



**PHYSICOCHEMICAL PROPERTIES AND POZZOLANIC
PERFORMANCE OF ULTRAFINE TREATED RICE HUSK ASH
(UFTRHA) AS ADDITIVE IN CONCRETE**

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Abstract

Rice husk ash (RHA) contains high amount of amorphous silica that is ubiquitous in the pozzolanic reaction of SCM in concrete. However, usage of conventional RHA is currently unfavourable in concrete industry due to its properties inconsistency. In this regard, improvement on the RHA properties by introduction of thermochemical pre-treatment prior to burning procedure is seen as an excellent way to reach the goal. In this paper, raw rice husk was pre-treated using 0.1N hydrochloric acid (HCl) and heated at 80°C. It was then mechanically activated by high energy planetary ball mill for 15 minutes at speed of 300rpm and ball-to-powder ratio (BPR) of 15:1. The chemical composition, mineralogical properties, particle size analysis, specific surface area as well as microstructure properties of ultrafine treated rice husk ash (UFTRHA) were determined accordingly. As for amorphous silica content of the optimum sample was recorded as 98.60% incinerated at 600°C with four hours of pre-treatment soaking duration. In terms of particle size and specific surface, it was also observed that, burning temperature of 600°C, pre-treated at four hours were recorded to produce finest size of UFTRHA where d(0.1), d(0.5) and d(0.9) were obtained as 1.416 µm, 4.364 µm and 14.043 µm respectively. Largest specific surface area value was obtained at 219.58 m²/g with the similar pre-treatment conditions. Meanwhile, the strength activity of UFTRHA from the optimum pre-treatment process was measured by testing the compressive strength of mortars. The highest compression value obtained was 50.17MPa with 3% UFTRHA replacement at 28 days.

Keyword: Ultrafine Treated Rice Husk Ash (UFTRHA), concrete additive material, rice husk ash, physicochemical, high energy grinding

INTRODUCTION

In current research trend, most researchers have promoted green technology application widely. This phenomenon encourages recent explorations of the application of additive materials in concrete industry. Additive materials are commonly used in concrete as admixtures to enhance its properties and also to promote greener concrete production. Rice husk ash (RHA) is regarded as one of concrete additive materials due to its high silica content. Production of RHA is done via thermal activation, which involves burning process of the rice husk from agricultural waste.

Rice plant is a type of plant that has the ability to absorb silica content from soil. The absorbed silica eventually assimilates into the plant structure during its growth. Therefore, the outer part, which is the rice husk, possesses high silica content with value of more than 80% (Juenger & Siddique, 2015). Approximately 1,000 million tons of rice are annually produced in the world, which usually leaves about 400 million tons of rice husks as waste material (Food Agriculture Organization (FAO), 2015). Hence, the potential of producing ash from husk is about 100 million tons per annum. Therefore, utilizing RHA in concrete is possible. Furthermore, high content of amorphous silica and high specific surface area (SSA) of RHA are possible to be achieved by adopting suitable burning condition (Mehta & Monteiro, 2006). Thus, incorporation of RHA in concrete production promotes environmental as well as economic relief. Compared to other additive types such as silica fume (SF) and fly ash (FA), RHA is proven to have greater reaction with portlandite (Ca(OH)_2) in pozzolanic reaction, contributes towards increment in compressive strength value and durability of high performance concrete (Feng, Yamamichi, Shoya, & Sugita, 2004; Salas, Delvasto, de Gutierrez, & Lange, 2009; Van, Rößler, Bui, & Ludwig, 2013) and ultra-high performance concrete as well (Van, Rößler, Bui, & Ludwig, 2014a; . Van, Rößler, Bui, & Ludwig, 2014b; Van Tuan, Ye, Van Breugel, & Copuroglu, 2011; Van Tuan, Ye, Van Breugel, Fraaij, & Bui, 2011).

In order to ascertain high amount of amorphous silica content from rice husk, metal impurities i.e. potassium and magnesium that encapsulate the rice husk surface should be removed. Elimination of these metal impurities is possible through thermochemical pre-treatment process using inorganic acid i.e. hydrochloric acid (HCl) and nitric acid (HNO_3) (Park, Salas, Chung, & Lee, 2014; Salas et al., 2009; Vayghan, Khaloo, & Rajabipour, 2013). The thermochemical pre-treatment process is able to reduce the sensitivity of RHA towards burning temperature (Feng et al., 2004). Therefore, in this paper, the main focus is to examine the optimum physicochemical attributes of treated RHA produced precisely.

METHODOLOGY

Ultrafine Treated Rice Husk Ash (UFTRHA) Pre-treatment Process Flow

Raw rice husk was obtained from local rice factory (BERNAS) located in Sungai Rangan, Perak. Prior to incineration procedure, the rice husk was treated with 0.1N analytical grade (A.G.) hydrochloric acid (HCl). The specimens were soaked and heated at 80°C in the acid solution. After completion of pre-treatment process, the samples were washed using distilled water until its neutral pH obtained and dried using laboratory oven at 110°C. It was then burned by using conventional furnace in laboratory. The burning process was done at 600°C, 700°C and 800°C with 1 hour retention time. The ultrafine treated rice husk ash (UFTRHA) was then ground using planetary ball mill for 15 minutes with ball-to-powder ratio (BPR) of 15:1 and rotation speed at 300rpm.

Physicochemical Characteristic of (UFTRHA)

In this study, chemical composition of UFTRHA prepared at various burning temperatures was examined using X-ray fluorescence (XRF) test. The test was done for UFTRHA sample that undergone pre-treatment in 0.1N HCl solution at 80°C. The analysis was done by using spectrometer of Bruker Axs S4 Pioneer. The test was in compliance with BS EN 12677. As for mineralogical properties determination, X-Ray diffraction (XRD) analysis was done accordingly. This test was conducted using Bruker Axs D8 Advance X-Ray Diffractometer instrument.

Brunnet emmet teller (BET) nitrogen adsorption test was done to examine particle specific surface area of the ground UFTRHA powder. The test was completed with degassing temperature of 300°C using surface area and pore analyser model micromeritics ASAP 2020. Meanwhile, particle size analysis (PSA) was done using Malvern instrument mastersizer, model Scirocco 2000.

Pozzolanic / Strength Activity Index

In order to ensure that the UFTRHA is a reactive pozzolan, it is vital to conduct strength activity index test. Thus, this test was completed in accordance to ASTM C311-98b specifically for ordinary Portland cement (OPC) mortar (ASTM, 2016). The mortars were prepared by blending OPC with the highest SiO₂ content of UFTRHA at 20% replacement level. The strength activity index was calculated as the following equation:

$$\text{Strength Activity Index (SAI)} = (B/A) \times 100$$

*Where B is the compressive strength value of blended cement at 20% replacement level; A is the compressive strength of control mix

RESULTS AND DISCUSSION

Chemical Composition of UFTRHA

Based on the experimental result, it can be observed that the predominant content of rice husk ash is silica (SiO_2). In addition, the SiO_2 composition in UFTRHA incinerated at 600°C has highest value among other samples that were prepared at 700°C and 800°C . According to the XRF analysis result, the SiO_2 content in UFTRHA sample produced at 600°C increased with percentage values of 1.62% and 8.82% as compared to the samples extracted at 700°C and 800°C respectively. This finding also indicate that the ideal burning temperature to produce UFTRHA is 600°C . The chemical composition determination of UFTRHA, X-Ray Fluorescence (XRF) data is summarized in Table 1.

In addition, the amount of alkali metal oxides i.e. sodium oxide (Na_2O), magnesium oxide (MgO), calcium oxide (CaO) and potassium oxide (K_2O) contents at all three different burning temperatures were obtained less than 1%. Less in amount of these metallic impurities is vital to enhance the purity of silica extracted from rice husk. By lowering the content of these metallic oxides, especially potassium and sodium, surface melting of SiO_2 particles can be reduced effectively. The surface melting of SiO_2 phenomenon will accelerate early crystallization of amorphous SiO_2 into cristobalite as suggested by several researches in this area (James & Subbarao, 1986; Kalapathy, Proctor, & Shultz, 2001; Krisnarao & Godkhindi, 1992; Real, Alcalá, & Criado, 1996).

Table 1: Chemical composition of UFTRHA treated for 4 hours at various burning temperature

Chemical composition	Chemical content of UFTRHA using 0.1N HCl with soaking duration at 4 hours (%)		
	600°C	700°C	800°C
CC			
SiO_2	98.60	97.00	89.90
P_2O_5	0.53	1.63	1.48
Fe_2O_3	0.06	0.25	6.62
CaO	0.36	0.46	0.48
Al_2O_3	0.13	0.09	-
K_2O	0.06	0.11	-
Na_2O	-	-	-
MgO	-	-	0.89
MnO	-	-	0.24
SO_3	-	-	-
Cl	-	-	-
ZrO_3	0.22	0.25	0.12

Minerological Characteristics of UFTRHA

Amorphousness and crystallinity degree of a material can be determined using the X-Ray diffraction analysis. This analysis was also utilized to determine

mineral presence in the tested material. Figure 1 illustrates the XRD patterns of UFTRHA incinerated at 600°C, 700°C and 800°C respectively.

Based on the XRD analysis, it was noted that all samples of UFTRHA prepared at all temperatures variation i.e. 600°C, 700°C and 800°C were amorphous and without the presence of high intensity peaks. Hence, it is proven that sensitivity towards burning temperature has been eliminated by removing impurities on the surface of the raw rice husk via the pre-treatment process prior to incineration stage. Amorphous state of silica content is vital in order to produce high quality additive material in concrete industry application.

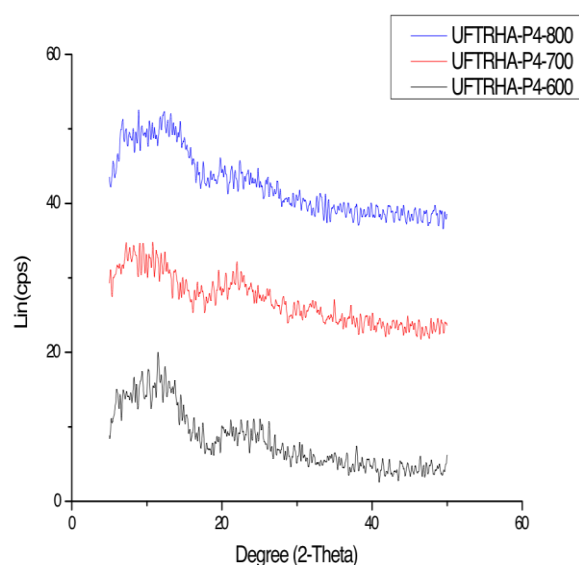


Figure 1: XRD patterns of UFTRHA incinerated at 600°C, 700°C and 800°C respectively

Physical Properties of UFTRHA

Among many of the feasible methods to be used for material size reduction is the mechanical milling process. Hence, this method was adopted in order to reduce size of UFTRHA powder particle. This milling mechanism is attainable using planetary ball mill (Saad, Nuruddin, Shafiq, & Ali, 2016). In this regard, several parameters of the mechanical milling process are to be considered namely milling speed, ball-to-powder ratio (BPR) and duration of grinding.

Table 2 tabulates the particle size analysis of UFTRHA at 4 hours pre-treatment duration and various burning temperature with milling speed, BPR and grinding duration of 300rpm, 15:1 and 15 minutes respectively.

Table 2: Particle size analysis of UFTRHA at various burning temperature at 4 hours of soaking time.

Milling Variable	Process	Pre-treatment Soaking (hrs)	Burning Temp. (°C)	Particle Size (µm)		
				d(0.1)	d(0.5)	d(0.9)
BPR: 15:1	speed: 300rpm Grinding time: 15 mins	4	600°C	1.416	4.364	14.043
Grinding			700°C	1.460	4.676	14.768
			800°C	1.205	4.948	21.638

High speed of the grinding process resulted in greater velocity of the ball movements in the milling bowl. Therefore, shearing impact between grinding media (balls) and feed stock (UFTRHA) occurs vigorously in the system hence the smaller particle size obtained (Saad et al., 2016). Based on the data in Table 3, UFTRHA that had been treated for four hours and incinerated at 600°C has finest particle size compared to other UFTRHA samples with d(0.1), d(0.5) and d(0.9) of 1.416µm, 4.364µm and 14.043µm respectively.

On the other hand, Table 3 shows the influence of different burning temperature towards specific surface area (SSA) value of UFTRHA pre-treated using 0.1N HCl for four hours as well. Specific surface area (SSA) value plays an important role in accelerating the pozzolanic reaction of additive materials. Furthermore, large surface area of the pozzolanic material particle also acts as seeds for the generation of denser calcium-silicate-hydrate phase (C-S-H) in enhancing concrete strength development. From the SSA analysis, the highest specific surface area of UFTRHA sample was obtained as 219.58 m²/g. This finding is in agreement with the previous experimental analysis where the highest SiO₂ content and finest median particle size were obtained from UFTRHA that was burned at 600°C with four hours of acid pre-treatment procedure. According to data in Table 3, the SSA values reduced as the burning temperature rose up to 800°C.

Table 3: Response of Brunnet Emmet Teller – Specific Surface Area (BET-SSA) values to different burning temperatures of UFTRHA pre-treated at 4 hours

BET-SSA Value for Different Sample Type (m ² /g)	Burning Temperature (°C)		
	600 °C	700 °C	800 °C
UFTRHA (acid pre-treated)	219.58	180.72	133.91

Pozzolanic / Strength Activity Index Analysis

For further examination of pozzolanic level of UFTRHA as additive material in concrete, strength activity index (SAI) test was done accordingly. The mix

proportion of SAI test is tabulated in Table 4, where compression values of 50mm³ cube samples with 20% of UFTRHA replacement were determined at 7 and 28 days respectively.

From the analysis, the SAI values of UFTRHA blended mortar were recorded as 137.17% and 148.21% at 7 and 28 days respectively. These findings give an indication that UFTRHA possesses an excellent pozzolanic / cementing properties, where minimum requirement of strength activity index (SAI) of 75% at both 7 and 28 days as per outlined in ASTM C618-00 (ASTM, 2015).

Table 4: Mix proportions for strength activity index (SAI) analysis

Constituent	Control Mix (A)	UFTRHA Blended Mix (B)
OPC (g)	450	360
Sand (g)	1350	1350
UFTRHA(g)	-	90
Water (g)	225	225

CONCLUSION

The results obtained shows that, the optimum conditions in pre-treatment process play important roles in terms of enhancing the physicochemical properties of UFTRHA. These properties are important in order to produce high quality additive material for concrete technology application. As for the chemical composition analysis, the highest purity of silica content (SiO₂) is achieved by incineration at 600°C of four hours pre-treated rice husk. On the other hand, the mineralogical assessment concluded that the silica is amorphous as no significant sharp peak presence in XRD analysis at all burning temperatures. The highest amorphous silica content (SiO₂) of the UFTRHA sample was recorded at 98.60% with particle size median of 4.364µm and specific surface area of 219.58 m²/g. Meanwhile, the strength activity index of UFTRHA than that of the control mortar at 7 and 28 days were calculated as 137.17% and 148.21% subsequently.

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