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Addition of Alkali Activator and Substitution of GGBFS in Hydraulic Cement for High Early Flexural Strength and High Slump Concrete

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ABSTRACT

To lower CO_2 emissions, the construction sector is increasingly adopting sustainable practices, such as cutting back on clinker usage in cement manufacturing. Hydraulic cement is an environmentally friendly cement material because it uses a smaller amount of clinker. The amount of industrial waste, including materials like Ground Granulated Blast Furnace Slag (GGBFS), keeps rising each year. Because of this, it is frequently used as an alternative to cement. However, concrete with GGBFS substitution generally experiences a delay in early strength development due to its low reactivity to water. To overcome this, adding an alkali activator in NaOH and Na_2SiO_3 is necessary. In this study, the dosage of alkali activator was varied at 0%, 2.5%, 5% and 7.5% by weight of GGBFS with *R* and *A* values set at 1.5 and 0.45. In addition, using GGBFS can also reduce the workability of concrete, so it is necessary to use a superplasticizer in the form of Sika® Viscocrete®-1050 to improve concrete flow properties. The dosage of superplasticizer used was 0.75% by weight with a target slump of 20 cm for ease of working. The amount of GGBFS used was 30% by weight. To evaluate the materials performance, test were carried out to measure the concrete workability, compressive strength of paste and concrete flexural strength after 3 days of curing. The results show that increasing the dosage of alkali activator can increase the paste compressive strength by more than 24 MPa according to the requirements of using hydraulic cement and concrete flexural strength by more than 3 MPa in 3 days. Concrete with a 7.5% alkali activator dosage can achieve a concrete flexural strength of 4.81 MPa at 3 days and has a slump value of 20 cm. This research can be a solution to reduce CO_2 emissions and is useful for construction projects that require high flexural strength values at early ages and high slump.

1. Introduction

The demand for concrete production continues to increase every year [1], this has led to a steady increase in cement production. However, cement production generates large CO_2 emissions, accounting for around 6% of greenhouse gas emissions [2]. Therefore, the industry construction must in innovate to engineer materials that are kinder to the environment. One of the most widely used methods is to substitute green materials for normal clinker during the cement production process, thereby reducing clinker usage and lowering CO_2 emissions [3] or commonly known as hydraulic cement. Following ASTM C1157 standards [4], hydraulic cement usually contains normal clinker mixed with renewable or green materials such as fly ash [5] and limestone [6]. Hydraulic cement in the construction industry is considered more environmentally friendly because its production process generates lower carbon emissions due to using less clinker than conventional cement, reducing CO_2 emissions [7].

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Another significant industrial byproduct is Ground Granulated Blast Furnace Slag (GGBFS), which continues to increase year after year and contributes to CO_2 emissions [8]. GGBFS is a by-product generated from the smelting of iron ore and rapidly cooled using water or steam [9]. In concrete applications, GGBFS can replace cement to its comparable chemical makeup to ordinary portland cement [10]-[11]. The chemical composition of GGBFS, such as silica, calcium, and alumina, can effectively increase the compressive strength of concrete [12]-[13]. Previous studies have shown that substituting GGBFS in OPC cement at a substitution rate of 30-45% can increase the compressive strength and flexural strength of concrete [14]-[15]. However, other researchers attempted to compare the strength of normal concrete and concrete with GGBFS substitution at 3, 7, and 28 days of age. The results showed that concrete with GGBFS substitution had lower strength at an early age compared to normal concrete [16]. This occurs because OPC contains C_3S and C_3A, which react quickly with water to produce high concrete strength at an early age, while GGBFS requires an alkali activator to accelerate the hydration reaction in concrete, thereby increasing concrete strength at an early age [17]. Although GGBFS has a slow reaction initially, it has high strength over a longer time. To overcome this problem, GGBFS requires an alkali activator solution [18] which can accelerate the reaction rate to produce high early strength concrete.

Sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) represent the most frequently employed alkaline activators in practice [19]. A mixture of NaOH and Na_2SiO_3 as an alkali activator has been proven to significantly improve the mechanical properties of concrete because it creates an alkaline environment that allows GGBFS to react more quickly [20]. Several factors must be considered in the alkali activator solution, such as; the ratio of Na_2SiO_3 and NaOH (R), the concentration of the NaOH solution (molarity), the ratio of alkali activator to cement (A), and the percentage of alkali activator solution to the amount of cement used. Several studies have found that the ideal ratio for R is 1.5–2.5, the ideal molarity is 10–16 M, and the value of A used is 0.45 to achieve concrete high early strength [21] - [22] - [18] and [23]. The amount of alkali activator solution greatly affects the hydration properties of concrete, this leads to changes in the concrete structural strength. Therefore, testing is necessary to determine the most effective dose of alkali activator to activate the chemical properties of the amount of GGBFS used in this study.

The demand for high early-strength concrete is increasing in line with developments in construction, as it can accelerate project implementation and reduce project costs [24]. However, using large amounts of cement to achieve this strength increases CO_2 emissions. Hydraulic cement and GGBFS are used as alternatives to reduce this. Although effective, GGBFS reduces the workability of concrete, which affects the ease of construction in the field. [25]. Since the slump target was 20 cm, Sika® Viscocrete®-1050 *HE* superplasticizer was added to improve workability without increasing the amount of water.

This study used HE (High Early) type hydraulic cement, which complies with ASTM C1157 [4]. The concrete is required to reach a compressive strength of 24 MPa within 3 days, which corresponds to a flexural strength of about 3 MPa. By incorporating GGBFS and using an alkali activator to accelerate hydration, it's anticipated that the flexural strength at 3 days can surpass 3 MPa due to the improved early-age strength development. This research is expected to reduce CO_2 emissions by using hydraulic cement with minimal clinker content, which is then substituted with 30% GGBFS, an industrial waste material. It is hoped that the combination of these two cementitious materials can produce high concrete strength at an early age by varying the dose of alkali activator and adding superplasticizer to obtain the best mechanical properties of concrete, thereby enabling its use in various constructions requiring high early flexural strength and high slump concrete.

2. Methods

2.1 Material

Hydraulic cement and GGBFS served as the fundamental materials in this study. Hydraulic cement and GGBFS were referred to as cement. The hydraulic cement used was sourced from PT. SBI with a specific gravity of 3.15. GGBFS was sourced from PT. Krakatau Indonesia has a specific gravity of 2.77, and the chemical content of GGBFS can be seen in the Table 1. Preliminary testing revealed that a 70:30 blend of hydraulic cement to GGBFS yielded the best performance.

The superplasticizer used is Sika® Viscocrete®-1050 HE type E, which reduces water usage and accelerates the initial setting process of concrete. This type of superplasticizer is suitable for application requiring rapid strength development concrete and can increase the slump value with a 30% reduction in water quantity [26].

Table 1. Chemical content of GGBFS

Components	Content (%)
Aluminium Trioxide (Al_2O_3)	15.75
Silicon Dioxide (SiO_2)	37.03
Iron Trioxide (Fe_2O_3)	0.67
Calcium Oxide (CaO)	42.61
Sulfur Trioxide (SO_3)	1.83
Potassium Oxide (K_2O)	0.30

Sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) are mixed to create the alkaline activator solution. NaOH pellets with a content of 98.5% have a specific gravity of 1.34, and Na_2SiO_3 has a specific gravity of 1.65. NaOH pellets are dissolved in distilled water at a concentration of 10 molar. After the NaOH has dissolved, the NaOH solution is left to stand for 24 hours. The NaOH solution is then mixed with Na_2SiO_3 in a ratio of R (Na_2SiO_3/NaOH) of 1.5 and cooled for one hour or until it reaches room temperature before use. The ratio of alkali activator to cement (A) is 0.45. The variations in the percentage of alkali activator in this study are 0%, 2.5%, 5%, and 7.5% of the weight of GGBFS, and the amount of alkali activator is reduced from the amount of water. The 10 Molar NaOH concentration, R ratio, and A ratio are the results of previous research on geopolymer paste, mortar, and concrete, which produced high mechanical strength in concrete [22]-[27].

The fine aggregates used are silica sand and Optima sand. Silica sand is sourced from Tayan with a specific gravity of 2.66 and a unit weight of 1390. Optima sand is sourced from Rumpin, Bogor, with a specific gravity of 2.53 and a unit weight 1430. Silica sand and Optima sand are used together in concrete mixtures at a ratio of 70:30. For coarse aggregate, crushed stone from Rumpin, Bogor, is used with a size of 10-20 mm, a specific gravity of 2.58, and a unit weight of 1480. Fine aggregate and coarse aggregate are prepared in the Saturated Surface Dry (*SSD*) condition, in accordance with the guidelines outlined in ASTM C136 [28].

2.2 Mix Design

In this research, the absolute volume method was employed to calculate paste, mortar, and concrete mixtures, as standardized guidelines for geopolymer concrete formulations are currently unavailable. This approach determines mix proportions by converting each material's absolute volume into the total volume of 1 m^3 of the final mixture [29]. The calculation of absolute volume starts from paste, mortar, to concrete in the following order:

The calculation of the proportion of the paste mixture based on absolute volume can be done using Equation (1).

$$V_s + V_{ggbfs} + V_{sv} + V_a + V_{ac} = 1m^3 \tag{1}$$

where, V_s is absolute volume of hydraulic cement, V_{ggbfs} is absolute volume of GGBFS, V_{sv} is absolute volume of Sika® Viscocrete®-1050, V_a is absolute volume of water, V_{ac} is absolute volume of alkali activator.

Equation (1) can be expanded into Equation (2) to calculate the weight of each material:

$$\frac{W_s}{G_{ss}\gamma_w} + \frac{W_{ggbfs}}{G_{sggbfs}\gamma_w} + \frac{W_{sv}}{G_{ssv}\gamma_w} + \frac{W_a}{G_{sa}\gamma_w} + \frac{W_{ac}}{G_{sac}\gamma_w} = 1m^3 \tag{2}$$

The above equation can then be further translated into Equation (3) with a cementitious weight (weight of hydraulic cement and GGBFS) of 70:30. The cementitious FAS (F_AS_m) is the weight of water and the weight of alkali activator to cementitious weight is 0.25

$$\frac{(1-X)W_{sm}}{G_{ss}\,\gamma_w} + \frac{XW_{sm}}{G_{sggbs}\,\gamma_w} + \frac{YW_{sm}}{G_{ssv}\,\gamma_w} + \frac{(FAS_m-ZAX)W_{sm}}{G_{sa}\,\gamma_w} + \frac{ZAXW_{sm}}{G_{sac}\,\gamma_w} = 1m^3 \tag{3}$$

where, X is percentage of GGBFS, Y is weight of Sika® Viscocrete®-1050, Z is percentage of alkali activator to GGBFS, F_AS_m is water cementitius ratio, A is Alkali activator/cement ratio, W_{sm} is weight of cementitius, Gss is specific gravity of hydraulic cement, G_{sggbfs} is specific gravity of GGBFS, G_{ssv} is specific gravity of Sika® Viscocrete®-1050, G_{sa} is specific gravity of water, G_{sac} is specific gravity of alkali activator, γw is density of water.

In the mortar mix design, the effect of the ratio between the absolute volume of paste to the absolute volume of fine aggregate voids (R_m) was set at 1.4 based on previous research [19]. The volume of fine aggregate voids (V_{ragh}) in 1 m^3 can be determined based on the unit weight of fine aggregate (B_{sagh}), the SSD specific gravity of fine aggregate (G_{sagh}) and the unit weight of water (γ_w). Then it can be calculated with Equation (4):

$$V_{ragh} = 1 - \frac{B_{sagh}}{G_{sagh}}\gamma_w \tag{2}$$

Furthermore, if V_{ragh} is known, the weight of cement (W_s), weight of GGBFS (W_{ggbfs}), weight of Sika® Viscocrete®-1050 (W_{sv}), weight of water (W_a) and weight of alkali activator (W_ac) required in 1 m^3 of mortar mix can be calculated with Equation (5):

$$\frac{(1-X)W_{sm}}{G_{ss}\,\gamma_w} + \frac{XW_{sm}}{G_{sggbs}\,\gamma_w} + \frac{YW_{sm}}{G_{ssv}\,\gamma_w} + \frac{(FAS_m-ZAX)W_{sm}}{G_{sa}\,\gamma_w} + \frac{ZAXW_{sm}}{G_{sac}\,\gamma_w} = R_mV_{ragh} \tag{5}$$

Furthermore, the weight of fine aggregate can be calculated with Equation (6):

$$V_{ragh}R_m + \frac{W_{agh}}{G_{sagh}\gamma_w} = 1m^3 \tag{3}$$

The research evaluates effect of the ratio between the absolute volume of mortar to the absolute volume of coarse aggregate voids (*R_b*) of 1.4 based on previous research [19] - [22]. The volume of voids between grains of coarse aggregate (Vragk) in 1 m^3 can be determined based on the unit weight of coarse aggregate (B_{sagk}), SSD specific gravity of coarse aggregate (G_{sagk}) and unit weight of water (γ_w). Then it can be calculated with Equation (7):

$$V_{ragk} = 1 - \frac{B_{sagk}}{G_{sagk}}\gamma_w \tag{4}$$

Furthermore, if Vragk is known, the weight of cement (W_s), weight of GGBFS (W_{ggbfs}), weight of Sika® Viscocrete®-1050 (W_{sv}), weight of water (W_a) and weight of alkali activator (W_{ac}) required in 1m^3 of concrete mix can be calculated with Equation (8):

$$\frac{(1-X)W_{sm}}{G_{ss}\,\gamma_w} + \frac{XW_{sm}}{G_{sggbs}\,\gamma_w} + \frac{YW_{sm}}{G_{ssv}\,\gamma_w} + \frac{(FAS_m - ZAX)W_{sm}}{G_{sa}\,\gamma_w} + \frac{ZAXW_{sm}}{G_{sac}\,\gamma_w} = R_m V_{ragh} R_b V_{ragk} \tag{8}$$

Furthermore, the weight of fine aggregate can be calculated with Equation (9):

$$V_{ragh}R_m\, V_{ragk}\, R_b + \frac{W_{agh}}{G_{sagh}\gamma_w} = V_{ragk}\, R_b \tag{5}$$

To calculate the coarse aggregat mass, apply the Equation (10):

$$V_{ragk}\, R_b + \frac{W_{agk}}{G_{sagk}\gamma_w} = 1m^3 \tag{6}$$

The results of material quantity calculations for 1 m^3 of concrete are available in Table 2. Material Requirements. Mix ID is a variation of the test variable, with *B* as the symbol for concrete, AG as the symbol for alkali activator and the numbers 0, 2.5, 5, and 7.5 are the percentage of alkali activator used.

2.3 Mixing and Casting

The process begins with the dry mixing of hydraulic cement and GGBFS until they become uniform. At this stage, it is recommended to wear a mask because fine particles of dry material can fly and endanger breathing. Then pour water that has been mixed with superplasticizer slowly while stirring for ± 3 minutes until evenly mixed, and there are no lumps, then pour the alkali activator and stir again until evenly mixed. The process continues by adding fine aggregate in the form of silica sand and optima sand in SSD (Saturated Surface Dry) and stirring again for ± 3 minutes until well blended.

To make the beam specimens, the fresh concrete mixture is then poured into a 150 x 150 x 600 mm steel beam mold and compacted to prevent air bubbles from being trapped in the concrete. Once the concrete has hardened, the steel beam mold is removed, and the specimen is ready for testing. To make cube specimens paste, use a 50 x 50 x 50 mm mold.

2.4 Testing

After the mixing process is complete, a slump test is carried out according to SNI 1972-2008 [30] to evaluate the workability of fresh concrete. Compressive strength testing of paste based on ASTM C109 [31] to determine the compressive strength of paste at 3 days of age before further testing of concrete specimens.

Flexural strength testing of concrete beams was conducted at 3 days of age. The flexural strength test was performed using a two-point loading method based on SNI 4431-2011 [31]. The beam specimens were placed on the testing machine with two-point loading along the horizontal axis and perpendicular to the testing machine. After testing the beam specimens for each test variable, the flexural strength values were calculated using the formula corresponding to the beam's fracture surface.

Table 2. Material requirements (1m^3)

Mix ID	Variable	Concrete Mix Design Proportion (kg/m^3)								
		HC	GGBFS	Water	SV	SS	SH	PS	PO	CA
BAG0	H70GGBFS30SV0.75AG0	463.1	198.5	165.4	5.0	-	-	382.1	163.7	1040
BAG2.5	H70GGBFS30SV0.75AG2.5	464.0	198.9	163.5	5.0	1.3	0.9	382.1	163.7	1040
BAG5	H70GGBFS30SV0.75AG5	465.0	199.3	161.6	5.0	2.7	1.8	382.1	163.7	1040
BAG7.5	H70GGBFS30SV0.75AG7.5	465.9	199.7	159.7	5.0	4.0	2.7	382.1	163.7	1040

3. Results and Discussion

The results of testing the workability of concrete, compressive strength of paste, and flexural strength of concrete are explained in the following points:

3.1 Workability

The test results showed that adding an alkali activator decreased the slump value of concrete. This can be seen in Figure 1, Concrete without the use of alkali activator (BAG0) has a slump of 23 cm, concrete with the use of 2.5% alkali activator (BAG2.5) has a slump value of 22.5 cm, concrete with the use of 5% alkali activator has a slump value of 22 cm. Concrete using 7.5% alkali activator has a slump value of 20 cm. Of the four test variables, the one that meets the target with a slump of 20 cm is the concrete with 7.5% alkali activator, indicating a 13% decrease in slump compared to concrete without alkali activator. It is observed that the slump value of concrete exceeds 20 cm with the use of superplasticizer, and there is a decrease in slump as the amount of alkali activator increases. According to Cornelis [27] Using Na_2SiO_3 and NaOH as alkali activators can affect the workability properties of fresh concrete and shorten the hardening time of concrete. Concrete with a high slump value of more than 20 cm can be used for precast prestressed concrete [32].

From this study, it can also be concluded that each addition of alkali activator percentage can make the consistency of concrete more homogeneous and prevent segregation, even though it has a high slump value when compared to concrete without the use of alkali activator [21]. As can be seen in Figure 2, concrete without alkali activator (BAG0) experienced segregation, where separation occurred between the paste and aggregate in the concrete. When 2.5% alkali activator (BAG2.5) was added, the concrete mixture still experienced segregation but not as much as BAG0 concrete. The concrete mixture begins to appear more homogeneous when 5% alkali activator (BAG5) is added, and the concrete mixture with 7.5% alkali activator (BAG7.5) is the most homogeneous and does not experience segregation despite having a slump value of 20 cm. Concrete with a high slump value can make work easier.

This slump test's results can also align with the function of Sika® Viscocrete®-1050 type HE as a superplasticizer with high workability. Sika® Viscocrete®-1050 type HE is a polycarboxylate-based superplasticizer that can improve the workability of concrete [33].

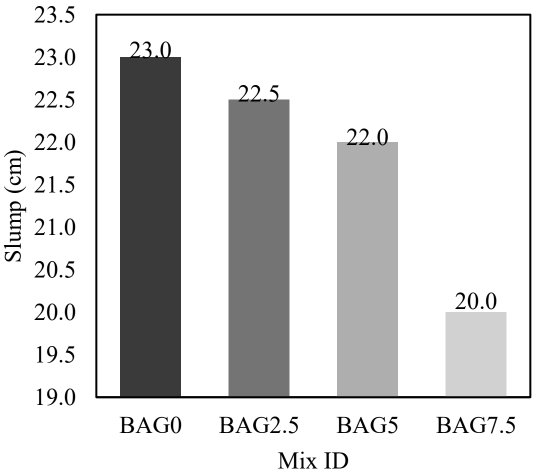

Figure 1. Percentage of alkali activator to concrete slump value

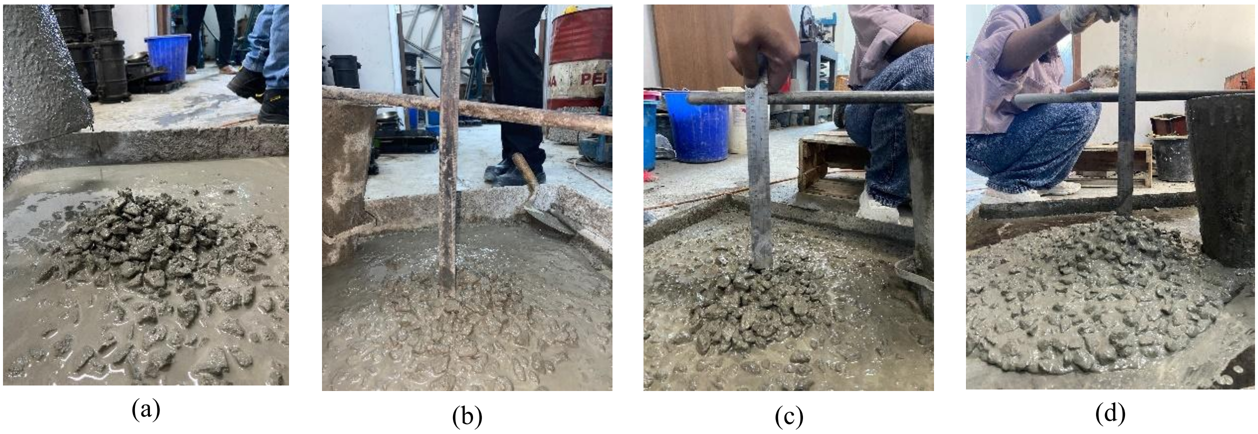

Figure 2. Concrete Slump Value Measurement **(a)** Without the use of alkali activator (BAG0); **(b)** Use of 2.5% alkali activator (BAG2.5); **(c)** Use of 5% alkali activator (BAG5); **(d)** Use of 7.5% alkali activator (BAG7.5)

3.2 Compressive Strength of Paste

Before making concrete, compressive strength testing is first carried out on the paste to determine the effect of using GGBFS and alkali activators on hydraulic cement, because, in general compressive strength and flexural strength have consistent results [34]. The results of the paste compressive strength test can be seen in Figure 3. Based on ASTM C1157 on hydraulic cement, the compressive strength requirement for HE type hydraulic cement paste after 3 days is 24 MPa [4]. The results of compressive strength testing of paste with 30% GGBFS substitution and the addition of alkali activator at 3 days of age in this study proved to increase compressive strength by up to 68.3% at 3 days of age. These test results indicate that adding 30% GGBFS and alkali activator significantly increases the compressive strength of hydraulic cement paste to over 24 MPa at the early age of 3 days.

3.3 Flexural Strength of Concrete

Figure 4. illustrates the flexural strength of concrete. At three days of curing, the flexural strength exhibits an upward trend as alkali activators are introduced. This improvement in strength results from the alkali activation process, where the reaction between the alkaline solution and GGBFS produces calcium silicate hydrate (C-S-H) gel and sodium alumino-silicate hydrate (N-A-S-H) gel, enhancing the concrete’s structural integrity [35]. This reaction creates strong bonds within the concrete aggregate, making the concrete mixture more homogeneous as the alkali activator is added [36]. As can be seen in Figure 5, segregation occurred in concrete that did not use an alkali activator (BAG0). In concrete with 2.5% (BAG2.5) and 5% (BAG5) alkali activator, segregation was minimal, and in concrete with 7.5% (BAG7.5) alkali activator, there was no segregation, resulting in higher concrete strength.

Alkali activators are very helpful in accelerating the rate of concrete strength gain in the early age because the chemical components in GGBFS become more reactive when mixed with alkali activators [37]. However, using less alkali activator may not react optimally with the amount of pozzolan used, which can cause segregation. Using too much alkali activator can also affect the workability of concrete and make it denser and more difficult to work with [36]. In addition, the CaO content in GGBFS also makes the concrete matrix denser, resulting in high concrete flexural strength [38]-[39]. The flexural strength of concrete with 7.5% alkali activator increased by 38% compared to concrete without alkali activator. The flexural strength of concrete increased with the addition of alkali activator, and the pattern of increase in concrete strength was similar to the results of previous paste tests, the inclusion of alkali activators has been shown to enchance concrete early strength development.

This study, the high flexural strength of concrete at an early age depends on the amount of alkali activator used and the amount of GGBFS used. The more alkali activator used, the higher the flexural strength of concrete, but it can reduce the workability of concrete [40]. Conversely, using a small alkali activator cannot react effectively with GGBFS. It cannot bind the aggregates well, which can cause segregation and reduce the flexural strength of the concrete.

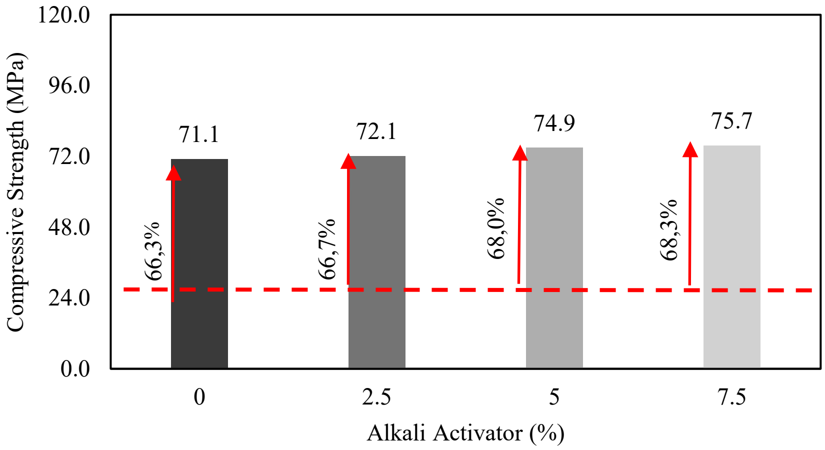

Figure 3. Percentage of alkali activator to compressive strength of paste at 3 days

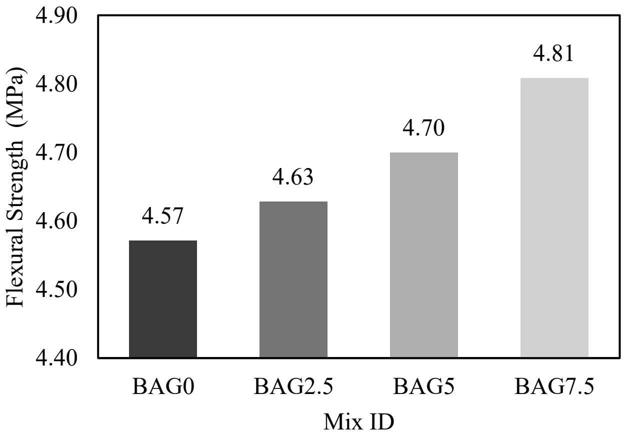

Figure 4 Flexural strength of concrete at 3 days

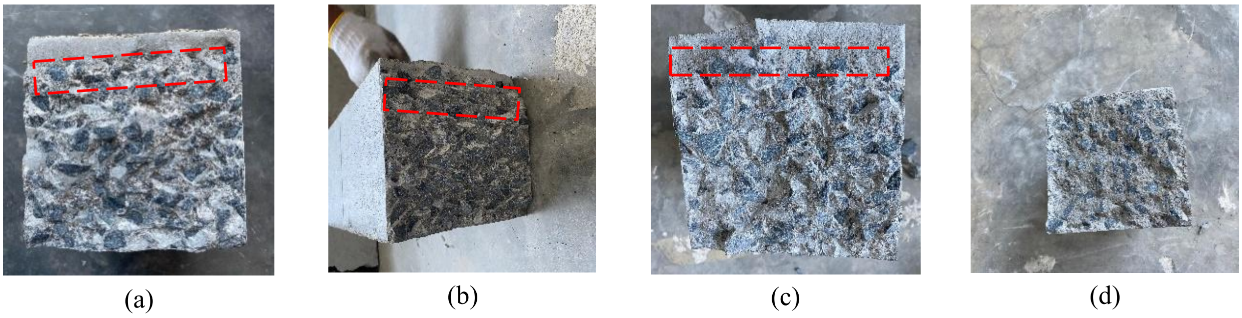

Figure 5 Concrete specimens **(a)** Without the use of alkali activator (BAG0); **(b)** Use of 2.5% alkali activator (BAG2.5); **(c)** Use of 5% alkali activator (BAG5); **(d)** Use of 7.5% alkali activator (BAG7.5)

4. Conclusions

The study's results indicate that using hydraulic cement with a 30% substitution of GGBFS can produce concrete with high flexural strength at an early age of 3 days. Concrete mixtures containing alkali activator show changed workability characteristics along with improved early strength. The higher the percentage of alkali activator used, the higher the flexural strength of the concrete achieved. However, the amount of alkali activator used must be limited to ensure the concrete's workability, thereby not impairing its performance. The optimal percentage of alkali activator to activate the pozzolanic properties of 30% GGBFS is 7.5%, as it results in a homogeneous mixture with good workability and high flexural strength. Concrete using 7.5% alkali activator has a slump value of 20 cm and high flexural strength up to 4.81 MPa at early age, making it suitable for precast prestressed concrete that requires high early-age concrete strength with a high slump. This research demonstrates the potential for more environmentally friendly concrete by reducing the use of OPC and utilizing industrial waste as an alternative cement substitute in concrete.

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