



## MECHANICAL PROPERTIES OF GEOPOLYMER PRODUCED BY RICE HUSK ASH CALCINED AT LOW TEMPERATURE

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### Abstract

Geopolymer is produced by the geopolymerization of the raw mixtures with high silica, alumina, calcium, and the alkali solution. However, it has deficiencies, such as the high heat release at the early age, high shrinkage, and strength reduction. In view of these issues, this study explored the geopolymer produced by replacing some portion of the slag by the rice husk ash (RHA) calcined at 400 °C. It is hoped to improve the mechanical properties of the geopolymer, resolve the problems of the treatment, and increase the practical application values of the waste rice husks. During the study, the mixing alkali activator was prepared by the sodium hydroxide and the sodium silicate (water glass) at various ratios and the liquid to the solids ratio was maintained at 0.6. Results showed that the ratio of the sodium hydroxide to the water glass influenced the compressive strengths. By replacing the slag with the 10% and 20% RHA, the compressive strength was reduced, and such results were attributed to the high silica content of the RHA, leading to excess silica in the resulting geopolymer. With optimization of the ratio of the sodium hydroxide to the water glass by the total silica content, the RHA effectively increased the strength. At 28 days, the 10% RHA even induced compressive strength higher than the plain.

### Keywords:

Low-temperature calcination; Rice husk ash; Geopolymer; Compressive strength; Slag

## 1 INTRODUCTION

The Portland cement is the most cementitious material used in civil engineering and its manufacturing process is always an environmental concern due to the carbon dioxide release and the energy consumption. To reduce the cement use, many kinds of alternative admixtures and binders have been developed to partially or fully replace the cement. The pozzolanic materials such as the fly ash, silica fume, and ground granulated blast-furnace slag (GGBS) are popular admixtures. They have high silica and alumina contents so that they are able to react with the  $\text{Ca}(\text{OH})_2$  in the hydrated cement and form C-S-H or C-A-H gel, improving the strength and durability of concrete.

The rice husk ash (RHA) is also a kind of pozzolanic material and it is produced from calcining the rice husk, in which most of the inorganic matters are amorphous  $\text{SiO}_2$ . By calcination, such  $\text{SiO}_2$  turns into crystalline. The calcination temperature is critical to the forms of  $\text{SiO}_2$ . It was reported that the crystalline  $\text{SiO}_2$  formed when the calcining temperature was above 500 °C [Onojah 2013]. The RHA was highly reactive when there was abundant oxygen during the calcination at 500-680 °C for a long time, [Mehta 1978]. By X-ray diffraction analyses (XRD), as the calcining temperature is increased, the light oxides are released, such as the sodium, sulfur, calcium, and magnesium, leaving the increased  $\text{SiO}_2$ , [Hwang 1989]. It was also found that the

calcining temperature at least 402 °C or above was required for the RHA to show  $\text{SiO}_2$  by removing the organic matters [Jose 1986]. Sufficient oxygen, time, and grinding time longer than 60 min. was suggested to produce RHA with good performance [Zain 2011]. When the calcining temperature was lower than 300 °C and the calcining time was shorter than 6 hours, the carbon inside was not completely removed, leading to high carbon content in the RHA [Nair 2008].

On the other hand, the geopolymer is an amorphous or semi-crystalline material produced by the mixture of the alkali-activating solution with the mineral or industrial wastes containing silicoaluminates. The alkali solution releases the  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  at the surface of the mineral and the additional alkali silicate solution provides the extra  $\text{Si}^{4+}$ , resulting in the polymerization with a three dimensional structure [Van Jaarsveld 1997]. Such geopolymer has high strength [Davidovits 1999; Van Jaarsveld 1997], high fire-resistance [Cheng 2003], and good fixation for heavy metals [Duxson 2007]. It is now drawing much attentions and expected to be a new binder in replacement of the Portland cement in the future. However, it has some deficiencies needed to be overcome. The geopolymerization can be rapid, leading to short setting time, large hydration heat, and lots of thermal cracks [Gebregziabihier 2016]. In the long term, the shrinkage can be high [Bakharev 1999], and the strength can be reduced if excess or high concentrated

alkali-activating solution is added [Xu 2001; Komnitsas 2009].

The RHA contains high silica content, and the reactive silica after calcination participates in the geopolymerization. Therefore, it has been used to produce the geopolymer [Hwang 2015; Chen 2017]. The application of the calcined RHA in the fly ash-based geopolymer was reported to have increased strength and improved durability by reducing the water content [Kusbianoro 2012].

In Taiwan, the japonica rice is the major crop and its production is around 1.27 million tons per year [Kao 2014]. The rice husk is voluminous so its transportation and treatment is always an issue. The rice husks can be used as fertilizers. However, the consumption is limited and most of them are treated as the waste. It is necessary to develop new applications for the rice husk and the production of the geopolymer can be a good candidate. With the growing diverse applications of the geopolymer, it is likely to consume most the rice husks. Although the RHA was reported to produce the geopolymer, the rice husk used in the past studies were calcined at high temperature even more than 1000 °C, implying high-energy consumption for the pretreatment. In view of these issues, this study tries to produce RHA calcined at low temperature of 400 °C, which is close to the ignition temperature in an open-air environment. The residual organic matter in the RHA is expected to be removed by the strong alkali solution and retard the aggressive early geopolymerization.

## 2 MATERIALS AND METHODS

### 2.1 Materials

The RHA was prepared by calcining the rice husk of the japonica rice from I-Lan, Taiwan. Each batch of 900-g rice husk was calcined at 400 °C for 10 hours. The residual ash was ground by a ball mill for 3 hours, and the resulting RHA had a median particle size ( $D_{50}$ ) of 7.8  $\mu\text{m}$  and specific weight of 2.1. The XRD pattern of the RHA shows a great portion of the amorphous silica (Fig. 1).

In this study, the slag-based geopolymer was produced. The slag had specific weight of 2.88 and the specific surface area was 604  $\text{m}^2/\text{kg}$ . The alkali-activating solution was prepared by the NaOH solution and the water glass (WG, sodium silicate ( $\text{Na}_2\text{O}\cdot n\text{SiO}_2$ ) solution). The NaOH solution had a molar concentration of 5 M and the specific weight of 1.2. The water glass had a specific weight of 1.35, modulus ( $n=\text{SiO}_2/\text{Na}_2\text{O}$ ) of 3, and  $\text{SiO}_2$  content of 25.4%.

The chemical compositions of the RHA are summarized in Tab. 1. The RHA had significant amount of Si while the slag had relatively more Al. It should be noted that chemical compositions were determined by X-ray fluorescence (XRF), in which the elements were expressed as oxides. Therefore, the Si could exist in the phases other than the silica.

### 2.2 Mix design

The experimental parameters are summarized in Tab.2. The liquid to solid ratio (w/s) was 0.6 (ml/g). The mix design I was used to explore the optimum NaOH/WG, which induced the highest strength of the slag-based geopolymer at 7 and 28 days in the absence of RHA. The mix design 2 was used to explore the influences of the RHA dosage, which partially replaced the slag by volume. By the results of the mix design II, the optimum

total silica content was obtained, which was used to determine the optimum NaOH/WG in the mix design III.

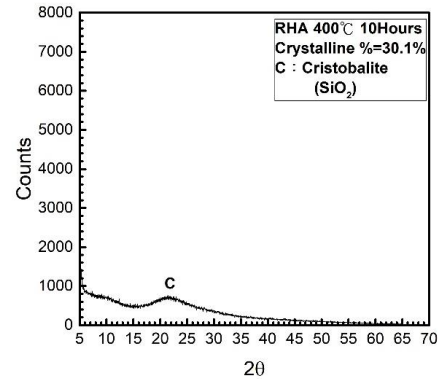


Fig. 1: XRD pattern of the RHA

Tab. 1: Chemical compositions of the slag and RHA

Chemical Oxides	RHA	Slag
$\text{SiO}_2$	76.8%	34.0%
$\text{Al}_2\text{O}_3$	1.4%	13.8%
FeO	0.1%	0.3%
CaO	0.5%	40.1%
MgO	0.5%	7.9%
$\text{SO}_3$	0.7%	0.7%
$\text{K}_2\text{O}$	3.7%	-
$\text{P}_2\text{O}_5$	0.6%	-

Tab. 2: Experimental parameters

Mix Design	Raw materials	RHA dosage	NaOH/WG (by volume)
I	Slag	0%	0-100%
II	Slag, RHA	0%, 10%	20-100%
III	Slag, RHA	10%, 20%	75.3%, 90.6%

### 2.3 Sample preparation

The slag and the RHA were premixed in a Humboldt mortar mixer before the NaOH solution was added. The resulting mixture was mixed at 140 rpm for 3 minutes, followed by the addition of WG and mixed at 285 rpm for another 2 minutes. Cubic specimens of 50 mm $\times$ 50 mm $\times$ 50 mm were casted, demolded after 24 hours, cured in air at 25 °C and 70% RH. The specimens were subjected to the compressive strength test in accordance with ASTM C109 at the desired ages.

## 3 RESULTS AND DISCUSSION

### 3.1 Effect of NaOH/WG

In Mix design I, the NaOH/WG was varied without changing the w/s. Results are shown in Fig. 2. It appears that an optimum ratio around 60% was required to achieve the highest strength at 7 days. In geopolymer, the NaOH is used to activate the slag by releasing the aluminates and silicates from the surface, and the WG is used to supply additional silicates. Therefore, it is likely to have an optimum ratio such that the maximum aluminate and silicate in the slag was released and fully reacted. However, at high ratios, the

long-term strength is reduced at 56 and 91 days (Fig. 3 in 3.2) due to the incomplete reaction. There remains too much unreacted silicates, possibly inducing the expansion.

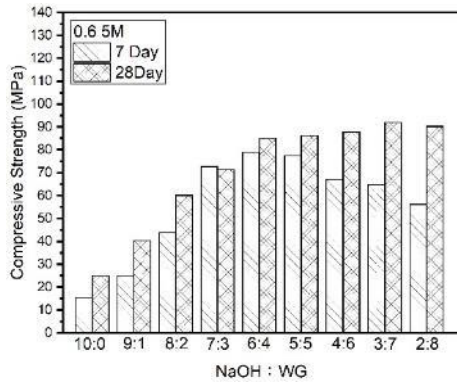
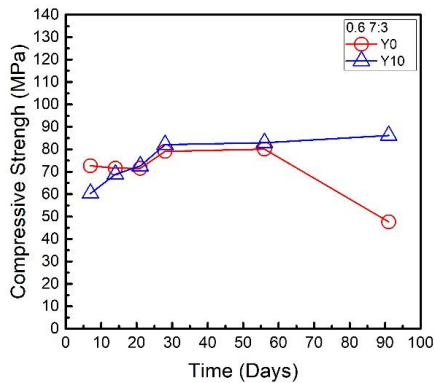


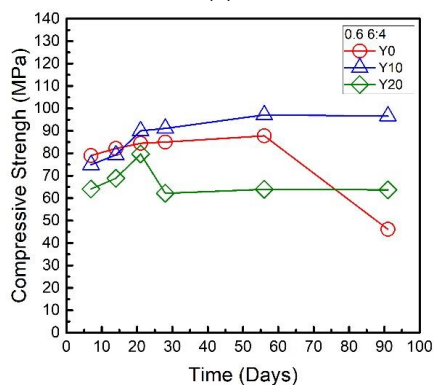
Fig. 2: Relationship between the compressive strength and the NaOH:WG for slag-based geopolymer

3.2 Effect of RHA replacement

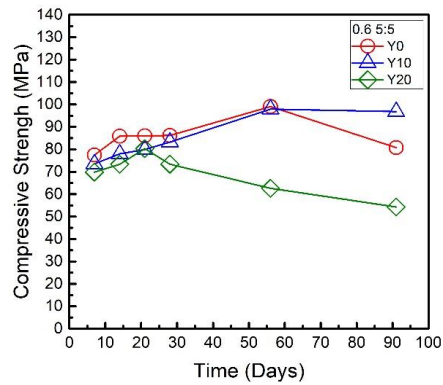
The influence of the RHA on the strength development of the geopolymer at different NaOH/WG ratios are shown in Fig. 3. Without the addition of the RHA, the geopolymer always had a reduced 90-day strength. With the addition of 20% RHA, in general, the strength was further reduced. With 10%, it is surprisingly to observe that the strength was increased and sustained until 90 days even though the early strength at 7 days was low. Such results imply that the 10% RHA mitigated the early severe geopolymerization. It is likely that the ash content in the RHA retarded the release of the silicate. However, with 20%, the strength was much reduced. Since the RHA had much more silicate than the slag, it is proposed that the extra silicate is unfavorable to the strength. Therefore, with addition of the RHA, the mix was later adjusted in consideration of the chemical compositions of the RHA.



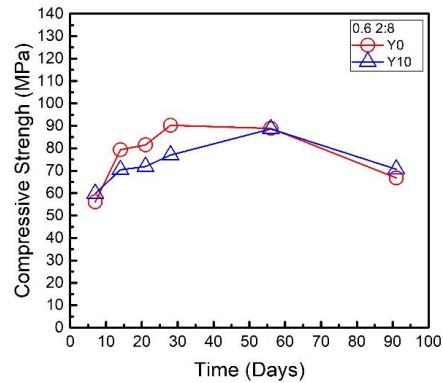
(a)



(b)



(c)



(d)

Fig. 3: Influence of RHA on the compressive strength at NaOH:WG of (a)7:3, (b)6:4, (c)5:5, and (d)2:8.

3.3 Optimum silicate content in geopolymer

The relative amounts of the released silicate and aluminate are critical to the properties of the geopolymer. Since both RHA and slag had Si as the major composition, the mix design of the geopolymer made by mixture of RHA and slag is supposed to be optimized by the total available SiO<sub>2</sub> content. The compressive strength was associated with the total SiO<sub>2</sub> content of the geopolymer weighted by the dosage of RHA and the NaOH/WG solution, as shown in Fig. 4. The highest strength occurred when the SiO<sub>2</sub> was in the range of 24-29%, suggesting that the NaOH/WG should be adjusted to reach the optimum SiO<sub>2</sub> content when the RHA was added. Those results showing low strengths in the presence of RHA in Fig.3 were likely due to excess silica content by the RHA. There was too much SiO<sub>2</sub>, resulting in the poor geopolymerization and the reduced strength. The optimum total SiO<sub>2</sub> content obtained through the mix design I, i.e. no RHA addition and NaOH:WG=6:4, was around 24.1%. The calculation is provided in Tab. 3 by assuming that the weight of the slag is 1 g for example.

After the RHA dosage was set (10%, 20%), the required SiO<sub>2</sub> from the WG was calculated through the optimum total SiO<sub>2</sub> content minus the SiO<sub>2</sub> provided by the RHA so the amount of the WG was determined.

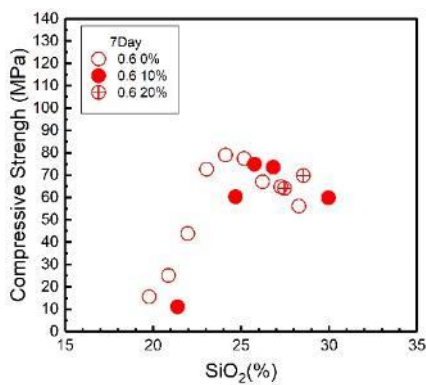
The resulting NaOH: WG was 7.53:2.47 and 9:06:0.94 for the RHA dosages of 10% and 20% (Mix design III). Since the RHA had much more SiO<sub>2</sub> than the slag, the WG dosage was decreased by the increase of the RHA dosage.

The results of the optimized mix design are shown in Figs 5(b) and (c). With 10% RHA, the optimized mix (Fig. 5(b)) had a higher strength than the plain. Without the optimization, the strength was lower than the plain

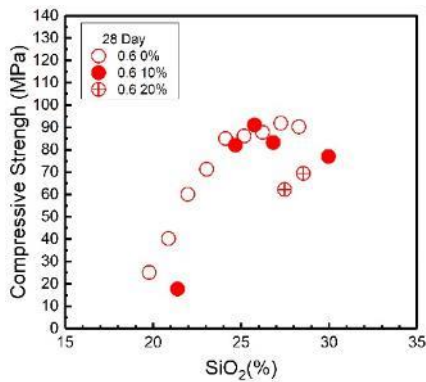
before the age of 28 days (Fig 5(a)). With 20% RHA, the strength difference between the mix and the plain (Fig 5(c)) was much smaller than those without optimization (Fig 5(a)). In addition, the strength in the mix with RHA was increased more than the plain. It appears that the addition of RHA helped to improve and sustain the strength of the geopolymer.

Tab. 3: Optimum total SiO<sub>2</sub> content for the mix design I

	Slag	NaOH	WG	Total
Weight (g)	1	1(g)×0.6(ml/g) ×60%×1.2 =0.432(g)	1(g)×0.6(ml/g) ×40%×1.35 =0.324(g)	1+0.432 +0.324 =1.756(g)
SiO <sub>2</sub> (g)	1(g)×34% =0.34(g)	-	0.324(g)× 25.7% =0.083(g)	0.34+0.083=0.423(g)
SiO <sub>2</sub> (%)				0.423/1.756 ×100% =24.1%

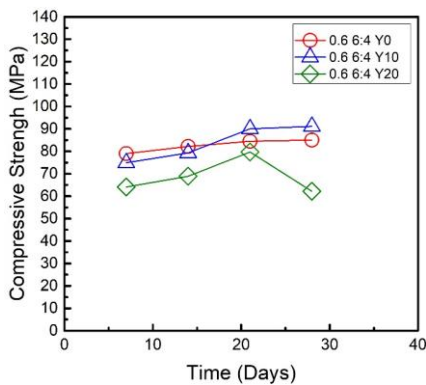


(a)

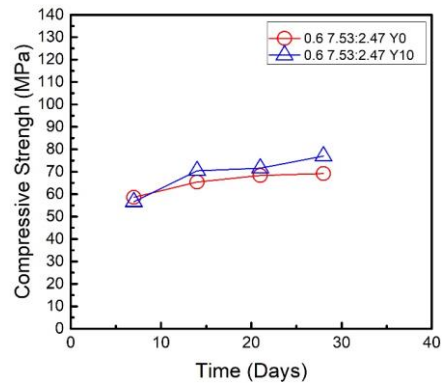


(b)

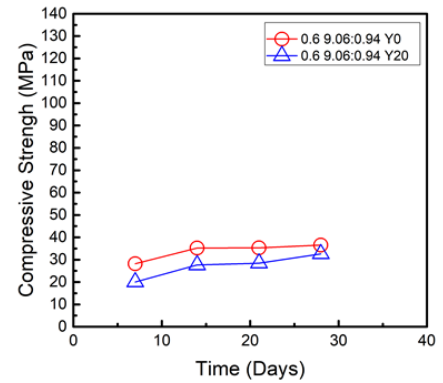
Fig. 4: Relationship between the compressive strength and the SiO<sub>2</sub> content at (a) 7days, or (b) 28 days.



(a)



(b)



(c)

Fig. 5: Influence of RHA dosage on the compressive strength at (a) NaOH:WG=6:4, and 10% or 20% RHA, (b) NaOH:WG=7.53:2.47 and 10% RHA, and (c) NaOH:WG=9.06:0.94 and 20% RHA.

#### 4 CONCLUSION

This study explored the application of the RHA in the production of the geopolymer. Results showed that the total SiO<sub>2</sub> content was critical to the strength development. The optimum NaOH:WG at liquid-solid ratio of 0.6 was 6:4, which is equivalent to the total SiO<sub>2</sub> content of 24.1%. With the addition of the RHA, the NaOH:WG should be adjusted accordingly to reach the optimum total SiO<sub>2</sub> content. After that, the strength of the mix with RHA addition was increased and sustained more than the plain.

#### 5 ACKNOWLEDGMENTS

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