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Low embodied energy cement containing untreated RHA: A strength development and durability study

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HIGHLIGHTS

- Lower carbon cement of acceptable strength can be produced with up to 15% untreated RHA.
- k of 0.5 implies a low (<10%) addition potential for coarse RHA in concrete.
- Untreated RHA improved mortar sorptivity by 50%. Resistivity was retained to baseline levels.
- Carbonation depth doubled with 15% RHA use. This also occurs in most treated SCMs.
- A less pronounced negative effect was recorded against chloride ingress.

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ABSTRACT

In contrast to common approach – that often involves extensive pre-grinding – the utilization potential of rice husk ash (RHA: by-product of rice industry) as a supplementary cementing material, in its untreated form was examined. This is to meet industry's increasing awareness for lower embodied energy cement and concrete. Given the availability of current raw materials in cement manufacturing, what is needed is to be able to achieve an optimum approach, between sustainability and durability when designing concrete structures. Under this frame, as-produced RHAs (D50 of approx. 70 μm) were examined with respect to their inherent characteristics and their impact on the performance of cement-based mortars. Strength, hydration and durability properties were considered. Untreated RHA exhibits moderate pozzolanicity and a low efficiency factor of approximately 0.5–0.6. Its very high chemical reactivity (active silica ratio of approx. 90%) cannot be exploited since the lack of adequate specific surface slows down its engagement in hydration reactions. Taking into consideration their untreated nature, it can be supported that they exhibit an acceptable strength potential after 28 days, complying – even marginally – with the strength class (42.5) of the used cement. Durability results revealed that there is no need to pre-treat RHA in order to achieve equal or even better performance than mortar with plain cement in terms of sorptivity (50% increase for 15% RHA usage) and resistivity. Untreated RHA however fails – as most SCMs do – to improve carbonation resistance since for a 15% cement replacement, carbonation depth was almost doubled. Overall, results indicate that usage of untreated RHA in cement-based systems is an alternative to decrease their carbon profile, as long as cement replacement is kept relatively low (below 15%).

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1. Introduction

Concrete is recognized to be the most widely used construction material, second only to water in total volumes consumed annually by society. It has been estimated that its average consumption is more than 1 m³ per year per every person on the planet [1]. However, production of cement and concrete is associated with a significant environmental burden. For instance, the cement manufacturing industry accounts for 5–7% of the total CO_2 anthropogenic emissions [2]. Similarly, concrete production embodies significant carbon and energy footprint. Embodied carbon (energy) has been defined as the total carbon released (energy consumed) from direct and indirect processes with a product or service and within the boundaries of cradle-to-gate [3]. With respect to concrete, cement is its ingredient that contributes most to its embodied energy. It has been proved that sustainable development of the

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Table 1
Chemistry and physical characteristics of raw materials.

	Cement	RHA A	RHA Θ	SF	RHA Umamaheswaran and Batra [38]	RHA Mehta [8]
Chemical analysis						
LOI	2.85	6.34	6.30		0.80	3–18
SiO_2	20.41	89.05	86.50	>90.00	93.52	80–95
Reactive SiO_2[a]	–	81.43	78.64			
γ_s[b]		0.91	0.91			
Al_2O_3	4.74	0.25	0.92		0.01	–
Fe_2O_3	3.08	0.41	0.56		0.51	–
CaO	62.28	0.85	1.12	<0.80	0.68	–
MgO	1.9	0.81	1.30		–	–
SO_3	2.82	0.01	0.05	<0.20	–	–
K_2O	0.59	1.32	1.58		–	1–2
Na_2O	0.19	0.17	0.43		–	–
MnO	0.02	0.13	0.12		–	–
Cl	0.01	0.09	0.09	<0.035	–	–
Particle size distribution			(µm)			
d(0.1)	2.43	15.63	17.29			
d(0.5)	19.91	65.93	70.46			
d(0.9)	55.76	206.56	226.24			
Mineralogical analysis						
Cristoballite		+++	+++			
Tridymite		+	+			

[a] The method specified in the European Standards EN 450-1 and 196-2 was followed for the estimation of the reactive silica of RHAs.
[b] γ_s: active ratio defined as the part of silica being reactive.
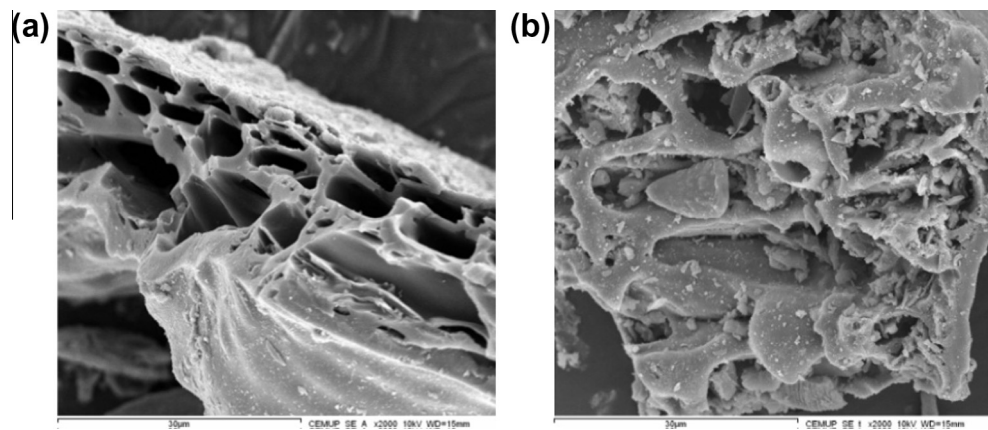
Fig. 1. Scanning electron microscopy pictures of (a) RHA A and (b) RHA Θ at ×2000.

Table 2
Mixture proportions.

	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
SCM (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 (mm)	210	210	204	210	203	206

content of the samples was calculated by using Eq. (1) proposed by Zhang et al. [17] after subtracting the amount of calcium carbonate present in all blended cements (as this was estimated from the data derived from the thermogravimetric analysis and the weight loss observed in the temperature area between 750 and 900 °C). Thermogravimetric analyses were performed in a Mettler STARe 851/LF/1600 TG/SDTA in a N_2-atmosphere (50 ml/min) at a heating rate of 10 °C/min.

$$W_n(\%) = \frac{W_1 - W_2}{W_2} - \frac{r_{fc}}{1 - r_{fc}} \cdot 100\% \qquad (1)$$

where W_n is the non-evaporable water content, W_1 and W_2 are the weight of specimens before and after ignition, respectively, and r_{fc} is a coefficient taking into account the loss on ignition and weights of the cement and RHA used in each blend. The latter is calculated as follows:

$$r_{fc} = p_f r_f + p_c r_c \qquad (2)$$

where p_f and p_c are the weight percentages of RHA and cement and r_f and r_c are the loss on ignition of RHA and cement respectively.

2.4. Durability

2.4.1. Capillary water absorption

To calculate the ability of the mortar surface to absorb water by capillary suction, the RILEM TC116-PCD [18] recommendation was adopted. It was performed after the specimens were cured for 56 days; this period was selected so as to ensure a good development of the pozzolanic reaction. The set up and conditioning of the test are shown in Fig. 2a and b. The absorption of water into the mortar under capillary action is dependent on the square-root of time and may be modeled as [19]:

$$A = a_0 + St^{0.5} \qquad (3)$$

where A (mg/mm^2) is the water absorption by unit area since the time the specimen was placed in the bath; S (mg/(mm$^2 \times$ 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.

2.4.2. Chloride ion penetration

All mortars were also tested for chloride ion penetration 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 (D_{ns}) from an accelerated test [20] by using a solution for Fick's 2nd Law of diffusion:

$$D_{ns} = \frac{0.0239(273 + T)L}{(U - 2)t}\left(x_d - 0.0238\sqrt{\frac{(273 + T)Lx_d}{U - 2}}\right) \quad (4)$$

where D_{ns} is the non-steady-state migration coefficient ($\times 10^{-12}$ 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 (°C), L is the thickness of the specimen, usually 50 mm, and t is the testing period (h). Finally x_d is the average value of measured chloride penetration depth (mm) based on a the depth of color change of a silver nitrate solution sprayed on the specimens (see Fig. 3).

2.4.3. Resistivity

Concrete resistivity is another parameter that contributes to durability assessment. Electric current flows more easily through the concrete mass when pores are saturated, 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 (Eq. (5)) in saturated conditions to compare different types of concrete, in this case, mortar.

$$\rho \equiv R \cdot \frac{A}{L} \equiv \frac{V \cdot A}{L \cdot I} \quad (5)$$

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.

2.4.4. Carbonation

Accelerated carbonation tests were carried out following the procedure described in RILEM CPC-18 [21], using a chamber with 5% carbon dioxide and relative humidity (RH) of approximately 65%. With respect to conditioning, it should be pointed out that for a low RH (below 50%) the diffusion of CO$_2$ into concrete is high but there is not enough water in the pores to generate carbonation. For a high RH, the diffusion of CO$_2$ is very low a fact also reducing carbonation rate [22]. This is why a RH of 65% is selected. In addition, given the correlation expressed by Limbachiya et al. [23] that one week exposure to 3.5% CO$_2$ concentration in the chamber equals to approximately 1-year exposure under natural environment conditions, the applied herein 5% concentration is rated adequate to provide a good long-term estimate. $40 \times 40 \times 160$ mm test specimens of each mortar type were kept in the chamber for two months, after 28 day curing in water at 20 °C. A slice from each test specimen was sawed off and sprayed with phenolphthalein solution, enabling the measurement of the carbonation depths (Fig. 4).

3. Results and discussion

3.1. Pozzolanic reactivity of untreated RHA

Results of the Chapelle test are summarized in Table 3 along with the respective values of other known SCMs from previous studies for comparative purposes. The amount of calcium hydroxide consumed by both RHAs is relatively low as a result of their coarse nature. As more or less expected, RHA A exhibits slightly higher capacity to bind lime compared to RHA Θ; this is probably the result of its higher fineness and reactive silica content. Despite

the high active ratio (γ_s) of both RHAs, test results are lower than other widely used SCMs. This indicates that fineness is a factor that contributes significantly to the pozzolanicity of RHA. Results testify that SCMs of lower active ratio and total active silica, like high or low calcium fly ash, exhibit higher capacities to bind lime under the same hydrothermal conditions. This is clearly attributed to their prior mechanical treatment that increased their specific surface largely compared to RHAs utilized herein.

Even though quite reliable for comparing the pozzolanic potential of different materials [24] earlier studies [25] have demonstrated that the Chapelle test cannot provide direct information on the future performance of the examined materials into a cementitious matrix under ambient temperatures; thus results should be treated cautiously and primarily under comparative perspective.

3.2. Workability of cement mortars

RHA presence in mortar requires the addition of SP for achieving the same workability with the no-RHA case; this indicates that despite RHA having not been previously ground to increased specific surface, it still increases somewhat the water demand of blended cement. Given the absence of any water-absorbing minerals, this increase can be mostly attributed to the porous nature of the RHA as testified by SEM examination. In an attempt to compare the two ashes, it may be argued that they didn't show any appreciable differences as SP requirement was identical for both replacement ratios (10% and 15%), even though initially a higher SP need was anticipated for RHA A due to its finer character. On the contrary, the specimen containing SF requested almost three times the quantity of SP that RHAs did for the same consistency. The relatively high water demand of silica fume in mortar has been established in numerous studies and linked to its very high specific surface. The relatively low water requirement of untreated RHAs – compared to respective values reported in the literature [6,13] for treated and especially over-ground ones – should be rated as a potential advantage for the concrete user since often strength benefit derived from grinding is – to an extent – compensated by the associated increased water demand.

3.3. Compressive strength

Strength results are summarized in Table 4. Mortars with 10% SF demonstrate superiority over all other mortars including the control case. This is reasonable – especially for early ages – and can be attributed to the amorphous siliceous nature and very high fineness of SF that make it a strong and readily reactive pozzolan. RHA-containing mortars are competitive after one week, but as hydration evolves they reduce strength compared with the control mortar by up to approximately 11% and 9% after one and three
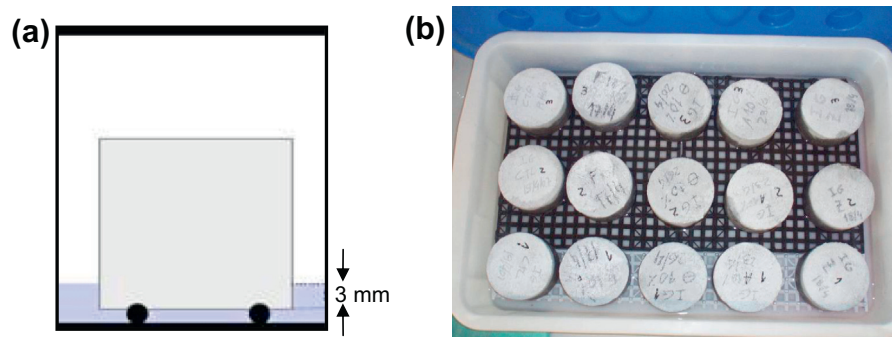

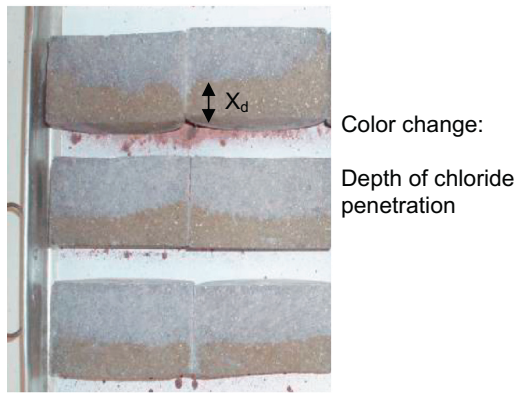**Fig. 2.** Testing capillary absorption.

Fig. 3. Measurement of chloride penetration depth with CTH rapid method.

Fig. 4. Carbonation depth measurement by spraying with phenolphthalein indicator.

months respectively. There is no clear explanation on the very satisfactory early-age performance of RHAs, given that their untreated nature cannot provide an adequate filler effect and since previous studies [10,17] have indicated that reactive silica cannot provide significant strength contribution unless hydration is at a progressed state. The latter can explain the decrease of the strength reduction after 28 days for all RHA mortars. In fact, after 90 days of hardening, the additional 5% RHA inclusion leads to similar final strength compared to mortars with less cement replacement (i.e. 10%). At maximum RHA content (15%), there is a small superiority of A sample which could be associated with its somewhat higher reactive silica content. Overall the performance of the two samples can be rated equal given the negligible strength differences at all ages.

Table 3
Chapelle test results for untreated RHAs and other SCMs.

SCM	g CH/g SCM
RHA A	0.51
RHA Θ	0.48
HCFA[a]	0.60
LCFA[b]	0.72
TLCFA[c]	0.84
FCC[d]	0.81

[a] HCFA: High Calcium Fly Ash [39].
[b] LCFA: Low Calcium Fly Ash [39].
[c] TLCFA: Processed Low Calcium Fly Ash [39].
[d] FCC: Spent Catalyst from oil-cracking refinery [40].

Strength gains are presented also in Table 4. They were determined for every mortar mix and age of hydration, using the following equation:

$$SG_i = R_i - \left(R_c \cdot \frac{C_{cem}}{C_{poz}} \right) \qquad (6)$$

where R_i is the compressive strength of the pozzolanic specimens at a given age, R_c is the compressive strength of the control at the same age, and C_{cem} and C_{poz} are the proportions by weight of cement and sum of cement and RHA in each mixture respectively.

Even though utilized in their as-received, coarse, state, RHAs exhibited a late-strength benefit with strength gains that reach approximately 3.7 MPa for the case of RHA A and 2.4 MPa for RHA Θ. Strong SF provided significantly better strength gain (SG) values as expected. There is no benchmark value for SG; however, in the frame of previous works with finely-ground RHAs in concrete, the respective SG values for a 10% cement replacement, reached significantly higher levels (10 MPa and 13 MPa at 28 and 90 days respectively for a RHA with a mean particle size of 5 μm) [26]. In general this denotes the dependency of RHA strength-contributing ability on fineness. Under this frame, it is postulated that for similar prior mechanical treatment, current RHAs (A, Θ) would reach similar SG values. Taking into consideration their untreated nature, it can be supported that they exhibit acceptable strength potential after 28 days, complying – even marginally – with the class strength of the used cement.

3.4. k Value and validation of analytical modeling expression

It has been well established [16] that in the case of mortars and concrete that incorporate supplementary cementing materials, the k-value derives from the following expression for the measured compressive strength (f_c):

$$f_c = K \cdot \left(\frac{1}{W/(C + kP)} - a \right) \qquad (7)$$

where K is a parameter depending on the cement type (here 38.8 MPa), C and P are the cement and RHA contents respectively in the mortar (kg/m³), W is the water content (kg/m³) kept constant in all the mixes and a parameter depending mainly on curing conditions (thus its numerical value for the tested samples changes with curing time). Using the mean measured values of the compressive strength of the control specimen, the parameter "a" was estimated as 1.00, 0.76, and 0.63 for 7, 28 and 90 days respectively. Based on the above expression and strength values, the k-values were determined and shown in Table 5 for RHA A and Θ mixtures.

Using the later ages (28 days and thereafter), we can report k-values for untreated RHA in the area of 0.5–0.6. This is significantly lower to k-values obtained by traditionally used SCMs (close to unity) that have been however previously ground to at least 4000 Blaine [6]. It reveals the inability of untreated RHA to equally replace cement even at small dosages of up to 15%. Practically, the k-value concept denotes that an untreated RHA can replace less than 10% by weight of cement in order to not alter early and later strength performance.

In a previous work [27] some of the authors of the present study have reported an analytical expression that related active silica of artificial pozzolans with k-value of their respective cementitious systems. The principal idea was to enable a first approximation of the future performance of those systems by knowing primarily the amount of silica present in the amorphous phase of the SCM. The authors concluded that for a SCM-system, k-value can be expressed as follows:

$$k = (\gamma_s \cdot f_{s,p}/f_{s,c}) \cdot (1 - a \cdot w/c) \qquad (8)$$

Table 4
Compressive strength and strength gain results of cement mortars.

Age	Property	CTL	$SF_{10\%}$	$A_{10\%}$	$A_{15\%}$	$\Theta_{10\%}$	$\Theta_{15\%}$
7 days	Compressive strength (MPa)	38.7	48.7	37.0	37.5	38.6	37.0
	Strength reduction (%)		−25.7	4.3	3.2	0.4	4.3
	Strength gain (MPa)		13.8	2.2	4.6	3.7	4.1
28 days	Compressive strength (MPa)	48.0	58.0	42.5	42.9	44.6	42.6
	Strength reduction (%)		−20.8	11.5	10.7	7.2	11.4
	Strength gain (MPa)		14.8	-0.7	2.1	1.3	1.7
90 days	Compressive strength (MPa)	53.3	58.8	48.4	49.0	49.1	47.7
	Strength reduction (%)		−10.2	9.3	8.1	7.9	10.5
	Strength gain (MPa)		10.8	0.4	3.7	1.1	2.4

where γ_S is the weight fraction of the oxide SiO_2 in the SCM (given in Table 1) which contributes to the pozzolanic reactions (i.e. the ratio of active silica to the total silica in the SCM), $f_{S,P}$ and $f_{S,C}$ are the weight fraction of silica in the SCM and cement respectively, whereas a is the parameter described above in Eq. (7). By applying the above equation for the blended cements of the present work at 28 and 90 days of hydration (stages at which reactive silica is considered to have a more drastic effect) k-values were calculated and presented in Table 5, together with the respective experimental ones.

It may be observed that for both RHA dosage ratios and hydration stages, there is a significant discrepancy between the theoretically calculated values and the experimental ones. In other words the predictive power of Eq. (8) is limited for the case of untreated RHA. This could be attributed to the absence of a fineness factor that in the case of RHA is of significant importance to strength contribution.

3.5. Non evaporable water content and gel/space ratio

Notwithstanding the fact that non-evaporable water content is not always safely associated with water that is chemically bound into hydration products [17], in most cases it can provide useful information about the rate of hydration of a cementitious system. Fig. 5 presents the relation between the W_n contents and the RHA addition in relation to their curing time. Naturally, W_n contents increase as the hydration continues and more hydration products are generated. Cements containing untreated RHA exhibit lower amounts of W_n compared to no-RHA sample throughout the testing period. As the hydration progresses the cements containing RHA reach slightly lower W_n contents, while in early ages the differences to control are more pronounced. This can be attributed to the slow development of the pozzolanic reaction, due to the coarse nature of the RHAs used herein. In general, W_n results are in agreement with the strength results explained in the previous sections, demonstrating thus an advantage for Θ 10% addition for early ages and a late but clear one for A 20% for later aging.

Gel/space ratio is defined as the ratio of the volume occupied by hydrated cement over the sum of the volumes occupied by hydrated cement and by capillary pores that are present in the matrix. Given that for a Portland cement paste, each ml of hydrated

cement occupies 2.06 ml, the gel/space ratio (X_c) can be calculated according to the following equation proposed by Neville [28]:

$$X_c = \frac{2.06 \cdot u_c \cdot a_c}{u_c \cdot a_c + \frac{w}{c}} \tag{9}$$

where u_c is the specific volume of anhydrous cement, a_c is the degree of cement hydration at a given curing stage, and w/c is the water-to-cement ratio used for preparing the paste.

Lam et al. [29] and Heikal [30] applied the above equation for pozzolanic cement specimens and assumed that the degree of cement hydration a_c is complete – therefore equals 1 – when the W_n is the one of fully hydrated cement paste (i.e. approximately 23%). Based on the above the measured density of cement (3.19 g/cm^2 corresponding to a value of $u_c = 1/3.19 = 0.313$) and the w/c 0.5 ratio applied in all pastes, gel/space ratios were calculated and presented in Table 6 in relation to curing time. The concept of gel/space ratio is essentially related with the durability properties of cement as it basically describes the pore size distribution and the volume the gel (hydration products) occupies in the cement matrix. Even though the RHA cements could not compensate the X_c of the control, their later age results indicate a promising durability performance.

3.6. Capillary water absorption

Absorption of water into dry mortar/concrete is considered to have two basic parameters: (1) the mass of water which is required to saturate the concrete (the effective porosity) and (2) the rate of penetration of the capillary rise (the sorptivity). Fig. 6 presents sorptivity results for all mortars tested. It may be seen that performance was enhanced with untreated RHA replacement percentage: a 32% increase was noticed for 10% RHA type Θ while a 65% increase was observed on the samples with 15% RHA type Θ. For mortars with RHA type A the increase observed was 18% for 10% cement replacement and 57% for 15% replacement. The sample incorporating silica fume also performed better than the control specimen (increase 42%).

The same conclusion was reached by a previous lab-study on the durability of concrete incorporating Portuguese rice husk ash and silica fume as cement replacements [9]. Sorptivity values for concrete specimens with 10%, 15% and 20% rice husk ash and for concrete specimens with 10% silica fume were lower compared

Table 5
Efficiency factors for untreated RHA A and Θ.

Mortar property		$A_{10\%}$	$A_{15\%}$	$\Theta_{10\%}$	$\Theta_{15\%}$
Strength, 28 days	Measured	0.29	0.56	0.56	0.54
	Calculated	2.30	2.20	2.22	2.12
Strength, 90 days	Measured	0.37	0.63	0.46	0.52
	Calculated	2.60	2.52	2.51	2.43

to control concrete. Saraswath and Song [31] reported the same trend, as they found that the coefficient of water absorption for rice husk ash replaced concrete at various replacement levels (up to 30%) was less when compared to control concrete. Kartini [32] also found that as the replacement percentage of OPC with treated RHA increases, the degree of water absorption reduces. This observation was attributed to reduction in the pore structure as pozzolanic material (RHA) occupies the empty space and reduces permeability of the concrete. However, given the coarse nature of the RHAs used here, the improved water resistance cannot be attributed to the pore filling effect but rather on the inherent water repellency of the RHA. It is not clear whether this is due to the hydrophobic nature of carbonaceous residues that are present in the ash.

3.7. Chloride ion penetration

Test results in terms of chloride ion penetration are shown in Fig. 7. The chloride diffusion coefficient (D_{ns}) was 15.31×10^{-12} m^2/s for the control mortar. The specimen incorporating 10% silica fume had a better performance with a D_{ns} of 2.44×10^{-12} m^2/s (enhancement 84%). On the contrary, both RHA mortars with 10% and 15% cement replacement performed similarly or slightly worse than the control regarding resistance to chloride penetration. Previous researchers have observed similar results concerning resistance to chloride ion penetration of concrete mixes containing rice husk ash. In particular, experiments conducted by Nehdi et al. [33] showed that proportions of non ground RHA did not change the rapid chloride penetrability classification of concrete to a significant extent, but the addition of finely ground RHA resulted in the reduction of the rapid chloride penetrability of concrete from a moderate rating to low or very low ratings depending on the type and addition level of RHA. Obviously, this behavior is related to gel/space ratio as well as to the active silica content able to create a pore refinement effect. The RHA grinding has a beneficial effect on pore refinement [34]; whereas the coarse character of the present RHA do not contribute in chloride resistance.

3.8. Resistivity

Fig. 7 presents the resistivity results for each mortar type. Samples incorporating 15% RHA produced an increase compared to control (9% and 15% for RHA type A and Θ respectively), while in samples with 10% RHA the resistivity was decreased (9% decrease for RHA type A and 16% decrease for RHA type Θ). In the case of silica fume the value of resistivity was much higher (279.5 Ω m), if compared to the resistivity value of control.

The electrical resistivity of a cementitious system is related to a number of factors such as paste microstructure, moisture content
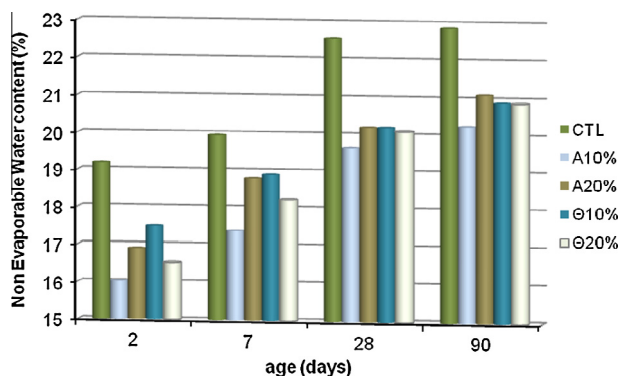
Table 6
Gel/space ratios for cement pastes with curing age.

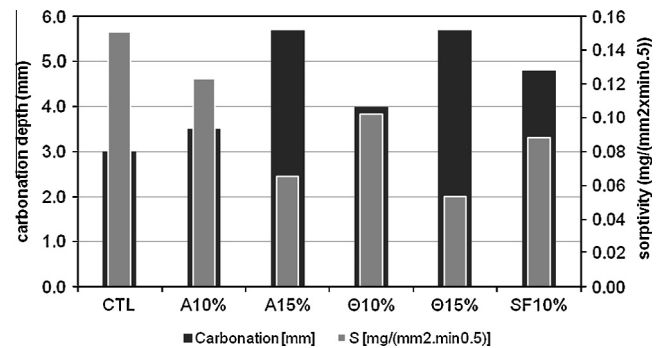| Cement	Age (days)			
	2	7	28	90
Control	0.707	0.725	0.784	0.791
A$_{10\%}$	0.626	0.662	0.718	0.732
A$_{20\%}$	0.649	0.698	0.731	0.752
Θ$_{10\%}$	0.665	0.700	0.731	0.747
Θ$_{20\%}$	0.639	0.683	0.729	0.747

Fig. 6. Sorptivity and carbonation results.

and temperature [35] and it is also affected by the presence of contaminants like chloride and sulfate ions [36]. Overall, results here verify a similar behavior to control, a fact that indicates that if initial resistivity is satisfactory there is no need to process RHA. If ground however, results produced by Gastaldini et al. [12] indicate that an increase of almost 100% in the values of electrical resistivity is anticipated for increases from 10% to 20% in the content of RHA for a similar w/b ratio in concrete.

3.9. Carbonation

Carbonation depths measured for all specimens are given in Fig. 6. The results for untreated RHA mortars and for mortar with 10% silica fume were unsatisfactory in comparison with those of control mortar. Samples incorporating 15% RHA produced much higher carbonation depths (89% increase for both types A and Θ) than those incorporating 10% (17% increase for RHA type A and 33% increase for RHA type Θ). The carbonation depth measured for silica fume mortar was 4.8 mm increased by 61% in comparison with the depth of 3 mm of the control mortar.

In principle, a higher extent of carbonation should be expected in systems that have or generate more Ca(OH)$_2$. Therefore when SCMs (i.e. portlandite consumers) are used to replace cement, carbonation should be minimized. However the complexity of the final resistance to carbonation is enhanced since SCMs can be less resistant to carbonation, mainly due to their low binding capacity of CO$_2$, caused by their smaller concentrations of Ca(OH)$_2$. In particular, it was shown by Papadakis et al. [22] that the carbonation depth increases, with the increasing content of every type of SCM used. Conflicting phenomena occur also with the generation of secondary CSH due to SCMs active ingredients (primarily silica) that aids resistance and – on the other hand – by the lowering down of cement hydration rate that increases permeability, thus ingress of CO$_2$.

Carbonation affects the durability of reinforced concrete structures. This results from the interaction of atmosphere's carbon dioxide (CO$_2$) with the alkaline products of the cementitious matrix. There is a large amount of solid Ca(OH)$_2$ in the hydration products of Portland cement that can be dissolved in water. This helps

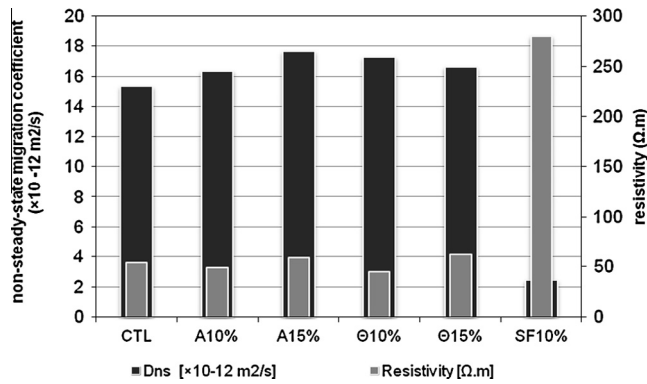**Fig. 5.** Non evaporable water content of control and RHA cements by curing time.

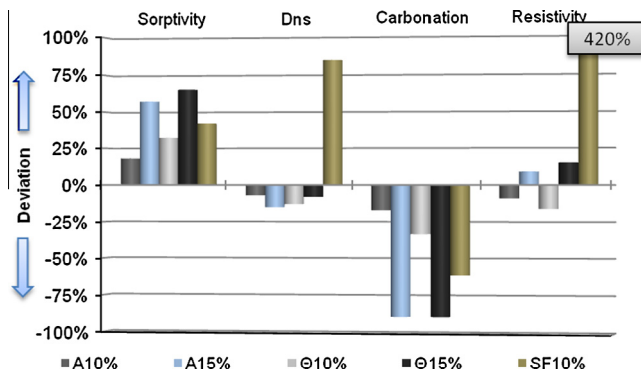**Fig. 7.** Chloride penetration and resistivity results.

Fig. 8. % Deviation from the non-RHA mortar with respect to durability properties.

to maintain the pH at 12–13. However, when all the available Ca(OH)$_2$ has reacted, the pH falls to a level below 11 which helps to promote corrosion [37]. As shown from Chapelle tests untreated RHAs exhibit pozzolanicity; being pozzolanic they consume Ca(OH)$_2$ to reduce the alkalinity and thus the rate of carbonation increases. This is the case for SF as well. However, the slow pozzolanic action evolution (as verified by W_n content development) inhibits the generation of adequate amounts of secondary CSH that could decrease permeability of the tested mortars. The latter was verified also through the gel/space ratios and provides an explanation of the inability of untreated RHA to suppress carbonation ingress.

An outlook of the effect of untreated RHA on mortar durability is provided in Fig. 8 where comparative results are given for all the durability tests in terms of % deviation from the CTL mortar results. Positive results indicate an improvement in durability whereas negative ones a deterioration on the mortar's performance.

4. Conclusions

Contrary to most studies available, RHA – not prior treated, with a D50 of 70 μm – were used as cement replacements. The aim was to assess their influence on mechanical and durability properties of cement-based mortars. Even though their mechanical pre-treatment has been shown to upgrade basic properties of the final product, it remains of interest to determine the respective RHA contribution in the absence of a preparation that is energy demanding (i.e. grinding or classifying). Major conclusions are as follows:

- Untreated RHAs exhibit pozzolanicity due to their siliceous character which is almost entirely (90%) amorphous. It is low compared to commonly used treated SCMs. Despite its porous

nature, untreated RHA does not increase appreciably the water requirement of cement for the same consistency. This is important for concrete applications since it won't compromise strength development.
- Untreated RHA exhibits a late-strength gain that reaches approximately 4 MPa. This is acceptable considering that the respective gain for a very reactive, extremely fine SCM (SF) is 10 MPa. Its efficiency was measured in the area of 0.5–0.6; that practically means that if added to concrete without prior grinding it could not replace more than half of the selected dosages (approx. 5%) for sustaining the non-RHA performance. A previously reported theoretical expression linking k-value with active silica ratio was not validated for untreated RHA. Modifications are required for untreated SCMs.
- Despite the high chemical reactivity of untreated RHA (γ_s of 90%), the lack of adequate specific surface slows down their engagement in hydration reactions. Both non-evaporable water content and strength results indicate an advantage of higher quality RHA (A) at later ages.
- Untreated RHA significantly aids sorptivity of mortar. Increases of up to 50% were achieved for 15% RHA incorporation. Performance increases with higher RHA inclusion exceeding even the water resistance of SF-based system. Given the coarse nature of the RHAs, the improved water resistance cannot be attributed to the pore filling effect but rather on the inherent water repellency of the RHA. It is not clear whether this is due to the hydrophobic nature of carbonaceous residues that are present in the ash. Resistivity was also found to be similar to the control specimen.
- On the contrary, the coarse nature of untreated RHA affects resistance against chloride penetration and – mainly – carbonation. When 15% of untreated RHA was used, carbonation depth was almost doubled. Being pozzolanic, RHAs consume Ca(OH)$_2$ which reduces alkalinity and increases the rate of carbonation. This is the case for SF as well. In addition, slow pozzolanic evolution of coarse RHA does not allow a quick and substantial formation of secondary hydration products that could assist pores closing, thus enhanced carbonation resistance.

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