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Rice Husk Ash - Importance of Fineness for its Use as a Pozzolanic and Chloride-Resistant Material

Joana Sousa-Coutinho[1]
Vagelis G. Papadakis[2]

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ABSTRACT

The cement industry contributes over 6% to global CO_2 emissions, thus making cement production an important sector for CO_2 emission mitigation strategies, such as increasing use of pozzolanic additions. The work presented herein involves two laboratory studies on mortar where cement was partially replaced by rice husk ash (RHA), a waste material made available from the rice industry.

In the first study, the cement replacement considered was 10% and 15% with two different types of RHA, with regular grinding. Mortars with 10% and 15% cement replacement with RHA were produced with the same workability as control mortar (0% RHA) and also as silica fume mortar with 10% cement replacement by commercial silica fume. Specimens were tested for strength, absorption by capillarity, chloride ion penetration, accelerated carbonation and resistivity. Both types of RHA mortar with 10% and 15% cement replacement performed worse than the control mortar regarding strength, resistance to chloride penetration and carbonation resistance. Perfomance in terms of resistivity was similar to control and in terms of sorptivity, performance increased with replacement percentage. Unsatisfactory results were explained by insufficient fineness evaluated by laser particle distribution on the RHA samples.

A second study involving cement replacement in mortar with 10 and 20% of RHA ground very finely (mean particle size of 6μm) led to equivalent or better results to control mortar, in terms of strength, but, principally, the chloride resistance was dramatically increased thus leading to the conclusion that fineness is a key issue in terms of RHA use as a cement replacement material.

KEYWORDS

Chrorides, additions, mortar, durability, RHA, rice husk ash, fineness

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[1] Faculty of Engineering of the University of Porto (FEUP), Porto, PORTUGAL, jcouti@fe.up.pt

[2] Department of Environmental and Natural Resources Management, University of Western Greece, Agrinio, GREECE, vgp@psp.org.gr

1 INTRODUCTION

Cement production growth is estimated to range between 120 and 180% in 2020 [Middendorf et al. 2005]. It is known that for every ton of portland cement produced, cement plants generate about the same amount of green house gases (GHG), primarily carbon dioxide – one of the main GHG, besides being an energy- intensive industry [Samarin 1999]. The cement industry contributes over 6% to global CO_2 emissions making this industry an important sector for CO_2 emission mitigation strategies such as the increase use of pozzolanic additions [Worrell et al. 2001; Naik 2005]. In fact, efforts have been made to promote the use of pozzolans. It has been shown that if just 30% of cement used globally was replaced with supplementary cementing materials (SCM), the rise in CO_2 emissions from cement production could be reversed [Ecosmart Concrete 2010]. Measures to decrease the rate of CO_2 emissions during cement manufacture can be classified into two main approaches:

a) attaining a higher efficiency in the production process, by decreasing fuel consumption;
b) reducing the rate of clinker production by using mineral replacements (additions or SCMs, added during manufacture or directly through cement replacement at the building site.

Experience from all over the world, both historically and during the last several decades, shows that the portland cement – pozzolanic/cementitious materials composite system will always be inherently superior to the portland cement system in its microstructural and durability properties. This implies that there are strong technical and economic arguments and evidence to modify the fineness of the industrial (or agricultural) byproducts rather than that of portland cement, and thus ensure that they are manufactured for durability rather than for strength [Swamy 2007; Papadakis 2000, Papadakis & Tsimas 2003]. The most commonly-used pozzollanic materials are fly ash, granulated slag, silica fume and various natural and calcined pozzolans such as rice husk ash and metakaolin, most of which are waste materials.

It is well known that rice husk ash (RHA), an agricultural waste material, can be a highly reactive pozzolanic material, produced by controlled burning of rice husk and providing several advantages, such as improved strength and durability properties, reduced materials cost due to cement savings and, environmental benefits. Reactivity of RHA is attributed to its high content of non-crystalline silica, and to its very large surface area governed by the cellular structure of the particles [Mehta 1994; Zhang & Malhorta 1996; Chandra 1997; Sousa-Coutinho 2003; Saraswathy 2007]. When pozzolanic materials are added to cement, the silica (SiO_2) present in these materials reacts with free lime released during the hydration of cement and forms additional calcium silicate hydrates as new hydration products which improve the mechanical properties of concrete formulation [Ganesan & Thangavel 2007].

Generally, reactivity of a pozzolanic material can be favored by increasing fineness [Mehta,1994; Saraswathy 2007]. When burning temperature exceeds 600ºC partially changing silica to cristobalite, quartz and trydimite (a crystalline material), grinding is especially important. The burning of rice husk generates a significant volume of RHA that commonly ends up being dumped, blemishing the environmental footprint of the rice industry. Given that rice husk comprises approximately 20% of the unrefined rice and that RHA is 18% of rice husk, it is estimated that the total quantity of RHA generated globally is close to 21 million tons per year. It has been demonstrated that RHA exhibits significant pozzolanic potential; however the way in which the material develops its potential is largely influenced by inherent factors, principally fineness and reactive silica [Mehta 1978; Mehta, 1992; Malhotra and Mehta 1996; Agarwal 2006].

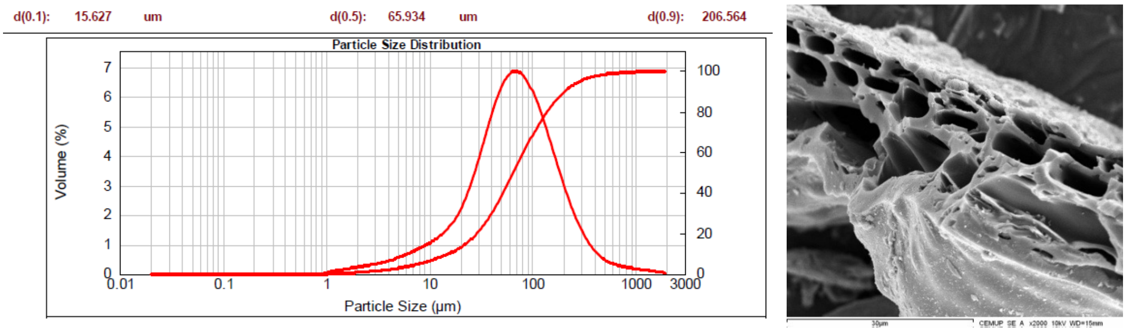
The study presented herein, examines the potential of a European RHA where two types were considered differing in reactive silica content and then fineness, in order to better understand the nature of this waste stream. Fineness levels were kept, for one RHA type, first at a regular level and then at a significantly lower level than those reported in the literature, in an effort to assess the reactivity of the material as a function of grinding. RHA was added in mortar systems and then in concrete and factors like strength and durability characteristics were determined to conclude on the potential of the local by-product.

2 RESEARCH PROGRAM

In a first study, the cement replacement considered was 10% and 15% with two different types of RHA obtained from a European industry, named A and Θ. Mortars with 10% and 15% cement (CEM I) replacement with each RHA were produced, as well as a silica fume mortar with 10% cement replacement by commercial silica fume. All mortars with the same water/binder ratio were dosed with superplasticizer in order to present equivalent workability. Specimens were tested for strength, absorption by capillarity, chloride ion penetration, accelerated carbonation and resistivity. In the first study, the fineness of RHA presented a mean particle diameter much greater than cement (65-70 μm for RHA in comparison to cement of 20 μm). In a second study, RHA (type A) was ground very finely (with mean particle size of 6μm) and the cement replacement was 10 and 20%.

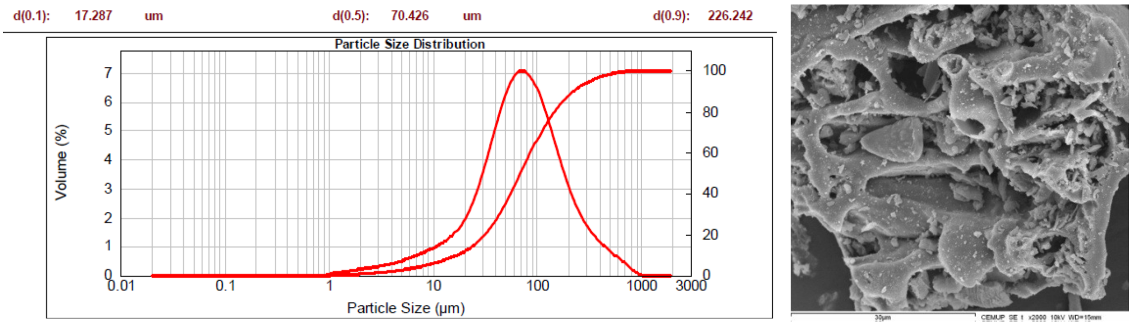
2.1 Materials

Materials used to produce mortar were tap water, CEM I 42,5 R type of cement, commercially available silica fume and the two experimental types of rice husk ash A and Θ, superplasticizer and standard CEN sand. Particle size distribution curves of RHA and cement and SEM photos of RHA are shown in Fig 1. Chemical analyses are shown in Table 1 and compaired to results by other authors.



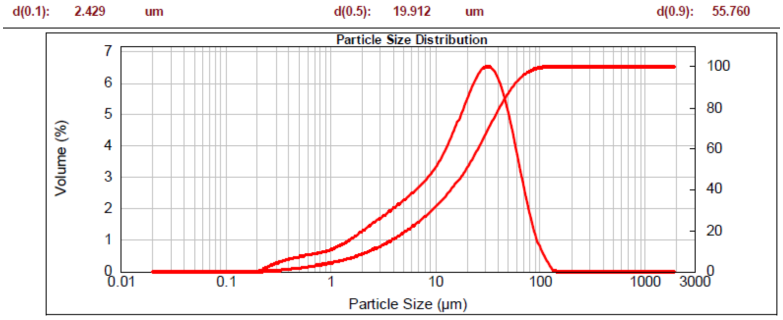
RHA A

RHA A ×2000



RHA Θ

RHA Θ ×2000



	A	Θ	CEM
		μm	
d(0,1)	15,63	17,29	2,43
d(0,5)	65,93	70,46	19,91
d(0,9)	206,56	19,91	55,76

Cement CEMI 42,5R

Figure 1. Particle size distribution curves of RHA (non-ground) and cement and SEM photos of RHA

Table 1. Chemical analysis for cement and RHA A and RHA Θ and results for RHA by other authors [Umamaheswaran & Batra 2008; Mehta 1994]

	cement	*RHA A*	*RHA A*	*RHA Θ*	*RHA Θ*	*RHA*	*RHA*
		IETCC	supplier	IETCC	supplier	Umamaheswaran & Batra 2008	Mehta 1994
LOI [%]	2,85	6,34	-	6,30		0,80	3-18
total SiO_2 [%]	20,41	89,05	88 - 98	86,50	88 - 98	93,52	80-95
reactive SiO_2 [%]	-	81,43	-	78,64	-	-	-
Al_2O_3 [%]	4,74	1,73	< 1	2,70	< 1	0,01	-
Fe_2O_3 [%]	3,08	1,31	-	0,00	-	0,51	-
CaO [%]	62,28	3,05	< 1	4,40	< 1	0,68	-
MgO [%]	1,90	2,15	-	1,97	-	-	-
free CaO [%]	1,01	0,46	-	0,0	-	-	-
K_2O [%]	-	-	< 1	-	< 1	-	1-2

Reactive SiO_2 *determined by EN -197-1*

2.2 Mixture proportions and workability

Mortar specimens according to mixture proportions shown in Table 2 were produced according to NP EN 196-1 [1996] after assessing workability. Workability was measured following the procedure described in ASTM C230 [2003] and ASTM 1437 [2001]. Control mortar (CTL) workability was set as target workability and superplasticizer added so as to obtain equivalent workability (±10mm) for all types of mortar. Average flow diameters for all batches are shown in Table 3.

Table 2. Mixture proportions and workability

	CTL	$SF_{10\%}$	$A_{10\%}$	$A_{15\%}$	$\Theta_{10\%}$	$\Theta_{15\%}$
sand (g)	1350	1350	1350	1350	1350	1350
Cement (g)	450	405	405	382,5	405	382,5
ash (g)	0	45	45	67,5	45	67,5
water (g)	225	225	225	225	225	225
Superplasticizer (g)	0	3.4	1.2	2.2	1.2	2.2
workability	210.2	210.1	204.4	209.6	203.3	206.1

2.3 Strength

Mortar strength was determined at 7, 28 and 90 days, following the standard procedure described in NP EN 196-1 [1996].

2.4 Absorption by Capillarity

Transport properties of the concrete surface, which play a major role in durability of reinforced concrete, are controlled by three mechanisms; namely, capillary absorption, permeability, and diffusion [Neville 1998]. Usually, concrete that is more resistant to the ingress of aggressive agents (water or carried ions, oxygen, and carbon dioxide) will be more durable. In the present study water absorption by capillarity, chloride ion migration, resistivity, and accelerated carbonation tests were carried out to assess durability. To consider the ability of the concrete surface to absorb water by capillary suction, the RILEM TC116-PCD [1999] recommendation was adopted as a basis. The molded side faces of 100 mm diameter and 50 mm height cylindrical specimens were tested, instead of the molded bottom face of 150 mm cube specimens used in the RILEM recommendation. The 56 (instead of 28) days old standard-cured (water at 20ºC) specimens were allowed to dry in a ventilated heater at 40ºC until constant mass was achieved. After cooling to 20ºC, the specimens were put on rods in a shallow bath of water at 20ºC, approximately 3 mm deep. The uptake of water by capillary absorption was measured through the weight gain of each specimen at time intervals until 4-1/2 h of contact with water. The absorption of water into concrete under capillary action is dependent on the square-root of time and may be modeled as [Hall 1989]:

$$A = a_0 + St^{0.5} \tag{1}$$

where, *A* (mg/mm^2) is the water absorption by unit area since the time the specimen was dipped in the shallow bath; *S* (mg/(mm^2×min.^{0,5})) is the "sorptivity" of the material; *t* is the elapsed time in minutes, and a_0 (mg/mm^2) is the water initially absorbed by pores in contact with water. Testing each specimen led to average (of 3) sorptivity results with correlation coefficients (R) over 0.978.

2.5 Chloride ion penetration

Chloride ion penetration was assessed by the Luping method, which is a non-steady state migration method based on a theoretical relation between diffusion and migration. The method enables the calculation of the apparent chloride diffusion coefficient (Dns) from an accelerated test [NT BUILD 492 1999]. It is based on measuring the depth of color change of a silver nitrate solution sprayed on the specimens previously submitted to a migration test. Specimens (100 mm diameter by 50 mm height) were submitted to an electrical current corresponding to a potential difference, in this case, of 30 V, during 24 h. Chloride ions are forced to migrate out of a NaCl solution subjected to a negative charge at the surface of the specimen, through the concrete into a NaOH solution maintained at a positive potential at the opposite surface of the specimen. The specimens are then split open, sprayed with nitrate solution and the chloride penetration depth (x_d) is measured in order to enable calculation of the apparent diffusion coefficient (D_{ns}) (Equation 2).

$$\mathrm{D}_{ns} = \frac{0.0239(273+\mathrm{T})\,\mathrm{L}}{(\mathrm{U}-2)\,\mathrm{t}}\left(x_d - 0.0238\sqrt{\frac{(273+T)Lx_d}{U-2}}\right) \tag{2}$$

where D_{ns} is the non-steady-state migration coefficient (×10 $^{-12}$ m^2/s), U is the absolute value of the applied voltage (V), T is the average value of the initial and final temperatures in the anodic solution (ºC), L is the thickness of the specimen, usually 50 mm, x_d is the average value of measured chloride penetration depth (mm), and t is the testing period (h).

2.6 Resistivity

Concrete resistivity is another parameter that contributes to durability assessment. When pores are saturated, electric current flows more easily depending on the pore structure. Prior to the chloride migration test described above, specimens are pre-saturated. Therefore, when current is imposed during the test it is possible to evaluate resistivity (Equation 3) in saturated conditions to compare different types of concrete, in this case, mortar.

$$\rho \equiv \mathrm{R}\cdot\frac{\mathrm{A}}{\mathrm{L}} \equiv \frac{\mathrm{V}\cdot\mathrm{A}}{\mathrm{L}\cdot\mathrm{I}} \tag{3}$$

where R is the electric resistance, (Ω - Ohm), I, current (A), V, voltage (V), ρ, electric resistivity (Ω.m), L, length (m), and A (m^2), the area of the test specimen across which current passes.

2.7 Carbonation

Accelerated carbonation tests were carried out following the procedure described in LNEC E391 [1993], using a chamber with 5% carbon dioxide and relative humidity (RH) of approximately 65%. 40×40×160 mm test specimens of each mortar type were kept in the chamber for two months, after 28 day curing in water at 20ºC. A slice from each test specimen was sawed off and sprayed with phenolphthalein solution, enabling the measurement of the carbonation depths.

3. TEST RESULTS AND DISCUSSION

Strength resutls at 7, 28 and 90 days, sorptivity results, resistance to chloride penetration, resistivity results at 56 days and carbonation results of each mortar type, are shown in Table 3. All these results refer to the regular ground form of RHA. Both types of RHA mortar with 10% and 15% cement replacement performed worse than the control mortar regarding strength, resistance to chloride penetration and carbonation resistance. Although a similar reduction, on average, in compressive strength was noticed at 28 and 90 days (10 % and 9% respectivelly) for all the RHA mortar samples, samples incorporating 15% RHA produced much higher carbonation depths (89% increase) than those incorporating 10% (17 % to 33 % increase).

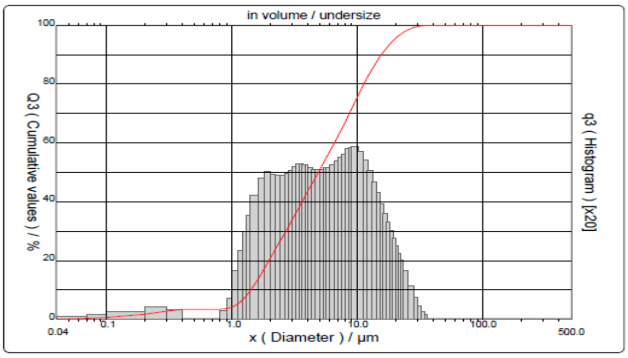
Table 3. Mechanical and durability test results and enhancement by the use of RHA (regular ground)

Results and Enhancement		*CTL*	$A_{10\%}$	$A_{15\%}$	$\Theta_{10\%}$	$\Theta_{15\%}$	$SF_{10\%}$
$\sigma_{7\ dias}$ [Mpa]	*Rslt.*	38,7	37,1	37,5	38,6	37,1	48,7
	Enh.		-4%	-3%	0%	-4%	26%
$\sigma_{28\ dias}$ [Mpa]	*Rslt.*	48,0	42,5	42,9	44,6	42,6	58,8
	Enh.		-11%	-11%	-7%	-11%	22%
$\sigma_{90\ dias}$ [Mpa]	*Rslt.*	53,3	48,4	49,0	49,1	47,7	58,0
	Enh.		-9%	-8%	-8%	-11%	9%
S [mg/(mm^2.min$^{1/2}$)]	*Rslt.*	0,1510	0,1233	0,0653	0,1023	0,0533	0,0883
	Enh.		18%	57%	32%	65%	42%
D_{ns} [$\times10^{-12}$ m^2/s]	*Rslt.*	15,31	16,32	17,62	17,24	16,59	2,44
	Enh.		-7%	-15%	-13%	-8%	84%
Carbonation [mm]	*Rslt.*	3,0	3,5	5,7	4,0	5,7	4,8
	Enh.		-17%	-89%	-33%	-89%	-61%
Resistivity [Ω.m]	*Rslt.*	53,7	48,6	58,4	44,9	61,8	279,5
	Enh.		-9%	9%	-16%	15%	420%

Enhancement (Enh.)=$(Rslt._{RHA}-Rslt._{CTL})/Rslt._{CTL}$

In terms of resistivity, samples incorporating 15% RHA produced an increase compared to control (9% and 15% for RHA type A and Θ respectively), while on samples with 10% RHA the resistivity was decreased (16% maximum decrease for RHA type Θ). In terms of sorptivity, performance increased with replacement percentage (a 65% increase was noticed on samples incorporating 15% RHA type Θ).

In Table 4, strength and accelerated chloride test results on concrete are given for the second study, where RHA (type A) was ground very finely to obtain SRHA (Fig. 2) and used as 10 and 20%cement replacement in concrete.



d(0,1): 1,41µm
d(0,5): 4,85µm
d(0,9): 15,43µm

Figure 2. Particle size distribution curve of SRHA

At 7 days the compressive strength proved to be similar to control samples (1% increase for both 10% and 20% levels of RHA), while at 28 days strength was slightly increased up to 7% for samples incorporating 10% RHA. Superfine RHA performs better than cement, even for 20% replacement. In this second study the chloride resistance of mortar incorporating SRHA was also evaluated, using the ASTM accelerated penetration test method. The samples before testing, were immersed for a period of 55 days in saturated $Ca(OH)_2$ solution. This period of time is more than adequate for a sufficient level of cement hydration and pozzolanic reactions of the ash used, as previously shown. The overall excellent behaviour of the samples tested (in comparison to control) is given in Table 4, right, where the electric charge passed through the samples is given for both levels of SRHA used.

Table 4. Mechanical test results, left and electric charge, right, in concrete with superfine RHA

	Control	*10% SRHA*	*20% SRHA*
7 d	38.7	39.2	38.9
28 d	48.0	51.2	50.2

	Charge passed [Coulombs]	*Permeability Class* [ASTM]
Control	2719	Moderate
10% SRHA	2569	Moderate
20% SRHA	864	Very Low

It is obvious that the mechanical grinding led to the development of smaller grain sizes than those of cement. It is generally acceptable that, at concrete level, the small grain sizes of ash strengthen (through the filler effect) packing among aggregates (specially in the case of fine aggregates) and cement grains. This is further enhanced with pozzolanic ash, reducing in this way the overall porosity (hence the permeability) of the final product. This is confirmed by results obtained according to the official classification by ASTM C1202 (see Table 4, right), where mortar incorporating SRHA exhibits low permeability to chloride ingress, in contrast to conventional mortar where permeability observed is of medium level.

CONCLUSIONS

The work presented in this study, examines the potential use of a European RHA where two types were considered differing in reactive silica and then fineness so as to better understand the nature of this waste stream. Fineness levels were kept, for one RHA type, first at a regular level and then at a significantly lower level than those reported in literature, in an effort to assess the reactivity of the material as a function of grinding. RHA was added in mortar systems and factors like strength and durability characteristics were determined to conclude on the potential of the local by-product. In the first study, cement replacement considered was 10 and 15% with the two different types of RHA, with regular grinding. Both types of RHA mortar with 10 and 15% cement replacement performed worse than control mortar in regard to strength, resistance to chloride penetration and carbonation resistance. Perfomance in terms of resistivity was similar to control and in terms of sorptivity, performance increased with replacement percentage. Unsatisfactory results were explained by insufficient fineness evaluated by laser particle distribution on the RHA samples. A second study involving cement replacement with 10 and 20% of RHA ground very finely, led to equivalent or better results compared to control concrete in terms of strength but, principally, chloride resistance was dramatically increased thus leading to the conclusion that fineness is a key issue in terms of RHA use as a cement replacement material.

As cement industry contributes significantly to global CO_2 emissions, making cement production greener is currently a very urgent challenge. Reducing the rate of clinker production by using mineral replacements, i.e., additions or supplementary cementing materials such as RHA with enhanced reactivity, contributes to greener concrete and thus sustainable construction.

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