The Effect of Acid Type in Mechanochemical Treatment of Rice Husk Ash for Concrete Application

J F Fatriansyah¹,*, S A Khairunnisa¹, D Dhaneswara¹, M Z Rahmatullah¹, B A Ramadhan¹

¹Metallurgical and Materials Engineering, Faculty of Engineering, Universitas Indonesia, Depok, Jawa Barat 16424

*Corresponding author: jakafajar@ui.ac.id

Abstract. Concrete was successfully produced using rice husk ash (RHA) as a partial cement substitute. RHA was mechanochemically treated using ball mill as mechanical force and acids (HCl and CH₃COOH) as chemical force. Mechanochemical treatment decreases particle size as demonstrated by particle size analyser test and reduces crystallinity of RHA as demonstrated by X-ray diffraction analyses. These characteristics make RHA more suitable as partial substitution of cement as well as pozzolanic material. The compressive strength of concrete increases 11-26 % by addition of RHA as cement substitution. The significant increase of compressive strength was obtained from RHA mechanochemically treated with HCl which has compressive strength of 14.8 MPa in comparison of standard concrete which has compressive strength of 11.72 MPa.

1. Introduction
Indonesia is an agricultural country which in 2017 produced paddy around 81 million tonnes [1]. Around 20 % of the total paddy production went as agricultural wastes. One of the agricultural wastes is rice husk. The rice husk contains 22% of silicon oxide (silica), 35 % carbon, 5% hydrogen, 36 % oxygen and the rests are nitrogen and sulphur [2]. Approximately for every ton of rice husk burning, around 0.19 ton of rice husk ash is produced [3]. This rice husk ash has greyish colour to white colour after complete burning. The burning process increases its silica content up to 90 % [3]. In addition, burning process below controlled temperature of 800 °C produces rice husk ash in its amorphous form [4]. Silica can be used as raw material for mesoporous silica, silicon carbide, silicon tetrachloride, pure silicon and zeolites even for hydrogen adsorption as shown in simulation [5–10].

Mechanical method using ball mills can be used to reduce the size of particles for example carbon [11–13] and amorphous silica grain/particle size [14]. Higher surface area of rice husk ash has high reactivity as active mineral mixing material for example as concrete mixing material [15]. The addition of rice husk ash in concrete increases compressive strength and impermeability of ultra-high-performance concrete (UHPC) due to silicas fine porous structure [16, 17]. Partial substitution of rice husk ash in Portland cement increases its working ability and mechanical durability on the economical point of view in construction industry [18–20]. In addition, substitution of some fraction in cement with rice husk ash can increase strength of concrete [4, 21- 24]. In this paper, we studied the effect of mechanochemical (mechanical plus chemical) treatment using ball mill as mechanical force and acids as chemical force in rice husk ash on mechanical properties of concrete produced partially using rice
husk as cement substitution. We suggested that the mechanochemical treatment on rice husk ash (RHA) can enhance mechanical properties of concrete.

2. Experimental Methods

2.1 Sample
Rice husk was obtained from paddy mills industry in Leuwiliyang area, West Java - Indonesia. HCl and CH\textsubscript{3}COOH was purchased from Mallinckrodt Pharmaceuticals and Emsure, respectively, and they were used without any further purification.

2.2 Preparations
Rice husk ash was dried under the sun for 8 hours to reduce water content. Dried rice husk was then burnt in a furnace for 5 hours at 700 °C resulting in a white powder. The white powder of RHA then mixed with 1M HCl with 10% w/w and ball milled with vertical planetary ball mill. In addition, the other sample of RHA powder was mixed with CH\textsubscript{3}COOH with 10% w/w and ball milled with vertical planetary ball mill. The speed of ball mill was set to 20 rpm within 15 minutes. In total, there were 3 samples, RHA without ball mill and acid treatment (X), RHA milled with CH\textsubscript{3}COOH (Y), and RHA with HCl (Z). The labelling of the samples is shown in Table 1.

| Name | Treatment                                      |
|------|------------------------------------------------|
| X    | RHA without ball mill and acid                |
| Y    | RHA milled with ball mill and CH\textsubscript{3}COOH addition |
| Z    | RHA milled with ball mill and HCl addition    |

Concrete was made by mixing cement, water, fine aggregates and coarse aggregates. Three RHA samples were added in modified concretes with the concentration of 10% of cement mass before RHA added. The detail of composition is shown in Table 2.

| Concrete types | RHA (g) | Cement (g) | Fine aggregates (g) | Coarse aggregates (g) | Water (g) |
|----------------|---------|------------|---------------------|----------------------|-----------|
| Concrete A     | 0       | 354.550    | 693.63              | 1007.34              | 195       |
| Concrete X     | 35.455  | 319.095    | 693.63              | 1007.34              | 195       |
| Concrete Y     | 35.455  | 319.095    | 693.63              | 1007.34              | 195       |
| Concrete Z     | 35.455  | 319.095    | 693.63              | 1007.34              | 195       |

The concrete was made with the composition as detailed in Table 2. All of materials were mixed and water was added slowly in order to bind all of materials. Mixed material was then poured in concrete mould and stand at room temperature for 1 day, followed by preserve it in water for 28 days.

2.3 Characterization
RHA composition was determined using X-Ray Fluorescence (XRF) (Panalitycal Epsilon). The size of RHA particles were measured using Particle Size Analyzer (PSA) (Nanoplus Particulate Systems). Concrete compressive strength was measured in civil engineering laboratory of Universitas Indonesia.

3. Results and Discussion
First, RHA compositions were obtained using XRF. The results were presented in Table 3. Table 3 shows that silica content in RHA is 88.13 %. This result shows that burning temperature of 700 °C is
suitable to reduce impurity in RHA. High silica content is important to improve concrete strength as well as a pozzolan material.

Table 3. RHA compositions measured using XRF.

| Compound | Concentration (%) |
|----------|-------------------|
| SiO$_2$  | 88.13             |
| K$_2$O   | 4.14              |
| Fe$_2$O$_3$ | 2.32            |
| P$_2$O$_5$ | 1.69             |
| MgO      | 1.55              |
| CaO      | 1.70              |
| Cl       | 0.37              |
| Ag$_2$O  | 0.12              |
| Total    | 100               |

The effect of mechanochemical treatment on particle size is shown in Table 4. The particle sizes were determined by PSA for all RHA samples. It is demonstrated that the addition of acids along mechanical treatment can reduce the size of RHA particles significantly. The decrease of particle size is plummeted for the addition of strong acid HCl in which the mean size of particles was reduced from 42.00 $\mu$m (concrete X) to 27.36 $\mu$m (concrete Z).

Table 4. PSA results of RHA samples.

| Concrete | Particle mean size ($\mu$m) |
|----------|----------------------------|
| X        | 42.00                      |
| Y        | 32.85                      |
| Z        | 27.36                      |

XRD results are shown in Figure 1 for all samples. The effect of mechanochemical treatment on particle crystallinity is shown in Table 5. All of RHA samples show almost identical diffraction pattern with one broadening peak with the centre around 22 degrees. This shows the characteristics of amorphous silica. However, the diffraction peak shows that all of the samples are not completely amorphous. Thus, the degree of crystallinity index needs to be quantified which can be calculated based on Equation 1 as follows

$$CI (%) = \frac{I_c - I_{am}}{I_c} \times 100, \quad (1)$$

where CI (%) is the crystallinity index, $I_c$ is the maximum diffraction intensity and $I_{am}$ is the amorphous index of crystallinity intensity. The crystallinity index of all samples calculated from Eq. (1) is presented in Table 5. Table 5 shows that the mechanochemical treatment reduces the crystallinity index of RHA. According to Akasaki et al. [22], more amorphous material has pozzolanic activity than less amorphous material. High pozzolanic activity is desired for the cement substitution application. Thus, it is expected that the mechanochemically treated samples are more suitable as cement substitution in comparison with untreated RHA.
The mechanical strength specifically measured in this work is compressive strength. The results are shown in Table 6 and Figure 2. Figure 2 shows that the substitution of RHA as pozzolanic material for cement in concrete yields higher compressive strength than that of unsubstituted concrete. Sample Z, which uses HCl, shows maximum compressive strength. It is suggested that smaller particle size and smaller crystallinity index resulting in higher compressive strength. Smaller particle size produces higher pozzolanic activity due to ability of smaller particles to fill empty space in concrete. Thus, it strengthens surrounding bonding as RHA transform into calcium silicate as a good binder after water addition. In addition, high crystallinity index in RHA shows low pozzolanic component inside because crystalline silica is not pozzolanic thus calcium silicate cannot be formed. As a result, low crystallinity index produces more calcium silicate as binder which in turn increase compressive strength of concrete. However, the fact that HCl treatment produces better result than that of CH₃COOH treatment is not yet understood. It is proposed that HCl produces smaller particle size due to stronger acidity nature in comparison with CH₃COOH thus increase the pozzolanic activity of RHA. The compressive strength of concrete increases 11-26 % by addition of RHA as cement substitution.

| Table 6. Compressive Strength of Concrete. |
|-------------------------------------------|
| Concrete | Compressive strength (Mpa) |
|-------------------------------------------|
| Standard concrete | 11.72 ± 0.42 |
| X | 13.03 ± 0.37 |
| Y | 12.92 ± 0.38 |
| Z | 14.8 ± 0.32 |
4. Conclusion
The mechanochemically treated RHA with ball mill and acids has been synthesized. The RHA was used as a cement substitution of concrete. Mechanochemically treated RHA shows smaller particle size and crystallinity index which is potential as pozzolanic material. The compressive strength of concrete increases 11-26% by addition of RHA as cement substitution. The significant increase of compressive strength was obtained from RHA that mechanochemically treated with HCl with a compressive strength of 14.8 MPa (26% higher than that of the standard concrete).

References
[1] Central Bureau of Statistics 2013 Keadaan Ketenagakerjaan (Jakarta: Central Bureau of Statistics)
[2] Nornikman H and Soh P J 2008 Progress in Electromagnetics Research 104 pp 145-166
[3] Sandhu R K and Siddique R 2017 Construction and Building Materials 153 pp 751–764
[4] Habeeb G A and Mahmud H Bin 2010 Materials Research 13(2) pp 185–190
[5] Sun L and Gong K 2001 Ind. Eng. Chem. Res 40 pp 5861 – 5877
[6] Dhaneswara D, Fatriansyah JF, Putranto DA, Utami SA, Delaoyri F. 2018 IOP Conference Series: Materials Science and Engineering Vol. 285 No. 1, p. 012032
[7] Fatriansyah J F, Dhaneswara D, Abdurrahman M H, Kuskendrianto F R, Yusuf M B. 2019 IOP Conference Series: Materials Science and Engineering 2019 Vol. 478 No. 1, p. 012034
[8] Dhaneswara D, Siti Agustina A A A, Putranto D A, Delaoyri F and Fatriansyah J F. 2018 IOP Conf. Series: Journal of Physics: Conf. Series 1011 012017
[9] Dhaneswara D, Fatriansyah J F, Wardana A K, Haqoh A N, Khairunnisa S A. 2019 IOP Conf. Series: Materials Science and Engineering 547 012032
[10] Dhaneswara D, Fatriansyah J F, Yusuf M B, Abdurrahman M H, Kuskendrianto F R. IOP Conf. Series: Materials Science and Engineering 547 012038
[11] Fatriansyah JF, Matari T, Harjanto S 2018 Materials Science Forum Vol. 929, p 50-55
[12] Fatriansyah JF, Dhaneswara D, Khairunnisa S A, Kusumawardhani D. 2019 IOP Conf. Series: Materials Science and Engineering 547 012034
[13] Harjanto S, Fatriansyah J F, Noviana L N, Yunior SW 2018 International Journal of Technology 9(5) pp 993-1005.
[14] Do J L and Friščič T 2017 ACS Central Science 3(1) pp 13–19
[15] Wang W, Meng Y and Wang D 2017 Kemija u Industriji 66(3–4) pp 157–164
[16] Huang H, Gao X, Wang, H and Ye H 2017 Construction and Building Materials 149 pp 621–628

Figure 2. Compressive strength of concrete with the RHA substitution.
[17] Zareei S A, Ameri F, Dorostkar F and Ahmadi M 2017 *Case Studies in Construction Materials* **7** pp 73–81

[18] Yalçin N and Seviç V 2001 *Ceramics International* **27**(2) pp 219–224

[19] Chopra D, Siddique R, Kunal 2015 *Biosyst. Eng.* **130** pp 72–80

[20] Chatveera B, Lertwattanaruk P 2011 *J. Environ. Manag.* **92** pp 59–66.

[21] Gosalvitr C, Srinophakun P, Kanchanapiya P and Danwittayakul S 2015 *Proceedings of the International Conference on Biological, Environment and Food Engineering (BEFE-2015)* pp 15-16.

[22] Akasaki J, Tashima M, Da Silva C A, Da Silva E, Barbosa M and Paya J 2005 *Congreso Nacional de Materiales Compuestos* 5

[23] Dhaneswara D, Fatriansyah J F, Kusumawardhani D P, Khairunnisa SA 2019 *IOP Conference Series: Materials Science and Engineering* **578** (1), 012063

[24] Fatriansyah J F, Dhaneswara D, Khairunnisa SA, Kusumawardhani D P, 2019 *IOP Conference Series: Materials Science and Engineering* **547** (1), 012034