). The purchasing power of emerging markets like India and China coupled with growing population led to high demand for residential buildings and infrastructural projects the world over. The construction industry is driven by the increase in the number of these projects, which in turn activates the demand for cement during the projected period. Presently, some countries are witnessing the large-scale urban migration of the populace, which strains the existing infrastructure and increases demand for real estate. The unanticipated increase in population makes the OPC limited in supply and the available ones to be very expensive. Supplementary cementitious materials like fly ash, silica fume, rice husk ash, POFA, etc have been used in previous researches to replace a sizeable and technical feasible percentage of cement in order to reduce overall construction costs. These costs can be further reduced through the utilization of large

quantity of POFA, a sustainable and environmentally friendly solution to fill the supply gap created by the growing demand for OPC, hence reduce cost.

1.2.3 Engineering problems

The development of EACC has as a major requirement, high OPC content, which is antithesis of global demand to reduce the production and utilization of cement as it generates CO₂, which is known to adversely affect the environment. There is need to do away with cement and replace wholly with POFA, a green material with qualifying properties of environmental friendliness and sustainability. The use of this material will eliminate a major problem of high heat of hydration associated with the high content use of OPC. This leads to undesirable access to the concrete matrix and embedded reinforcement by deleterious materials like sulfates and acids, through the shrinkage-induced cracks formed as a result of the adverse effect of the heat of hydration. Pozzolanic materials like the mineral admixtures have been used to lower drastically the heat of hydration and POFA identified as a good pozzolanic material will cancel totally the adiabatic heat in concrete mass. This encourages its use as base material for not only alkali-activated binder but also for EACC, which is strongly believed will improve the engineering properties and performance of the developed EACC.

1.2.4 Social problems

In a world of growing urbanization, cement industry still stands advantageous in that there is a lot of demand for it. Due to this high demand, there are some social impacts, which focusses on the community well-being to include public health and safety, the living environment, satisfaction of basic needs (housing, sanitation, water supply etc.), access to public services (health, education, training and recreation), jobs creation and landscape

aesthetics. At the local level, cement production has significant positive and negative impacts. The negative impacts, which is crucial, include disturbance to the landscape, dust, and noise, disruption to local biodiversity from quarrying limestone (the raw materials for cement) and dangerous conditions that local cement plant workers are exposed to. Utilization of supplementary cementitious materials like POFA will positively impact the community through the creation of jobs, reduction in the cost of infrastructure by using POFA material and keeping their environment less of CO₂.

1.3 Justification of research work

The development of engineered cementitious composite (ECC) as part of its requirements is the high binder content. Portland cement has been the most commonly used base material in matrix development of ECC where its hardening process is through an exothermic cement hydration process. Apart from its huge threat to the environment due to the high CO₂ emission, its exothermic hydration process puts a question mark on its shrinkage properties, which directly affect its durability properties. On the other hand, the indiscriminate disposal of POFA by the palm oil industries has been a challenging issue demanding urgent solution because of the declining effect of the material on the environment and the hazardous risk it pose to the health of community people.

This material is thought to find beneficial use in the development of POFA alkali activated mortar for two major reasons. One is that POFA contributed extremely less CO₂ than Portland cement when used and two, its usage can lead to environmental cleaning and landscape saving from the POFA waste. In the overall, utilization of POFA as the only aluminosilicate material in alkaline activation will lead to reduced CO₂ emissions, reduced construction costs, infrastructure development and creation of job within the communities where POFA is generated. . Despite all the studies into the alkaline activation technology,

no study has been devoted to the exploration of the POFA-based alkali-activated binder. Bearing this in mind, this study provides additional insight into the world of alkaline activation first and secondly, to develop EACC utilizing activated POFA. Hence, this research is justifiable in the potential it offers to save the environment and its ability to drastically reduce the cost of infrastructures in Malaysia and other places

1.4 Thesis aim and objectives

Partial replacement of cement with supplementary materials has been one of the ways to reduce the consumption of cement, however, the impact of reduction does not reflect positively on the environment. Hence, the aim of the study is to completely replace cement by POFA in the development of EACC, which will make a valuable contribution to the promotion of high volume utilization of POFA in alkali-activated binder. In order for the intended aim to be achieved, the following specific objectives have been set:

- i. To synthesize POFA-based alkali-activated mortar from treated POFA to be used as matrix for the POFA-EACC and assess its properties through compressive strength properties and microstructural studies.
- ii. To investigate the durability characteristics of selected mixtures from the optimized POFA alkali-activated binder in (i) above through exposures to sulfate and acid environments.
- iii. To evaluate the mechanical composite performances of the POFA-EACC in terms of flexural, tensile and compressive strength.

1.5 Scope of work

This study contributes to the development of engineered cementitious composite based on alkaline activation technology using POFA, a newly found environmentally friendly and

sustainable material. The POFA-based engineered alkali-activated cementitious composite (POFA-EACC) mortar was developed with POFA as the only base material, alkali activator and polyvinyl alcohol (PVA) fibers as reinforcement. Due to low Ca(OH)_2 and alumina content, the developed POFA alkali-activated binder recorded strength below the expected strength. In order to improve the matrix strength of the developed POFA alkali activated mortar, Al(OH)_3 was added.

The base material was obtained raw locally from United Palm Oil Mill Sdn. Bhd. in Nibong Tebal, Penang, Malaysia. The untreated POFA was processed to improve its efficiency and properties in the laboratory before it is fit for use as a base material for the synthesis of the alkali-activated binder. The POFA was activated by alkaline solution (Na_2SiO_3 with silica modulus of 3.3 and NaOH with molarity of 10 M, 12 M, 14 M).

The experimental investigation involves prior characteristics study of POFA based on its chemical composition, physical properties and morphology of its particles. The synthesis of the POFA alkali-activated binder followed and was studied under five factors in order to enhance the developed binder. The POFA alkali-activated mixtures with relatively high compressive strength at 28 days was used to study the tensile and flexural properties of the POFA-EACC binder mortar developed. The curing temperature was 60 °C for 24 hours were chosen to be studied in order to establish efficient curing conditions. The effect of water to solid ratio on the strength development of the POFA binder mortar was also investigated.

1.6 Outline of thesis

This research work is reported in this thesis in seven chapters. Following this introductory chapter, which describes the overview of the present research, the other chapters are organized as follows:

Chapter two presents a review of the literature available on the subject of alkali-activated technology and the different materials used from previous works in the production of alkali-activated mortar. This includes a review of the reaction mechanism of alkali-activated and the different testing techniques used in the characterization of the alkali-activated binder. It presents also the review of engineered cementitious composites, micromechanics of strain hardening, conditions for strain hardening and applications of ECC.

Chapter three presents the materials and experimental design, which covers the mixture proportions and the methodology of research employed to achieve the objectives of the study. The material properties, mixture proportion, mixing procedure and test methods used in evaluating the properties of the alkali-activated POFA system are presented in this chapter. The experimental methodology is divided into two parts. The first part develops the POFA alkali-activated mortar with the required matrix strength prior to the introduction of PVA fiber using compressive strength as decision metric. The second part is the development of the POFA-EACC using optimized mixtures from the first part based on better strength performance. The chapter also elucidates on the experimental procedures undertaken in studying the durability performance of the POFA-based alkali-activated binder.

Chapter four presents the experimental results of the physical and mechanical properties of the POFA alkali-activated cementitious composite mortar. The effects of NaOH molarity, alkaline activators/POFA ratio and alkaline activator ratio on the mechanical properties of the POFA alkali-activated binder are presented. Results of the improvement of the matrix strength after the addition of $\text{Al}(\text{OH})_3$ are also included. SEM/EDX, XRD and FTIR were used to study the microstructural properties of the developed POFA-based alkali-activated binder and the results shown in this chapter.

Chapter five discusses the properties of POFA-EACC due to the introduction of PVA fibers to engineer the mixtures, the POFA-EACC mortar is tested for flexural and tensile strength, and the results are also shown in this chapter.

Chapter six presents the experimental studies on the durability properties POFA-based alkali-activated binder including when exposed to sulfate salts and acid attacks. All results were compared with the unexposed POFA-based alkali-activated binder. Like chapter five, XRD, SEM/EDX and FTIR were used to study respectively the compositional and interfacial properties of the binder after exposure to salts and acids.

Chapter seven presents the conclusions drawn from the research work and highlights some recommended areas of further research work in the future.

CHAPTER TWO

LITERATURE REVIEW

2.1 Background

Alkaline-activated binders (AAB) represent a broad range of materials characterized by chains or networks of inorganic molecules. These AAB rely on thermally activated natural materials (e.g. kaolinite clay) or industrial byproducts (e.g. fly ash or slag) or agro-waste (e.g. POFA) to provide a source of silica (SiO_2) and alumina (Al_2O_3), which when dissolved in an alkali-activating solution, subsequently polymerizes into molecular chains and networks to create the hardened binder. AAB share similarities with the natural zeolite materials, in that AAB are inorganic polymers but with amorphous or semi-crystalline microstructure instead of the crystalline microstructure of the zeolites. The polymerization process is a fast chemical reaction between alkaline solutions and Si-Al minerals whose result is a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O bonds. The geopolymerization reaction is exothermic and takes place under atmospheric pressure at temperatures below 100 °C. The exact mechanism by which geopolymer setting and hardening occurs is not yet fully understood. However, according to most researchers (Provis and van Deventer 2013; Palomo et al. 2014; Provis and Bernal 2015), the proposed mechanisms for the geopolymerization occur in four stages. These stages occur simultaneously thus made it impossible to be distinguished, they are:

- (i) Dissolution of Si and Al from the solid aluminosilicate materials in the strongly alkaline aqueous solution.
- (ii) Formation of oligomers species (geopolymers precursors) consisting of polymeric bonds of Si-O-Si and/or Si-O-Al type.

- (iii) Polycondensation of the oligomers to form a three-dimensional aluminosilicate framework and;
- (iv) Bonding of the unreacted solid particles and filler materials into the geopolymeric framework and hardening of the whole system into a final solid polymeric structure.

2.2 Aluminosilicate source materials (ASM)

The two most vital ingredients of the alkali-activated binder are alkaline activators and the aluminosilicate source materials (ASM). ASM that are the prime ingredients for alkaline activation are materials, which are rich in silica (SiO_2) and alumina (Al_2O_3). In this category are thermally activated materials like metakaolin or industrial by-products such as fly ash, silica fume, GGBFS, steel slag, etc. Alternatively, agricultural waste like almond shell ash (AA), Olive Bagasse Ash (OBA), chestnut peel ash (CPA), grape bagasse fly ash (BGFA), grape bagasse bottom ash (BGBA), digested filtering waste (lees) from the wine industry (DFW) and palm oil fuel ash (POFA) in the case of this study can be used as source materials for alkaline activation (Matos et al. 2012). Generally, the selection of aluminosilicate source materials depends mainly on the availability of the materials, cost of acquiring the material, particular demands from the users, type of application intended and other similar factors (Nawy 2008).

Bearing in mind the above factors, alkaline activation has been studied by numerous researchers, documenting the effect of different source materials in different combinations of natural, agricultural and industrial by-products, the addition of different admixtures and other ways to improve the process of alkali activation. The reaction between ASM and alkaline solution allows for a very quick dissolution and gelation of the aluminosilicate

species. This process results in the formation of compounds, which are made up of mixtures of amorphous, semi-amorphous or micro-crystalline structures (Khale and Chaudhary 2007).

There are two main categories of ASM based on the nature of their oxide components ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$), the low calcium (Si + Al) and high calcium (Si + Ca) ASM materials (Li et al. 2010; Pacheco-Torgal et al. 2014). For both categories, the process of achieving alkali activation distinctively differs. High calcium ASM requires moderate alkaline concentration or condition (Bakharev et al. 2000; Shi et al. 2006) to achieve activation and the main alkaline activation product is $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ (calcium silicate hydrate) gel. The product shares semblance with the C-S-H gel, a product of OPC hydration but takes up Al in its gel structure. For low calcium ASM, an aggressive condition (highly alkaline solution and curing temperature 60 – 200 °C) is required to start the alkaline activation reaction (Pacheco-Torgal et al. 2014). The prime reaction product in the case of low calcium ASM is $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ (alkaline aluminosilicate hydrate) gel referred to zeolite precursor (Palomo et al. 1999; Duxson et al. 2006; Provis and Deventer 2009).

There is a third category of ASM material called hybrid alkaline cement formed as a result of alkaline activation of materials with CaO, SiO_2 and Al_2O_3 content greater than 20% (Alonso and Palomo 2001; Yip et al. 2005; Palomo et al. 2007; García-Lodeiro et al. 2013). This hybrid category is also divided into two groups; first is the group of OPC and ASM (over 70%) (Palomo et al. 2007), for example, cement + GGBFS, cement + fly ash, cement + slag + fly ash. The second group is a blend of different ASM but no OPC such as GGBFS + fly ash, natural pozzolan + silica fume + fly ash and similar (Pacheco-Torgal et al. 2014). The alkaline activation reaction products of a combination of different ASM

is complex, which comprises of a mixture of cementitious gels such as C-A-S-H (which contains sodium in its structure or composition) and (N,C)-A-S-H (high calcium content N-A-S-H) gels (Garcia-Lodeiro et al. 2013).

2.3 Palm oil fuel ash (POFA)

In addition to other ASM, palm oil fuel ash (POFA) has also been seen as a very capable source material in the development of alkali-activated binder. POFA is an agricultural waste product recovered in the form of ash from the burning of palm oil fibre, kernel shell and empty fruit bunches as fuel, at a controlled temperature of 800 –1000 °C to power the palm oil boiler for the generation of electricity for the mill (Awal and Hussin 2011; Kroehong et al. 2011). POFA, now accepted as pozzolanic material (Sata et al. 2007; Tangchirapat, Jaturapitakkul and Chindaprasirt 2009; Awal and Hussin 2011) contains a high amount of silicon and some aluminum oxides in its amorphous state.

Many researchers (Tay and Show 1995; Awal and Hussin 1999; Chindaprasirt et al. 2007; Hussin et al. 2009; Johari et al. 2012; Chandara et al. 2012; Aldahdooh et al. 2014; Yusuf 2015) have found beneficial use for POFA to develop mortar and concrete with excellent strength and durability properties in order to save the land from soil contamination, underground and surface water pollutions. The pioneering work by Tay (1990) into the use POFA as cement replacement started where 10% of cement content was replaced with POFA in concrete. The motivation came from the high silica content of POFA, which encouraged the idea of cement replacement because of its conceived pozzolanic properties. In addition, two works by Tangchirapat et al. (2007) and Chindaprasirt et al. (2008) were also reported that 10% of the binder mass should be the limit for POFA because of its low pozzolanic properties. Slowly, the quantity of POFA replacement

increased with replacing cement with 20% ground POFA (GPOFA) and observing that its compressive strength was similar to OPC concrete (Chindaprasirt et al. 2007). Similar results were reported Sumadi and Hussin (1995) in that by replacing 20% GPOFA with an equal weight of OPC, durable concrete can be produced that is almost identical to OPC concrete. However, they found that by increasing the amount of GPOFA, the compressive strength decreased because of its higher water demand. To increase the achievable quantity of POFA, pozzolanic reactivity of POFA was enhanced by Tangchirapat et al. (2009) and Hussin and Awal (1998) using GPOFA with improved fineness to achieve 30% by binder mass. After this increase in achievable quantity with GPOFA, the potential to produce high-strength concrete with POFA was proved in the works of Johari et al. (2012) and Sata et al. (2004). High-strength concrete was developed by Sata et al. (2004) using superplasticizer (SP) to largely reduce the water demand of POFA initially seen impeding higher quantity use of POFA. They revealed that the concrete containing 30% GPOFA showed a higher strength than OPC concrete at 28 days.

It was also shown by Johari et al. (2012) that by using treated GPOFA, high-strength concrete can be produced by reducing the unburned carbon and smaller-sized GPOFA particles. In an additional effort to reduce the use of OPC, some other works Johari et al (2012; 2013) have reported that the maximum achievable quantity that can be replaced with OPC was 60% POFA. With continual improvement and increase in the quantity of POFA replaced with OPC, there is bound to be more eco-friendly concrete, thus contributing to a greener and more sustainable environment by reducing cement consumption (Altwair, Megat Johari, et al. 2012).

2.3.1 Physico-chemical properties of POFA

The performance of any ASM depends on its physicochemical properties. The POFA used by researchers have different properties depending on the source of the waste material and the quality of treatment through the condition of burning temperature (Abdullah et al. 2006). The different chemical compositions of POFA used in various studies from different sources are shown in Table 2.1. As revealed in the table, the prime compositions in POFA include silica (SiO_2), alumina (Al_2O_3), ferric oxide (Fe_2O_3), calcium oxide (CaO), magnesium oxide (MgO) and potassium oxide (K_2O). POFA has a high amount of SiO_2 in its chemical composition, which gives it a high potential of being used as a binder. The performance of POFA as a binder depends on the quantity of the prime compositions especially the SiO_2 , Al_2O_3 and CaO , which depends on the burning time and temperature level. According to ASTM C618 specification (ASTM C618 2012), POFA is pozzolanic and hence grouped as Class F, however within the research community, there is no consensus on which class POFA should belong. Strictly looking at the specification, POFA falls between Class C and Class F because $(\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3)$ is between 50 and 70% respectively for individual class. This difference is as a result of the condition of the raw materials at the mill and the burning condition during treatment.

Table 2.1: Comparative chemical compositions of different POFA sources

Oxides	(Saharudin et al. 2017)	(Ranjbar et al. 2014)	(Islam et al. 2014)	(Tangchirapat, Jaturapitakkul and Kiattikomol 2009)	(Jaturapitakkul et al. 2011)	(Kroehong et al. 2011)	(Huseien et al. 2016)
SiO₂	61.57	64.17	63.41	55.50	65.30	54.00	64.20
Al₂O₃	4.12	3.73	5.55	9.20	2.56	0.90	4.25
Fe₂O₃	2.96	6.33	4.19	5.60	1.98	2.00	3.13
CaO	7.08	5.80	4.34	12.40	6.42	12.90	10.20
MgO	1.92	4.87	3.74	4.60	3.08	4.90	5.90
K₂O	7.99	8.25	6.33	0.00	5.72	13.50	8.64
SO₃	1.17	0.72	0.91	2.30	0.47	4.00	0.09
MnO	-	0.18	0.17	0.00	0.00	0.00	0.00
P₂O₅	3.36	5.18	3.78	0.00	0.00	0.00	0.00
Na₂O	0.03	0.18	0.16	0.00	0.36	1.00	0.10
SiO₂+Fe₂O₃+Al₂O₃	68.65	74.23	73.15	70.30	69.84	56.90	71.58
LOI	1.13	16.30	6.20	7.90	10.05	3.70	1.73

The physical properties of POFA are hugely dependent on burning time which is around 90 minutes and with a temperature of 550 °C. Other factors that influence POFA properties significantly are the intensity of grinding and duration, this is to improve its reactivity and with that, higher POFA quantity can be used. The carbon content in the POFA affects the color variation moving from dark shades (high carbon content) to greyish white (low carbon content). The carbon content of POFA can be drastically reduced through the application of heat with higher temperature on it (Abdullah et al. 2006; Altwair et al. 2011; Safiuddin et al. 2011).

Prior to milling, the POFA particles sizes and shapes are mostly large, spherical and porous as seen on the SEM micrograph in Figure 2.1. After the milling process, POFA shares particle shape irregularity and angularity with Portland cement as shown in Figure

2.2 (Jaturapitakkul et al. 2007). The unmilled POFA particle sizes are larger than Portland cement particles, however, after milling, the particle sizes became smaller than that of the Portland cement. The median particle size of unground POFA is about 54 – 183 μm , which is larger than Portland cement particles which are in the range of 10 – 20 μm . However, the particle sizes of POFA decreases to 7.2 – 10.1 μm after the process of grinding (Sata et al. 2004; Jaturapitakkul et al. 2007).

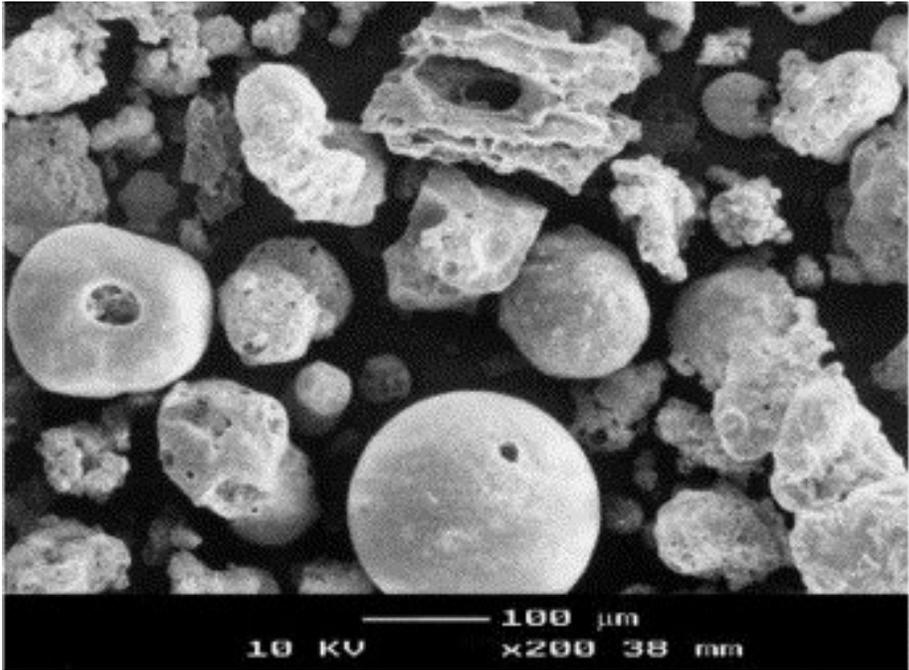


Figure 2.1: SEM micrographs of unground POFA (Jaturapitakkul et al., 2007a)

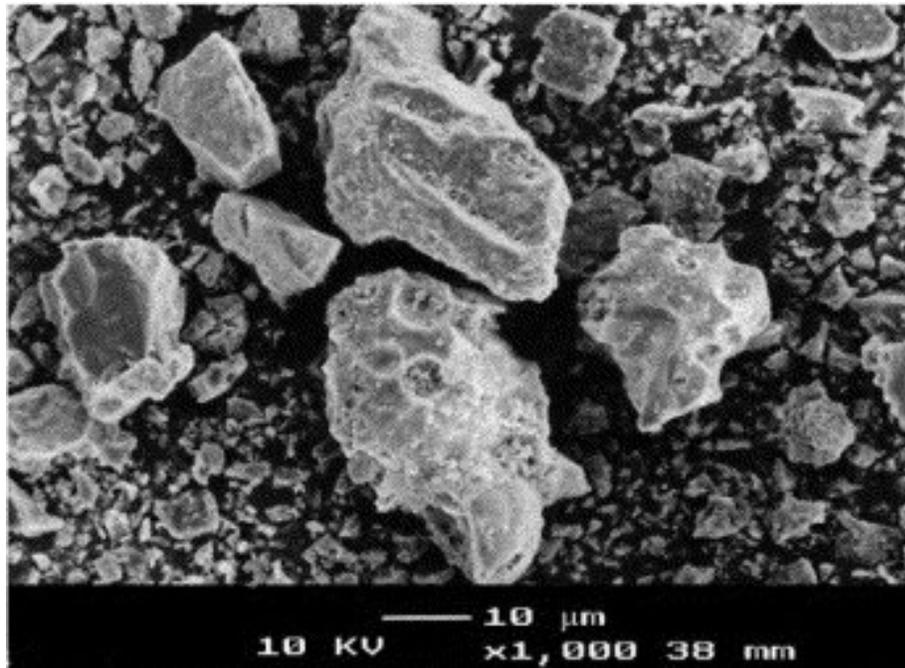


Figure 2.2: SEM micrographs of ground POFA (Jaturapitakkul et al., 2007a)

2.3.2 Effect of POFA on fresh properties of alkali-activated binder

The fresh properties of POFA-based alkali-activated mortar are vital in that it indirectly determines the mechanical and durability of hardened alkali activated mortar. After the heat and physical treatment of POFA, its fineness increased which makes it hydrophilic, an ability that increases its ability to consume more water. It was reported in a study by Alsubari et al. (2014) that as the quantity of POFA increases, the slump flow of the concrete decreases. This is attributed to the porosity and high surface area of the POFA particles. This POFA porosity and fineness affords it the tendency to absorb more water in the mixture, hence reducing the quantity of water needed to work the fresh POFA mortar (Safiuddin and Jumaat 2011). The effect on the workability of fresh alkali activated POFA mortar comes from two sources; the alkaline activators and the free water added to the mixture. In a study by Moslih et al. (2013) where POFA-based alkali-activated binder was developed, the slump flow was reported to be affected by both NaOH concentration

and the water/binder ratio. As the NaOH concentration increases, the slump flow decreases due to the increase in the NaOH solute and decrease in its water content. The silicate content of alkali-activated binder has also been reported by Qureshi and Ghosh (2014) to affect the fresh properties of blast furnace slag paste. It was shown that the flow diameter of the slag paste increases from 110 – 175 mm as the silicate content ($\text{SiO}_2/\text{Na}_2\text{O}$) increases from 0.2 to 1.2.

2.3.3 Effect of POFA on compressive strength of alkali-activated binder

The compressive strength of alkali-activated binder utilizing any aluminosilicate such as POFA is dependent on the chemical compositions and physical properties of the base materials, strength of the alkali activators and curing temperature. The prime factor is the composition of aluminosilicate materials, which is assessed for quality based on the quantity levels of the main oxides. The presence or absence of main oxides in these materials defines the quality of the engineering properties of the developed alkali-activated binder. The health of the microstructure gives an indication of the engineering properties of the binder and that depends largely on the quantity of the major oxides such as SiO_2 , Al_2O_3 , Na_2O and CaO in the base material. The chemical composition of POFA contain a high amount of SiO_2 but in varying quantities depending on the region and treatment. A common property in all is the deficiencies in Al_2O_3 and CaO , which affects the engineering properties of POFA. It was reported by Silva et al. (2007) that Al_2O_3 accelerates the setting of alkali-activated binder while setting of the alkali-activated binder is inhibited by increasing SiO_2 . However, in the overall, strength is improved when SiO_2 is increased due to low porosity. One of the critical parameters used by researchers in understanding the roles silica and alumina species played in the properties of the activated

binder is Si/Al ratio and the calcium content. The role of calcium is evident in the formation of the alkali-activated gel and the calcium silicate hydrate with substituting aluminum (C-(A)-S-H). To achieve suitable or adequate strength for the POFA-based alkali activated paste, mortar or concrete, physical (fineness) and chemical (addition of $\text{Al}(\text{OH})_3$ or supplementary blend (Ariffin et al. 2011; Ismail et al. 2013) or both $\text{Al}(\text{OH})_3$ and supplementary blends need to be explored (Yusuf, Megat Azmi Megat Johari, Ahmad and Mohammad Maslehuddin 2014a).

Kroehong et al. (2011) investigated the effect of utilization of POFA to the tune of 40% maximum replacement of OPC on the compressive strength. It was reported that the compressive strength of blended cement paste with POFA increased with curing time but decreased with an increase in the replacement of OPC with POFA. With the increase in the fineness of POFA, the rate of compressive strength gain of the blended cement paste improved significantly due to the increased hydration reaction, nucleation effect, improved packing effect and increased pozzolanic reaction. The high fineness of POFA catalyzes its pozzolanic reaction, which makes it faster than POFA with low fineness (Tangchirapat, Jaturapitakkul and Kiattikomol 2009; Sata et al. 2010). This is because POFA with high fineness comes with better particle packing, which makes the paste, mortar or concrete homogeneous and dense, a panacea to compressive strength improvement.

2.4 Alkali Activation of Source Materials

2.4.1 Historical background of alkaline activation

The publication of 1908 patent by Kuhl (1908), a German chemist was the first to be published with respect to alkali-activated binder technology (Provis and Bernal 2015). He