Characterization, Microstructure Properties and Impurities Removal of Treated Rice Husk Ash (TRHA) as Supplementary Cementing Material (SCM) in Concrete using Hydrochloric Acid Pretreatment Process

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ABSTRACT
Recently, the need towards production of environmental friendly and excellent performance cementitious material has been outlined properly. Based on extensive researches done since 1970s, it is proven that rice husk ash (RHA) is silica-rich material and hence categorized as pozzolans in concrete. Nevertheless, the usage of this material in real construction industries is still under expectation. This is simply due to instability of the chemical components, especially amorphous silica content in the material after burning process. The aim of this paper is to present the characteristics and unwanted metal leaching evaluation of treated rice husk ash (TRHA) to be utilized as supplementary cementing material (SCM) in concrete. In this regard, raw rice husk was treated by adopting hydrochloric acid (HCl) pretreatment method prior to burning process. Several tests have been conducted to analyze the chemical compositions, specific surface area (SSA), microstructure properties and concentration of alkali metal removal of TRHA and compared to non-treated rice husk ash (NTRHA). In this paper, the effect of soaking time in acid solution from 1 to 4 hours is also presented and discussed accordingly.

INTRODUCTION
Usage of non-renewable sources in construction industry has been given a considerable highlight nowadays. Conventional concrete structure is mainly made of Portland cement, in which the raw material originates from limestone, the non-renewable sources. Regardless of this fact, the cement production rate around the world was approximately 1.2 billion tons/year in 2001 and expected to grow progressively to about 3.5 billion tons/year by 2015 (Bryant, 1997). Therefore, the usage of supplementary cementing material (SCM) is highly promoted in order to reduce the consumption of the non-renewable resources materials. SCMs are commonly used in concrete as admixtures to enhance its properties and also to positively contribute from environmental point of view. In light of incorporating SCM into concrete production, rice husk ash (RHA) is regarded as one of them due to high silica content. Production of RHA is done via thermal activation, which is burning process of the rice husk from agricultural waste.

According to United Nation Food Agriculture Organization (FAO), world rice consumption per capita in 2013 is about 57 kilograms (FAO Rice Market Monitor, 2014). In Asian countries, the average annual consumption of rice is around 100 kilograms per capita (Adjao and Staaz, 2013). Hence, the potential of producing ash from husk is about 100 million tons per annum. Realizing this fact, utilizing RHA in concrete is practical. It is known that high content of amorphous silica and specific surface area (SSA) of RHA are possible to be achieved by adopting suitable burning condition (Mehta, 1994).

Recently, an extensive research on incorporation RHA in concrete has been done due to high in silica content. Despite of high number of experimental works done in this area, quality of rice husk ash produced is still compromised. The rice husk is very sensitive towards incineration or burning process (International Rice Research Institute, 2005). The sensitivity towards burning condition causes inconsistency of the properties of rice husk ash produced. Hence, it is regarded as the main reason that leads towards unfavorable usage of this material as SCM in current construction sector (Mehta, 1997; Feng et al., 2004). Several researches reported...
that the impurities can be greatly eliminated via acid-leaching treatment (Feng et al., 2004; Salas et al., 2009; Vayghan et al., 2013; Park et al., 2014). Hence, removal of impurities on the rice husk surface prior to incineration process completion is essential to improve the quality of RHA as SCM.

Methodology:

**Preparation of Treated Rice Husk Ash (TRHA):**

The agricultural waste material used in this research was rice husk. The rice husk was obtained from local rice factory (BERNAS) in Sungai Ranggam, Perak. Prior to burning process, 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 for 1 to 4 hours. After completion of pretreatment process, the samples were washed using distilled water until it neutral pH obtained and dried using laboratory oven at 110°C. It was then burned by using conventional furnace model Protherm in laboratory. The burning process was done at the temperature of 700°C with 2 hours retention time. The treated rice husk ash (TRHA) was then ground using planetary ball mill for 1 hour with ball-to-powder ratio of 15:1 and rotation speed at 300rpm. Figure 1 showed process flow of the pretreatment procedures adopted in this research.

**Fig. 1:** Process flow chart of treated rice husk ash (TRHA) sample preparation.

**Characterization of Treated Rice Husk Ash (TRHA) and Alkali Metal Removal Test:**

In order to determine the acid pretreatment effect before burning process of rice husk, several tests have been conducted. In this regard, chemical composition of both non-treated rice husk ash (NTRHA) and treated rice husk ash (TRHA) were examined using X-ray fluorescence (XRF) test. As of TRHA, the test was done for sample that undergone pretreatment in 0.1N HCl solution at 4 hours soaking period only. The analysis was done by using spectrometer of Bruker Axs S4 Pioneer. The test was in accordance to BS EN 12677.

Particle surface area of the ground TRHA was determined using Brunnet Emmet Teller (BET) nitrogen adsorption method with degassing temperature of 300°C. The test was conducted using surface area and pore analyzer model micromeritics ASAP 2020.

On the other hand, microstructure analysis of both unground NTRHA and TRHA was also performed in this research. The test was carried out by using Field Emmision Scanning Electron Microscopy (FESEM), model Zeiss Supra 55 VP instrument.

In addition, examination of alkali metal impurities that leached out from the acid pretreatment procedure was done using atomic absorption spectrophotometer (AAS) instrument. The leachate samples were collected at 1, 2, 3 and 4 hours soaking duration respectively.

**RESULTS AND DISCUSSIONS**

**Chemical Composition of Non-treated Rice Husk Ash (NTRHA) and Treated Rice Husk Ash (TRHA):**

According to the XRF results tabulated in Table 1, it can be seen that silicon dioxide (SiO$_2$) content of TRHA was slightly increased as compared to the NTRHA. Referring to ASTM C-618, pozzolanic material that can be adopted as supplementary cementing material (SCM) in concrete should contain cumulative percentage of 3 reactive components at least 70%. The 3 components are silicon dioxide (SiO$_2$), aluminium oxide (Al$_2$O$_3$) and iron oxide (Fe$_2$O$_3$). Therefore, increment in silicon dioxide content in TRHA is crucial in order to enhance the performance of rice husk ash as SCM in concrete.

**Table 1:** Chemical composition of treated and non-treated agricultural wastes at 80°C pretreatment temperature for 4 hours and burned at 700°C for 2 hours.

<table>
<thead>
<tr>
<th>Components</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>P$_2$O$_5$</th>
<th>TiO$_2$</th>
<th>SO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Code</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TRHA</td>
<td>91.1</td>
<td>0.11</td>
<td>2.06</td>
<td>0.59</td>
<td>0.10</td>
<td>-</td>
<td>0.12</td>
<td>1.52</td>
<td>0.02</td>
<td>-</td>
</tr>
<tr>
<td>NTRHA</td>
<td>81.9</td>
<td>0.17</td>
<td>0.33</td>
<td>2.23</td>
<td>0.34</td>
<td>-</td>
<td>8.21</td>
<td>3.95</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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Journal of Applied Science and Agriculture, 10(3) Special 2015, Pages: 1-4
Particle Surface Area:

Surface area of pozzolanic material is vital in order to promote pozzolanic reaction for calcium-silicate-hydrate (C-S-H) formation in concrete strength development. Based on the particle surface area test results, TRHA has larger surface area of 40.3132m²/g to that NTRHA at 30.3235m²/g. Hence, it was proven that the acid pretreatment process improved the quality of the rice husk ash produced. Table 2 shows the detail parameters of the test and surface area of both NTRHA and TRHA accordingly.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Material Type</th>
<th>Pretreatment, burning and grinding parameters</th>
<th>BET nitrogen adsorption (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTRHA</td>
<td>Non-treated rice husk ash</td>
<td>Burning Temperature: 700°C Retention time: 2 hours BPR: 15:1 Grinding speed: 300rpm Grinding duration: 1 hour</td>
<td>30.3235</td>
</tr>
<tr>
<td>TRHA</td>
<td>Treated rice husk ash</td>
<td>Pretreatment Temperature: 80°C Soaking time: 4 hours Burning Temperature: 700°C Retention time: 2 hours BPR: 15:1 Grinding speed: 300rpm Grinding duration: 1 hour</td>
<td>40.3132</td>
</tr>
</tbody>
</table>

Microstructure Analysis of Non-treated Rice Husk Ash (NTRHA) and Treated Rice Husk Ash (TRHA):

As for microstructure properties investigation, the SEM analysis was conducted on both NTRHA and TRHA samples. Figure 2 (a) and 2 (b) displayed the SEM images for unground NTRHA and TRHA respectively. From investigation, it was observed that the outer surface of NTRHA was rough and has sharp edges. Moreover, these particles were vesicular, in which it had membranous cavity in nature and having hard shell-like surface. On the other hand, TRHA samples that undergone the pretreatment at 80°C for 4 hours soaking time and burned at 700°C at 2 hours indicated that the hard shell-like surface was broken into small sections and inner part of the particle can be clearly seen without any aid of milling or grinding process. This was due to completion of the acid pretreatment process prior to burning procedure that has remarkably removed the impurities on the surface of the rice husk.

Acid Pretreatment and Alkali Metal Removal:

Acid pretreatment is one of the effective processes to remove alkali metals that exist on the material surface namely magnesium (Mg), sodium (Na) and calcium (Ca). These alkali metals will melt during the burning process and hence causing sensitivity towards burning temperature. Realizing this fact, this leaching procedure is vital in order to enhance the characteristics of the produced rice husk ash. Figure 3 illustrated the removed alkali metals in terms of concentration (ppm) of Mg, Na and Ca components respectively.

Conclusion:

Based on the results, calcium concentration removal was found to be higher than magnesium and sodium components. The finding was also in agreement with the XRF result where amount of CaO component in TRHA was reduced from 2.23% to 0.59%. Overall, it can be deduced that longer soaking time resulted in increment of leaching rates of all alkali metals components.
Fig. 3: Magnesium (Mg), calcium (Ca) and sodium (Na) concentration leached out from the acid solution after rice husk pretreatment process.

ACKNOWLEDGEMENT

The author would like to thank Ministry of Education Malaysia for funding the research under MyRa Incentive Grant (0153AB-J12), Civil Engineering Department and Centralized Analytical Laboratory (CAL) of Universiti Teknologi PETRONAS for their assistance and technical advice throughout this research.

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BS EN 12677, 2003. Chemical Analysis of Refractory Products by XRF.