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THE EFFECT OF ADMIXTURE VARIATIONS ON WORKABILITY AND COMPRESSIVE STRENGTH OF GEOPOLYMER CONCRETE FLY ASH BASED WITH HIGH CALCIUM CONTENT

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ABSTRACT: The use of class C fly ash on geopolymer concrete causes flash setting characteristics. The objective of this research is to analyze how the addition of admixture as an alternative delay flash setting increases the workability of concrete. In this study, geopolymer concrete was made with admixture variations of 0%, 0.5%, 1%, 1.5%. The alkaline activator used in this study was 10 M NaOH and Na2SiO3, and the activator ratio was 1:1. The type of admixture used is sucrose. The tests carried out were: compressive strength at the age of 7, 14, 28, 56 days, slump test, permeability test, porosity test, and resistivity test. The mixing method applied was the dry mixing method, where the alkaline activator used was in a dry form (solid) crushed with fly ash to produce geopolymer cement. Geopolymer cement was mixed with water fine and coarse aggregates to make geopolymer concrete. The results of this research show that the slump values for the 0%, 0.5%, 1%, and 1.5% are 12.5 cm, 16.5 cm, 18.5 cm, and 19.5 cm, respectively. Whereas the average compressive strength of 3 cylinders of geopolymer concrete aged 28 days is 16.58 MPa, 29.55 MPa, 35.29 MPa, and 29.05 MPa, respectively. The effective admixture in this study is 1%. Since the addition, 1% admixture increases the workability of geopolymer concrete without reducing its compressive strength. The admixture used in this study is 1%. It is the most effective amount as it increases the workability of geopolymer concrete without reducing the compressive strength.

Keywords: Admixture, Geopolymer Concrete, Fly ash, Compressive Strength, Workability

1. INTRODUCTION

Portland cement is the most common type of cement in construction use around the world. The usage harms the environment because the cement production process produces CO2 gas [1]. Joseph Davidovits found innovation to reduce the use of Portland cement using its replacement called geopolymer. Geopolymer can reduce CO2 production because it is a synthesis of non-organic natural materials through a polymerization process, which uses Fly ash as a binder [2]. Geopolymer concrete also has the advantage of being resistant to corrosive environments and impressive durability [3]. According to SNI 2847 - 2019, the minimum compressive strength for concrete in a corrosive environment is 35 MPa. A precursor in the form of fly ash was applied in this research. It was chosen because of the high silica (Si) and alumina (Al) that it contains [4].

The fly ash used in this study is high-calcium fly ash (type C) with pozzolanic and cementitious properties [5]. This fly ash type has CaO content greater than 10%, which is rarely used for geopolymer concrete. The mixture of geopolymer concrete with type C fly ash waste binder has rigid viscosity properties because it contains calcium (CaO) in it, which causes double reactions called polymerization and hydration [6]. The result of the hydration reaction is the formation of a calcium aluminosilicate-hydrate (C-A-S-H) phase/gel, which coexists with alkali aluminosilicate (N–A–S–H) [7]. The C-A-S-H phase causes the geopolymer concrete to experience a flash setting [8]. The phenomenon causes geopolymer concrete based on fly ash type C to be challenging to be implemented. However, this C-A-S-H phase also has an essential role in increasing the compressive strength of geopolymer concrete [9].

The use of admixture is one of the solutions to increase the workability of concrete. Kusbiantoro [10] implemented sucrose as an admixture on geopolymer concrete based on fly ash type F. Experimental results in that study show that sucrose can significantly increase the setting time. This is related to the carbohydrate composition of sucrose which changes in a high alkaline environment and interferes with the development of C-A-S-H gels in the geopolymer mixture. When the formation of C-A-S-H is inhibited, the workability of geopolymer concrete increases.

On the other side, a significant result was obtained from the addition of polycarboxilate-based admixture [11]–[12]. These results occur due to the absorption from the carboxyl group (-COOH) and dispersion from hindering flocculation due to ethylene oxide (-CH_2CH_2O-) that comes from the chemical structure of polycarboxylate-based superplasticizer.

Dosage limits for admixtures, Hardjito [13] stated that superplasticizer-based admixtures effectively increased workability in the range of 0.8%-2%. The highest compressive strength with good workability was obtained when the geopolymer concrete mixture used 0.5% admixture, which was 14.28 MPa. Geopolymer concrete based-high calcium fly ash achieves high workability of ±20 cm. This concrete has a compressive strength of 15-35 MPa, uses an additional 1% admixture in the wet method [14]. However, the wet process is complicated to implement in common because it must involve chemical calculations [15].

This study discusses the effect of admixture variations on workability and compressive strength of geopolymer concrete made from fly ash with sodium hydroxide molarity of 10 M. The admixture uses sucrose. The mixing method used dry mixing. The tests used as parameters in this study are the resistivity test, permeability test, and porosity test. The results of these tests are correlated with the compressive strength of geopolymer concrete. This study investigates the percentage of admixture with high workability and compressive strength of 35 MPa.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Fly Ash

The type C fly ash used in this study was collected from Paiton Jawa Power Plant. Type C fly ash has a hydration reaction (due to the CaO content) which produces heat resulting in flash setting (fast setting time) [8, 16]; therefore, the admixture is needed.

2.1.2 Alkali Activator

The alkaline activator used was sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) in solid form. The molarity of NaOH used in this study was 10 M with an activator ratio of 1:1. The OH- ion in NaOH is an essential element in the geopolymerization process. This ion is vital in increasing the decomposition reaction rate of alumina and silica bonds [17]. In contrast, sodium silicate accelerates the polymerization reaction and binds the material to form a solid paste [18].

2.1.3 Admixture

The admixture used is sucrose, which was applied to increase workability [13], and characterized by the magnitude of the slump value. Sucrose was chosen because it can significantly increase the final setting time of pasta. This is because sucrose can cover fly ash particles from alkaline solutions [12].

2.2 Methods

2.2.1 Material Characteristics

The Fly ash material was characterized by conducting SEM, XRD, XRF, and specific gravity tests. Then the aggregate test includes; Sieve analysis, specific gravity test, volume weight test, and abrasion test (for coarse aggregate).

2.2.2 Specimens Variation

The specimens made in this study consisted of 4 variations of admixture. Table 1 shows the detail of the addition of admixture.

Table 1 Variation of admixture (sucrose)

Variation of admixture	Percentage of binders (%)
V.C	0 %
V.1	0,5 %
V.2	1%
V.3	1,5 %

2.2.3 Specimens Production

The steps for making the mix design are based on the journal by Phoo-ngernkham [14] and converted to the dry method [15]. The dry method implemented in the manufacture of geopolymer cement is conducted by using an alkali activator used in the solid form, which is then crushed with fly ash into geopolymer cement. Geopolymer cement is mixed with aggregate and water to form geopolymer concrete.

Table 2 Summary of the mix design composition

Materials	V.C	V.1	V.2	V.3
	kg/m^3			
FA	600.5	600.5	600.5	600.5
MRS	507.9	507.9	507.9	507.9
MLS	1140.6	1140.6	1140.6	1140.6
NaOH	36.6	36.6	36.6	36.6
$Na_2SiO_3.5H_2O$	55.9	55.9	55.9	55.9
Water	149.3	149.3	149.3	149.3
Sucrose	0	3.0	6.0	9.0

Note: FA = Fly Ash, MRS = Fine Aggregate, MLS = Coarse Aggregate

The dry method mixing orders carried out in this study are as follows; gravel and sand were added first, followed by sucrose as admixture. After being mixed relatively even, the fly ash was added. When the time was set and it was well mixed, then water was added [19]. The summary of the mixed design composition can be seen in Table 2.

2.2.4 Specimens Curing

The chosen curing method implemented in this study was ambient curing. Curing was done by placing a concrete sample at room temperature. Curing at room temperature was determined for this study because it was easier to apply in the study field compared to other curing or treatment methods. The curing temperature in this study ranged from 35℃ - 40℃ with an inertia of 40% - 50%.

2.2.5 Specimens Test

The tests carried out were slump test to determine workability as ASTM C 143 [20], compressive strength test at the age of 7, 14, 28, and 56 days as ASTM C-39 [21], resistivity test as AASHTO T358, and porosity test of concrete at 28 days old as ASTM C 642 [22].

3. RESULT AND DISCUSSIONS

3.1 Materials Characteristics

3.1.1 Fly Ash

The SEM test illustrates microstructural arrangements of particles and not the pozzolanic reactions. It indicates that the higher the amorphous phase, the more reactive the fly ash is. Table 3 shows the results of the XRD test. Specific gravity test of fly ash applied in this research refers to ASTM C188. Table 4 shows the specific gravity test results.

Table 3 Mineral Content XRD Test Results of Fly Ash

Mineral	Compound	Test results (%)
Amorphous	-	54.72
Quartz	O_2 Si	4.30
Brownmillerite	Al Ca_2 Fe O_5	7.4
Periclase	Mg O	9.24
Magnesite	C Mg O_3	18.40
Anhydrite	Ca O_4 S	3.00
Maghmemite	Fe_2 O_3	1.5
Lime	Ca O	1.4

3.1.2 Coarse and Fine Aggregate

The results of the coarse aggregate test to determine its characteristics can be seen in Table 5. In contrast, the characteristics of the fine aggregate of Lumajang sand used in this study can be seen in Table 6.

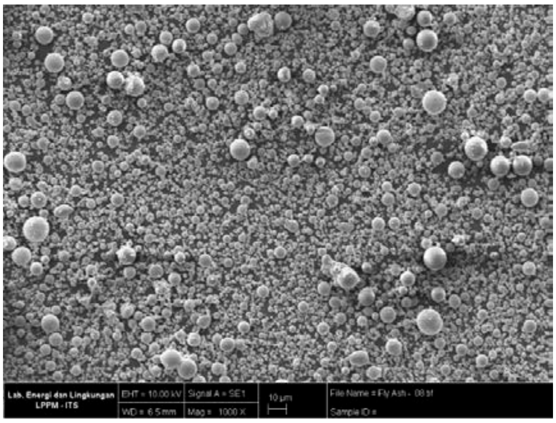

Fig. 1 The results of the SEM (1000x) fly ash test

Table 4 Specific Gravity Fly Ash Test Results

Items	Weight 1 (gr)	Weight 2 (gr)	Weight 3 (gr)
Pikno A	178.3	191.4	191.4
Pikno A + Oil	572.9	586	586
Pikno A + Oil + Fly Ash	754.7	767.6	767.6
Oil + Fly Ash (B)	576.4	576.2	576.2
Oil (C)	394.6	394.6	394.6
Fly Ash (A)	250	250	250
Specific grafity	2.93	2.92	2.92
Average		2,92	

Table 5 Specification of Crushed Stone Coarse Aggregate max. 20 mm

No	Test Type	Result
1	Coarse Aggregate Gradation Analysis (ASTM C136)	
	- Fineness Modulus (FM) (ASTM C-33)	6.92
	- Zone (Max)	2
2	Specific gravity SSD (ASTM C127)	2.678
3	Release Volume Weight (ASTM C29)	4594.4 kg/m^3
4	Aggregate Wear (SNI-2417-2008)	20.39 %

3.1.3 Alkali Activator

This study used NaOH and $Na_2SiO_3.5H_2O$ in solid form as an alkali activator. Typical chemical specifications of 98% NaOH flake used in this study can be seen in Table 7.

Table 6 Specification of Lumajang Sand Fine Aggregate

No	Test Type	Result
1	Coarse Aggregate Gradation Analysis (ASTM C136)	
	- Fineness Modulus (FM) (ASTM C-33)	2,65
	- Zona (Maks)	4
2	Specific gravity SSD (ASTM C127)	2,78
3	Release Volume Weight (ASTM C29)	1573,3 kg/m^3

Table 7 Typical Chemical Composition of Sodium Hydroxide Flake 98%

Parameter	Value
Sodium Hydroxide (NaOH)	98 min (%)
Residual Water (H_2O)	1 max. (ppm)
Sodium Carbonate ($NaCO_3$)	0,5 max. (ppm)
Chloride (NaCl)	150 max. (ppm)
Iron (Fe)	5 max. (ppm)
Nickel (Ni)	5 max. (ppm)

3.2 Test Result

3.2.1 Slump Test

Figure 2 shows the results of the slump test. The addition of admixture in sucrose increases the slump value by 4-7 cm or 21% - 36%. This shows an increase in the workability of geopolymer concrete. From the graph, it can be seen that the more sucrose content is given, the higher the slump value becomes. It means that the workability of the geopolymer becomes higher. This is because the addition of sucrose can liquefy the concrete mixture so that the slump value increases and workability increases. However, the difference in slump values between variations using admixture: V.1, V.2, V.3 is slightly different.

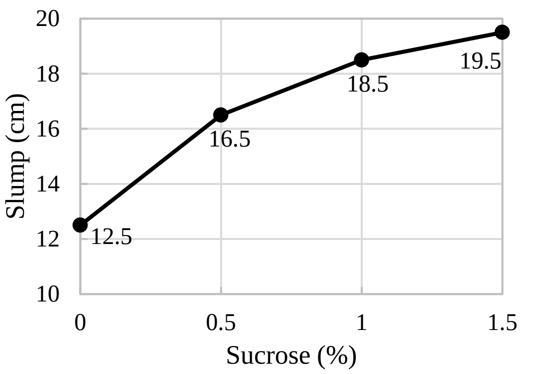

Fig. 2 Slump Value Based on % Addition of Sucrose

3.2.2 Compressive Strength

The average test results for three samples of all variations can be seen in Figure 3. Figure 3 shows that the highest compressive strength value is V.2 of 47.4 MPa with 1% sucrose, followed by V.1 at 40.8 Mpa with sucrose of 0.5%. In comparison, the lowest compressive strength is V.C which is without sucrose. The target compressive strength of 35 MPa has also been obtained at V.2 at 28 days of concrete (35.3 MPa). However, the age of 28 days has not shown the maximum acceptable compressive strength of geopolymer concrete in this study. It can be seen by the increase in the compressive strength of geopolymer concrete by 14% - 28%.

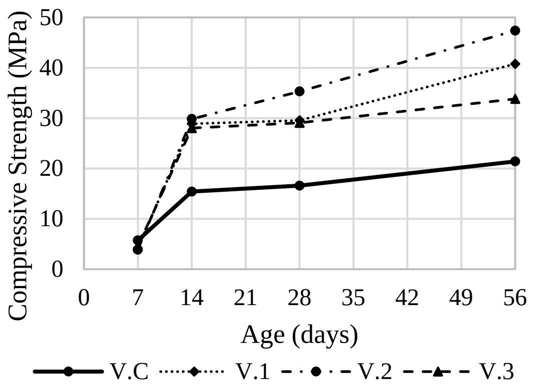

Fig. 3 Compressive Strength of All Geopolymer Concrete Variations

3.2.3 Resistivity

The resistivity test uses the Resipod Proceq tool. The test results can be seen in Figure 4.

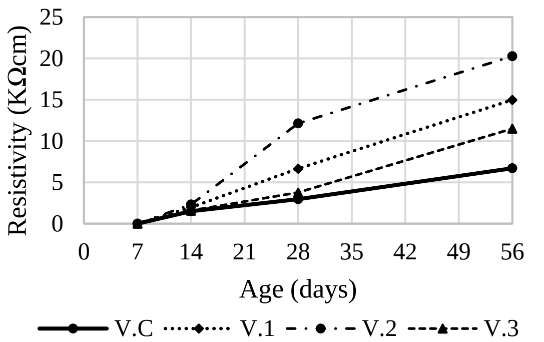

Fig. 4 Resistivity Value of All Geopolymer Concrete Variations

The resistivity test results in variations of geopolymer concrete producing resistivity value throughout the life of the concrete. The highest resistivity is V.2 of 20.3 KΩcm with an admixture composition (sucrose) 1%— followed by V.1 at 14.98 KΩcm with a design of 0.5% sucrose. In contrast, the lowest resistivity value is V.C variation without sucrose. Although the highest value is in

V.2, the quality of the geopolymer concrete is still classified in the category of moderate corrosion risk; therefore, it is still prone to corrosive substances.

Porosity

The porosity test in this research uses ASTM C 642 [21] standard without vacuum, where the 10 x 20 cm test object will be cut into 3, it is shown in Figure 5, and the test results can be seen in Figure 6. Porosity testing is carried out when the concrete is 28 days old.

Fig. 5 Sample pieces for porosity test at 28 days old

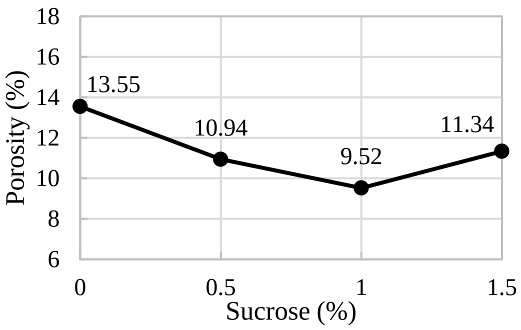

Fig. 6 Porosity of All Geopolymer Concrete Variations

Figure 6 shows the lowest porosity value throughout the life of the concrete is V.2 of 9.52% with admixture sucrose 1%. The lower the porosity value of concrete, the better the quality. Then it is followed by V.1 of 10.94% with a composition of 0.5% sucrose. In contrast, the highest porosity value is V. C without sucrose. There is no category of % pore on the quality of concrete. However, concrete with too many pores can undoubtedly be quickly passed by water seepage or chemical compounds (which are corrosive), affecting the performance and durability of geopolymer concrete.

3.3 Effect of Admixture (Sucrose) adding to the Compressive Strength and Workability of Geopolymer Concrete Analysis

Figure 7 shows the relationship between compressive strength and workability. Figure 7 shows that adding a sucrose admixture increases the compressive strength value and increases the slump value. The addition of sucrose affects the microstructure of the polymerization reaction. It dilutes the geopolymer concrete mixture. This causes the workability to increase, which is indicated by an increase in the slump value [23]. The high viscosity at the V.C, characterized by a low slump value, causes the reaction to occur unevenly/not all of the reaction perfectly. The addition of admixture in the form of sucrose can reduce viscosity which is indicated by an increase in the slump value, and slow down the reaction between fly ash particles and alkaline activator [12]. The polymerization reaction can be more evenly distributed [24]. This is indicated by a significant increase in compressive strength, which is 37% - 55%.

However, a decrease in compressive strength was experienced when the admixture composition was 1.5%. This is because the CHOH molecule in sucrose covers the fly ash particles too much, and the addition of admixture can affect the behavior of the alkaline activator in the geopolymer concrete binding process [25], thus inhibiting the polymerization reaction. This weakens the bond between fly ash particles and alkali activators. This also shows that the addition of too much sucrose can also reduce the compressive strength of geopolymer concrete. In this study, the most effective admixture sucrose for geopolymer concrete with 10 M NaOH and activator ratio of 1:1 is 1% admixture. This mix design improves the workability of geopolymer concrete without reducing its compressive strength.

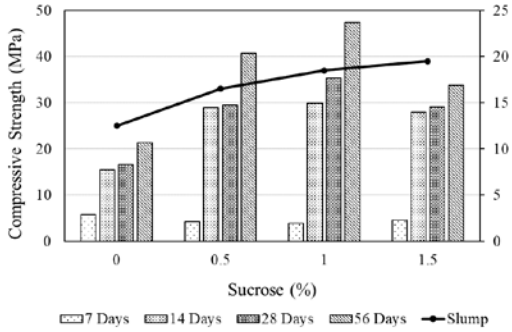

Fig. 7 Relationship between Compressive Strength and Workability

3.4 Effect of Adding Admixture (Sucrose) on Compressive Strength with Other Testing Parameters

3.4.1. Compressive Strength with Porosity Test

Figure 8 shows the correlation between compressive strength and porosity. Figure 8 shows that sucrose admixture can reduce porosity in concrete. An increase follows the tiny pores contained in the concrete in the compressive strength of the geopolymer concrete. Sucrose application can reduce the porosity of geopolymer concrete by 13% - 30%. This is because variations that do not use admixture (V.C) have gaps in the interfacial transition zone. The interfacial transition zone is the confluence zone between aggregate and binder minerals in a cementitious system. This gap then becomes a pore in the concrete. The addition of admixture can fill the gaps that are difficult to reach by the cement particles so that the gaps in the interfacial transition zone are closed. The more percentage of sucrose added, the more closed the gap in the interfacial zone.

However, the porosity value increased when 1.5% admixture was added (in sample V.3). 2 things probably caused this. First, because there is less vibration during the implementation, the voids in the geopolymer concrete are still trapped, causing pores. Second, because this study uses an activator in the form of NaOH of 10 M (including low molarity), the ability to react with fly ash is also low. The cause of porosity in geopolymer concrete (in particular) depends on the alkali activator itself and the silica content in the fly ash. When the ability to react is low, the possibility of forming a solid geopolymer concrete product is also reduced, indicated by the appearance of pores in the concrete. This is indicated by the decrease in the compressive strength of V.3.

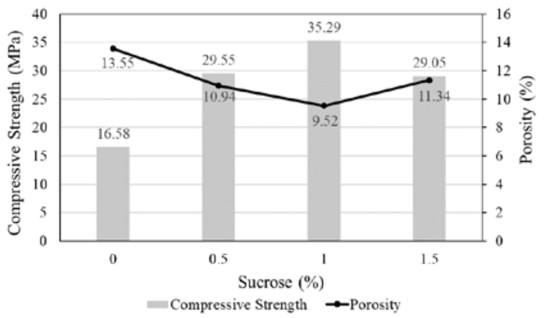

Fig. 8 Relationship between Compressive Strength and Porosity

3.4.2. Compressive Strength with Resistivity

Figure 9 shows the relationship between compressive strength and resistivity. Figure 8 shows that adding admixture sucrose increases the compressive strength while increasing the resistivity value. The addition of sucrose increased the resistivity value by 42% - 68% of the variation without sucrose V.C. The greater the resistivity value, the greater the compressive strength of geopolymer concrete. This is because the porosity of the concrete itself influences the resistivity value. The greater the porosity of concrete, the lower the resistivity value. It also affects the compressive strength of the concrete.

As the age of the concrete increases, the resistivity value also increases, followed by the increase in compressive strength. The resistivity value indicates that this is still not readable at the age of 7 days, as the compressive strength of geopolymer concrete at 7 day-olds is also still low. The greater the resistivity value in a concrete, the greater the energy required for an electron to pass through; the transfer of ions at the anode and cathode will be more difficult; therefore, the concrete will be more resistant to corrosion. This is also related to chloride penetration. Chloride penetration will quickly enter the concrete, which has low resistivity [26].

The composition of geopolymer concrete uses fly ash type C with alkaline activator NaOH of 10 M and the ratio of activator ratio of 1:1. This study has not shown the superiority of geopolymer concrete in terms of resistance to corrosive chemicals, as mentioned in the journal by Tajunnisa [3], because the level of corrosion is still moderate. There is a need for further research on the effect of fly ash type C (high calcium fly ash), the concentration of alkaline activator, and the addition of admixture on geopolymer concrete resistance to corrosive. The curing temperature also needs to be considered because it can significantly affect the resistivity value [27].

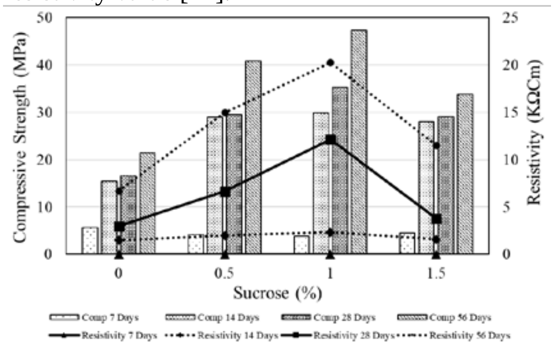

Fig. 9 Relationship between Compressive Strength and Resistivity

4. CONCLUSIONS

Based on the description above, some conclusions can be drawn as follows:

1. Admixture sucrose addition improves the workability of high calcium fly ash-based geopolymer concrete. This is indicated by the increase in the slump value from 12.5 cm to 19.5 cm.
2. The targetted compressive strength of 35 MPa is met by V.2 with a 1% admixture at 28 days, which is 35,3 MPa.
3. The most effective addition of admixture for geopolymer concrete with a NaOH concentration of 10 M; the ratio of NaOH: Na_2SiO_3 is 1:1, and by using 1% (V2) of dry mixing method.
4. The relationship between compressive strength results and other parameters such as compressive strength and resistivity is directly proportional. It is indicated by the values of

compressive strength and resistivity; the higher the resistivity value is, the higher the compressive strength value becomes. Meanwhile, the relationship between compressive strength and porosity is inversely proportional; the smaller the % of the porosity value, the greater the compressive strength value of geopolymer concrete is.

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