PROPERTIES AND HYDRATION OF BLENDED CEMENTS WITH RICE HUSK ASH

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Key Words: rice husk ash, blended cement, micro analysis, hydration.

ABSTRACT

This research investigates the properties and hydration of blended cements with rice husk ash. A reference sample and three cements replacement 5%, 10% and 20% weight % rice husk ash were tested. Setting time, flowability, pozzolan activity index, autoclave expansion, compressive strength and flexural strength were measured. The hydrated products were identified by X-ray diffraction. The microstructure of the hardened cement paste and their morphological characteristics were examined by scanning electron microscopy. It is concluded that the increase of rice husk ash content reduces the cement content in the mix, and the hydration process slows down causing setting time to increase. The calcium hydroxide decreases and the hydration product C-S-H gel increases as a result of the pozzolanic reaction, the microstructure becomes denser and the strength is increased.
I. INTRODUCTION

Rice husk (RH) is an important agricultural residue. It contains a high amount of SiO₂ [1]. It was reported that the annual output of RH of the world and China was about 80 and 40 million tons, respectively [2, 3]. Most RH is burned as fuel to generate energy resulting in the waste product, rice husk ash (RHA). If RHA are not utilized, it will result in tremendous waste generation, energy loss and environmental pollution [4]. Many researchers [5-7] indicated that RHA, burned at a controlled temperature, had a high pozzolanic property. Utilizing rice husk ash as a substitute for cement and constituents of concrete is a valuable and effective way to produce sustainable concrete from a waste material and to support sustainable development for the comfortable and continued existence of present and future generations [8].

Waste rice husk-bark ash was utilized to improve the durability of concrete in a marine environment. The durability of concrete in terms of chloride diffusion coefficient, chloride binding capacity, and resistance to corrosion of embedded steel could be considerably improved as high as 35% [9]. From the viewpoint of cement chemistry, the husk contains approximately 75% volatile organic matter, and the remaining 25% is converted into ash during the firing process and is known as rice husk ash. RHA contains approximately 85%-90% amorphous silica [10-12], and RHA has been shown to be suitable for use as a supplementary cementitious material to partially replace Portland cement [13, 14].

RHA has been used in concrete abroad since 1978. Rodríguez de Sensale, Ribeiro, and Gonçalves suggested that a positive quality of RHA is that it greatly decreases the autogenous shrinkage and produces an autogenous relative humidity change. An increase in the RHA content in cement decreases the autogenous deformation [15]. RHA is a highly siliceous material that can be used as an additive in concrete if the rice husk is burned in a specific manner. Huang and Agarwal suggested that burning rice husk under controlled temperature-time conditions produces ash containing silica in an amorphous form [16, 17]. During the burning process, the carbon content is burned off and all that remains is the silica content. The silica must be kept at a non-crystalline state in order to produce an ash with high pozzolanic activity. The high pozzolanic behavior is a necessity if you intend to use it as a substitute or additive in concrete. It has been tested and found that the ideal temperature for producing such results is between 600°C and 700°C [18]. The ash produced by controlled burning of the rice husk between 550°C and 700°C incinerating temperature for 1 hour transforms the silica content of the ash into an amorphous phase. The reactivity of amorphous silica is directly proportional to the specific surface area of ash. The RHA so produced is pulverized or ground to required fineness and mixed with cement to produce blended cement [19]. Thermo-gravimetric and differential thermo-gravimetric analyses were performance to study the effect of temperature on the mineralogical compositions of RHA subjected to different grinding time. The rice husk samples were prepared by burning at 700°C for six hours in Gas Furnace with a heating rate of 10°C/min. From the experiment, it was found that the greater the weight loss, the less the crystallinity of the RHA. In addition, there are no significant differences in chemical compositions of the rice husk ashes with different grinding time. Furthermore, when the grinding time increased from 1 hour and 30 minutes to 5 hours, there was a significant drop in the pozzolanic index [20]. Chindaprasirt found that paste and concrete containing RHA can improve the durability of concrete at various ages [21]. Rashid et al. showed that partial replacement of OPC (Ordinary Portland Cement) with RHA will improve the concrete performance, either its strength or durability [22, 23].

Multiple studies of applying RHA to cement engineering have described the potential of utilizing rice husks to manufacture RHA for industrial applications, especially as a highly reactive pozzolanic material in cement and concrete production [24]. Being rich in silica, RHA can be used as a source material to make geopolymer [25], and RHA generally performs better than other pozzolans in general, and silica fumes in particular [26]. This study evaluates how different amounts of RHA added to concrete may influence its physical and mechanical properties. The feasibility of the practical application of RHA is discussed in regard to the concepts of "durability, workability, economy, and ecology" through observation, experiment and theoretical analysis in order to provide references for future application of RHA to the cement industry.

II. EXPERIMENTAL PROGRAM

1. Materials

Cement: Type I Portland cement produced by a Taiwan cement company; its properties conform to ASTM
Table 1  Physical properties of type I Portland cement and RHA

<table>
<thead>
<tr>
<th>Materials</th>
<th>Specific gravity</th>
<th>Specific surface (cm²/g)</th>
<th>Median particle size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>3.15</td>
<td>3800</td>
<td>14.6</td>
</tr>
<tr>
<td>RHA</td>
<td>2.24</td>
<td>5200</td>
<td>10.3</td>
</tr>
</tbody>
</table>

Table 2  Chemical compositions of type I Portland cement and RHA

<table>
<thead>
<tr>
<th>Chemical compositions (%)</th>
<th>Cement</th>
<th>RHA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon dioxide (SiO₂)</td>
<td>20.18</td>
<td>85.62</td>
</tr>
<tr>
<td>Aluminium oxide (Al₂O₃)</td>
<td>4.57</td>
<td>0.10</td>
</tr>
<tr>
<td>Iron oxide (Fe₂O₃)</td>
<td>3.07</td>
<td>4.68</td>
</tr>
<tr>
<td>Calcium oxide (CaO)</td>
<td>63.34</td>
<td>1.19</td>
</tr>
<tr>
<td>Magnesium oxide (MgO)</td>
<td>3.21</td>
<td>0.93</td>
</tr>
<tr>
<td>Sulfur trioxide (SO₃)</td>
<td>3.00</td>
<td>0.60</td>
</tr>
<tr>
<td>Potassium oxide (K₂O)</td>
<td>0.69</td>
<td>4.41</td>
</tr>
<tr>
<td>Sodium oxide (Na₂O)</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>Loss on ignition (LOI)</td>
<td>1.50</td>
<td>2.30</td>
</tr>
<tr>
<td>SiO₂ + Al₂O₃ + Fe₂O₃</td>
<td>27.82</td>
<td>90.40</td>
</tr>
</tbody>
</table>

C114-05. RHA: Pozzolanic activity of RHA depends on silica content, silica crystallization phase, and size and surface area of ash particles. Ideally, ash must contain a limited amount of unburned carbon. RHA that has amorphous silica content and large surface area can be produced by combustion of rice husk at controlled temperature [27] and these factors are mainly responsible for its high reactivity [28, 29], so the kiln temperature and duration can affect the qualities of the ash. This study hopes through self-developed high-temperature furnace at different calcination temperature, test optimum combustion temperature and duration to get the best results, and through after the combustion RHA color, preliminary screening. This study used rice husk that was dried at 100°C for 24 hours and then sintered from 600°C to 750°C (heating rate was 5°C/minute, lasting 4 hours). The results showed that if the rice husk is burned at a temperature of lower than 600°C the RHA will contain too large an amount of un-burned carbon, the color was gray white; and when sintered at a temperature of higher than 750°C the silica content will become a crystalline structure, and RHA color deep pink. When sintered at 700°C, the color is pale pink, the RHA additive test result matches the glassiness diffusion zone, are shown in Fig. 1. Their physical and chemical properties are shown in Tables 1 and 2, respectively. Fig. 2 shows the scanning electron microscopy (SEM) of RHA. It reveals that the particle shapes are irregular, and angular and crushed shape. The median particle sizes (d50), as presented in Table 1, of RHA are 10.3 μm, which are less than that of Portland cement type I (14.6 μm). RHA is much lower than that of cement. The particle floating should be observed during mixing to avoid no uniform mixing from affecting the test result. Chemical composition analysis, as shown in Table 2, indicates that RHA oxide is mainly SiO₂, which is the first cause of the pozzolanic active reaction. The activity of the reaction between glassiness and other substances will be increased relatively, which is an advantage of the pozzolanic reaction. According to ASTM C 618, can be said to be Class N pozzolan since the sum of SiO₂, Al₂O₃, and Fe₂O₃ are higher than or equal to 70%, SO₃ are not higher than 4%, and LOI are not higher than 10%.

2. Mixture proportions and testing methods

The test mix proportion used in this study includes cement replacement ratios of 0, 5, 10, and 20% by weight, a water-binder ratio of 0.47, and curing ages of 7, 28, 56, 90 and 120 days. The compressive strength test was carried out according to ASTM C109. The flexural strength test was carried out according to CNS 1234. The specific gravity test was carried out according to ASTM C188.
Table 3  Physical properties of tested cements

<table>
<thead>
<tr>
<th>Sample</th>
<th>RHA (%)</th>
<th>Setting time (min)</th>
<th>Autoclave Expansion (%)</th>
<th>Flowability (%)</th>
<th>Pozzolan activity index (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial</td>
<td>Final</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OPC</td>
<td>0</td>
<td>315</td>
<td>400</td>
<td>0.07</td>
<td>103</td>
</tr>
<tr>
<td>R5</td>
<td>5</td>
<td>340</td>
<td>455</td>
<td>0.09</td>
<td>109</td>
</tr>
<tr>
<td>R10</td>
<td>10</td>
<td>393</td>
<td>490</td>
<td>0.12</td>
<td>113</td>
</tr>
<tr>
<td>R20</td>
<td>20</td>
<td>460</td>
<td>545</td>
<td>0.14</td>
<td>98</td>
</tr>
</tbody>
</table>

The setting time test was carried out according to ASTM C191. The flow test was carried out according to ASTM C1437 “Standard Test Method for Flow of Hydraulic Cement Mortar”. The pozzolan activity index test was carried out according to ASTM C311-98a. The autoclave expansion test was carried out according to ASTM C151. For X-ray diffraction (XRD), verification mode was adopted with D-5000 data processing software and complete JCPDS data. Scanning electron microscopy (SEM) was used for image observation, and the X-ray derived from electron impact was used for Energy Dispersive Analysis of X-ray (EDAX) to analyze the chemical elements of the solid qualitatively. Thermogravimetric-differential thermal analysis (TG-DTA) was used to analyze the thermal behavior of paste. Mercury intrusion porosimetry (MIP) was used to analyze the cumulative porosity. The variance in the microstructure and the variance in the hydration product composition ratio of RHA paste at 56 days were observed.

III. RESULTS AND DISCUSSION

1. Physical properties of blended cements

Table 3 presents the cement setting time, the flowability and the pozzolan activity of the tested samples. The water demand is less, the higher the RHA content of the cement. The decreased water demand is attributed to the delayed hydration of the RHA, due to its mineralogical composition. The flow tests confirm the above results and show that the RHA addition improves the paste workability. When the replacement is 20% of cement with RHA, elevates the amount of ettringite formed during the late hydration thus resulting in lower workability of the paste. The blended cements showed longer setting times than pure cement. This is expected as the increase of RHA content reduces the cement content in the mix. As a result, the hydration process slows down causing setting time to increase. The results of the autoclave expansion are presented in Table 3. The changes in length of the test specimens are high enough, they satisfy the standard requirements of ASTM C151 (max autoclave expansion: 0.8%). With three different replacements, the Pozzolan Activity Index exceeds 90% higher than the required Pozzolan Activity Index standard on Day 28 for fly ash, they satisfy the standard requirements of ASTM C151. Meanwhile, the high content of CaO, Al₂O₃ and Fe₂O₃ in RHA influences the active reaction of the pozzolanic material.

2. Mechanical properties of blended cements

Fig. 3 shows that the compressive strength development of the cements. Compressive strength increases with age. This result is consistent with the results of Safuuddin [30], who found that the compressive strength of the paste mixed with RHA increases with age. When replacement is less than 10% for the best, replace 20% of the results with the OPC similar, but the strength development was significantly lower than within 10% replacement. In many cases - depending on the nature of husks and burning/cooling conditions - the total silica of RHA exceeds 90% with most of it being non-crystalline, thus reactive under alkaline conditions [31]. Table 2 shows the content of SiO₂ is not particularly high, only 85.62%.
As RHA contain of un-burned completely carbon, thus cause strength decreases, because pozzolanic activity depends on silica content, silica crystallization phase and size and surface area of ash particles. This result is consistent with the literature [32], when the SiO₂ content is lower, the higher the replacement will lead to compressive strength decreased. After 90 days, the compressive strength development of the slows. Fig. 4 presents the compressive relative strength of tested cements in relation to curing age and replacement level. Relative strength is the ratio of the strength of the RHA cement to the strength of the pure cement at each particular curing time. The rate of strength development of reference cement depends mainly on its hydration rate. Therefore, the relative strength-time plots provide an insight into the rates of reaction in the blended system relative to the pure cement [33]. At 7 days, the RHA cements present a compressive strength that equals the 171%, 193% and 119% of the reference cement strength for 5%, 10% and 20% RHA content respectively. At 90 days, the RHA cements present a compressive strength that equals the 172%, 184% and 97%. Fig. 5 shows that the flexural strength development of the cements. When a portion of cement is replaced by RHA, the flexural strength increases with the age. At different ages are approximately 1~2 MPa higher than that of OPC, showing the RHA fiber-strengthened characteristic. Fig. 6 presents the flexural relative strength of tested cements in relation to curing age and replacement level. At 7 days, the RHA cements present a compressive strength that equals the 107%, 122% and 99% of the reference cement strength for 5%, 10% and 20% RHA content respectively.

3. Cement hydration

Fig. 7 shows the X-ray diffraction patterns of cement with 0%, 5%, 10% and 20% RHA hydrated for 56 days. It can be seen that the decrease in the amplitude of the peak slows down as the replacement of RHA increases, the hydration rate decreases as the replacement increases. The main hydration products were C-S-H, Ca(OH)₂ and ettringite (C₃A · 3C₃S · H₉₂) as well as unhydrated C₃S and C₂S. Fig. 8 shows the results of TG-DTA of the hydrated cement paste. The TGA curves showed mass loss at or around 150°C and 450°C, representing dehydration, decomposition of Ca(OH)₂ and decarbonation of calcium carbonate. In the 110°C-200°C and 400°C-500°C zone, the dehydration of the C-S-H gels takes place. It can be observed as a wide band that shifts to higher temperatures
when the hydration age increases. Heat absorption valley at about 450°C, OPC is maximum, but it decreases gradually as the RHA replacement increases. This suggests that the Ca(OH)$_2$ content in grout decreases gradually, and the decreasing amplitude of peak and the Ca(OH)$_2$ content decrease as the replacement of RHA increases. In DTA shows that there is a weight loss at 105°C-440°C, it may be resulted from decomposition of C-S-H gel and other possible components. The weight losses are 12% when RHA replacement is 5%, 11% when RHA replacement is 10%, and 9% when RHA replacement is 20% respectively. Which is attributed to the decomposition of crystalline Ca(OH)$_2$ produced by the hydration of calcium silicate phases of the blended cements. It is observed when the RHA replacement is 20%, there are fewer hydration products formed on the contrary. Fig. 9 shows that the cumulative pore volume increases with the replacement of RHA for cement. For RHA paste with a replacement of less than 10%, compared with OPC, the pore size and diameter are almost equivalent within the range of 0.008~0.1 μm. According to the compressive strength test result, the strength of RHA paste is higher than OPC. This result is consistent with the results of Safiuddin [30], who found that the compressive strength of the paste mixed with RHA increases with age. When replacing less than 10%, after the period of 90 days, the long age strength difference is even more significant. This result is consistent with Ramezanianpour [34], who found that RHA concrete has a higher compressive strength at various ages up to 90 days when compared with the control concrete. Fig. 10 show that the SEM photos of blended cements, hydrated at 56 days. RHA replacement of cement increases, structure becomes more compacted. Shows that the amount of crystallized needle-shaped ettringite inside pores, a high density of typical hexagonal plates of Ca(OH)$_2$ can be observed inside the capillary pores. Furthermore, hydraulic reactions of RHA mineral phases took place and their products filled the paste pores, generated high-compaction C-S-H gel, forming a continuous matrix. The pores decreased greatly, and other hydration products fill up all pores, forming a dense structure. The CH product of RHA paste decreases as the age increases, and a C-S-H gel hydration product forms. The low content of CH reduces the formation of gypsum, reduces the permeability, and reduces the strength reduction relatively. The C-S-H gel forms a continuous matrix to fill up the pores in the paste, so the structure becomes denser, and the strength is increased.

### IV. CONCLUSIONS

1. The RHA additive test result is consistent with the glassiness diffusion zone. The activity of reaction between glassiness and other substances is relatively increased, which is advantageous to the pozzolanic reaction.
2. When sintered at 700°C, the color is pale pink, the RHA additive test result matches the glassiness diffusion zone.

3. The blended cements showed longer setting times than the pure cement. This is expected as the increase of RHA content reduces the cement content in the mix.

4. The mechanical property performance of 5% and 10% RHA cement are better than that of the pure cement, at all ages.

5. The decrease in the amplitude of the peak slows down as the replacement of RHA increases, the hydration rate decreases as the replacement increases. The main hydration products were C-S-H, Ca(OH)₂ and ettringite (Ca₆Al₂(SO₄)₃·32H₂O) as well as unhydrated C₃S and C₂S.

6. SEM observation shows denser bonding when the cement is replaced by RHA, and the generated high-compaction C-S-H gel forms a continuous matrix to fill up the pores in the paste, so the structure becomes denser, and the strength is increased.

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