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MOHD MUSTAFA AL BAKRI ABDULLAH^{1,2*}, IKMAL HAKEM A AZIZ¹,
WARID WAZIEN AHMAD ZAILANI³, SHAYFULL ZAMREE ABD RAHIM¹,
HEAH CHENG YONG^{1,2}, ANDREI VICTOR SANDU⁴, LOKE SIU PENG¹

SILICA BONDING REACTION ON FLY ASH BASED GEOPOLYMER REPAIR MATERIAL SYSTEM WITH INCORPORATION OF VARIOUS CONCRETE SUBSTRATES

This paper presents an experimental investigation on the mechanical properties and microstructure of geopolymer repair materials mixed using fly ash (FA) and concrete substrates. An optimal combination of FA and concrete substrate was determined using the compressive test of geopolymer mortar mixed with various concrete substrate classes. It was found that the contribution of (C35/45) concrete substrates with the FA geopolymer mortar increases the 28-day bonding strength by 25.74 MPa. The microstructure analysis of the samples using scanning electron microscopy showed the denser structure owing to the availability of high calcium and iron elements distribution. These metal cations (Ca^{2+} and Fe^{3+}) are available at OPC concrete substrate as a result from the hydration process reacted with alumina-silica sources of FA and formed calcium aluminate silicate hydrate (C-A-S-H) gels and Fe-bonding linkages.

Keyword: Fly ash geopolymer; Repair material; Concrete substrate; Interfacial zone transition

1. Introduction

Traditionally, Ordinary Portland cement (OPC) has been used as a binder material in concrete. Deterioration of OPC concrete can occur from or near the surface which caused by the exposure conditions such as marine environments as well as factors with shrinkage, excessive loads, settlement of support, and also insufficient concrete cover [1]. Those factors will contribute to the cracking, spalling, seepage, and delamination. The deteriorated concrete structure should be repaired as the deterioration phenomenon will affect the behaviour of the concrete materials in the exposure conditions [2,3]. Therefore, deteriorated OPC concrete structure are repaired with repaired material to utilize for longer service-life and to assure the safety of the associated components [4]. The durability of the damaged concrete structure should be extended with high performance repair materials. Suitable material is then selected for repairing of damaged concrete surface or rehabilitating works which requires an understanding of bonding strength between the concrete substrate and repair materials. Geopolymer is an inorganic based concrete repair

material which introduced as an alternative binder for rehabilitation or surface treatment of concrete.

Geopolymer is produced by condense alumina-silicates in alkalized environment with the mixing of alkaline solution and activator solution. Geopolymer material is produced with industrial by-product, earth's crust and power plant waste such as slag, kaolin and fly ash [5]. The durability of geopolymer as repair material is based on the bonding strength at the interfacial transition zone (ITZ) between concrete substrate and geopolymer composites [6]. Repair material with strong bonding indicates strong linkage at ITZ bond is crucial in order to strengthen deteriorated concrete structure. Good, efficient and durable bonding strength is required for the effective and successful repair of deteriorated concrete [7].

This research aims to determine the optimum formulation of geopolymer for concrete repair and rehabilitation through the geopolymerization process via fly ash. It involved OPC concrete substrate class were carried out regarding compressive strength and durability of the geopolymer especially at the interfacial transition zone. In this regard, this current research aims at

¹ UNIVERSITI MALAYSIA PERLIS (UNIMAP), CENTRE OF EXCELLENCE GEOPOLYMER AND GREEN TECHNOLOGY (CEGEOGTECH), PERLIS, MALAYSIA

² UNIVERSITI MALAYSIA PERLIS (UNIMAP), FACULTY OF CHEMICAL ENGINEERING TECHNOLOGY, PERLIS, MALAYSIA

³ UNIVERSITI TEKNOLOGI MARA (UITM), FACULTY OF CIVIL ENGINEERING, SHAH ALAM, SELANGOR, MALAYSIA

⁴ "GHEORGHE ASACHI" TECHNICAL UNIVERSITY OF IASI, FACULTY OF MATERIALS SCIENCE AND ENGINEERING, ROMANIA

* Corresponding author: mustafa_albakri@unimap.edu.my



studying the concrete behaviour based on the strength and assessed the bonding mechanism of fly ash based geopolymer for use as a repair binder.

2. Material and method

The geopolymer paste was made from fly ash Class F (FA) from Manjung power plant in Perak, Malaysia. Ordinary Portland cement (OPC) is required for the production of concrete substrate as binder. The mixture of sodium hydroxide (NaOH) and sodium silicate solution (30.1% SiO₂, 9.4% Na₂O, and 60.5% H₂O) was used as the alkaline activator solution. The NaOH flake (99% in purity, purchased from Formosa Plastic Corporation, Taiwan) were dissolved in distilled water to produce sodium hydroxide solution. Three class of OPC are produced (C25/30, C30/37 and C35/45). The mix of cement, water and aggregates produced the concrete. The chemical composition of FA and OPC are tabulated in TABLE 1.

TABLE 1
 Chemical composition of FA and OPC (by weight)

Materials	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	LOI
FA	38.40	14.50	19.57	18.40	3.60	1.71	2.83	1.56	1.05
OPC	22.02	6.19	2.65	59.99	2.53	0.40	0.10	2.84	0.90

The mix proportions of OPC substrate are shown in TABLE 2. The OPC substrate was prepared by mixing the OPC cement, coarse aggregate, fine aggregates and water. By referring to the Faury concrete mix design method, a C30/37 strength class of OPC concrete was designed [8]. The hardened OPC concrete substrate is used to attach with the geopolymer paste in order to evaluate the bonding strength. For the mixing of paste, NaOH and Na₂SiO₃ solutions were mixed and cooled down at room temperature a day prior to mixing. The steel prism mould was divided into two equal layers where half was filled with fresh geopolymer and the other half was filled by OPC concrete substrate. The samples were covered with vinyl sheet and were cured at ambient temperature. The mix proportions OPC/FA repair materials are shown in TABLE 3. The average of three samples for each testing was reported.

TABLE 2
 Mix proportions and strength of OPC concrete

Component	OPC (kg/m ³)	Water (kg/m ³)	Aggregate (kg/m ³)		Compressive Strength (MPa)
			Fine	Coarse	
C25/30	446	205	617	1147	25
C30/37	436	205	639	1135	30
C35/45	427	205	660	1123	35

TABLE 3

Mix proportions FA geopolymer paste

Sample	Fly ash	NaOH (kg/m ³)	Na ₂ SiO ₃ (kg/m ³)	Solid/liquid ratio
FA paste	833.3	119.1	297.6	2.1

3. Experimental test and characterization

3.1. Compressive strength test

The compressive strength was evaluated using Instron machine series 5569 Mechanical Tester with a loading capacity of 3000 kN using a loading rate of 0.5 MPa/s. The maximum load is recorded, and the strength was calculated by dividing the maximum load with the area of the face subjected to loading. The strength was recorded in N/mm² to nearest 0.1 N/mm² or MPa unit.

3.2. Bonding strength

The slant shear test of samples geopolymer and hardened OPC concrete substrate is used to evaluate the bonding strength as described in ASTM C882 with angle 30°. The specimen consists two parts into 50 mm × 50 mm × 125 mm prism mould as shown in Fig. 1. Half part of the samples was made up of geopolymer and the remaining half cast with OPC concrete substrate. This geopolymer/concrete substrate was used to investigate the strength and performance of the bond between repair materials and concrete substrate.

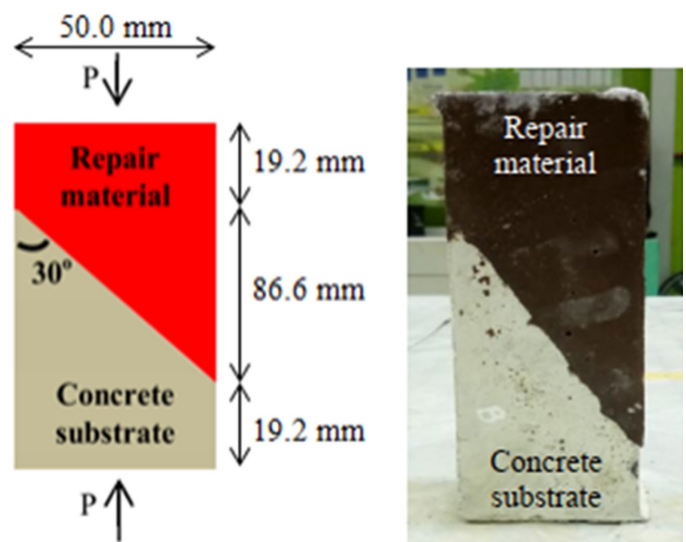


Fig. 1. Schematic diagram and experimental design of the repair material

3.3. Scanning electron microscopy (SEM)

The microstructure of the fly ash geopolymer/OPC concrete substrate were obtained using JSM-6460LA model Scanning

Electron Microscope (JEOL) utilizing the secondary electron detectors. The cross sectioned was taken from the cutting process of the samples. Then, all the specimens were coated with palladium by using Auto Fine Coater JEOL JFC 1600 model before the testing. At the same time, the surface elemental composition was taken by energy dispersive spectroscopy (EDS) using the same procedure.

4. Result and discussion

4.1. Strength and density measurement of OPC concrete substrate class

The compressive strength and density of various concrete substrate class are shown in Fig. 2. The strength and density of concrete substrate increased with higher concrete substrate class. The noticeable increase in density was due to the amount of voids and porosity within the system. Higher class of concrete substrate or denser concrete has fewer amounts of voids and porous structure, hence, the concrete structure is difficult to break [9].

Furthermore, the higher class of concrete substrate also lead to higher compressive strength as shows in Fig. 2. Higher compressive strength of concrete provides higher durability prevents for initial cracked and withstand higher load or external stress. The concrete substrate class of C35/45 obtained higher compressive strength which can withstand higher applied load with less crack appearance compared to C35/30 and C0/37.

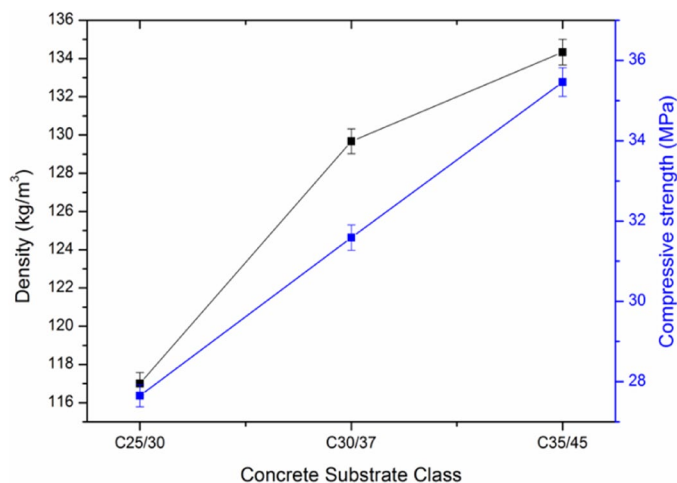


Fig. 2. Compressive strength and density of various substrate concrete class (a) C25/30, (b) C30/37 and C35/45

4.2. Bonding strength analysis of Fly Ash based geopolymer repair material/Concrete substrate composites

The value of bonding strength at interface transition zone (ITZ) between fly ash based geopolymer repair material and OPC substrate composite which obtained from compression test as illustrates in Fig. 3. The concrete substrate class (C25/30,

C30/37 and C35/45) was applied to study the bonding strength with the contribution of fly ash based geopolymers as a repair material at fixed 12 M of NaOH concentration. It was observed that the ITZ bonding strength increased with the higher class of OPC concrete substrate. The maximum ITZ bonding strength can be achieved at 25.74 MPa (FA/C35/45) while the lowest strength at 16.66 MPa (FA/C25/30). The maximum compressive strength of fly ash based geopolymer/concrete substrate composites (FA/C35/45) has been selected for microstructure analysis in further section.

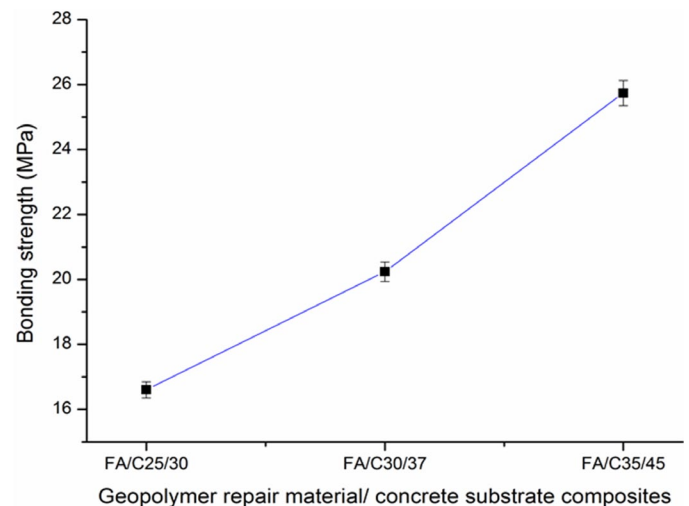


Fig. 3. Bond strength of fly ash based geopolymer/concrete substrate composites

4.3. Microstructure analysis of geopolymer/OPC concrete substrate composites

In order to obtain an overview regarding microstructure, as well as the potential chemical bonding formation at interfacial zone of the maximum bonding strength, the FA/C35/45 were further analysed via SEM-EDS mapping as depicted in Fig. 4 and Fig. 5. The SEM image revealed that the ettringite (yellow mark) or $\text{Ca}(\text{OH})_2$ is clearly observed in the transition zone, which corresponds to the substrate. Strength development of OPC involves the formation of ettringite and it is believed that the C-S-H component gives strength to the binder. Based on EDS data, at the OPC area, the Ca/Si averaged compositional ratios of 4.5 were measured which confirmed the high calcium content of substrate [10]. The concrete substrate surfaces contains large amount of calcium due to the existing of calcium hydroxide C-S-H and $(\text{Ca}(\text{OH})_2)$ as a result of the hydration process of OPC.

While the unreacted fly ash presented in the area of geopolymer repair materials (12 M NaOH). SEM and EDS analyses of the geopolymer repair materials getting insight into the role of calcium and iron in the geopolymerization process. The SEM result of the optimum formulation shows a dense microstructure that stated clearly indicates stronger bond to the concrete substrate.

EDS result reveals the presence of a large amount of calcium and iron, which can be partly attributed to the gel develop-

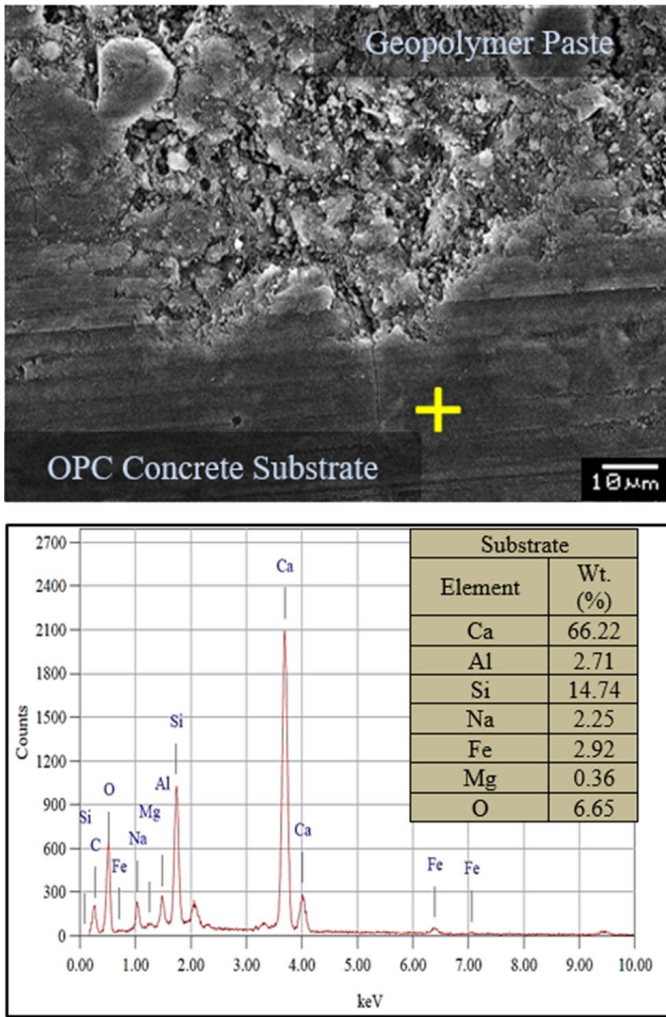


Fig. 4. SEM-EDS result at interface transition zone (ITZ) of FA/C35/45

ment and contribute to the bond strength development between geopolymer and concrete substrate. The significant amount of silica, alumina, calcium and iron as detected in the Fig. 5 become evidence for primarily composed C-A-S-H gel at the interface transition zone and the formation of ferro-sialate bond within the geopolymer system. The occurrences of these phases are due to the availability of metal cations (Ca^{2+} and Fe^{3+}) to form the stronger calcium-silica and iron-silica bonding reaction. Fig. 5 illustrates the localised area and the SEM elemental mapping in Si-Al-Ca-Fe at interfacial transition zone, signifying that these elements are mostly located within the samples.

The explanation for the bonding strength development at contact zone is in the fact that OPC concrete substrate surface are rich in calcium hydroxide, that reacts with geopolymeric based binder due to the need of metal cations such as Ca^{2+} and Fe^{3+} to be present in the framework cavities to balance the electronegativity of the geopolymer system [11]. The electronegativity of geopolymer system was influenced by the negative charge of Al^{3+} ions connected with Si^{4+} ions. The system consisting of a three-dimensional framework of SiO_4 and AlO_4 tetrahedra interlinked by shared oxygen atoms. The negatively charged Al and tetrahedrally coordinated Al (III) atoms inside the network are charge-balanced by alkali metal cations such as Na^+ , K^+ ,

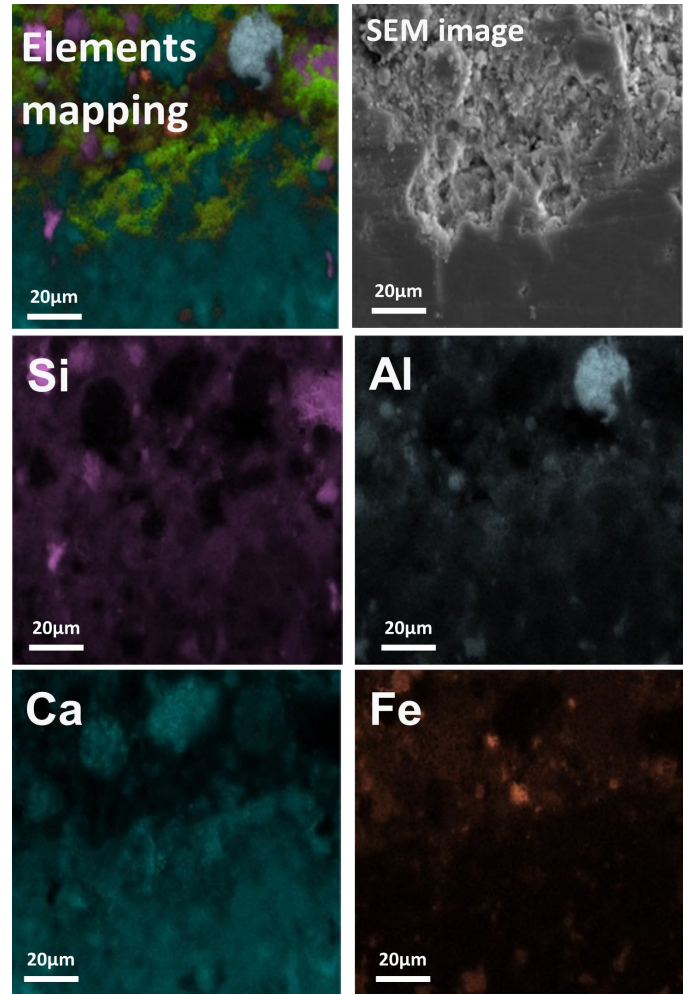


Fig. 5. SEM elemental distribution maps of Si, Al, Ca and Fe at the interfacial transition zone of FA/C35/45

Ca^{2+} and Fe^{3+} . Portland cement grains react with $\text{Ca}(\text{OH})_2$ at the surface of substrate leading to bonding strength development at the contact zone as described in the Fig. 6.

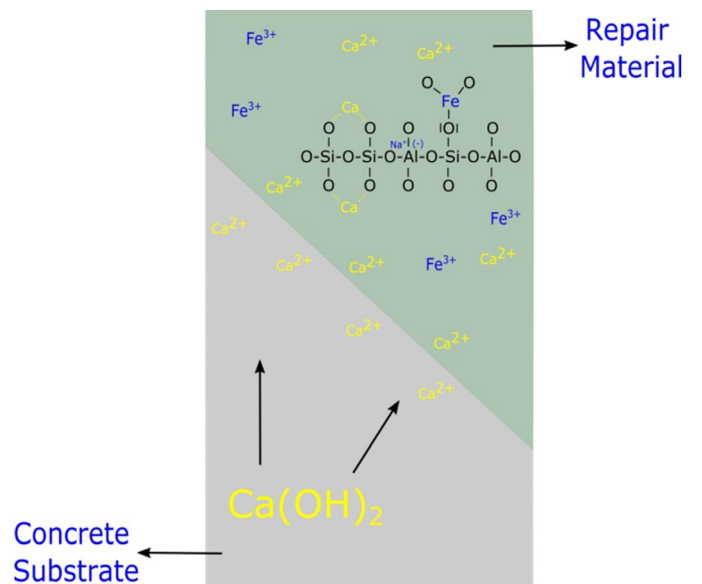


Fig. 6. The schematic diagram of interface transition zone of fly ash based geopolymer/ concrete substrate

5. Conclusion

In this work, the interfacial transition zone of geopolymer repair material with concrete substrate was synthesized. The utilization of fly ash geopolymer reported better bonding strength with higher concrete substrate class. It can be concluded that, the optimal concrete substrate class was C35/45 for pure concrete as it reported the highest compressive strength. The contribution of fly ash geopolymer as repair material enhances the interfacial transition zone (ITZ) of concrete substrate. The SEM-EDS reveal the impact of Ca^{2+} and Fe^{3+} with silica bonding reaction obtained the denser microstructure with the formation of ferro-sialate and calcium alumina silicate hydrate (C-A-S-H) gel.

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REFERENCES

- [1] H. Alanazi, M. Yang, D. Zhang, Z.J. Gao, *Cem. Concr. Compos.* **65**, 75-82 (2016).
- [2] K. Pandurangan, M. Thennavan, A. Muthadhi, *Mater. Today-Proc.* **5** (5), 12725-12733 (2018).
- [3] I.H. Aziz, M.M.A.B. Abdullah, H.C. Yong, L.Y. Ming, K. Husin, A.A. Kadir, E.A. Azimi, Manufacturing of fire resistance geopolymer: A review, in: *MATEC Web of Conferences 2016*, EDP Sciences (2016).
- [4] G.F. Huseien, J. Mirza, M. Ismail, S. Ghoshal, A.A. Hussein, *Renew. Sust. Energ. Rev.* **80**, 54-74 (2017).
- [5] I.H. Aziz, M.M.A.B. Abdullah, C.-Y. Heah, Y.-M. Liew, *Adv. Cem. Res.* **32** (10), 465-475 (2020).
- [6] M.B.gundiran, S. Kumar, *Constr. Build. Mater.* **125**, 450-457 (2016).
- [7] T. Phoo-ngernkham, A. Maegawa, N. Mishima, S. Hatanaka, P. Chindapasirt, *Constr. Build. Mater.* **91**, 1-8 (2015).
- [8] F. Pacheco-Torgal, J. Castro-Gomes, S. Jalali, *Constr. Build. Mater.* **22** (3), 154-161 (2008).
- [9] S.-Y.Guo, X. Zhang, J.-Z. Chen, B. Mou, H.-S. Shang, P. Wang, L. Zhang, J. Ren, *Constr. Build. Mater.* **264**, 120715 (2020).
- [10] F. Moghaddam, V. Sirivivatnanon, K. Vessalas, *Case Studies in Construction Materials* **10**, e00218 (2019).
- [11] T. Phoo-ngernkham, C. Phiangphimai, D. Intarabut, S. Hanjitsuwana, N. Damrongwiriyanupap, L.-Y. Li, P. Chindapasirt, *Constr. Build. Mater.* **247**, 118543 (2020).