

THE HYBRIDIZATION OF FLY ASH AND GROUND GRANULATED BLAST-FURNACE SLAG GEOPOLYMER MATERIALS AS CEMENT REPLACEMENT

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ABSTRACT

Geopolymers is essentially amorphous polymers that's belonging to the same aluminasilicate family as zeolites but have a significant difference from them. Their properties are also different: they possess high strength, thermal stability, high surface smoothness and precision, and high surface hardness. One of the main objectives in achieving sustainable construction materials is to reduce the over use of virgin materials used to produce cement, coarse and fine aggregates. The utilization of industrial by-products such as fly ash (FA), silica fume, ground granulated blast furnace slag (GGBS), and rice husk ash, as the cement replacement or as the additional cementitious materials has had a constructive effect in minimizing greenhouse gas emissions. The study prescribed herewith proposes the ash hybridization approach between Class F pulverised fuel ash (PFA) and ground granulated blast furnace slag (GGBS) as cement replacement to fabricate a geopolymer mortar with adequate mechanical and durability performance for industrial application. A total of 53 different mix designs of geopolymer mortar were fabricated with PFA-GGBS hybridization ratio of 0:0-80, 10:0-80, 20:0-80, 30:0-80, 40:0-80, 50:0-80, 60:0-80, 70:0-80 and 80:0-80 as cement replacement with constant water/binder ratio of 0.25. This geopolymer mortar was fabricated by using 50 x 50 x 50 mm and 40 x 40 x 160 mm steel mould for assessment of mechanical and durability performances. The mechanical performance of the PFA-GGBS mortar block was assessed in terms of compressive strength and flexural strength after water curing for 28 days. The durability assessments performed include tests on water absorption and total porosity. Moreover, the hybridization of PFA and GGBS at mass ratio of 10:30 and 10:40 can be suitably implemented for the fabrication of mortar block with adequate mechanical strength, stiffness and durability performance to be classified as load bearing masonry unit for building construction.

Keywords: hybridization, PFA, GGBS, mechanical performance, durability assessments.

1. Introduction

The high demand for concrete using Ordinary Portland Cement (OPC) has resulted in high volume of CO₂ emission, and lead to eco- logical imbalance due to continuous depletion of natural resources. The reality of air pollution through carbon dioxide (CO₂) emission into the atmosphere from the production of cement is well known. A major challenge faced in the construction industry is the heavy reliance on the use of ordinary Portland cement as a primary binder for concrete, blockwork and bricks production. The cement manufacturing sector contributes to 7% of the global anthropogenic carbon dioxide emission (Malhotra, 2002). The significant carbon dioxide emission from cement production is contributed mainly by the energy intensive process to convert native limestone into reactive cementitious phases. In addition, a significant amount of carbon dioxide is being produced from the decomposition of limestone during the calcination process of cement production. Hence, the production of a tonne of cement produces 222 kg of carbon dioxide gases (Worrell, Price, Martin, Hendriks, & Meida, 2001).

In the realization of the adverse environmental effect due to the use of Portland cement, the cement and concrete manufacturing sector had initiated a number of approaches to minimize carbon emission such as capture and storage of CO₂ emission and partial replacement of clinker with supplementary binder material and limestone powder. Since early 1970s numerous studies has been performed to develop a new class of binder material (popularly known as Since early 1970s numerous studies has been performed to develop a new class of binder material (popularly known as Geopolymer) which can be used as a complete replacement of Portland cement as the primary binder in concrete production (Juenger, Winnefeld, Provis, & Ideker, 2011).

Geopolymer or Alkali activated binder is collectively viewed as an efficient approach to reduce CO₂ emission in concrete manufacturing sector. Geopolymer is an inorganic mineral binder produced from the dissolution and polycondensation of aluminasilicate rich finely divided ash material in the presence of high alkalinity pore solution (Davidovits, 2015). Geopolymers

can be classified into two major groups which is pure inorganic geopolymers and organic containing geopolymers, synthetic analogues of naturally occurring macromolecules (Kim, Lai, Chilingar, & Yen, 2006). Nowadays, geopolymers are usually produced by alkali activation of aluminasilicate rich industrial and agricultural waste ashes namely coal fly ash (Chindaprasirt & Chalee, 2014; Hanjitsuwan et al., 2014), ground granulated blast furnace slag (Puligilla & Mondal, 2013)(Islam, Alengaram, Jumaat, & Bashar, 2014), palm oil fuel ash (Ranjbar, Mehrali, Alengaram, Metselaar, & Jumaat, 2014) and rice husk ash (He, Jie, Zhang, Yu, & Zhang, 2013). In order to achieve an environmentally friendly concrete and mortar, several studies are on-going on the utilization of waste materials to produce green concrete. The significant research in geopolymer includes thermal behaviour (Bakharev, 2006), durability in sodium and magnesium sulphate solutions (Bakharev, 2005a), and resistance to acid attack (Bakharev, 2005b) of geopolymeric materials.

Geopolymer is an inorganic alumina hydroxide polymer synthesized from predominantly silicon and aluminium materials of geological origin and industrial by-product material such as FA. Fly ash is an industrial by-product generated during the combustion of coal for energy production. Currently the annual production of coal ash worldwide is estimated around 600 million tons, with fly ash constituting about 500 million tons at 75–80% of the total ash produced (Ahmaruzzaman, 2010). FA is a fine powder of mainly spherical glass particles having pozzolanic properties which shall consist essentially of reactive silicon dioxide (SiO₂) and aluminium oxide (Al₂O₃), the remainder being iron (III) oxide (Fe₂O₃) and other oxides. It can be obtained by electrostatic or mechanical precipitation of dust-like particles from the flue gases of power station furnaces fired with pulverized bituminous or other hard coal (BSI, 2008). The government of Malaysia decided that by 2010 the share of coal in the fuel mix for electricity generation would rise to about 40% (Kupaei, Alengaram, Jumaat, & Nikraz, 2013). The increased use of coal burning in thermal power plants has increased the production of FA to an estimated 3 million tons per annum. The abundance of FA in Malaysia could pave way for the development of geopolymer concrete.

The other waste material that is abundant in Malaysia is GGBS, a by-product of the production of iron in a blast furnace and it is composed chiefly of calcium and magnesium silicates and aluminosilicates. The history of slags used for cement is not new. A quite number of investigations have been performed on the use of GGBS as a cementitious material in cement production since 1939 and to evaluate its performance (Li, Sun, & Li, 2010). GGBS can be used for producing high quality self-compacting concrete (100 MPa) (Dinakar, Sethy, & Sahoo, 2013). In this study, the hybridization of fly ash and ground granulated blast-furnace slag geopolymer materials as cement replacement were studied.

2. Materials And Methods

2.1. Material

2.1.1. Ordinary Portland Cement (Opc)

ASTM Type I Portland cement (PC) with median particle size of 3.9 μm , specific surface area of 1.0432 m^2/g and specific gravity of 3.02 was used in this study. Both the physical and chemical properties of cement used comply with specification in ASTM Standard C150. The chemical composition of PC used is presented in Table 1.

2.1.2 PULVERISED FUEL ASH (PFA)

Pulverised fuel ash (PFA) used in this study was collected from the precipitator unit of local coal fuelled power plant. Based on Blaine fineness analysis, the result show that PFA used in this study had a specific surface area of 3.244 m^2/g . The specific gravity of PFA was determined to be 2.8. The chemical composition of PFA used is summarized in Table 1.

2.1.3 GROUND GRANULATED BLAST-FURNACE SLAG (GGBS)

Ground granulated blast-furnace slag (GGBS) is a by-product from the blast-furnaces used to make iron. Mixtures of iron-ore, coke and limestone are fed into blast-furnaces which operates at a temperature of about 1500°C. Two products: molten iron, and molten slag are produced when iron-ore, coke and limestone melt in the blast furnace, and the molten slag is lighter and floats on the top of the molten iron. The molten slag comprises mostly silicates and alumina. The specific surface area of 4.65 m^2/g and specific gravity of 2.86 was used in this study. Typical chemical composition of GGBS as shown in Table 1.

Table 1. Chemical compositions of Portland cement, PFA and GGBS.

Chemical Compound	% by total mass		
	Portland Cement	PFA	GGBS
MgO	1.50	5.94	5.01
Al ₂ O ₃	3.60	17.61	12.59
SiO ₂	22.40	43.22	32.62
P ₂ O ₅	0.06	0.23	0.01
SO ₃	3.10	-	-
Cl	-	-	-
K ₂ O	0.34	1.31	0.32
CaO	65.60	11.28	37.87
TiO ₂	0.17	0.88	0.50

MnO	0.03	0.14	0.25
Fe ₂ O ₃	2.90	13.73	2.00
ZnO	trace*	-	-
SrO	0.04	-	-
PbO	0.01	-	-
CuO	-	-	-
Rb ₂ O	trace*	-	-
C	-	1.80	-
Na ₂ O	-	0.43	0.25
C ₃ S	59.58	-	-
C ₂ S	19.60	-	-
C ₃ A	4.64	-	-
C ₄ AF	8.82	-	-
Loss on ignition (%)	2.53	1.80	1.50

*Very small amount – not presented

2.1.4. Aggregates

Fine aggregates used were locally sourced quartzitic natural river sand in uncrushed form with a specific gravity of 2.65 and a maximum aggregate size of 5 mm. Fine aggregates were dried to saturated surface dry conditions for use as a constituent material in mortar mixes. Fine aggregates were graded in accordance to BS 812: Part 102 and the grading of fine aggregates used were in compliance with overall grading limits of BS 882. The fineness modulus of the fine aggregates was determined to be 3.26.

2.1.5 Superplasticizer And Mixing Water

The high range water reduction agent used in the study was a polycarboxylic ether based superplasticizer with a relative density of 1.10 at 25 °C. Mixing water was attained from the potable water supply network.

2.2. Methods

2.2.1. Mixture Proportioning And Mixing

The binder: sand were maintained constant at 1:0.35 for all mortar mixes produced. The OPC was partially replaced using PFA and GGBS at substitution levels of 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70% and 80% by total binder weight. These correspond to PFA:GGBS hybridization ratio of 0:0-80, 10:0-80, 20:0-80, 30:0-80, 40:0-80, 50:0-80, 60:0-80, 70:0-80 and 80:0-80, respectively. A corresponding set of hydrated ash paste was produced using the aforementioned ash hybridization ratio while maintaining the water/binder ratio constant at 0.25 for the mineralogical phase change study. The various mix proportions of PFA-GGBS geopolymer mortar based on ratio of material by total binder weight are summarized in Table 2.

Table 2: The mix proportions of PFA-GGBS geopolymer.

Mix designation	Portland cement	PFA	GGBS	Sand (s/b)	Water (w/b)	SP* (%)
Control	1.00	0.00	0.00	0.35	0.25	1.0
PFA 0 %	0.90	0.00	0.10	0.35	0.25	1.0
GGBS 0-80 %	0.80	0.00	0.20	0.35	0.25	1.0
	0.70	0.00	0.30	0.35	0.25	1.0
	0.60	0.00	0.40	0.35	0.25	1.0
	0.50	0.00	0.50	0.35	0.25	1.5
	0.40	0.00	0.60	0.35	0.25	2.0
	0.30	0.00	0.70	0.35	0.25	3.0
	0.20	0.00	0.80	0.35	0.25	4.0
PFA 10 %	0.90	0.10	0.00	0.35	0.25	1.0
GGBS 0-80 %	0.80	0.10	0.10	0.35	0.25	1.0
	0.70	0.10	0.20	0.35	0.25	1
	0.60	0.10	0.30	0.35	0.25	1
	0.50	0.10	0.40	0.35	0.25	1.5
	0.40	0.10	0.50	0.35	0.25	1.5
	0.30	0.10	0.60	0.35	0.25	3
	0.20	0.10	0.70	0.35	0.25	4

	18	0.10	0.10	0.80	0.35	0.25	5.0
PFA 20 %	19	0.80	0.20	0.00	0.35	0.25	1.0
GGBS 0-80 %	20	0.70	0.20	0.10	0.35	0.25	1.0
	21	0.60	0.20	0.20	0.35	0.25	1.0
	22	0.50	0.20	0.30	0.35	0.25	1.0
	23	0.40	0.20	0.40	0.35	0.25	1.0
	24	0.30	0.20	0.50	0.35	0.25	2.0
	25	0.20	0.20	0.60	0.35	0.25	2.5
	26	0.10	0.20	0.70	0.35	0.25	3.0
PFA 30 %	27	0.70	0.30	0.00	0.35	0.25	1.0
GGBS 0-80 %	28	0.60	0.30	0.10	0.35	0.25	1.0
	29	0.50	0.30	0.20	0.35	0.25	1.0
	30	0.40	0.30	0.30	0.35	0.25	1.0
	31	0.30	0.30	0.40	0.35	0.25	1.0
	32	0.20	0.30	0.50	0.35	0.25	1.5
	33	0.10	0.30	0.60	0.35	0.25	2.0
PFA 40 %	34	0.60	0.40	0.00	0.35	0.25	0.0
GGBS 0-80 %	35	0.50	0.40	0.10	0.35	0.25	0.0
	36	0.40	0.40	0.20	0.35	0.25	0.5
	37	0.30	0.40	0.30	0.35	0.25	1.0
	38	0.20	0.40	0.40	0.35	0.25	1.0
	39	0.10	0.40	0.50	0.35	0.25	1.5
PFA 50 %	40	0.50	0.50	0.00	0.35	0.25	0.0
GGBS 0-80 %	41	0.40	0.50	0.10	0.35	0.25	0.0
	42	0.30	0.50	0.20	0.35	0.25	0.0
	43	0.20	0.50	0.30	0.35	0.25	1.0
	44	0.10	0.50	0.40	0.35	0.25	1.0
PFA 60 %	45	0.40	0.60	0.00	0.35	0.25	0.0
GGBS 0-80 %	46	0.30	0.60	0.10	0.35	0.25	0.0
	47	0.20	0.60	0.20	0.35	0.25	0.0
	48	0.10	0.60	0.30	0.35	0.25	0.5
PFA 70 %	49	0.30	0.70	0.00	0.35	0.25	0.0
GGBS 0-80 %	50	0.20	0.70	0.10	0.35	0.25	0.0
	51	0.10	0.70	0.20	0.35	0.25	0.5
PFA 80 %	52	0.20	0.80	0.00	0.35	0.25	0.0
GGBS 0-80 %	53	0.10	0.80	0.10	0.35	0.25	0.0

* superplasticizer for the mortar workability and target slump.

2.2.2. Mixing, Forming And Curing

From each batch of mortar produced, a total of 3 units of 50 x 50 x 50mm mortar cubes and 3 units of 40 x 40 x 160mm mortar prisms were moulded. The mortar specimens were used for compressive strength and flexure strength tests. During the mixing of mortar mixes containing OPC, PFA and GGBS (binder materials) were initially dry mixed at a low mixing speed for 3 min prior to the addition of other constituent materials. Further mixing sequences and durations were performed in accordance to standard procedures prescribed in ASTM Standard C305 (ASTM, 2011). The superplasticizer will be added until reach the slump is needed. Upon completion of the mixing, the slump test will be determined by using flow table test. The target slump for all sample is about 200 mm. After that, the fresh mortar mix was then poured into the mould in three layers. For proper compaction, each layer of the mix was vibrated for 10 s on a vibrating table. Moulded specimens were then cured in mould for 24 h prior, removed from their moulds, and immersed in the curing tank till the testing ages of 28 days.

2.2.3. Mechanical And Durability Analysis

The compressive and flexural strength of PFA-GGBS geopolymer mortar blocks were determined in accordance with the procedures prescribed in ASTM Standard C140 and ASTM C348 as shown in Figure 1, respectively. The reported flexural and compressive strengths at given ages of mortar are the average of the three numbers of specimens tested. The water absorption test is performed on the three representative from broken prism specimens in accordance to procedures prescribed in the ASTM C 140. The vacuum intrusion porosimetry was performed to determine the total porosity of the mortar blocks produced. Vacuum saturation method described by RILEM (TC, 1994) was used for the measurement of porosity of all mortar specimens. The bulk density also be measured before the cube and prism mortar has been tested.

Figure 1: Mechanical testing of sample using Universal Testing Machine.



(a) Compressive strength testing



(b) Flexural strength testing



(c) Vacuum intrusion porosimetry testing



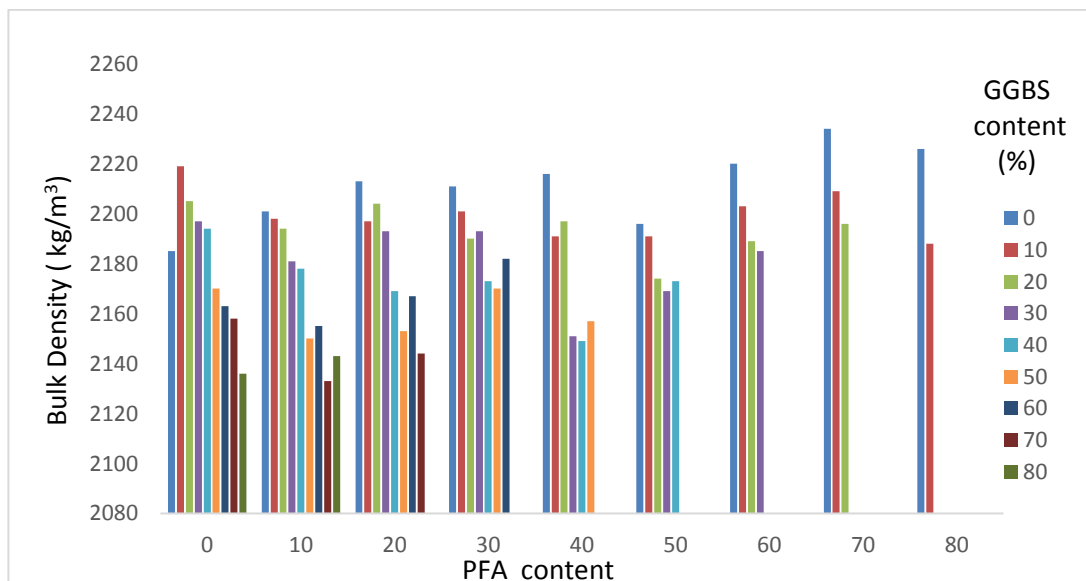
(d) Water absorption

3. Result And Discussion

3.1. Bulk Density

Based on Fig. 2, the overall average of bulk density for all specimens between 2133 to 2234 kg/m³. The highest bulk density is 2234 kg/m³ which content 70% of PFA without GGBS content. Therefore, the lowest bulk density is hybridization between 10% of PFA content and 70% of GGBS content with 2133 kg/m³. However, the overall bulk density for others is good which is more than 2000 kg/m³ and still can be categorized as normal weight grout and concrete composite.

Figure 2: Bulk density at the age of 28 days.

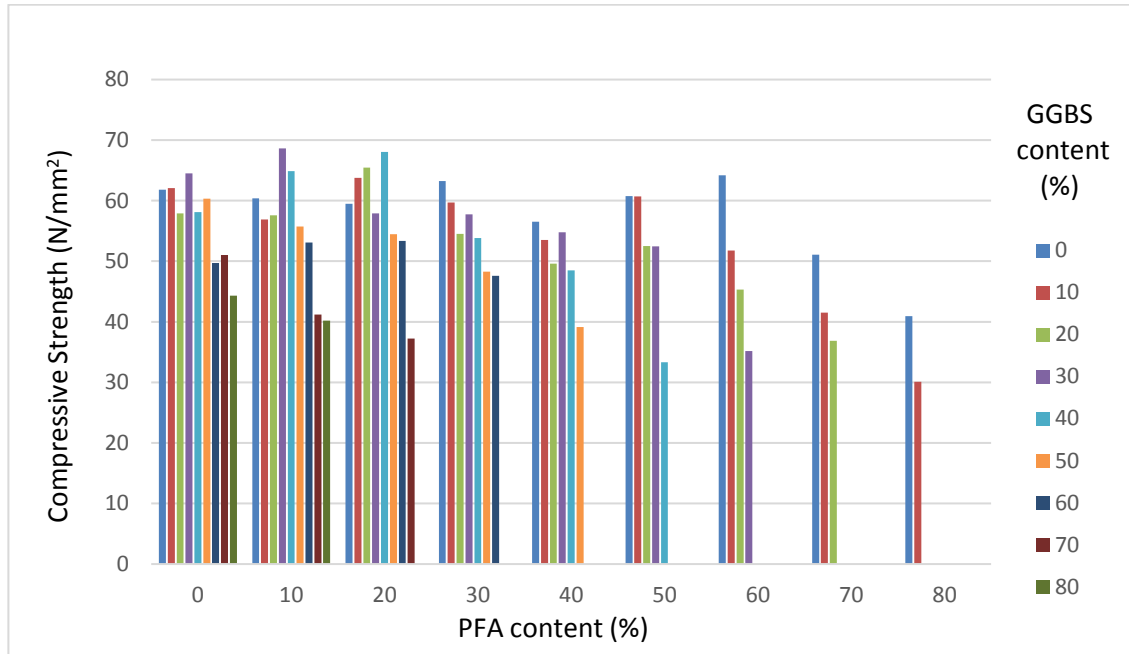


3.2. Compressive Strength

In order to establish the quality of geopolymer mortar block produced from the various hybridization ratio, the ultimate compressive strength of the geopolymer mortar blocks was examined. The compressive strength of PFA-GGBS geopolymer mortar with water to binder ratio of 0.25 at the age of 28 days are shown in Fig. 3. With reference to the compressive strength

results obtained, the rate of compressive strength is from 30.1 MPa to 68.6 MPa for the hybridization of PFA-GGBS mortar. For hybridization of PFA and GGBS as cement replacement, there are five sample that highest strength compared to control when PFA:GGBS is 10:30, 10:40, 20:10, 20:20 and 20:40 with percentages of 11%, 5%, 3%, 5.8% and 10.2% compared to control mortar. Figure 3 also show the highest compressive strength for PFA and GGBS mortar without hybridization compared to control mortar. At PFA is zero percentage, the GGBS mortar containing 10% and 30% is 0.5% and 1.7% higher compare to control mortar. On the other hand, at GGBS is zero percentage the PFA mortar containing 30% and 60% is 2.3% and 3.9% higher compare to control mortar. On the other hand, the result can be observed that the increasing combination ratio between PFA and GGBS is decrease the compressive strength of specimens compare to the control mortar.

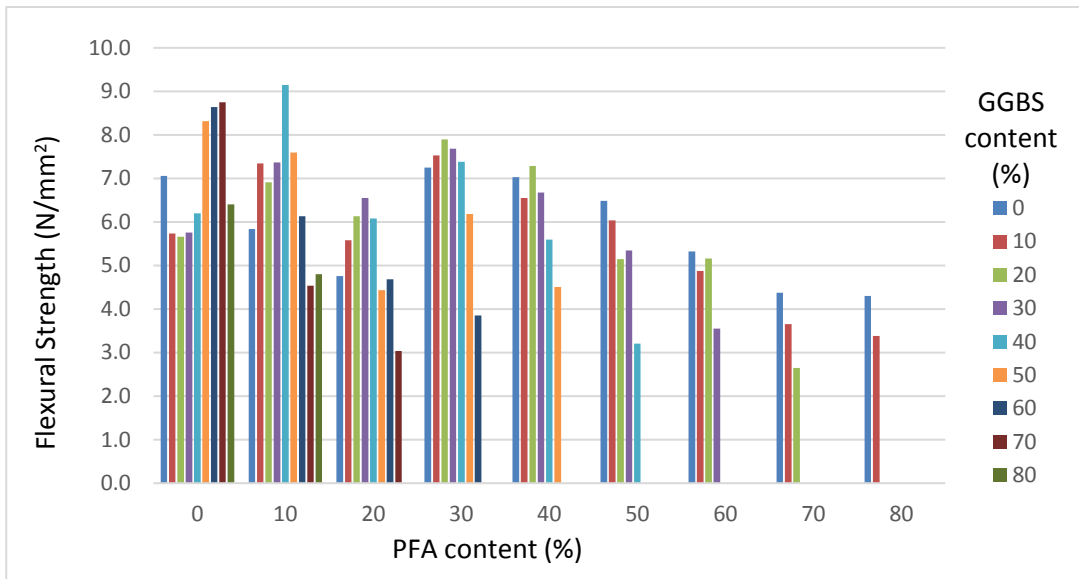
Figure 3: Compressive strength of mortar mixes of various PFA-GGBS content at 28 days



3.3 Flexural Strength

The flexural strength of PFA-GGBS geopolymer mortar as cement replacement with water to binder ratio of 0.25 are shown in Fig. 4. The rate of flexural strength is from 2.6 MPa to 9.1 MPa. With reference to the flexural strength results, for PFA contents (20%, 40%, 50%, 60%, 70% and 80%) and GGBS contents (60%, 70% and 80%) almost all is lower compare that to control mortar. At PFA content is zero percentage, there are three mix design has highest flexural strength when GGBS contents is 50%, 60% and 70% with the percentage of 16.3, 21.1 and 23.9 highest compare to control mortar. When GGBS is zero percent, 30% of PFA content has higher flexural strength with the percentage different is 2.82% as compared to the control mortar. For the hybridization of PFA and GGBS, there are several mix design that have higher strength compared to the control mortar. The hybrid contents of PFA: GGBS is 10:10, 10:30, 10:40, 10:50, 30:10, 30:20, 30:30, 30:40 and 40:20 with the different of percentage from 2.82 to 28, respectively. The highest flexural strength was exhibited by mortar mix with hybridization of PFA: GGBS of 10%: 40% which exhibited flexural strength which is 28 % higher as compared to the control mortar.

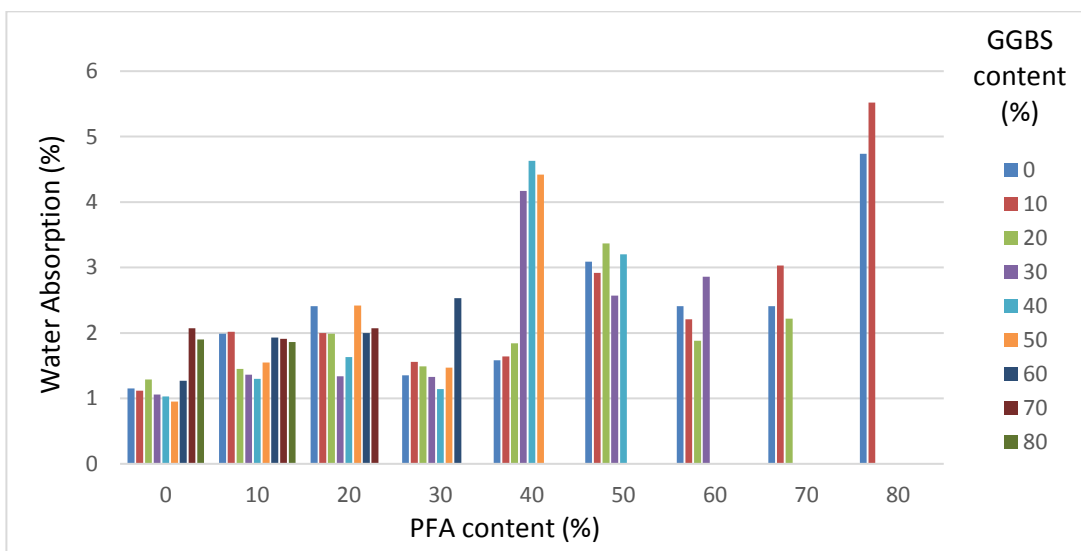
Figure 4: Flexural strength of mortar mixes of various PFA-GGBS content at 28 days



3.4 Water Absorption

The results of water absorption of geopolymer mortars with various content of PFA and GGBS are presented in Fig. 5. From the water absorption results, it was observed that mixes with zero percentage of PFA content and various GGBS contents (10%, 30%, 40% and 50%) by total weight of binder exhibited lower degree of water absorption as compared to mortar containing 100% OPC (control) by total weight of binder. At the age of 28 days, the reduction in the value of water absorption of geopolymer mortar with zero percentage of PFA content and various GGBS contents (10%, 30%, 40% and 50%) as compared to the control mortar were 2.6%, 7.8%, 10.4% and 17.4%, respectively. The PFA contents is more than 40% show that the degree of water absorption higher compare to the PFA content is less than 40%. The highest percentage of the degree of water absorption when PFA content is 80% and GGBS content is 10% which is 380% as compared to the control mortar. This can be observed the porous (void) inside the specimens is higher compare to other specimens that can be related with reducing the strength of the mortar in Fig 3 and Fig. 4.

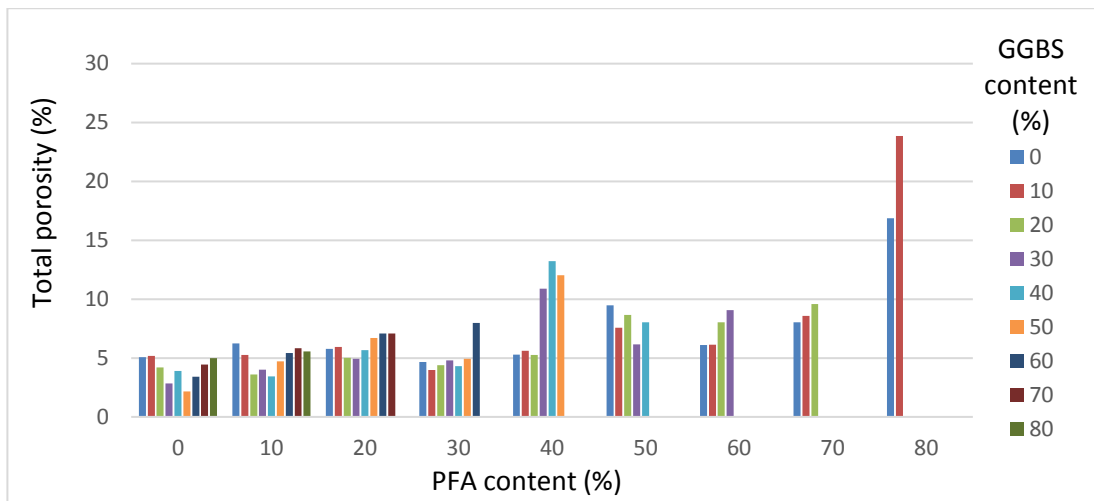
Figure 5: Water absorption of mortar mixes of various PFA-GGBS content at 28 days.



3.5 Total Porosity

The results of total porosity of hardened mortars with various content of PFA and GGBS for curing durations at 28 days are presented in Fig. 6. Based on the total porosity results obtained, it was observed that mixes with PFA:GGBS content between 0:20-80%, 10:20-50%, 20:20-30% and 30: 0-50% by total weight of binder exhibited lower total porosity as compared to the control mortar by total weight of binder. The reduction in the value of total porosity of geopolymer mortar with PFA: GGBS content between 0:20-80%, 10:20-50%, 20:20-30% and 30: 0-50% compared to the control mortar were 9.1%, 13.1% and 16.3%, respectively. It's can be related with the void inside the specimens is higher compare to the control mortar. The observation shown by increasing of PFA and GGBS with high percent will increase the total porosity that will decrease the strength of the specimens.

Figure 6: Total porosity of mortar mixes of various PFA-GGBS content at 28 days.



4.0. Conclusions

The hybridization of fly ash and ground granulated blast-furnace slag geopolymer materials as cement replacement have been successful in this study. The hybridization of fly ash and ground granulated blast-furnace slag with the percentages from 0% to 80% show that the result of hybridization between of PFA and GGBS at mass ratio of 10:30 and 10:40 as cement replacement has higher performances in mechanical properties. The compressive strength for this both specimens is 68.6 and 64.9 N/mm² and flexural strength is 7.4 and 9.1 N/mm². The durability performance for both specimens also show the good result which is lower percentages of water absorption and porosity because of the void (porous) inside the specimens is very low. It's can be suitably implemented for the fabrication of mortar block with adequate mechanical strength, stiffness and durability performance to be classified as load bearing masonry unit for building construction.

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