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Rice Husk Ash Pozzolanicity Assessment by Resistivity Method

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Abstract: Assessment of pozzolanic reactivity is commonly based on a direct and indirect method which mostly used the electrical conductivity method. However, these methods are limited by long-duration requirements or need to be done in the laboratory. By modifying the sandbox test to measure the electrical resistivity of Rice Husk Ash (RHA) as pozzolan, this investigation tries to offer a simpler method that can be done in situ. The RHA was heated in the oven with several temperatures varying from 100°C to 600°C and tested for its electrical resistivity by mixing it with laboratory-grade lime. The value of electrical resistivity is then compared with the value of the Luxan method by using the same materials. The results showed a similar trend with the electrical conductivity method. Hence new pozzolanic classification was proposed in line with this new pozzolanic assessment.

Keywords: electrical conductivity, pozzolanicity, resistivity, rice husk ash

1. Introduction

Rice husk ash (RHA) is an abundantly available and renewable agriculture by-product from rice milling in the rice producing country which has highest proportion of silica content among all plant residues [1]-[3]. Rice mill turns the paddy into 78% rice, 20% rice husk and 2% lost in process [4]. Rice husk also generates most ashes and the ash content of rice husk is around 17-26%, a lot higher than fuels (wood 0.2-2% and coal 12.2%) while the nature of the ash is slagging and fouling will create new problem [5]. Also silica content of rice husk is highest among various plants [6].

The end product of rice husk in the boiler is RHA which for the most part will end up as a waste since it has little or no commercial value and its disposal also evoke environmental problem. This because RHA does not biodegrade easily as a result of high silica content [7] and generate pollution which caused health problems to the inhabitants. In Uruguay, RHA was thrown into the river and bring about great contamination and ecological concern [8].

The rice husk (RH) contains about 50% cellulose, 25-30% lignin and 15-20% silica [9] then after the combustion, one fifth to 25% of the rice husk will change into RHA. Origin of amorphous silica in rice husk according to studies at University of Berkeley [10] is from silica in the soil that migrates in the plant in the shape of monosilic acid and concentrated by evaporation. Study by Kamiya et al. [11] explained further that rice plant ingests ortho-silicic acid from ground water which is polymerized to form amorphous silica in the hulls. The amorphous silica occurs principally on the external face of the husk and to a lesser concentration on the inner surface where the crystalline silica found on the husk before calcinations in the ash probably due to contamination by sand [10].

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High content of silica in amorphous form of RHA is known to be very active. According to ASTM C-618, pozzolan is "siliceous or siliceous and aluminous material which in themselves possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically reacts with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties".

It was found that RHA will produce calcium silicate hydrate (C-S-H) gel if combine with lime as a function of RHA burnt temperature at range 400°C to 900°C [12]. With simple notations, when silicon was burnt in the presence of oxygen, it will produce silica (Eq. (1)). Cement hydration will release calcium silicate hydrate and calcium hydroxide (Eq. (2)). The same calcium silicate hydrate of cement hydration will also be generated when the silica mixed with calcium hydroxide (Eq. (3)). This reaction between silicate and lime produced Pozzolanic reaction which converts the less dense CH phase and larger pores into denser C-S-H and smaller pore due to the pore refinement. However, C-S-H of cement hydration has higher density than the C-S-H of pozzolanic [13]. Previous studies suggested that the pozzolanic reaction may be accelerated by temperature [14]-[16].

$$Si + O_2 \rightarrow SiO_2 \tag{1}$$

$$\begin{gathered} C_3S + H_2O \rightarrow C_3S_2H_X + Ca(OH)_2 \\ \text{Cement + water} \rightarrow \text{hydrated gel + calcium hydroxide} \end{gathered} \tag{2}$$

$$\begin{gathered} SiO_2 + Ca(OH)_2 \rightarrow \text{C-S-H} \\ \text{Silicate + calcium hydroxide} \rightarrow \text{hydrated gel} \end{gathered} \tag{3}$$

Reactivity of certain pozzolanic material should be assessed to determine its ability to create cementitious properties. The level of pozzolanic activity may indicate the strength of end product. The pozzolanic reactivity describes the reaction rate or a measure for the degree of reaction over time between pozzolan and calcium (Ca^{2+}) or $Ca(OH)_2$ in the presence of water.

Previous researchers have developed some methods to assess the pozzolanic reactivity, both direct and indirect methods as follows:

(a) Chapelle test. Basically, this test is an accelerated lime consumption test. The test can be completed in 16 hours by determining the calcium concentration as a result of $Ca(OH)_2$ reacted with the pozzolanic material [15].
(b) Fratini test. This method conforms to BS-EN 196-5:1995, Part 5. Concentration of $Ca(OH)_2$ which has solubilised in aqueous solution in the presence of cement was evaluated. If the concentration of hardened paste below the saturation curve of $Ca(OH)_2$ in function of alkalinity then the paste considered has pozzolanic properties [17].
(c) Rapid analytical method based on treating the siliceous non-crystalline fraction of the pozzolan with glycerol and the titration of the resulting solution is performed with an aqueous glycerol solution of barium hydroxide [18].
(d) By determining the amount of methylene blue to change the colour of suspension of 1 gram pozzolan ash in 25 ml distilled water by titration [19].
(e) Strength activity index method. This is an indirect and standardized method, which used in ASTM C 311-04: Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland Cement Concrete. Basically, compressive strength of 50 mm pozzolan mortar cube was determined and compared to the strength of control cube.
(f) Monitoring electrical conductivity change. Pozzolanic activity of rice husk ash can be measured by comparing the difference of electrical conductivity of saturated calcium hydroxide $Ca(OH)_2$ solution with pozzolan added to this solution [20]. Several researchers have had investigated this electrical conductivity method as follow:

Meanwhile, for the electrical conductivity measurement, several researchers have done the investigations using various approaches and techniques, such as:

(a) Luxan Method. Measured the conductivity change when 5 grams of pozzolan reacts with 200 ml saturated $Ca(OH)_2$ solution at 40°C. There are three categories where $\Delta\sigma > 1.2$ has good pozzolanic activity, $0.4 < \Delta\sigma < 1.2$ variable pozzolanic activity and if $\Delta\sigma < 0.4$ means it has no pozzolanic properties [21]. This method quite simple and fast, except it can only be done in the laboratory.
(b) Tashiro Method. Measured electrical resistivity (opposite of conductivity) from paste of pozzolan mixed with $Ca(OH)_2$ solution under steam curing at 70°C [22]. This method required complex equipment.
(c) McCarter & Trans Method. Conductivity of pozzolan and $Ca(OH)_2$ mixtures monitored at ambient temperature for over two days. Using electrical impedance method to investigate the chemical activity development in the mixture. There were four stages of chemical activity identified i.e. initial period, dormant/induction period, rapid chemical activity resulted in an increase in rigidity of the mixture, and the last was much slower reaction rate [23]. The difference with Luxan method is Luxan used direct current source and McCarter using alternating current source with fixed frequency of 5 kHz for 48 hours.
(d) Tashima Method. Investigated the pozzolanic reactivity by measuring of electrical conductivity in saturated lime suspension and variation of pH. Siliceous pozzolan was added to achieve unsaturated condition where in this state the loss of electrical conductivity was measured [24], [25].

2. Experimental Study

The reactivity of RHA in this study was measured by three different methods. First, the reactivity of all the RHA burnt in controlled temperature and uncontrolled RHA was measured by established conductivity method and resistivity method that was specially developed in this project. Then the controlled burnt RHA which has optimum amorphous content was compared with RHA in term of its reactivity by Strength Activity Index method.

2.1 Conductivity Method

To determine the pozzolanicity of RHA, the experiment of electrical conductivity method developed by Luxan was carried out. The material and equipment used were as follows:

(a) Calcium hydroxide reagent laboratory grade.
(b) Conductivity meter Hach Sension5 (mili Siemens per centimeter or mS/cm).
(c) Digital stirring hot plate Corning PC-420D (Fig. 1).
(d) Magnetic bar stirrer.

The test was conducted by measuring the conductivity of 5 grams of RHA in 200 ml warm saturated lime solution at 40 ºC. The RHA that was tested is as follows: RHA 400°C, RHA 500°C, RHA 600°C, RHA 700°C, RHA 800°C, RHA 900°C, RHA 1000°C and uncontrolled burnt RHA.

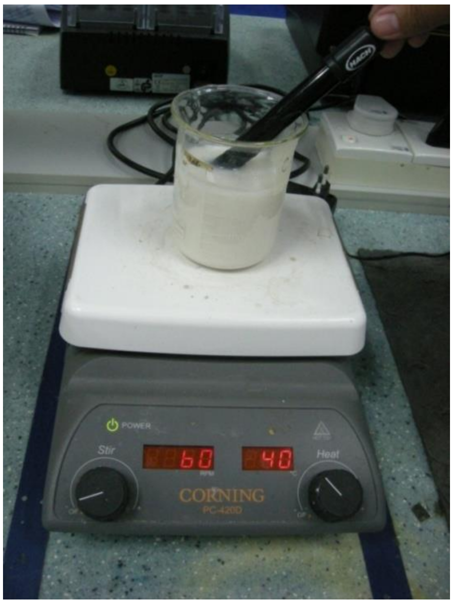

Fig. 1 - Digital stirring hot plate Corning PC-420D

2.2 Modified Resistivity Method

This study tried to explore an equivalent assessment of pozzolanicity compared to conductivity method. Inversely proportionate to conductivity, reasonably pozzolanicity can be measured by resistivity hence the name resistivity method. Modified from soil box test, this test was specifically developed for this study. The resistivity of $Ca(OH)_2$ solution with RHA was measured. Using combination of custom made acrylic box, meters and batteries, resistivity test apparatus was set. The dimension of the box was exactly the same with that of original soil box test. The schematic of modified soil box is shown in Fig. 2.

Fig. 3 showed the apparatus used for this developed resistivity method test by using two multimeters and batteries. Dimension (inside): 2.946cm wide x 11.15cm long x 2.3876 deep, rounding: 3 cm wide x 11.15 cm long x 2.4 cm deep. Two multimeters were used to measure the voltage between two positions and electric current from the batteries. The principles of this developed resistivity method can be defined as inverse of conductivity as stated in Eq. (4) to Eq. (5).

$$\sigma = \frac{1}{\rho} \tag{4}$$

$$R = \frac{V}{I} = \frac{\rho l}{A} \tag{5}$$

$$\rho = \frac{RA}{l} = \frac{VA}{Il} \tag{6}$$

$$R = \frac{\left(V_{on} - V_{off}\right)}{l} \tag{7}$$

where σ = Conductivity, R = Electrical resistance (Ohm or Ω), V = Electric potential difference (Volt or V), V_{on} = Electric potential difference when the battery on (Volt or V), V_{off} = Electric potential difference when the battery off (Volt or V), I = Electric current (Ampere or A), ρ = Electrical resistivity (Ohm-meter or Ω.m), A = cross sectional area (m^2), and l = length (m).

This test was conducted by measuring the electrical resistivity of the mixture of RHA and $Ca(OH)_2$ solution. Ratio of RHA and $Ca(OH)_2$ laboratory reagent is 9:1 by weight where water/solid ratio 9:10 also by weight. The measurements at the test are as follows: (i) RHA = 18 gr, (ii) $Ca(OH)_2$ = 2 gr, and (iii) Water = 18 gr. After all the materials were mixed, then put into the acrylic box evenly to all direction. Turn on all the devices and start to measure the electrical current (Ampere) and voltage (Volt). The electrical resistivity was calculated from these results by using Eq. (6).

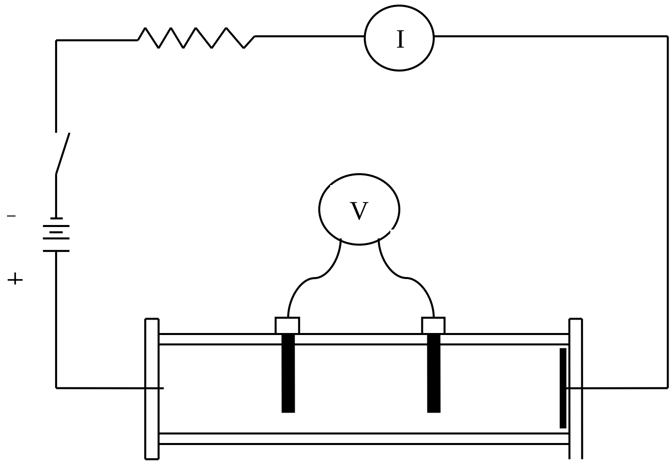

Fig. 2 - Schematic diagram of modified soil box for resistivity measurement

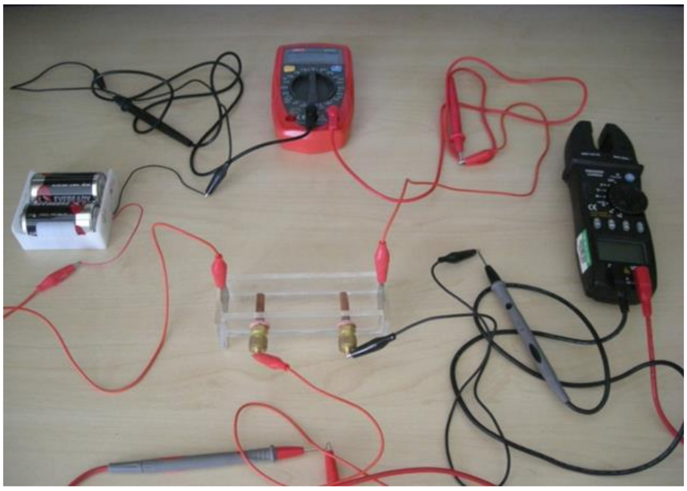

Fig. 3 - Modified soil box resistivity test equipment

3. Results and Discussion

3.1 Resistivity Values

From a series of experiments, the result of all the controlled and uncontrolled RHA pozzolanic reactivity is shown in Fig. 4. The initial conductivity value refers to the conductivity of RHA and calcium hydroxide solution before heated. And the final conductivity value is the conductivity of RHA and calcium hydroxide solution after heated at 40°C. However, according to category developed by Luxan et al if the pozzolanic reactivity below 0.4 mS/cm it means the materials possessed no pozzolanic property. The low electrical conductivity value of RHA might be originated from the particle size that was not ground to achieve fine particles. Since none of the RHA sample was finely ground, it just sieved through 200 µm mesh. Because as stated by previous researchers that fine particle plays very important role to the pozzolanic reactivity [26]. Fig. 5 shows the resistivity value of the RHA and also the value of its conductivity and conductivity after compensate at 20°C. Resistivity value (ρ) was converted to conductivity value (σ) by using Eq. (6).

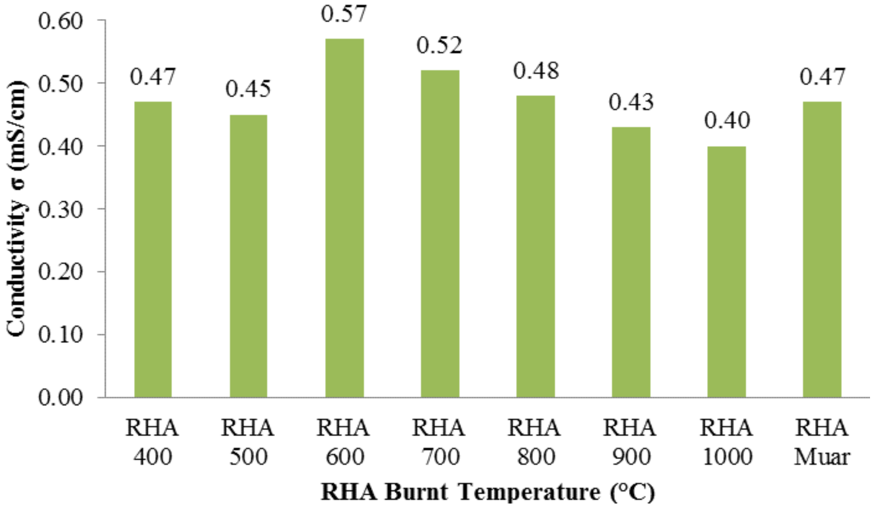

Fig. 4 - Pozzolanic reactivity with conductivity method

From the Table 1, the lowest resistivity 2.31 Ohm.meter (the highest conductivity 0.33 mS/cm) was possessed by RHA burnt at 600°C. This indicates that RHA 600ºC has the highest reactivity. While lowest reactive RHA burnt at 400°C has the resistivity 3.27 Ohm.meter (conductivity after compensate with 20°C is 0.23 mS/cm).

Table 1 - Resistivity values of RHA by resistivity method

RHA	I (µA)	V on (volt)	V off (volt)	ρ (Ωm)	σ (mS/cm)	Compensate (σ20)
RHA 400	345	0.715	0	3.27	0.31	0.23
RHA 500	432	0.811	-0.011	2.99	0.33	0.26
RHA 600	478	0.845	0	2.31	0.43	0.33
RHA 700	498	0.915	0	2.83	0.35	0.27
RHA 800	456	0.885	-0.003	3.13	0.32	0.25
RHA 900	437	0.89	0.023	3.25	0.31	0.24
RHA 1000	329	0.752	0.004	2.98	0.34	0.26
Waste RHA	377	0.736	-0.012	3.02	0.33	0.25

3.2 Validation of New Method

Conductivity of RHA from the new resistivity method need to be validated statistically to ensure this new method is valid and reliable. From the graphic in Fig. 5, conductivity values from the resistivity method are lower than that of conductivity method. This might be due to the conductivity method used lime solutions that was heated to 40°C makes the RHA pozzolanicity more reactive, while resistivity method used drier materials to test. Overall, the trends between two methods are almost the same which indicated two methods to obtain pozzolanicity of RHA from different burnt temperature and places are quite similar.

First the correlation coefficient from conductivity and resistivity method data set were checked to ensure the type and dependence from both data set. By running both data set as in Table 2 in correlation analysis in Excel, the result shows the value of correlation coefficient from conductivity and resistivity method is 0.76 and that indicates positive linear correlation.

The normality of conductivity data distribution for new developed and Luxan method are checked by looking at its skewness value. From descriptive statistical analysis in Excel, the skewness value for new developed method is 2.0 and Luxan method is 0.6 as stated in Table 4. According to George and Mallery (2011) skewness value in the range of ± 2 is considered normal and can be accepted.

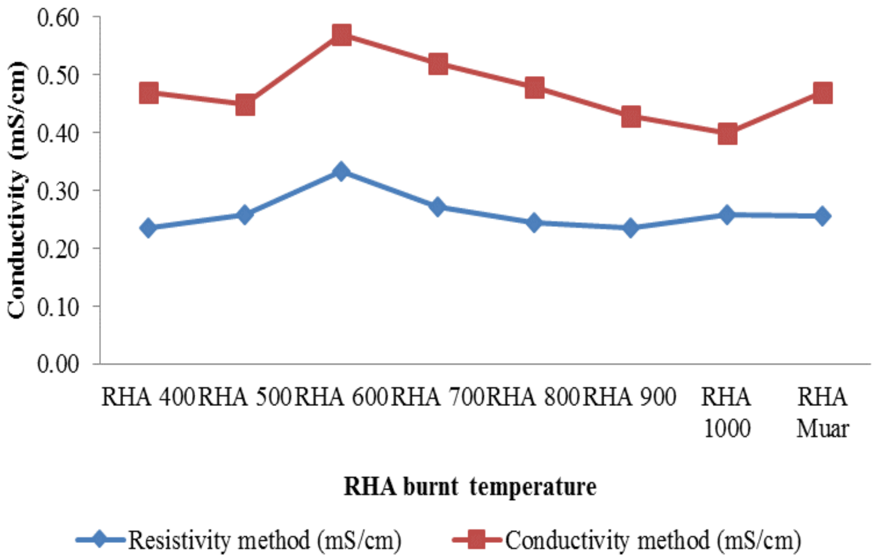

Fig. 5 - Comparison conductivity and resistivity method after compensate

Table 2 - Data entry for comparison resistivity and conductivity method

Type of RHA	Resistivity method (mS/cm)	Conductivity method (mS/cm)
RHA 400	0.23	0.47
RHA 500	0.26	0.45
RHA 600	0.33	0.57
RHA 700	0.27	0.52
RHA 800	0.25	0.48
RHA 900	0.24	0.43
RHA 1000	0.26	0.4
Waste RHA	0.25	0.47

Table 3 - Correlation coefficient from resistivity and conductivity method

	Resistivity method (mS/cm)	Conductivity method (mS/cm)
Resistivity method (mS/cm)	1	
Conductivity method (mS/cm)	0.76	1

Table 4 - Descriptive statistical analysis from resistivity and conductivity method

	Resistivity method (mS/cm)	Conductivity method (mS/cm)
Mean	0.3	0.5
Standard Error	0.0	0.0
Median	0.3	0.5
Mode	#N/A	#N/A
Standard Deviation	0.0	0.1
Sample Variance	0.0	0.0
Kurtosis	4.7	0.6
Skewness	2.0	0.6

Range	0.1	0.2
Minimum	0.2	0.4
Maximum	0.3	0.6
Sum	2.1	3.8
Count	8	8
Confidence Level (95.0%)	0.0	0.0

After regression analysis is executed in Excel, to see how many percent of variance explain by the model, the Coefficient of Determination (R^2) value for these two data set is known 0.58 (as shown in Table 5) which indicates the two data sets has acceptable correlation if R^2 is higher than 0.5 [27].

Table 5 - Regression analysis of resistivity and conductivity method

Regression Statistics	
Multiple R	0.76
R Square	0.58
Adjusted R Square	0.51
Standard Error	0.02
Observations	8

From the regression analysis result, new equation is developed to establish the relationship between conductivity values from this new resistivity method with Luxan method as stated in Eq. (8).

$$\sigma_{\text{resistivity method}} = 0.0464 + 0.454\sigma_{\text{Luxan method}} \tag{8}$$

This resistivity method needs to propose new classification pozzolanic value since the category developed by Luxan to classified pozzolanicity cannot be applied in the resistivity method because Luxan stated that the value below 0.4 mS/cm do not possess pozzolanic property. To set new classification for this new resistivity method, the equation from regression analysis as stated in Eq. (8) is used and the classification for new resistivity method is illustrated in Table 6.

Table 6 - Pozzolanic classification of new resistivity method

σ of New Resistivity Method (mS/cm)	**Remarks**
< 0.23	Do not possess pozzolanic properties
σ< σ < 0.42	Having pozzolanic properties
>0.42	Good pozzolanic properties

From the table above, the pozzolan need to have conductivity value at least 0.23 mS/cm to be considered to have pozzolanic properties if tested by the new resistivity method. And if the pozzolan has conductivity above 0.42 mS/cm, then it has good pozzolanic properties

4. Conclusion

The electrical resistivity of RHA by sand box method can be compared with electrical conductivity of Luxan method by converting resistivity value to conductivity. The result showed that the value from new method have similarity with that of Luxan method. This corroborated the hypothesis that the electrical resistivity can display the same trend for pozzolanicity with existing method. However, even though the trend is quite similar but the value were not. For this issue, new classification of pozzolanicity has been created in line with the new method.

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