THE COMBINED EFFECT OF DIPOTASSIUM HYDROGEN PHOSPHATE AND PAPER MILL SLUDGE ASH TOWARDS FORMATION OF EFFLORESCENCE AND PROPERTIES OF FLY ASH GEOPOLYMER MORTAR

NORBAIZURAH BINTI RAHMAN

Doctor of Philosophy

UNIVERSITI MALAYSIA PAHANG

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy.

_____

(Supervisor's Signature)

Full Name : ASSOC. PROF. DR. ANDRI KUSBIANTORO

Position : ASSOCIATE PROFESSOR

Date : 06 AUGUST 2018

_____

(Co-supervisor's Signature)

Full Name : ASSOC. PROF. DR. KHAIRUNISA MUTHUSAMY

Position : ASSOCIATE PROFESSOR

Date : 06 AUGUST 2018

STUDENT'S DECLARATION

I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

_____

(Student's Signature)

Full Name : NORBAIZURAH BINTI RAHMAN

ID Number : PAC15003

Date : 6 AUGUST 2018

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LIST OF SYMBOLS

%	Percentage
°C	Degree celcius
µL	Microliter
Al	Aluminium
$Al(OH)_4$	Aluminate
Al_2O_3	Aluminium oxide
Ca	Calcium
$Ca(OH)_2$	Calcium hydroxide
CaO	Calcium oxide
cm	Centrimeter
CO_2	Carbon dioxide
CO_3	Carbonate
Fe	Ferum
Fe_2O_3	Iron oxide
g	Gram
H_2O	Water
HCl	Hydrochloric acid
K	Potassium
K_2HPO_4	Dipotassium hydrogen phosphate
K_2O	Potassium oxide
K_2SiO_3	Potassium silicate
Kg/m^3	Kilogram per meter cubes
KOH	Potassium hydroxide
M	Molar
Mg	Magnesium
MgO	Magnesium oxide
min	Minutes
ml	Millilitre
mm	Millimetre
mN/m	Millinewton per meter
MPa	Megapascal
Na	Sodium
Na_2CO_3	Sodium carbonate
Na_2O	Sodium oxide

Na_2SiO_3	Sodium silicate
NaOH	Sodium hydroxide
O	Oxygen
OH	Hydroxide
P_2O_5	Phosphorus pentoxide
PO_4	Phosphate
ppm	Parts per million
rpm	Revolutions per minute
s	Second
Si	Silicon
SiO_2	Silicon dioxide/Silica
SO_3	Sulphur trioxide
SrO	Strontium oxide
TiO_2	Titanium dioxide
g/mol	Gram per mol
N/s	Newton per second

LIST OF ABBREVIATIONS

ASTM	American society for testing and materials
CSH	Calcium silicate hydrate
DTG	Differential thermagravimetry
EDX	Energy dipersion x-ray
FTIR	Fourier transform infrared spectroscopy
ICPMS	Inductively coupled plasma mass spectrometry
LOI	Loss on ignition
MLS	Modified lignosulphonates
Ms	Modulus ratio
MS	Malaysia Standard
NASH	Sodium aluminosilicate hydrate
OPC	Ordinary portland cement
PMSA	Paper mill sludge ash
RHA	Rice husk ash
RM	Red mud
SEM	Scanning electron microscopy
SMF	Sulphonated melamine formaldehyde
SNF	Sulphonated naphthalene formaldehyde
TGA	Thermogravimetric analysis
UCS	Unconfined compressive strength

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ABSTRAK

Penggunaan aluminosilikat yang mempunyai jumlah CaO yang tinggi telah di aplikasikan secara meluas ke dalam geopolimer. Ini adalah kerana kekuatan mampatan yang tinggi pada awal usia. Kehadiran Ca^{2+} mempercepatkan proses geopolimerisasi, oleh itu telah menghasilkan gel geopolimer yang banyak. Walau bagaimanapun, jumlah Ca^{2+} yang berlebihan menyumbang kepada kadar pengerasan yang cepat dan kebolehkerjaan yang rendah. Masa pengerasan yang cepat dan kebolehkerjaan yang rendah mendorong kepada kesukaran semasa pengangkutan, pembancuhan, pemadatan dan menyebabkan kemusnahan struktur. Ini disebabkan oleh strukturnya yang berpori dan berlubang. Dalam campuran konkrit Portland konvensional, bahan tambah berasaskan fosfat telah dikaji secara meluas untuk menghalang masa penetapan simen, namun ia jarang dikaji dalam sistem geopolimer. Walaupun lanjutan pada masa penetapan pes geopolimer, penggunaan berlebihan campuran ini mengakibatkan pembentukan peroi yang akan merosakkan integriti geopolimer. Oleh itu, kajian ini dilakukan untuk mengkaji kesan bahan sumber sekunder yakni abu kumbahan kilang kertas (PMSA) dan pelbagai suhu pengawetan (30 ℃, 60 ℃ dan 90 ℃), sifat-sifat mortar geopolimer yang mengandungi dipotassium hidrogen fosfat (K_2HPO_4) terutamanya pada peranannya untuk meminimumkan pembentukan peroi dalam spesimen geopolimer. Satu siri ujian dijalankan untuk menentukan sifat rheologi, mekanikal dan mikrostruktur geopolimer yang mengandungi K_2HPO_4 pada pelbagai peratusan 0.1%, 0.2%, 0.3%, 0.4% dan 0.5% (berat abu terbang) dan PMSA. Untuk menentukan sifat rheologi, penetapan masa, kebolehkerjaan, kelikatan dan ujian ketegangan permukaan dilakukan manakala tahap tindak balas, kekuatan mampatan dan ujian keliangan dilakukan untuk mengetahui sifat mekanikal. Pelepasan logam alkali ditentukan oleh Inductively Coupled Plasma Mass Spectrometry (ICPMS) dan ujian pH. Sementara itu, ujian Fourier Transform Infrared Spectroscopy (FTIR) dijalankan untuk mengenal pasti ikatan kimia dalam molekul dan analisis Thermogravimetric (TGA) menentukan produk geopolimerisasi. Sementara itu, Ujian Mikroskopi Penyebaran Tenaga (EDX) dan Pengimbasan Mikroskopik Elektronik (SEM) dijalankan untuk mengetahui komposisi mikro dan unsur-unsur yang menyumbang kepada peningkatan kekuatan geopolimer. Berdasarkan keputusan, menunjukkan bahawa kemasukan peratus optimum PMSA dalam geopolimer adalah 5%. Gabungan 0.5% K_2HPO_4 dengan 5% PMSA telah memanjangkan masa pengerasan, kekuatan mampatan yang tinggi, mengurangkan keliangan dan menghasilkan struktur mikro yang padat. Suhu pengerasan yang tinggi telah mempercepatkan proses geopolimerisasi dengan meningkatkan pembentukan gel geopolimer dalam rangka kerja geopolimer dan menunjukkan kesan positif terhadap pengurangan pembentukan peroi di permukaan geopolimer dan nilai pH pelepasan logam alkali berkurangan. Tambahan CaO di dalam geopolimer telah menghasilkan produk sekunder iaitu gel CSH. Ini kerana Ca-O lebih mudah dipecahkan ikatan daripada Al-O dan Si-O. Ca^{2+} yang belum diikat bercantum dengan Si untuk membentuk gel CSH. Berdasarkan statistik analisis Si dan Ca berpotensi penting manakala Na, Al, Fe dan Mg mungkin penting terhadap struktur geopolimer. Setiap alkali kation dan anion mempunyai kesan tersendiri pada setiap peringkat proses geopolimerisasi dalam penghasilan struktur akhir dengan mengawal gel geopolimer dan pertumbuhan kristal. Ini menyumbang kepada pembentukan struktur alumina-silikat. Oleh itu, penggunaan sisa industri (abu kumbahan kilang kertas) digabungkan dengan pengawetan suhu tinggi akan membawa kepada bahan binaan hijau yang mampan yang akan membantu mengekalkan kualiti alam sekitar dan sumber semula jadi.

ABSTRACT

The use of aluminosilicate source with high amount of CaO has been widely used in geopolymer due to its high compressive strength at early age. The presence of Ca^{2+} is able to accelerate the geopolymerization process, hence produces large amount of geopolymer matrices. Nevertheless, excessive amount of Ca^{2+} in geopolymer also contribute to the rapid setting time and low workability. Short setting time and low workability will obstruct the process of transporting, casting and compacting, which might cause the structural disintegration due to its porous and honeycomb structure. In conventional Portland cement mixture, phosphate based admixtures have been extensively studied to retard the setting time of cement paste, yet it is scarcely studied for the use in geopolymer system. Despite of the extension on the setting time of geopolymer paste, the excessive use of this admixture may result in the formation of efflorescence that would damage the integrity of hardened geopolymer. Therefore this study was proposed to investigate the effect of secondary source material i.e. paper mill sludge ash (PMSA) and various curing temperature (30°C, 60°C and 90°C), on the properties of geopolymer mortar containing dipotassium hydrogen phosphate (K_2HPO_4) particularly on its role to minimize the formation of efflorescence in hardened geopolymer specimen. A series of tests were conducted to determine the rheological, mechanical and microstructural properties of geopolymer containing K_2HPO_4 at various percentages of 0.1%, 0.2%, 0.3%, 0.4% and 0.5% (by weight of fly ash) and PMSA. To determine the rheological properties, setting time, workability, viscosity and surface tension test were conducted while degree of reaction, compressive strength and porosity test were done to determine the mechanical properties. The leaching of alkali metal was determined using Inductively Coupled Plasma Mass Spectrometry (ICPMS) and pH test. Meanwhile, Fourier Transform Infrared Spectroscopy (FTIR) testing was conducted to identify chemical bonds and Thermogravimetric analysis (TGA) was done to determine geopolymerization products. Energy Dispersion X-Ray (EDX) and Scanning Electron Microscopy (SEM) test were conducted to investigate the microstructure and elemental composition that contributes to the strength performance of fly ash based geopolymer. Based on the experimental results, it shows that the optimum percentages inclusion of PMSA in geopolymer was 5%. The combination of 0.5% K_2HPO_4 with 5% PMSA has significantly prolonged the setting time, higher in compressive strength, reduce the porosity and produce denser microstructure. Higher curing temperature has accelerated the geopolymerization process and enhances the formation of geopolymer gel in geopolymer framework. In addition, it also shows the positive effect on reducing the formation of efflorescence at the surface of hardened geopolymer and lowers the pH value of leaching. Addition of CaO in geopolymer matrix has formed secondary product which is CSH gel as Ca-O bond is more susceptible to break the bonds than Al-O and Si-O. Free Ca^{2+} would bond with Si to form CSH gel. Based on the statistical analysis Si and Ca had "potentially important" effect while Na, Al, Fe and Mg had "possibly important" effect towards the structural disintegration of geopolymer. Each type of alkali cation and anion had its own effects on every stage of geopolymerization process. They played the vital role in the production of final structure by controlling the geopolymer gel and crystal growth hence contribute to the structural development by forming alumino-silicate structures. Therefore, the use of industrial waste (paper mill sludge ash) combined with elevated temperature curing would lead to the sustainable green construction materials that would help to preserve environment quality and natural resources.

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