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Pozzolanic contribution of rice husk ash in cementitious system

M. Jamil *, A.B.M.A. Kaish *, S.N. Raman, M.F.M. Zain

Sustainable Construction Materials and Building Systems (SUCOMBS) Research Group, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

HIGHLIGHTS

- Pozzolanic effect of RHA in cementitious system is determined.
- Pozzolanic effect is determined in terms of replacement percentage.
- Finding is based on cement hydration and reaction between RHA & hydration products.

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ABSTRACT

Rice husk ash (RHA) is an established supplementary cementitious material (SCM). Extensive research has been carried out to incorporate RHA as a SCM in casting concrete and mortar. RHA contributes in two fold of effects in concrete or mortar; i.e. filler effect and pozzolanic effect. Replacement percentages of RHA used in various previous studies were chosen arbitrarily like 5%, 10%, 20% and so on to determine the total effect of RHA. But the unique filler effect or pozzolanic effect of RHA in cementitious system is yet to be investigated comprehensively by the scientific community. This study was carried out to find the maximum pozzolanic (chemical) contribution of RHA in cementitious system in terms of replacement percentage. The determination is analytical and based on the hydration reaction of cement and the pozzolanic reaction of RHA with the hydration product. The obtained result was also verified with the experimental results available from published literatures.

1. Introduction

The annual production of rice from across the globe is around 600 million tons per year. Thailand alone produces approximately 5 million tons annually [1]. The outer shell of rice grain, often called as rice husk, generated from the rice milling industries is a well known agro-industrial by-product in many parts of the world. Raw rice husk (RRH) consists of about 40% cellulose, 30% lignin group and 20% silica. This RRH is normally used as a fuel in the parboiling process in rice milling industries. On combustion, the cellulose–lignin matrix of RRH burns away and leaves only a porous silica skeleton. Therefore, RHA contains a large volume of silica [2–4]. After grinding the porous silica skeleton of rice husk a fine powder with high surface area, called rice husk ash (RHA) is produced [5]. Due to its high silica content, RHA is considered as a highly reactive pozzolanic material in the production of concrete. The reactivity of RHA is attributed to the high amorphous silica content and the very large surface area governed by the porous structure of the particles. Highly reactive RHA is found when it is burnt under controlled conditions. This RHA contains high silica content in the amorphous form of silica up to 95% or even 100%. Its reactivity is also favored by increasing its fineness [6–9]. Ismail and Waliuddin reported that the fineness of RHA may have influence to activate the pozzolanic properties of RHA of crystalline form [10]. Chopra also obtained good results by grinding RHA of crystalline form [11]. Zerbino et al. and Cordeiro et al. reported that the pozzolanic reactivity of residual RHA can be improved by grinding up to an appropriate particle size [12,13]. However, Mehta suggested avoiding grinding of amorphous RHA to a high degree of fineness since it mainly derives its pozzolanic activity from the internal surface area of the particles [2]. Zain et al. stated that grinding of partially crystalline RHA for 30 min in a Los Angeles machine with a combination of 10 mm and 20 mm diameter steel rod produce good quality RHA [14]. But they suggested grinding for 60 min or more to achieve standard fineness of RHA. The optimized RHA, under controlled burning and/or grinding, could be used as a pozzolanic material in cement and concrete. Using RHA in concrete provides several advantages, such as improved strength and durability properties of concrete, reduction of environmental impact

* Corresponding authors. Tel.: +60 123120002; fax: +60 89252546 (M. Jamil).
E-mail addresses: mjamil.ukm@gmail.com, lynyeeha@gmail.com (M. Jamil), amrul.cuet@gmail.com (A.B.M.A. Kaish), snraman@gmail.com (S.N. Raman), fauzi@vlsi.eng.ukm.my, fauzizain@gmail.com (M.F.M. Zain).

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related to the disposal of waste materials and also reduction of carbon dioxide emissions [8,12,15–18].

RHA obtained by controlled combustion contains high volume of silica (SiO_2) mostly in amorphous form [14]. This form of silica present in RHA reacts with the hydration product of cement, $Ca(OH)_2$ to form a secondary type of Calcium–Silicate–Hydrated (C–S–H) gel [19–22]. This C–S–H gel is mainly responsible for hardening of concrete or mortar. $Ca(OH)_2$ comes only from the hydration of siliceous compound of cement. Siliceous compounds present in cement are only in the form of tri-calcium silicate (C_3S) and di-calcium silicate (C_2S). Ordinary Portland cement (OPC) contains a specific percentage of C_3S and C_2S that yields a specific amount of $Ca(OH)_2$. Therefore, a specific amount of RHA reacts chemically with a specific amount of $Ca(OH)_2$ to form the secondary C–S–H gel.

Previously, researchers used both amorphous and crystalline (residual) RHA in concrete or mortar in different replacement percentages (like 5%, 10%, 15%, 20% and so on) and investigated their mechanical and durability properties. Mixed ratios used in their studies were neither based on any scientific basis nor the chemistry of Portland cement hydration and the chemical reaction between RHA and $Ca(OH)_2$. The extra amount of RHA, after reacting chemically with $Ca(OH)_2$, used as a filler material in concrete or mortar. The exact contribution of RHA as a filler or as a pozzolanic material separately is still unknown to the scientific community. It is also not clear whether the advantageous use of RHA is due to filler or chemical (pozzolanic) effect. This difficulty is due to the fact that most of the time; the concomitant action of both effect influences the results evaluated from the most commonly used methods. It is claimed that the chemical or pozzolanic effect is dominating in case of amorphous RHA and the physical or filler effect is dominating when the RHA is mainly in crystalline form. There are many studies available in the published literature that determines the total pozzolanic activity (exerted by chemical and physical effects) of RHA having both partially and mostly crystalline parts in concrete and mortar [13,21–25]. However, none of the published studies reported the individual contribution from chemical (or pozzolanic) effect and/or physical (or filler) effect on the strength properties of concrete and mortar. Therefore, this study aims to determine the contribution of RHA from only its chemical/pozzolanic effect in cementitious system based on the hydration reaction of Portland cement and the chemical (pozzolanic) reaction between RHA and $Ca(OH)_2$.

2. Hydration of Portland cement

The hydration of OPC involves a series of reactions of the anhydrous calcium silicates (C_3S and C_2S) and aluminates (C_3A and C_4AF) phases with water to form hydrated phases [26]. This process is the involvement of different chemical reaction schemes. However, only the chemical reactions which are related to the tri-calcium silicate (C_3S) and di-calcium silicate (C_2S) compounds of cement have only been discussed in this article. Because, only the hydration of C_3S and C_2S produces calcium hydroxide ($Ca(OH)_2$).

Both C_3S and C_2S react with water and produce similar type of C–S–H gel which is the main 'glue' that binds the sand and aggregate particles together in concrete and mortar. The chemical formula of tri calcium silicate (C_3S) is $(CaO)_3{\cdot}SiO_2$ (or Ca_3SiO_5), where the molecular weight ratio of Ca to Si is 3:1 (i.e., Ca/Si = 3). This ratio in di calcium silicate (C_2S) is 2:1 (i.e., Ca/Si = 2). But, Chen et al. reported that the Ca/Si ratio in C–S–H gel (produced either from C_3S or C_2S) varies from 1.30 to 1.80 depending upon the condition of reaction [27]. Le Chatelier, Flint and Wells and Kalousek found this ratio to be 1.7 in normal temperature [28–30]. Newman and Choo also reported the ratio to be approximately 1.7 and the chemical formula of C–S–H gel is $C_{1.7}SH_3$ [i. e, $(CaO)_{1.7}{\cdot}SiO_2.(H_2O)_3$] [26]. Therefore, there is always an extra amount of calcium in the system after the hydration of C_3S and C_2S which are precipitated as calcium hydroxide ($Ca(OH)_2$ or CH).

The hydration reactions of C_3S and C_2S are summarized by the following equations [31].

$$\underset{\substack{2[3*(40+16)+\{28+(16*2)\}] \\ =456\text{gm}}}{2(3CaO.SiO_2)} + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + \underset{\substack{3*\{40+2*(16+1)\} \\ =222\text{gm}}}{3\,Ca(OH)_2} \quad (1)$$

$$\underset{\substack{2[2*(40+16)+\{28+(16*2)\}] \\ =344\text{gm}}}{2(2CaO.SiO_2)} + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + \underset{\substack{\{40+2*(16+1)\} \\ =74\text{gm}}}{Ca(OH)_2} \quad (2)$$

From these reactions, knowing the amount of C_3S and C_2S in OPC, one can easily calculate the amount of $Ca(OH)_2$ produced from a certain amount of OPC. For instance, ASTM type-I cement contains 55% C_3S and 19% C_2S [32]. Therefore, based on chemical Eqs. (1) and (2), 55 gm C_3S produces 26.776 gm $Ca(OH)_2$ and 19 gm C_2S produces 4.087 gm $Ca(OH)_2$. Hence, 100 gm ASTM type-I cement will produce 30.8635 gm $Ca(OH)_2$.

3. Chemical reaction between $Ca(OH)_2$ and SiO_2

James and Rao reported for the very first time that the reaction product of $Ca(OH)_2$ and silica from rice husk ash is a type of C–S–H gel [33]. Sugita et al. also discussed the possibilities of C–S–H gel formation in RHA concrete due to the reaction between the silica in RHA and the $Ca(OH)_2$ in hydrating cement [20,21]. Later Yu et al. confirmed that the amorphous silica exists in RHA reacts with $Ca(OH)_2$ to form one kind of C–S–H gel [22]. They reported the chemical structure of that secondary C–S–H gel as $Ca_{1.5}SiO_{3.5}{\cdot}xH_2O$.

Based on the chemical equilibrium, possible reaction between silica and $Ca(OH)_2$ in the presence of water is as follows:

$$\underset{\substack{2*(28+16*2) \\ =120\text{gm}}}{2SiO_2} + \underset{\substack{3*\{40+2*(16+1)\} \\ =222\text{gm}}}{3Ca(OH)_2} + H_2O \rightarrow 2Ca_{1.5}SiO_{3.5}{\cdot}2H_2O \quad (3)$$

It can be found from the above chemical reaction that 120 gm silica (SiO_2) reacts with 222 gm $Ca(OH)_2$ to form the secondary C–S–H gel. Therefore, according to the chemical Eq. (3) the molar ratio of SiO_2 and $Ca(OH)_2$ (S/CH ratio) in this C–S–H gel is 0.54054.

4. Chemical contribution of RHA in case of ASTM type-I cement

ASTM type-I OPC contains typically 55% C_3S and 19% C_2S [32]. The maximum chemical contribution of RHA is that replacement percentage of cement that will give the S/CH ratio as 0.54054. Summarized calculation of maximum cement replacement percentage by 100% amorphous RHA is given in Table 1.

Table 1 revealed that 12% replacement of RHA gives the S/CH ratio of 0.4418; whereas this ratio is seen to be 0.5718 when 15% replacement is done. Therefore, the optimum cement replacement percentage by RHA lies in between 12% and 15% to obtain maximum possible secondary C–S–H gel. This ratio is calculated as approximately 14.3%. The typical percentage of C_3S and C_2S may vary depending upon the raw materials used in the production of cement. In that case, the calculated chemical contribution will also vary accordingly.

The sample calculation of data of this table is given in Appendix A.