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The effect of rice husk ash addition as pozzolan on geopolymer binder using alkali activators

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Abstract. Geopolymer concrete is an example of innovative concrete that does not use cement as a binder and generally fly ash used in recent research. However, fly ash is categorized as a hazardous and toxic waste [8]. This research studied about another binder, besides fly ash, in this case is rice husk ash made as a geopolymer paste alkali activated by a chemical mixture of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) confronted to a fly ash mixture paste as comparative material. The compositions made were, 100% rice husk ash, a mixture of 50% rice husk ash and 50% fly ash, and 100% fly ash as control mixture. After making the mixture, the composition will be tested to setting time-test in the form of paste. The size of specimen was cylindrical 2,5 cm in diameter 5 cm in height and cube size 15 cm x 15 cm x 5 cm. Each type of specimen was projected to porosity test, compressive strength test, UPV (Ultrasonic Pulse Velocity) and permeability test on 3 days, 28 days and 56 days of sample's age. From the result of setting time, it was found that the composition of 100% rice husk ash had the longest on binding, which were 129 minutes for early binding and 170 minutes for late binding. The lowest result of porosity test was 100% of fly ash at 56 days of sample's age testing with a porosity of 20%. The lowest result of compressive strength was 100% of rice husk ash tested in 3 days of sample's age showed a compressive strength at 0.65 MPa. Based on the test results of UPV (Ultrasonic Pulse Velocity), the lowest value of wave velocity was 531.667 m/s, belong to 100% rice husk ash mixture at 3 days of sample's age testing, with very poor binder quality qualification. The test result of highest permeability kT value with very poor-quality index binder was 100% rice husk ash with period of testing time in 3 days 0,047.10-16 m².

1. Introduction

Concrete as one of building structures' materials already widely known because almost all existing buildings now use concrete as basic materials. The strength of concrete is very dependent to the composition and strength of each of its constituent materials, one of those is cement. From the earth conference, which was held in Bali on December 2007 themed about climate change, it was stated that the total number of cement production in the world was recorded 1.5 billion tons. In this case, cement industries release 1.5 billion tons carbon dioxide into nature. According to The International Energy Authority: World Energy Outlook, the amount of carbon dioxide produced in 1995 was 23.8 billion tons. Another fact, based on these data, Portland cement production accounts for seven percent of the carbon dioxide produced from a variety of sources that may lead to global warming. There are several



researches concern in the concept of cement replacement in concrete production, in this particular case is rice husk ash mixed with fly ash. As it is well known that fly ash has high silica content and can be used as a binder (pozzolan) for the partially replacement of cement in concrete production. In addition, since fly ash is classified as a waste, which is hazardous and toxic materials, it should be deprecated [8]. This problem becomes a factor to reduce the usage of fly ash as a geopolymer binder, substituting materials in example rice husk ash and alkali activator. Rice husk is burned at high temperatures (400-800°C) to produce rice husk ash containing high silica (SiO_2), or known as pozzolan in rice husk ash, is 94-96% and pass a sieve no. 200 so that the rice husk ash can fill in the empty spaces between grains in order to increase the adhesion between the particle. Silica content in 10% rice husk ash usage, in the mixture, improves compressive strength. Alkaline activator used was sodium silicate (Na_2SiO_3) which serves acceleration of the polymerization reaction and alkali solution used was sodium hydroxide (NaOH), which serves to assist the process of bonding between the particles [6]. In this study, the researcher used a binder mixture of rice husk ash and fly ash with the intention of determining the effect of rice husk ash addition in binder geopolymer using comparative other binder, namely fly ash, with alkali activator sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH). The samples were then examined in setting time, porosity, UPV, permeability, and compressive strength tests during the binding process up to its paste form.

2. Composing Materials

Fly ash is one of by-product material in coal industry, which is used as a binder in geopolymer concrete. Fly ash is determined as a pozzolanic material for it is consisted of alumina-silica compounds. These compounds potentially react to calcium hydroxide of conventional cement and water and then forms a strength compound into the hydrating cement. It is indicating the ability of fly ash to chemically reacts and performs, also having properties similar to pozzolanic material, presented by nature, i.e. the volcanoes ashes or other sedimentary materials [1].

Rice husk is the result of a rice mill industry, burned at 400-800°C temperature [7]. The highest content of silica (SiO_2), which is obtained by sun drying for 1 hour, amounted up to 88.97%, compared to the oven drying (190°C) for 1 hour was up to 83.15%. The most common amount of the silica content of rice husk ash is up to 90-96%. Silica, contained in rice husk ash, has hydrated amorphous structure [5].

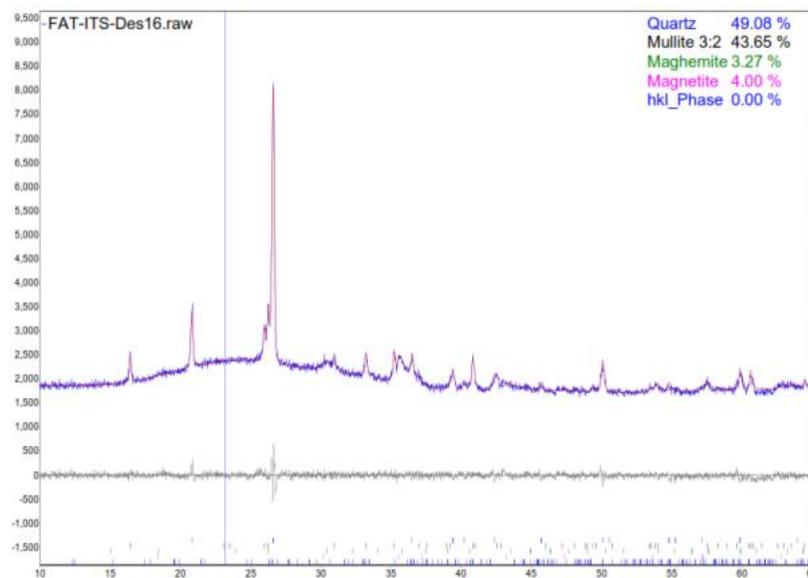
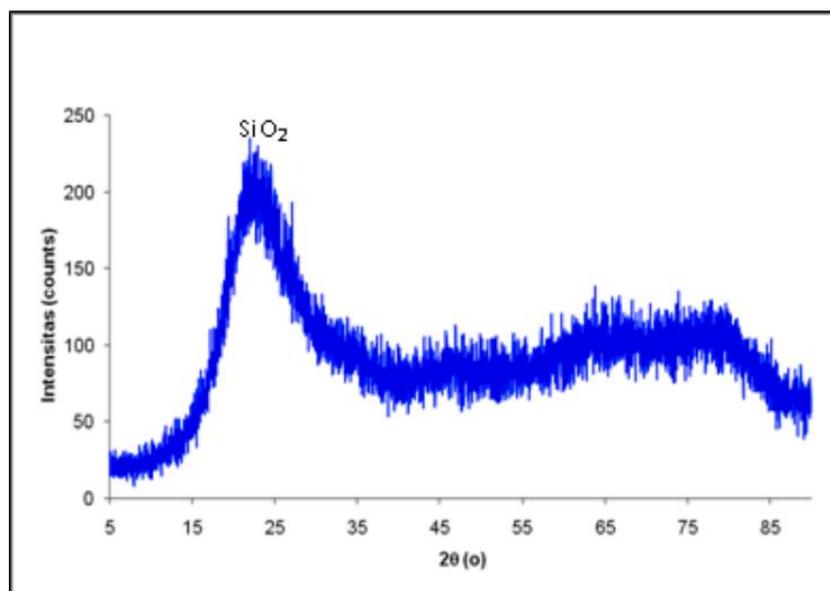
Fly ash and rice husk ash are material that would be made as a geopolymer binder. Before making a geopolymer concrete, the researcher tested chemical compound of the material. The tests conducted were XRF (X-Ray Fluorescence), XRD (X-Ray Diffraction), and SEM-EDX (Scanning Electron Microscope). The results of these tests can be seen in Table.1, Table.2, Figure.1, Figure.2, Figure.3, and Figure.4 as following:

Table 1. The Test result of XRF Fly Ash of Paiton Power Plant

Compound	Content (%)
SiO_2	47,10
Al_2O_3	24,25
Fe_2O_3	16,07
CaO	5,830
SO_3	0,206
MgO	2,620
Na_2O	0,645
K_2O	1,640

Table 2. The test result of XRF Rice Husk Ash

Compound	Content (%)
SiO ₂	96,40
K ₂ O	2,720
CaO	0,639
MnO	0,073
Fe ₂ O	0,093
CuO	0,028
ZnO	0,042
Re ₂ O ₇	0,021

**Figure 1.** The Test Result of XRD Fly Ash Paition**Figure 2.** The Test Result of XRD Rice Husk Ash

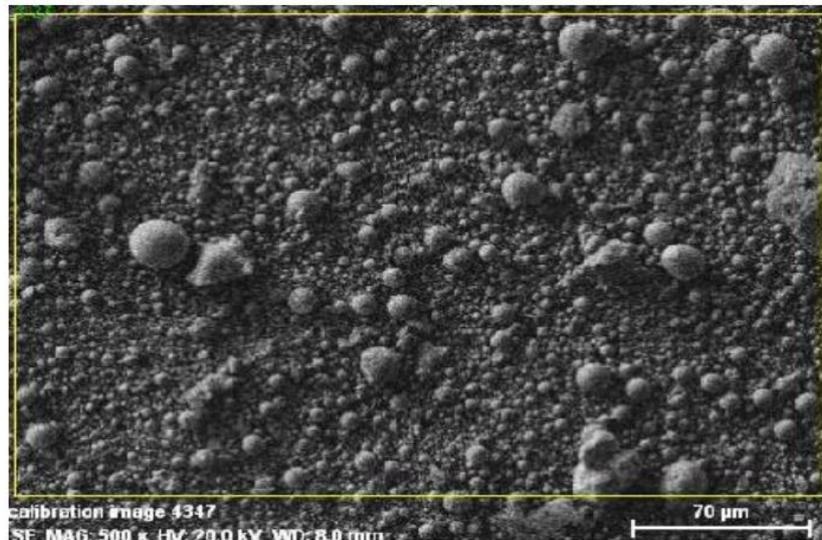


Figure 3. The Test Result of SEM-EDX Fly Ash Paiton

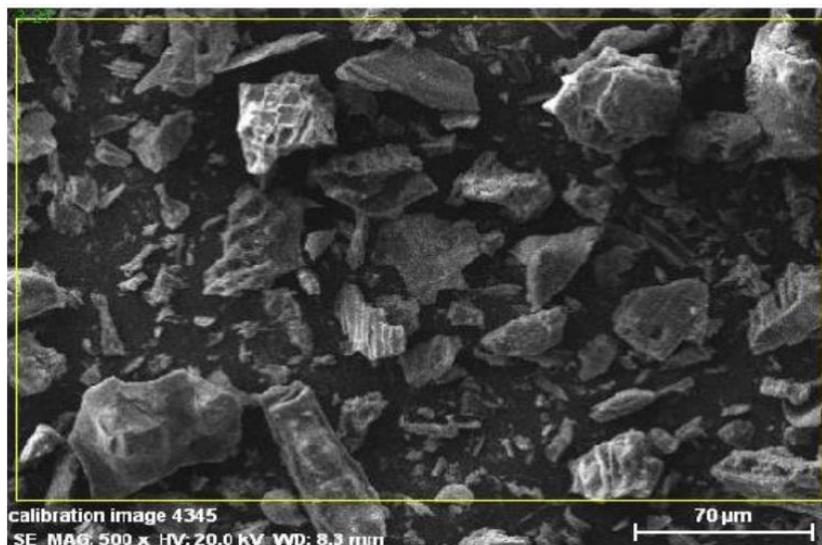


Figure 4. The Test Result of SEM-EDX Rice Husk Ash

Referring to the compound test, XRF (X-Ray Fluorescence), fly ash had a CaO content of less than 10% is 5.83%, in this research, the researcher used fly ash type F [1]. From the compound test XRD (X-Ray Diffraction) of fly ash, could be seen there was SiO₂ content of 49.08% and the test results of SEM-EDX (Scanning Electron Microscope) shown the form of spherical particles of fly ash that improves workability, so it could reduce the use of water, simplify the binding inter-particles and minimize the space between the mixed material [4]. From the test results of the compound, XRF (XRay Fluorescence) of rice husk ash, the SiO₂ content of rice husk ash was 96.40%, the addition of rice husk ash proportion circa 10% improves the compressive strength. This was occurred as rice husk ash is a pozzolanic material. Based on XRD, crystal content of rice husk ash is shown as the highest peak on the XRD diagram, specifically at 2θ°. Crystal silica could improve the compressive strength as rice husk ash is a pozzolanic material [3] and from the results of SEM-EDX (Scanning Electron Microscope) test, the form of rice husk ash particle, which resembles as a hollow sponge, requires a high-water demand. This shape of particle caused the involvement of rice husk ash affects to a very slow process in specimen hardening [2].

The combination of Sodium Silicate (Na_2SiO_3) and Sodium Hydroxide (NaOH) liquid were aimed to help prevent chemical reactions among aluminum and silica, contained in fly ash and rice husk ash. Sodium hydroxide is an alkaline compound that is very reactive when mixed with water or distilled water [9].

3. Methodology

The methodology used in this research was an experimental study with direct examination in the laboratory. This research intentioned to know the effect of rice husk ash to replace fly ash in geopolymer binder with alkali activator mixture of Sodium Silicate (Na_2SiO_3) and Sodium Hydroxide (NaOH).

In the production of this geopolymer binder, fly ash was taken from PT. PJB UP Unit 1-2 Paiton (Power Plant), Probolinggo, East Java. Rice husk was taken from the rice milling in Situbondo, East Java. Rice husk was burned in the charcoal factory in Balongbendo, Krian, Sidoarjo, East Java

Geopolymer binder compositions made were 100% rice husk ash, a mixture of 50% rice husk ash and 50% fly ash, and 100% fly ash, blended with the alkali activator molarity of 12 M, weight ratio of Na_2SiO_3 to NaOH statically maintained at 1,5. Every pastes of composition mixtures were examined into setting time. The specimen made into cylindrical shape of 2,5 cm in diameter and 5 cm in height were attempted into porosity test and compressive strength test. Meanwhile, the specimen of cubical shape of 15 cm x 15 cm x 5 cm were directed into UPV test (Ultrasonic Pulse Velocity) and permeability test, at the age of 3 days, 28 days and 56 days of samples.

The production of specimens:

1. Material preparation, consisting of rice husk, fly ash, NaOH solution and Na_2SiO_3
2. Rice husk drying under the sunlight for 3 hours, repeat until dry
3. Burning the rice husk at $\pm 700^\circ\text{C}$ temperature up to 4 hours
4. Sift the rice husk ash using a sieve No. 200
5. Test the chemical properties of fly ash and rice husk ash
6. The mixture of Na_2SiO_3 and NaOH is made to approach 1.5 in weight ratio.
7. The composition of geopolymer binder mixture in weight ratio of fly ash and rice husk ash (materials) to alkali activator can be seen in Table.3 following:

Table 3. Comparison of Weight Mixed

Fly ash : Husk ash (%)	Material : Alkali (%)
100 : 0	45 : 55
50 : 50	74 : 26
0 : 100	65 : 35

8. Vicat test (initial setting time and final setting time) 12M ratio of 1.5. Following Table.4. lists the results:

Table 4. The Result of Setting Time

Binder Name	Binder Code	Setting Time (minute)	
		Initial	Final
100% of Rice husk ash	ASP12-1,5	129	170
100% of fly ash	FA12-1,5	18	45
Mix 50% of fly ash dan 50% of rice husk ash	ASPFA12-1,5	73	110

9. Amount of each samples' mixtures attempted into tests :

Table 5. The Variation of Object Test

Test	Ratio of Fly ash to Husk ash			Total
	100:0	50:50	100:0	
Compressive Strength	9	9	9	27
Porosity	9	9	9	27
UPV dan Permeability	9	9	9	27

10. Cylindrical sample of 2,5cm in diameter and 5cm in height, examined at the age of 3 days, 28 days and 56 days of samples. The results presented in Table.6 :

Table 6. The Result of Cylinders Testing

Binder Name	Binder Code	Binder's Age/Time	compressive strength (MPa)	Porosity (%)
100% Rice husk ash	ASP 12-1,5	3 days	0,65	FAILED
		28 days	1,62	
		56 days	2,58	
100% fly ash	FA 12-1,5	3 days	19,12	26,2
		28 days	34,90	21,6
		56 days	43,32	20,0
mix 50% fly ash and 50% Rice husk ash	ASPFA 12-1,5	3 days	1,53	58,0
		28 days	3,33	55,2
		56 days	7,65	45,1
75% fly ash and 25% Rice husk ash	ASPFA [B]	3 days	7,95	-
25% fly ash and 75% Rice husk ash	ASPFA [A]	3 days	0,95	-

11. Cubical sample of 15 cm x 15 cm x 5 cm test at the age of 3 days, 28 days and 56 days of samples. Obtained the results as Table.7. following:

Table 7. The Results of Cube Testing

Binder Name	Binder Code	Binder's Age/ time	UPV (m/s)	Permeability (10^{-16} m^2)
100% rice husk ash	ASP 12-1,5	3 days	531,7	FAILED
		28 days	810,0	
		56 days	1635	
100% fly ash	FA 12-1,5	3 days	1711,7	0,020
		28 days	2187,5	0,004
		56 days	2777,5	0,002
Mix of 50% fly ash and 50% rice husk ash	ASPFA 12-1,5	3 days	679,17	0,047
		28 days	1074,2	0,016
		56 days	1140,0	0,010

12. Analyzing the result of testing

13. Making conclusion based on the analysis

4. Data Analysis

Hereby the results of examination undergone into the specimens, specifically setting time, porosity, compressive strength, permeability, and UPV tests of geopolymer binders' specimens (12M with 1,5

ratio of alkali activator) presented in Figure 5 and Figure 10. From the graphic, the longest time setting (initial setting time and final setting time) had by the mixture of 100% rice husk ash composition, the initial setting time is 129 minutes and the final setting time is 170 minutes. The fastest setting time (initial setting time and final setting time) had by 100% fly ash composition that has initial time setting time 18 minutes and the final setting time is 45 minutes. Due to the shape of rice husk ash particles, that resembles as a hollow sponge captured on Figure.4, the mixture requires a high-water demand and might need an addition of superplasticizer, a chemical functioning to reduce the use of excess water, so it's taking a longer time to set, compared to fly ash' control mixture.

Otherwise, the fly ash has a spherical particle shape, shown in Fig.3, which increases the workability and reduces the water usage, in other word, the mixture is easier to bind to each other and minimize the space between materials mixed. Highest compressive strength was tested at the age of 56-day of 100% fly ash mixture, resulted 43.32 MPa. Highest compressive strength tested at the age of 3-day held into the composition of 75% fly ash : 25% rice husk ash (ASPFA [B]) 12M-1,5 mixture and 25% fly ash : 75% rice husk ash (ASPFA [A]) 12M-1.5 is 100% fly ash mixture, which is 21.12 MPa. Moreover, the results of the lowest compressive strength tested on 3-day sample's age of 100% rice husk ash composition at 0.65 MPa. So, it could be concluded, when the matrices of materials perfectly bind each other, the compressive strength tend to be higher. The highest porosity was found on 3-day of sample's age of 50% rice husk ash and 50% fly ash composition by 58% in value, but the lowest porosity test resulted on 56 days of sample's age of 100% fly ash composition by 20% in value. The failure of permeability examination was occurred on 100% rice husk ash composition, at all age testing of 56 days, 28 days and 3 days. It was caused by the form of hollow particles that degrade the adhesion of particles. The highest UPV test results held on 56 days examination of 100% fly ash composition in the amount of 2777.5 m/s (shoddy binder quality) and for the lowest UPV test results was 3 days of 100% rice husk ash composition amounted to 531.6 m/s (binder quality was very poor). The highest permeability testing held on 3-days sample's age of 100% rice husk ash and fly ash by 100% 0,047.10-16 m² including normal binder quality and for the lowest permeability test result was the testing of 56-day 100% fly ash composition by 0,00233.10-16 m² (binders' quality is very good). There was a failure in testing permeability to 100% rice husk ash in all age testing at 56 days, 28 days, and 3 days. It was caused of the form of hollow particles results in lower adhesion between the particles.

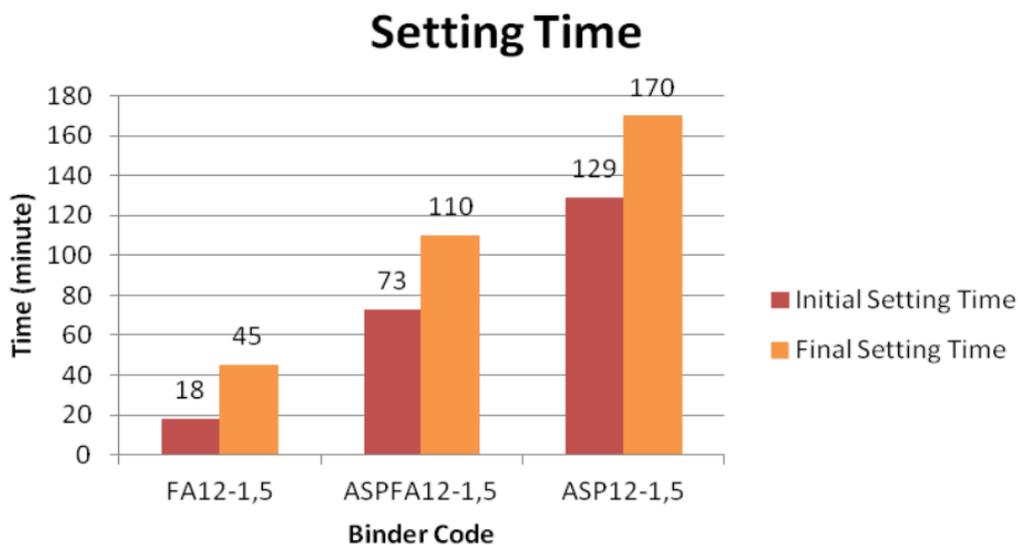


Figure 5. The Test Result of Setting Time (initial and final time)

Compressive Strength

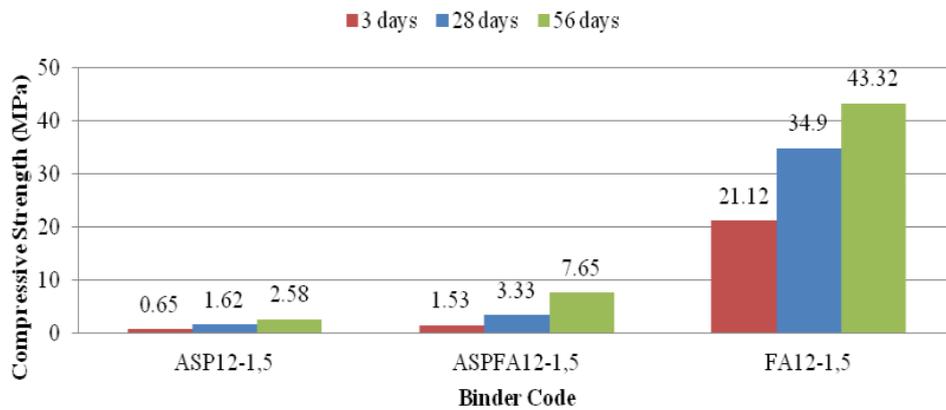


Figure 6. Compressive Strength Test Results 3 Days, 28 days, and 56 days

Compressive Strength 3 days

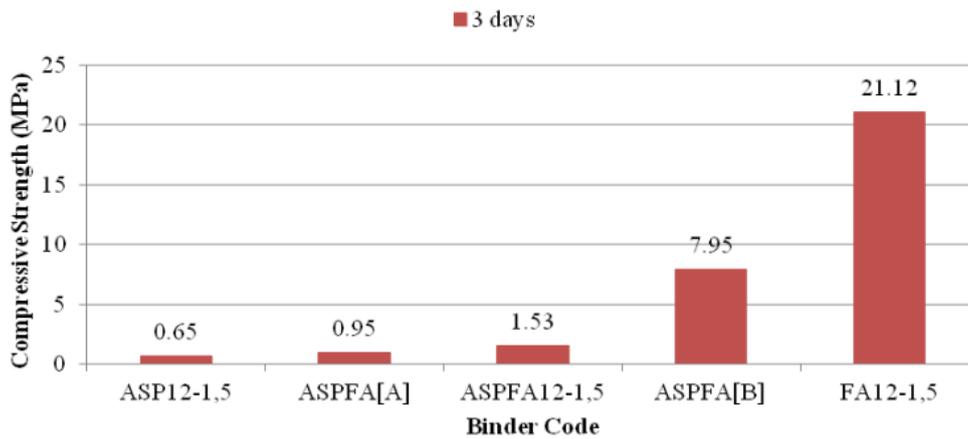


Figure 7. Compressive Strength Test Results 3 Days

Porosity

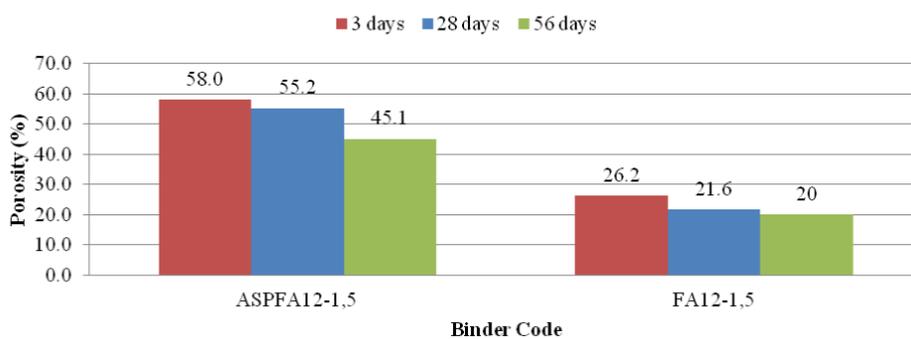


Figure 8. Porosity Test Results

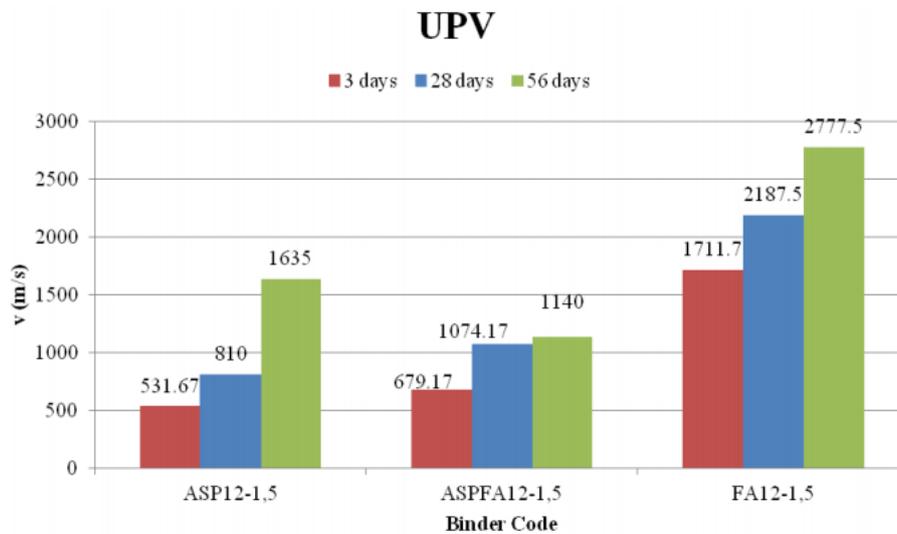


Figure 9. UPV Test Results (Ultrasonic Pulse Velocity)

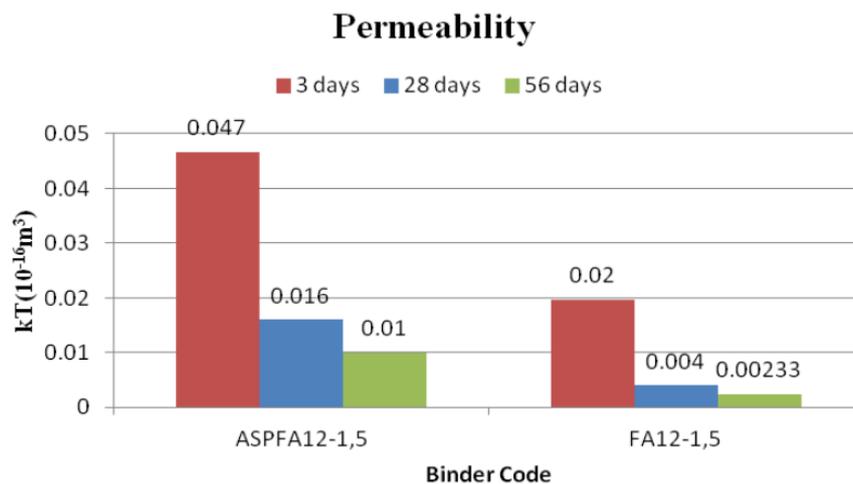


Figure 10. Permeability Test Results

5. Conclusion

The best mixture is presented in the composition of 100% fly ash with the compressive strength up to 43,32 MPa. The inclusion of ash to the geopolymer concrete in big quantities could provide high compressive strength. The use of rice husk ash in binder decreases the compressive strength and its sponge-like particles tend to absorb more water into the mixture and low the reactivity. The advantage of rice husk ash usage is seen from its slowing setting time-characteristic. As it is well known, the problem of Indonesian material geopolymer binder is its rapid setting time, which interferes the usage of geopolymer binder for industrial usage.

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