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Durability of Concrete Using Rice Husk Ash as Cement Substitution Exposed To Acid Rain

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ABSTRACT
The acidity of rainfall in major areas of Indonesia is under neutral pH. Average pH of rainfall is between 3 and 5. Free lime within concrete will react with acid and cause a decrease in the strength of concrete. A means to anticipate the damage is to reduce the content of free lime within concrete. Silicon oxide contained in rice husk ash can react with free lime to form a new compound that is harder and denser. It became the basis for the use of rice husk ash in concrete mixtures. The mixtures were prepared by replacing 5% and 10% of cement with rice husk ash and the results were compared with a reference mix with 100% cement. This paper presents the results of an experimental investigation on the mechanical characteristics of concrete specimens as durability parameters. Then to evaluate the mechanical characteristics, microstructure test was conducted. The lower the mechanical properties of the concrete, the higher the level of gypsum contained within concrete. The percentage of 5% rice husk ash of the cement weight has a lower compressive strength decrease than the 10% rice husk ash. In addition, the proposed durability model is a model of polynomial equation with two variables.
***Keywords* –** acid rain, binder, durability, microstructure, rice husk ash.

I. INTRODUCTION

Concrete material is one of many materials used in construction field. The strength of concrete is generally regarded as the most important properties to be considered. This is because the strength of concrete can provide an overall picture of the concrete quality. However, it is also important to note that the concrete must withstand the conditions that had been designed, without damage, over a period of years. So, in addition to its strength, it should also be durable or have a high durability.

The durable nature of the concrete will be impaired if it has a contact with acidic environment. In concrete, cement functions as an aggregate binder and therefore it is a decisive factor for concrete quality. Cement mainly contains lime, silica, alumina, and iron oxide. Acidic environment contains sulfuric acid which can react with free lime contained in cement and form a component of a larger volume. This process causes expansion and cracking in concrete. The boundary line of normal pH rain level is 5.6. Acidity rain level in Indonesia territory measured on March 2011 pH showed that majority areas have pH rain level under 5.6 [1]. This gives an illustration that acid rain has occurred in Indonesia.
Cement replacement materials have been widely used to improve the strength and durability of concrete, such as silica fume or slag or fly ash. Rice husk ash (RHA) is one alternative for cement replacement materials, which has been widely studied for its benefit in the concrete mixture. However, compared to other substitute materials, rice husk ash applications in the field and daily life is still minimal. Rice production in South Sulawesi was 4.38 million ton of milled rice, which consisted of 4.35 million ton of paddy rice and 0.03 million ton of paddy fields [2]. Meanwhile rice production in 2011 was estimated to be 4.54 million ton of milled rice, which consisted of 4.51 million ton of paddy rice and 0.03 million ton of paddy fields. If the rice milling process produced 20% of husk waste, it means that South Sulawesi produced about 908 million ton of husk waste. Furthermore, if the burning of rice husk yield ash for about 15%, it will produce RHA of 136,200 ton.

There are many studies of the possibility to use RHA as a replacement for cement in concrete mixtures. One of them [3] examined the chloride penetration resistance of concrete with RHA. The result suggested that there was an increase in compressive strength and durability when using 20% rice husk ash. A study conducted by [4] concluded that the use of RHA up to 40% of cement weight can increase corrosion resistance. Furthermore, [5] examined the durability of concrete with RHA. The use of rice husk ash up to 15% of cement weight may increase the resistance to penetration of chloride ions. The purpose of this study was to determine the effect of RHA on mechanical properties and microstructure of concrete due to acid rain. After that, a model of mechanical characteristics of concrete due to acid rain was formulated. The benefit of this study is by gaining illustration of the effect of RHA as a cement substitution for the mechanical characteristics of concrete due to acid rain, it is expected to contribute to the fundamental science of concrete technology, especially on the durability properties of concrete due to acid rain. The resulting model can be used as theoretical basis and reference in terms of the durability of concrete against acid rain.

II. METHODS

The chemical and physical characteristics of RHA as substitution material were investigated. Concrete specimens consist of two types namely cylinder and prism. All the specimens are immersed in mixing nitric acid and sulfuric acid solution. Specimens that immersed in water were also made and used as controlled specimens.

The ash which will be used as an added ingredient was examined for its chemical and physical characteristics. There are two types of concrete test specimens with rice husk ash; cylinders and prisms. The entire specimens were immersed in a bath of nitric acid and sulfuric acid solution. Concrete specimen of rice husk ash immersed in a water bath (normal treatment) was also made and used as control test specimen.

In this study, the independent variable was the percentage of RHA, which is 5% and 10% of the cement weight. Meanwhile, the dependent variable was mechanical characteristics of concrete as durability parameters.

Mechanical property tests consisted of compression test [6], modulus of rupture test [7] and water absorption. Microstructure tests consisted of scanning electron microscopy test (SEM) and X-ray power diffraction test (XRD). Acid rain simulation was completed by immersing it in a solution of sulfuric acid and nitric acid. Specimens without RHA and immersed in normal water were made for control specimens. The collected data was used to create a proposed model of concrete with rice husk ash due to acid rain.

Vega3tescan SEM-EDX and Rigaku Miniflex II XRD were used for microstructure test in this research while Universal Testing Machine (UTM) for mechanical test. The materials used in this research is Portland Composite Cement, aggregate (fine and course), water, RHA and Superplaticiezer (Sikamen-LN).

III. RESULTS AND DISCUSSION

3.1. Rice Husk Ash

RHA was taken from the burning husk which was used as fuel for furnace brick making. The results of XRD characterization showed an amorphous phase (Fig. 1). Amorphous phase was resulted from the burning of rice husks above 400^0C. The shape of amorphous phase allowed RHA to be pozzolan materials. From the result of EDS, we obtained RHA composition, which was dominated by SiO_2 levels, of 95.23% as shown in Table 1.

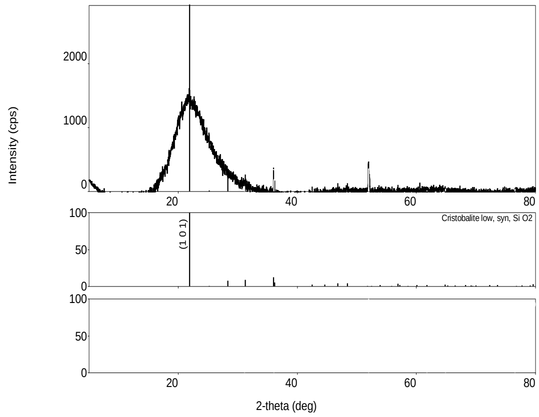

Figure 1. XRD of RHA test

Table 1. RHA Chemical Composition

Oxide Compound	Chemical Composition (%)
SiO_2	95.23
Al_2O_3	1.24
K_2O	1.80
Na_2O	0.21
MgO	0.52
P_2O_5	1.00

3.2. Mechanical Properties

As we know, the use of RHA in concrete can improve the strength of concrete. The same result was produced from compression test study. Although specimen used 10% RHA, compressive strength decreased compared to the other two test specimens. However, under acidic conditions, a decrease in compressive strength RHA which used 10% was smaller when compared to the test specimen without RHA.

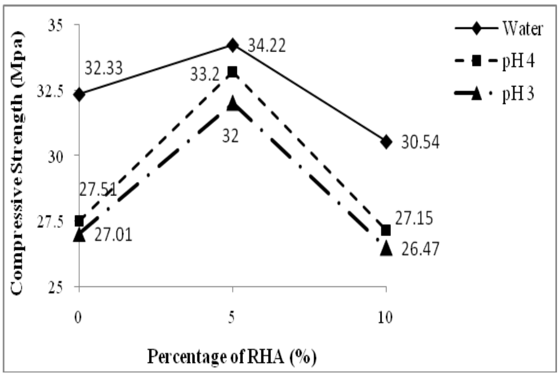

Figure 2. relationship between % RHA and compressive strength (28 days)

Broadly speaking, Fig. 2 shows that the compressive strength decreased if it had been immersed for 28 days in an acid solution (either pH 4 or pH 3). However, compressive strength of the 5% RHA specimens was higher than other specimens. Meanwhile the compressive strength of the test specimens in solution of pH 4 and pH 3was only slightly different.

Fig. 3 shows the compressive strength of the specimens after immersion for 90 days. The pattern was similar to the 28 days-immersion test specimen. Test specimens using 5% RHA had the highest compressive strength both in normal water or acid solutions. The difference lies only in the magnitude of reduction in compressive strength for each test specimen.

Modulus rupture test, which was conducted for all prism-shaped specimens with size of 15 cm x 15 cm x 60 cm, was performed to find out the tensile strength of the concrete. According to the theory, the concrete has a greater compressive strength than its tensile strength. Therefore, to determine the correlation between the magnitude of the tensile strength of the test specimen and RHA use, a graph as shown in Fig. 4 and Fig. 5 was created.

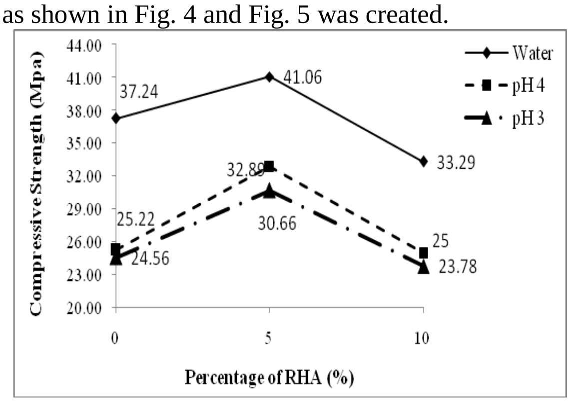

Figure 3. relationship between % RHA and compressive strength (90 days)

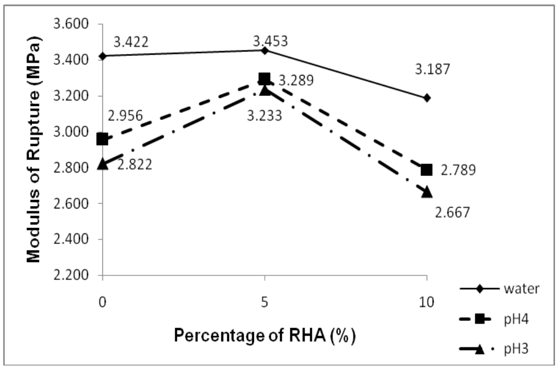

Figure 4. relationship between % RHA and modulus of rupture (28 days)

Similar to compression test results, the use of 5% RHA in concrete can increase the modulus of rupture of concrete at 28 days and 90 days compared to the modulus of rupture of the specimen without RHA. However, the use of 10% RHA in concrete was unable to increase flexural strength, even if the value was smaller than the modulus of rupture of the specimen without RHA.

In general, Fig. 4 shows the modulus of rupture decreased if it had been immersed for 28 days in an acid solution (either pH 4 or pH 3). However, modulus of rupture of 5% RHA test specimens was higher than other specimens. Although the compressive strength of the specimen in a solution of pH 4 and pH 3 was only slightly different, but other test specimens (without RHA and 10% RHA) had a greater decrease in modulus of rupture.

Modulus of rupture of the specimen after immersion for 90 days is presented in Fig. 5. Trends of rise and fall of the modulus of rupture is similar to that of the specimen that had been immersed for 28 days. Specimens with 5% RHA had the highest modulus of rupture both in normal water or acid solutions immersion. The only difference lies in the magnitude of decrease in modulus of rupture for each specimen.

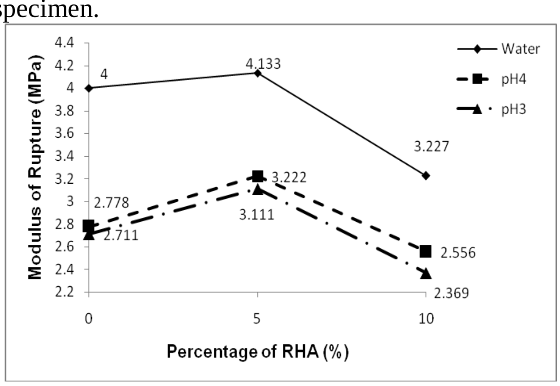

Figure 5. relationship between % RHA and modulus of rupture (90 days)

3.3. Microstructure Properties of Concrete

Fig. 6 and Fig. 7 present the amount of water absorption which occurred in the cylinder specimens. Fig. 6 shows that the water absorption increased if it had been immersed for 28 days in acid solution (either pH 4 or pH 3). However, the water absorption of 5% RHA specimen was the least of other test specimens. Meanwhile, the test specimen water absorption in solution of pH 4 and pH 3 was only slightly different.

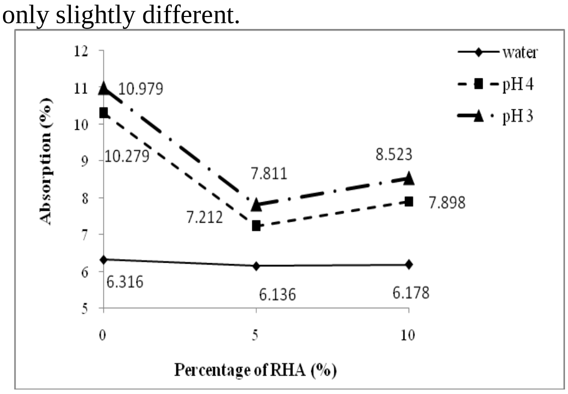

Figure 6. relationship between % RHA and water absorption (28 days)

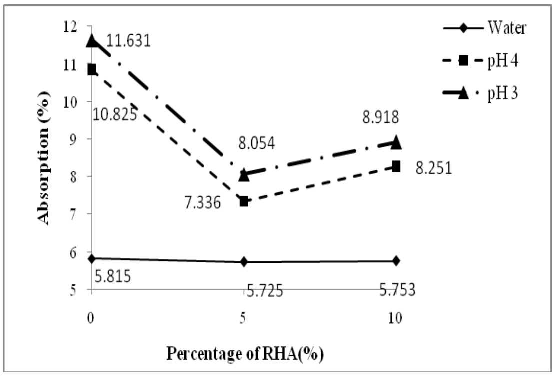

Figure 7. relationship between % RHA and water absorption (90 days)

Fig. 7 shows the water absorption of the specimen after immersion for 90 days. The pattern of water absorption was similar to that of the specimen after immersion for 28 days. Specimen with 5% RHA had the lowest water absorption, both in normal water and acid solution immersion. The difference lies only in the magnitude of reduction in water absorption for each test specimen.

The effect of RHA percentage to $Ca(OH)_2$ and gypsum levels in all environments (normal water, pH 4 and pH 3), is presented in Fig. 8 and Fig. 9. Broadly speaking, both normal and acidic water environment showed similar graphs, the only difference was the magnitude.

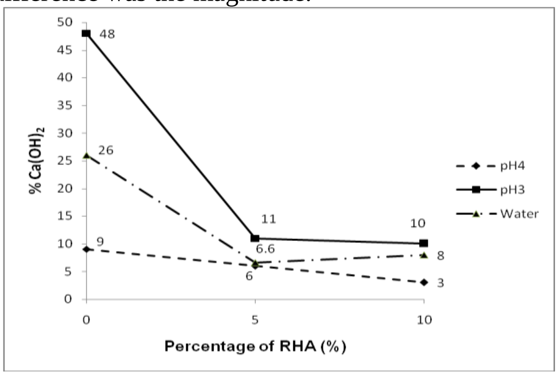

Figure 8. relationship between % RHA and % $CaOH)_2$ (90 days)

Fig. 8 shows that immersion in pH 4 environment caused a decrease in $Ca(OH)_2$ level compared to the level in test specimen without RHA. But immersion in pH 3 environment (more acid) caused an increase in $Ca(OH)_2$ level compared to the level in test specimen without RHA. Basically, the use of RHA was intended to reduce $Ca(OH)_2$ level in the concrete. Then by immersing in acid solution, it was expected to decrease the $Ca(OH)_2$ level, as it reacted with acid. This is what happened on the test specimen immersed in a solution of pH 4.

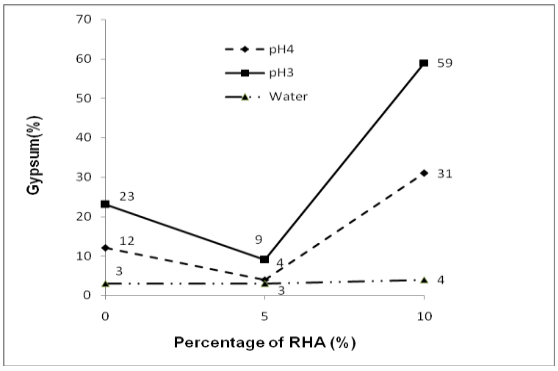

Figure 9. relationship between % RHA and % $CaOH)_2$ (90 days)

Conditions during the immersion in pH 3solution should further reduce the $Ca(OH)_2$ level, but this is not the case. This condition can occur if the gypsum (the result of the reaction of $Ca(OH)_2$ and acid) further reacts with calcium hydrate alumina and generates a new compound and $Ca(OH)_2$. The presence of $Ca(OH)_2$ in this continuous reaction caused a higher $Ca(OH)_2$ level.

Fig. 9 shows that immersion in an acidic environment causes an increase in gypsum level, only differ in magnitude. This can occur because gypsum is a product of concrete in an acidic environment, and therefore it is obvious gypsum level is greater when compared to normal aquatic environment.

3.4. Durability Model of Concrete

The proposed model is a function of polynomial equation that has two variables. Function with two variables, x and y, is generally expressed in the form *z = f(x,y)*. Graph of function z is a curve surface or blanket and the base is z-y plane. Thus, the values of z lie on the surface. If this is converted to the condition in this study, we can conclude that the compressive strength and the modulus of rupture are the function z. Meanwhile the two variables are the percentage of RHA (y) and the duration of immersion (x).

To compare the strength and rupture modulus deterioration trend of the concrete specimen immersed in acid solutions (Table 2), relative strength and rupture modulus variation ratio are defined as equation (1) and (2) :

$$ID_{fc} = \frac{fc_{a,t}}{fc_{n,28}} \quad (1)$$

$$ID_{fr} = \frac{fr_{a,t}}{fr_{n,28}} \quad (2)$$

where ID_{fc} is the relative strength degradation ratio of compressive strength for deteriorated concrete specimen, $fc_{a,t}$ is the compressive strength for concrete exposed to the acid solution for t days; and $fc_{n,28}$ is the compressive strength of control specimens cured in water at 28 days. ID_{fr} is the relative rupture modulus degradation ratio of rupture modulus for deteriorated concrete specimen, $fr_{a,t}$ is the modulus of rupture for concrete exposed to the acid solution for t days; and $fc_{n,28}$ is the modulus of rupture of control specimens cured in water at 28 days.

Table 2. Durability Ratio of Mechanical Properties

No.	x	y	z	
	%RHA	Immersed Time (day)	ID_{fc}	ID_{fr}
1	0	0	1.00	1.00
2	0	28	0.84	0.82
3	0	90	0.76	0.79
4	5	0	1.27	1.01
5	5	28	0.99	0.94
6	5	90	0.95	0.91
7	10	0	1.03	0.93
8	10	28	0.82	0.78
9	10	90	0.74	0.69

R2013a Matlab program was used to assist the establishment of each function z, followed by the depiction of surface shape. The results revealed that the shape of the model was a polynomial equation with each of the x and y direction in order 2, as in equation 3 and equation 4, where a is the percentage of RHA (%) and t is duration of immersion (days)

$$ID_{fc} = 1.024 + 0.0835a - 0.0096t - 0.0082a^2 - 0.00005at + 0.00007t^2 \quad (3)$$

$$ID_{fr} = 0.9917 + 0.026a - 0.0073t - 0.0034aa^2 + 0.0002at - 0.00006t^2 \quad (4)$$

Thus, in order to find the effect of independent variables on the dependent variables, the determinant coefficient value (R^2) was measured. Because independent variables consisted of two variables, it is important to note the *Adjusted Rsquare* which value is always smaller than R^2. Table 3 shows the results of the above values. The Standard Error of Estimate (SEE) value was used to determine the accuracy of the model in predicting the dependent variable.

Tabel 3. The values of R^2, adj. R^2 dan SEE

ID	R^2	Adj. R^2	SEE
Compressive Strength	0,9845	0,9586	0,0034
Modulus of Rupture	0,9410	0,8426	0,0034

The model for compressive strength has Adj. R^2 value of 0.9586, which it means that 95.86 % variation in compressive strength could be explained either by the percentage of RHA or duration of immersion (simulated acid rain). The remaining 4.14 % should be explained by other causes. SEE value of 0.0034 indicates that the model is able to clearly explain the correlation. Then for a model of rupture modulus, the condition is similar to that of compressive strength. 94.10% of variation in rupture modulus could be explained either by the percentage of RHA or duration of immersion (simulated acid rain), while the remaining 5.90 % should be explained by other causes. SEE value of 0.0034 indicates that the model is able to clearly explain the correlation.

IV. CONCLUSION

This study concludes that :

1. The use of 5% rice husk ash gives a positive impact on the mechanical characteristic of concrete exposed to acid rain, because it has been proved to have the highest relative degradation ratio (compressive strength and flexural strength).
2. The use of 5 % rice husk ash gives a positive impact on the microstructure properties of concrete exposed to acid rain, because it has been proved to have the smallest water absorption, the least amount of gypsum and $Ca(OH)_2$.
3. Model for durability of concrete with rice husk ash as a cement substitution exposed to acid rain is created using polynomial equation with two variables; the percentage of rice husk ash and duration of immersion.

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