



# Rice husk ash (RHA) effectiveness in cement and concrete as a function of reactive silica and fineness



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## ABSTRACT

Research on ash from burning of rice husks (RHA) has already demonstrated that it is one of the most promising supplementary cementing materials (SCM), given its high specific surface and great amount of silica soluble in alkaline conditions. Indeed, RHA could be a product of added value if it wasn't for its limited availability and periodically high residual carbon content, factors inhibiting its wider use in building materials. Most of the published work has exploited the effectiveness of RHA of very high specific surface and reactive silica, without really investigating the effect of these factors with respect to mechanical and durability characteristics of the derived cement and concrete. This is of crucial importance since someone could falsely rate RHA of moderate fineness and chemical reactivity as potentially reject, constituting thus a significant portion of this by-product unutilised. Reactive silica and fineness effect was assessed in this study by examining two different RHAs, both in blended cement and concrete level. It was found out that RHA is a material extremely "sensitive" to fineness changes; the higher being the fineness the more positive is the effect of RHA inclusion in the mix. Not surprisingly, active silica holds a key role especially for later-age strength gain, indicating that pozzolanic effect takes over from the "physical" effect of the pozzolan as hydration evolves. Pozzolanic potential, strength development of mortars and concrete, efficiency factors (k-values) estimation and resistance against chloride penetration are part of the testing performed and reveal the importance of the binary action of RHA in producing competitive blended cement and concrete.

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## 1. Introduction

Rice husk ash (hereafter RHA), is the solid residue derived from burning rice husks. In many cases – depending on the nature of husks and burning/cooling conditions – the total silica of RHA exceeds 90%. At lower temperatures the nature of RHA silica is predominantly amorphous, thus reactive under alkaline conditions like the ones created in the hydrating cement paste. By heating at higher than approximately 700 °C, crystallization of the ash occurs from amorphous SiO<sub>2</sub> to cristobalite or tridymite [1,2]. When the husk is subjected to the typical thermal treatment in the rice industry – without modifications of the burning and/or cooling conditions – it is possible that the derived ash will be enriched in residual carbon and exhibit different mineralogy and lower glassy phase, factors compromising its reactivity, grindability and ultimately its applicability.

By applying different techniques, it has been demonstrated that RHA exhibits significant pozzolanic potential [3,4]; however the way the material is developing its potential is largely influenced by inherent factors, principally amorphous silica and fineness. Agarwal's study [5] highlighted some of these factors, by measuring the pozzolanicity of RHA of different specific surfaces and LOI. He concluded that as-received RHA exhibited 16% less reactivity compared to its finer granulometric fractions, thus confirming previous observations about RHA being a highly reactive material due to its micro-porous nature, high specific surface and high silica content [3,6,7]. Feng et al. [6] and Sugita et al. [7] have also provided useful data by dealing with the pozzolanic properties of RHA after pre-treating the material with hydrochloric acid. The value of those papers lies in the three different methods employed (i.e. heat of hydration, Ca(OH)<sub>2</sub> content and pore size distribution) for assessing – and ultimately confirming – the high pozzolanicity of this by-product. In application level, the first attempts of Mehta [4,8] in the early nineties are well-known. Later studies highlighted the effectiveness of RHA to replace parts of cement in hydraulic binders and mortars. In concrete, several studies have been conducted, with those of Nehdi et al. [2], de Sensale [9], Ganesan et al. [10], Coutinho [11], Givi et al. [12], Saffudin [13], and Van Tuan [14]

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demonstrating the applicability of RHA. What seems to be common in the majority of those studies is the very high specific surface that RHA was ground to before use, in order to ensure high reactivity.

Despite research on RHA utilization in construction materials is not new, the Hellenic by-product and its reuse potential has not been examined before. To obtain a representative view on the local waste stream, it was decided to experiment with ashes of different chemistry and fineness. Chemical factor differentiation was achieved by investigating two RHAs of different reactive silica. Local RHA exhibits a deviation in that respect since husk origin and process parameters (i.e. burning temperature, cooling rate) are not the same in the two plants of the producer (Agrino SA). With respect to fineness, the raw materials were laboratory ground to two different levels. In both cases, specific surfaces were kept lower than what is reported in the literature (values of  $>15,000 \text{ cm}^2/\text{g}$  are usually attained before usage) in order to avoid excessive grinding. By incorporating these RHAs in mortar and concrete, the study reports – among others – data on the reaction degree of RHA with hydration age and its efficiency factor (known as *k*-value); to the authors' knowledge, both parameters have not been reported elsewhere for any type of RHA. By comparing RHA *k*-value with the respective ones of other commonly used supplementary cementing materials (i.e. fly ash, silica fume) a good indication on its future applicability is obtained.

## 2. Experimental part

### 2.1. Sample selection and processing

The main physicochemical characteristics of the two samples (designated as RHA8 and RHA12) are summarized in Table 1. RHAs originate from the two plants of the supplier, where feed rice husk and burning/cooling mode are different; in particular, in the case of RHA12 production slightly lower burning temperatures were applied (by approximately  $50 \text{ }^\circ\text{C}$ ) than in the case of RHA8 production, resulting in increase on amorphous silica content (by approximately 7%) but also

**Table 1**  
Chemical composition (% by mass) and main physical characteristics of raw materials.

	Cement	RHA8	RHA12
Moisture <sup>a</sup>	n.a.	0.01	0.01
SiO <sub>2</sub>	19.96	89.47	93.15
SiO <sub>2</sub> (reactive) <sup>b</sup>	n.a.	52.38	59.15
$\gamma\text{S}^c$	n.a.	58.57	63.50
CaO	64.72	1.10	0.89
Al <sub>2</sub> O <sub>3</sub>	4.71	0.18	0.13
MgO	3.65	0.44	0.40
SO <sub>3</sub>	2.62	0.11	0.10
K <sub>2</sub> O	0.55	1.32	1.63
P <sub>2</sub> O <sub>5</sub>	0.12	0.74	0.51
Fe <sub>2</sub> O <sub>3</sub>	3.68	0.25 (ppm)	0.18 (ppm)
Na <sub>2</sub> O	0.21	620.00 (ppm)	160.00 (ppm)
Cl		910.00 (ppm)	410.00 (ppm)
LOI	2.91	4.06	5.61
IR <sup>b</sup>	0.21	41.33	36.29
pH <sup>d</sup>		8.64	9.21
Glass phase <sup>e</sup>		58.67	63.71
R45 – as received (%) <sup>f</sup>	6.63	81.7	91.7
R45 – P level (%)		29.7	27.2
R45 – U level (%)		6.5	7.4
Blaine – P level (cm <sup>2</sup> /g)	3865	3820	3930
Blaine – U level (cm <sup>2</sup> /g)		7000	6550

<sup>a</sup> Determined according to ASTM C311-98b.

<sup>b</sup> The method described in EN 196-2 was followed for insoluble residue and reactive silica determination.

<sup>c</sup> Active ratio, defined as the part of silica being reactive.

<sup>d</sup> Determined according to ISO 6588.

<sup>e</sup> The procedure described in RILEM Recommendations (TC FAB-67 Use of Fly Ash in Building) was followed for determining the glass phase content of RHA.

<sup>f</sup> All 45-micron residues were determined with the aid of Alpine apparatus.

on increase of LOI as well. XRD examination was performed with a Siemens D 5000 X-ray diffractometer (CuK<sub>α</sub> radiation, 40 kV, 30 mA) operated at  $0.02^\circ/\text{s}$  in a  $2\theta$  scale. It revealed that the samples exhibited similarities with a typical broad hump confirming their amorphous structure and a distinct peak of SiO<sub>2</sub> in the form of cristobalite (see Fig. 1).

As-received RHAs were ground in a lab ball mill; the aim was to produce samples with similar particle size distribution (PSD) at two levels of Blaine fineness, i.e. 4000 and 7000 cm<sup>2</sup>/g. The respective samples were annotated as P (for 4000 cm<sup>2</sup>/g) and U (7000 cm<sup>2</sup>/g) respectively. This approach would enable to record (a) the pure effect of fineness on RHA reactivity (physical effect) and (b) the effect of active components (chemical effect) by neutralizing PSD differences between RHA8 and 12. Those effects were monitored in mortar and concrete. No notable differences were observed in the energy consumption of the ball mill when grinding the two samples, which can be characterized as “easy-to-grind”, due to the absence of hard and abrasive quartz. The success of the grinding procedure is verified from the Blaine values, 45-micron sieve residues (Table 1) and the similar PSD of the ground ashes (Fig. 2). The latter was measured with the aid of Cilas 1064 laser particle size analyser.

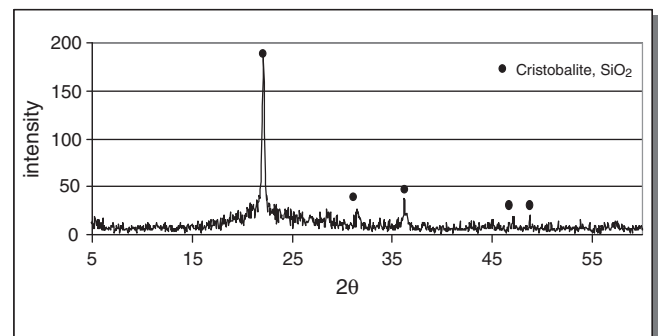
### 2.2. Pozzolanic activity

Even though they do not fully represent the complex evolution of hydration reactions with cement, accelerated pozzolanic tests may be employed for a quick approximation of the RHA reactivity. This is further necessitated given that inherent characteristics such as reactive silica cannot be rated as an absolute index of the reactivity of the RHA (or any other SCM) in blended cement [15]. Considering the above, the Fratini test [16] was used to derive information on the potential reactivity of RHA; the test involves hydrothermal curing of the suspensions (RHA-to-cement ratio equal to 1:5) for 8 days at  $40 \text{ }^\circ\text{C}$  and 100% RH. At the end of the curing period, the suspensions are analysed for Ca content and alkalinity. Each mixture was tested twice and the mean values are reported. Comparisons are made using the solubility curve of Ca(OH)<sub>2</sub>.

### 2.3. Testing in mortar and paste

#### 2.3.1. Mortars and compressive strength

Compressive strength development was monitored on mortar specimens prepared in accordance with EN 196-1 (cementitious materials-to-sand ratio of 1:3 and W/C<sub>M</sub> of 0.5). 10%, 20% and 30% replacements of cement by each RHA (U and P levels) were adopted. CEM I 42,5N was used and its main physicochemical characteristics are shown in Table 1. Standard silica sand according to EN 196-1 requirements was used as the mortar aggregate. Compression tests were conducted at 2, 7, 28, 90 and 365 days after mixing. Mortar with no RHA was also



**Fig. 1.** X-ray diffraction graph of RHA8 (identical to RHA12).

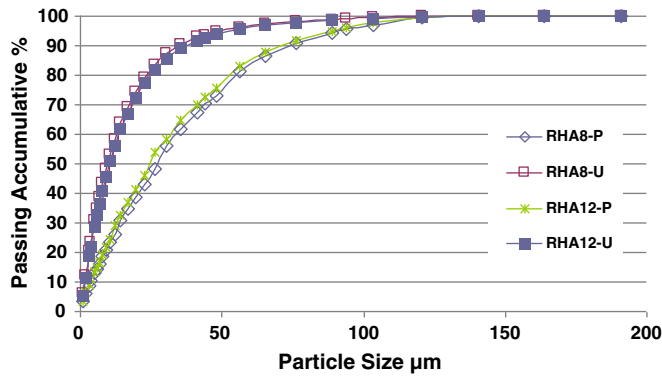


Fig. 2. Particle size distribution of RHA8 and RHA12 ground to two levels of fineness.

prepared (reference) for comparison. Mix design is summarized in Table 2.

### 2.3.2. Pastes and pozzolanic reaction

Similarly to the procedure above, but with no aggregate, paste specimens were also prepared and cast in plastic vials after being intensively shaken to remove any air content. Hydration was terminated at the strength testing intervals using a procedure where the paste prisms are soaked in ethanol and diethylether for 30 min and subsequently dried at 40 °C under vacuum [17]. The evolution of the pozzolanic reaction in pastes was monitored by thermogravimetric analysis (TG). This can be achieved by determining the amount of unbound  $\text{Ca}(\text{OH})_2$  (expressed as the sum of the weight loss occurring in the temperature region of 400–550 °C and the free- $\text{Ca}(\text{OH})_2$  transformed into calcium carbonate) in the hardened paste at the testing ages. The measurements were performed in a Mettler STARE 851/LF/1600 TG/SDTA. A platinum crucible with 70  $\mu\text{l}$  capacity was used and the mass of the examined samples ranged from 45 to 55 mg. The samples were tested in a nitrogen atmosphere (50 ml/min) at a heating rate of 10 °C/min from ambient temperature to 1000 °C.

### 2.3.3. RHA reaction degree

For measuring the reacted fraction of RHA, the insoluble residues of the cement and RHA were determined after a 1-hour treatment with picric acid-methanol and water solution. Briefly, 1 g of each specimen was added to a beaker containing a well-stirred solution of 9 g picric acid and 60 ml of methanol. After a 15-min stirring, approximately 40 ml of deionised water was added and stirring continued for another 45-min. Then it was filtered through a medium pore size filter paper and the filter was then washed with methanol (until the yellow colour diminished) and about 250 ml of deionised water. The residue was then transferred into a platinum crucible and ignited in an electric furnace at

Table 2  
Mixtures prepared for mortar testing with two levels of fineness for each RHA (quantities in grammes).

	Cement	RHA8 <sub>p</sub>	RHA8 <sub>u</sub>	RHA12 <sub>p</sub>	RHA12 <sub>u</sub>	Sand	Water
Reference	450	0	0	0	0	1350	225
RHA8 <sub>p</sub> – 10%	405	45	0	0	0	1350	225
RHA8 <sub>p</sub> – 20%	360	90	0	0	0	1350	225
RHA8 <sub>p</sub> – 30%	315	135	0	0	0	1350	225
RHA12 <sub>p</sub> – 10%	405	0	0	45	0	1350	225
RHA12 <sub>p</sub> – 20%	360	0	0	90	0	1350	225
RHA12 <sub>p</sub> – 30%	315	0	0	135	0	1350	225
RHA8 <sub>u</sub> – 10%	405	0	45	0	0	1350	225
RHA8 <sub>u</sub> – 20%	360	0	90	0	0	1350	225
RHA8 <sub>u</sub> – 30%	315	0	135	0	0	1350	225
RHA12 <sub>u</sub> – 10%	405	0	0	0	45	1350	225
RHA12 <sub>u</sub> – 20%	360	0	0	0	90	1350	225
RHA12 <sub>u</sub> – 30%	315	0	0	0	135	1350	225

950 °C for 60 min. Corrections were made carrying out blank tests with no sample. The same procedure was performed for the paste samples whose hydration was terminated at selected ages. Then the reacted fraction ( $R_{\%}$ ) of each RHA in the different hydrating systems was calculated with the use of Eq. (1) [18]:

$$R_{\%} = 1 - \frac{S_s - P_c S_c}{P_f S_f} \quad (1)$$

where  $S_s$  is the residue per gramme of the paste specimen,  $S_c$  and  $S_f$  are the residue per gramme of plain cement paste and residue per gramme of RHA,  $P_c$  and  $P_f$  are the weight percentage of cement and RHA of each specimen tested respectively.

### 2.4. RHA concrete

During preparation of concrete mixtures, RHA (ground to P-level) replaced 10 and 20% b.w. of cement, both cement (annotation: CEM) and aggregates (AGGR). This addition was selected because it is not too high (that could change drastically the hydration rate of the binder) nor too low (so as to enable to monitor its effect). Further, it is realistic since even if utilized in blended cement, RHA inclusion is not expected to be higher than 20–30%, a fact that coincides with literature findings that indicate an optimum addition of 10–15% [9–11]. The water content for all specimens was kept constant (186 kg/m<sup>3</sup>), while a polycarboxylate-based superplasticizer (SP) was added when required to retain slump of the fresh concrete at desired levels (60–70 mm). The same type of SP was used for all mixtures. Coarse (31.5 mm maximum size) and fine (4 mm) limestone aggregates were added during mixing. Table 3 summarizes the concrete mix designs.

Cubic specimens of 10 × 10 × 10 cm<sup>3</sup> were moulded for strength monitoring, while cylindrical specimens (h = 20 cm, d = 10 cm) were also prepared for testing the concrete resistance to chloride attack using ASTM C1202. In accordance to the latter, concrete samples 50 mm thick were cut off from the middle of the cylindrical moulds, after curing for 55 days in water saturated with hydrated lime (adequate time to assure that pozzolanic reactions are developing); the specimens were then coated (twice) on the cylindrical surface with epoxy resin and subjected on a potential of 60 V DC. The charge passing through the specimens was recorded. Two specimens of each mixture were tested and the mean value is reported. Concrete strength results were used to estimate the efficiency factors (or k-values) of RHA-based concrete. Comparison was made with the respective values of other commonly used SCMs, such as fly ash and silica fume.

## 3. Results and discussion

### 3.1. Fratini test

Results are shown in Fig. 3. Almost all systems with RHA ground to 4000 cm<sup>2</sup>/g exhibited adequate pozzolanic activity. The only system that was measured above the  $\text{Ca}(\text{OH})_2$  saturation curve was 10RHA8. On the contrary, the respective cement with 10RHA12 was measured below the saturation curve. Similarly, all RHA12-based cements exhibited a lower  $\text{Ca}^{2+}$ /alkalinity profile compared to the cements with equal replacement ratio by RHA8. Given that cement content is the same (thus expected CH due to cement hydration is also expected to be more or less the same) and the fact that the two RHAs are of the same fineness and PSD, the superiority of RHA12 cements should be attributed to its enrichment in reactive silica. The reactivity of RHA is enhanced with grinding as shown by further decreasing  $\text{Ca}^{2+}$ /alkalinity levels for the same RHA participation (Fig. 3(b)). This is due to faster  $\text{Ca}(\text{OH})_2$  consumption compared to the respective systems with the P-ground RHA. Having higher specific surface, U-RHA provides more space for reaction, thus CH depletion by RHA active component is greater.

**Table 3**  
Concrete mix designs.

Components in kg/m <sup>3</sup>	REF	Cement replacement				Aggregate replacement			
		10RHA8	20RHA8	10RHA12	20RHA12	10RHA8	20RHA8	10RHA12	20RHA12
Cement (C)	310	279	248	279	248	310	310	310	310
RHA (P)	0	31	62	31	62	31	62	31	62
Water (W)	186	186	186	186	186	186	186	186	186
W/(C + P)	0.60	0.60	0.60	0.60	0.60	0.55	0.50	0.55	0.50
Coarse aggr (max size 31.5 mm)	840	835	840	840	840	828	795	828	795
Fine aggr (max size 4 mm)	1030	1020	1030	1030	1030	1012	993	1012	993
SP (g/lt)	20.0	24.0	28.9	25.5	28.9	30.6	48.1	34.0	49.3

The Fratini test results demonstrate that amorphous silica and fineness have a significant effect on the reactivity of RHA in alkaline environment. Although this was anticipated from the beginning, results herein should be utilized cautiously and for obtaining a comparative view on the samples tested. Primal reason for that is the fact that the test is being carried out under controlled conditions that might have little to do with the actual hydrating environment of the hardened mortar or concrete under normal conditions.

### 3.2. Strength development

Table 4 summarizes the strength profile of the P-ground RHA with time. Over the examined period, the reference sample exhibits strength superiority at all ages, but that is especially pronounced at early ages. After the first week, the RHA samples develop strength faster than the reference and for RHA content up to 20% they reach competitive strength values at 90 days. In the case of 30% replacement, it is evident that RHA activity cannot compensate for the equal loss of clinker minerals. Grinding as low as to 4000 cm<sup>2</sup>/g, results in RHA that can

only be rated efficient after the first month of hydration. Still at all replacement levels RHA12 samples outperform RHA8. As explained above, this is normally the result of its higher reactive silica content since the ashes used are of the same fineness level.

When grinding was extended to 7000 cm<sup>2</sup>/g, RHA performance was notably improved at all ages, as seen in Table 5. Both types of RHA are now more reactive and supply extra strength to their systems. The more reactive RHA12 remains clearly more effective at all ages when compared to RHA8 that lacks almost a 7% in reactive silica. In fact, the 10RHA12<sub>p</sub> sample exhibits a strength profile similar to the reference cement with no RHA; this indicates that RHA12 ground to 7000 cm<sup>2</sup>/g is equivalent to CEM I 42,5N, as long as replacement is limited to 10% b.w. As replacement of the basic binder increases, the strength decreases but the beneficial influence of the supplementary grinding (compared to cements with P-level RHA) is still evident. This is depicted in Fig. 4, where it may be seen that the major benefit of the extra grinding is mainly located in the 28 days values (i.e. gain of 7–9 MPa is recorded), while the respective benefit at 2 days is limited. This is consistent with previous works on RHA, both on the optimal level to achieve maximum strength (10–15% by cement weight) [12,19,20] and the specific surface optimize in terms of packing and filler effect. The latter confirm the sensitivity of RHA performance to fineness changes and explain to a big extent the satisfactory results of U-ground RHA cements.

### 3.3. Fixing lime ability

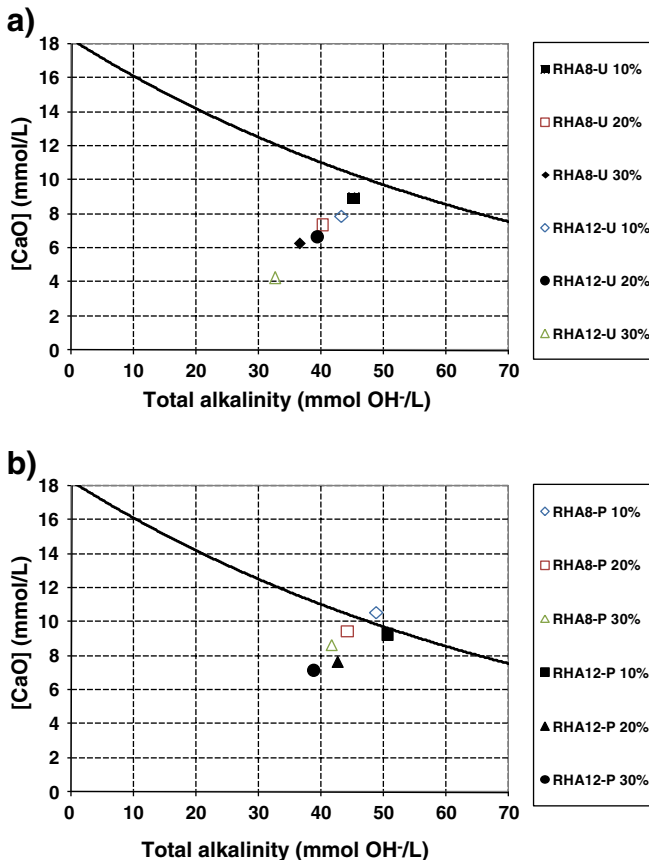
Thermal analysis was employed, not to identify the resulting hydration products, but mainly to obtain a quantitative evaluation of the CH content of the RHA-cement matrix. By estimating this quantity at different stages of curing, the rate at which pozzolanic reactions are progressing can be obtained. For that reason, Eq. (2) proposed by Paya et al. [18] was used to calculate the percentage of fixed lime (FL);

$$\text{Fixed Lime (\%)} = \frac{(\text{CH}_c \cdot C_{\%}) - \text{CH}_p}{\text{CH}_c \cdot C_{\%}} \times 100 \quad (2)$$

where CH<sub>c</sub> is the CH content of the no-RHA paste for a given curing time, CH<sub>p</sub> is the CH content of the RHA-cement paste at the same age and C<sub>%</sub> is the proportion of cement in the examined paste. Results are shown in Fig. 5 and refer to P-ground RHA samples and hydration intervals of 2, 7, 28 and 90 days after mixing.

**Table 4**  
Compressive strength profile of RHA-containing cements (P-level of grinding).

	2 days	7 days	28 days	90 days
Reference	23.7	37.8	54.6	61.3
RHA8 <sub>p</sub> – 10%	22.0	34.6	47.8	57.9
RHA8 <sub>p</sub> – 20%	18.9	31.8	40.8	55.7
RHA8 <sub>p</sub> – 30%	14.9	24.8	39.7	48.1
RHA12 <sub>p</sub> – 10%	21.0	33.8	44.4	58.5
RHA12 <sub>p</sub> – 20%	18.8	31.3	44.7	57.2
RHA12 <sub>p</sub> – 30%	15.5	25.3	39.8	48.5



**Fig. 3.** Fratini test results for (a) P-level and (b) U-level ground RHA.

**Table 5**  
Compressive strength profile of RHA-containing cements (U-level of grinding).

	2 days	7 days	28 days
Reference	23.7	37.8	54.6
RHA8 <sub>U</sub> – 10%	20.5	36.4	50.7
RHA8 <sub>U</sub> – 20%	18.9	32.3	49.5
RHA8 <sub>U</sub> – 30%	16.1	28.3	47.3
RHA12 <sub>U</sub> – 10%	22.8	38.2	53.8
RHA12 <sub>U</sub> – 20%	19.8	33.6	51.4
RHA12 <sub>U</sub> – 30%	17.1	30.1	48.8

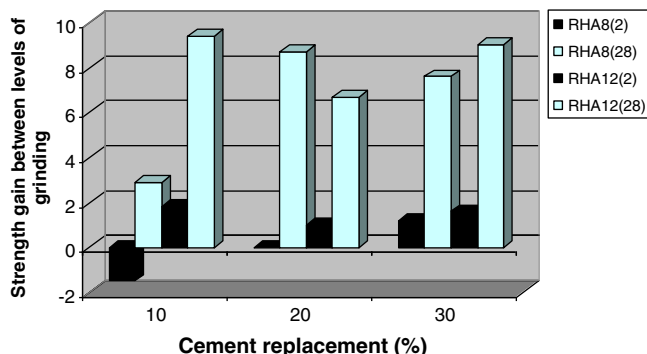
Contrary to cement blended with other SCMs (e.g. fly ash), no negative values were recorded even at early curing. A FL value below zero usually denotes the inability of the SCM to act early. It can also be the outcome of excessive CH coming from the hydration of free CaO in the SCM (e.g. high-calcium fly ash), which obviously is not the case here. FL increases with curing time and increasing RHA-to-cement ratios and is greatest for 30% RHA at the end of curing, with values of 55% and 44% for RHA12 and 8 respectively. Generally, RHA12 produces higher FL values for all cement replacements compared to RHA8. This is in agreement with strength results presented earlier. For anticipating the importance of the latter values, a comparative overview of FL achieved by other local SCMs (commonly used in cement industry) is given in Table 6.

Even though HCFA is underestimated with the FL approach (due to its own CH contribution), a reactive RHA (12) is at least equally effective in consuming CH with both types of fly ashes [21], but normally (due to the extremely high specific surface) less reactive than a residue from oil cracking process (FCC) [22]. The results are even more encouraging considering the low level of RHA fineness; with the strength results in mind, it is postulated that even higher FL values can be obtained if RHA is further mechanically treated.

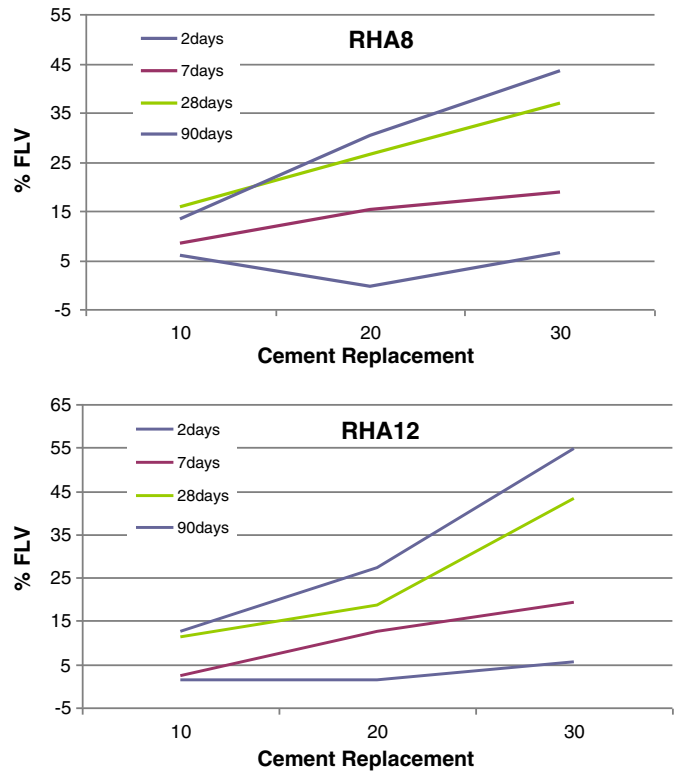
### 3.4. RHA reaction degree

Reacted fraction results for RHA-cements are shown in Fig. 6. After as little as 2 days of hydration, a significant part of RHA (almost a third) has undergone reaction. RHA continues to react over time and more than half of both samples have reacted after 3 months. Until the first week, the samples with higher RHA contents (>20%) react slower than the 10%-specimens, probably as a result of the lack of CH in the respective systems that lowers alkalinity of the system. A similar trend has been reported in cementitious systems with fly ash, where according to Zhang et al. [19], increasing fly ash percentage leads to acceleration of the cement hydration and a slowing down of the pozzolanic reaction rate.

Contrary to what is observed during the early ages, at the end of 28 days and onwards, the reaction of the samples with significant RHA content is accelerated compared to the 10%-RHA samples; this is in alignment with the strength gain results of the respective mortars



**Fig. 4.** Strength gain of RHA-blended cements with age and grinding level.



**Fig. 5.** Fixed lime values with curing age and RHA content for P-ground samples.

during the same period (see Fig. 4). Comparing the two RHA samples, sample 12 reacts somewhat faster than 8. Although the factors that affect RH participation in the hydrating scheme have not been fully explored, the critical factors seem to be the amorphousness of the material (primarily), the alkalinity of the pore solution, fineness and alkali content of the SCM. Based on the above and given the similar PSD and low alkali content of the RHA tested, the faster RHA12 reaction should be attributed to its higher glass content. Even though differences are not very large (approx. 4–5%), the combined effect of faster dissolution and higher silica content can explain the strength superiority of the RHA12 systems at later ages. Others [14] have provided data showing that the main reason for the later stage strength increase was the pore structure of RHA which induced the so called “internal curing” of concrete.

### 3.5. RHA concrete

#### 3.5.1. Workability

Slump is a direct indication of the workability of a concrete and a comparative factor between mixtures where same amount of water has been used. With common slump target and similar water added for all mixtures, the parameter that can allow conclusions on workability is the amount of SP used for attaining the desired slump. With all other factors constant, the physicochemical characteristics of the ashes

**Table 6**  
FL ability of different SCMs used as cement additives (replacement ratio: 20%).

	Specific surface area (cm <sup>2</sup> /g)	28 days
RHA <sup>a</sup>	7.000	26.6
HCFA <sup>b</sup>	5.450	8.7
LCFA <sup>b</sup>	5.600	26.3
FCC <sup>b</sup>	79.000	56.6

<sup>a</sup> This work.

<sup>b</sup> Earlier works [21,22], HCFA: High calcium fly ash, LCFA: Low calcium fly ash, FCC: Catalyst from refinery cracking unit.

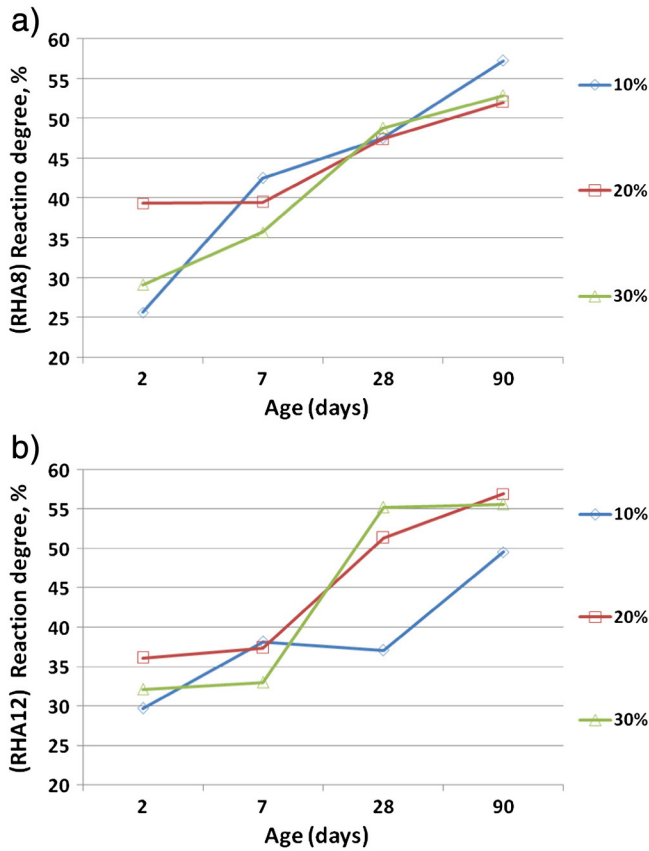


Fig. 6. Reaction degree for (a) RHA8 and (b) RHA12 in relation to curing age and cement replacement.

used are responsible for any differences. As seen in Table 3 any RHA addition increased the SP demand (or else the water requirement of concrete). This demand is proportional – for both types of replacement applied (cement and aggregates) – to the amount of RHA used, with the maximum increase being recorded in the cases that RHA replaced aggregates. This is obviously not only due to higher binder content but also due to lower  $W/(C + P)$  ratio, and the fact that RHA didn't replace only the very fine (filler) part of the aggregates.

Results related to the RHA effect on workability are conflicting in the literature; water demand increase has been reported [2,12] and explained through the hydrophilic nature of RHA and its – usually very high – specific surface that requires more water. The latter however is also responsible for particles packing improvement, thus flow characteristics, assuming almost spherical shaping. Similarly, theories about the absorption of fine particles of RHA on the oppositely charged surfaces of cement particles and subsequent avoidance of flocculation work in water demand decreasing directions. In any case, in the frame of this work, water demand increase was kept low, while the quality of RHA had no effect on these requirements as revealed by the similar SP addition levels for concrete made either with RHA8 or 12. This was more or less expected due to their identical PSD and the absence of any mineral components that can be associated with water absorptivity (e.g. anhydrite,  $C_3A$ , etc.).

### 3.5.2. Strength results and modelling

The experimental results from compressive strength tests are summarized in Fig. 7 (7a for RHA8 and 7b for RHA12). It is generally observed that when RHA substitutes aggregates, strengths higher than the reference concrete are achieved. The strength increase is due to the higher content of calcium silicate hydrate (C–S–H; the main carrier of strength in hardened cement) in the RHA specimens, due to the reaction of the calcium hydroxide produced from cement hydration with the

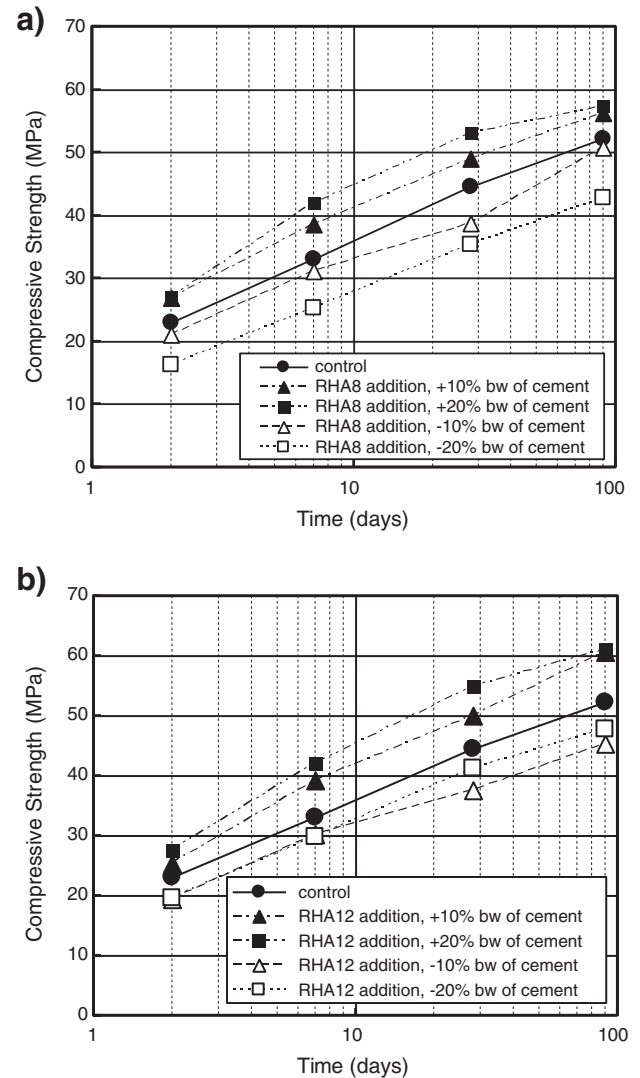


Fig. 7. Compressive strength development for concrete incorporating (a) RHA8 and (b) RHA12. The +10% and +20% addition of RHA by weight (bw) of cement refers to the case of aggregate replacement by RHA (constant water and cement content) and the –10% and –20% addition of RHA by weight (bw) of cement refers to the case of cement replacement by RHA (constant water and almost constant aggregate content).

active silica of the RHA. This is testified by fixed lime values shown earlier. There is a reasonable distribution of the strength increase according to the RHA content. On the contrary, when RHA replaced part of cement, a strength decrease was recorded. Higher addition of RHA8 (i.e. 20% b.w. of cement) brings about a strength decrease throughout the hydrating period, a fact not occurring with more reactive RHA12, where the concrete with 20% RHA usage has higher strength than that of 10% RHA usage. In any case – and compared to the no-RHA concrete – all four concretes that replaced part of the basic binder exhibit strength very close to the control specimen, both in the early and later stage of curing.

In order to estimate the  $k$ -values, the following procedure was followed. The compressive strength,  $f_c$  (MPa), of a Portland cement concrete can be estimated by the following empirical equation [21]:

$$f_c = K \left( \frac{1}{W/C} - a \right) \quad (3)$$

where  $W$  is the water content in the initial concrete mix ( $\text{kg}/\text{m}^3$ ),  $C$  is the cement content in the concrete ( $\text{kg}/\text{m}^3$ ),  $K$  is a parameter depending on the cement type (MPa) and  $a$  a parameter depending mainly on time and curing. For the cement used in this work,  $K$  was calculated as

**Table 7**  
Efficiency factors (k-values) for various supplementary cementing materials.

Concrete property	RHA8 <sup>a</sup>	RHA12 <sup>a</sup>	HCFA <sup>b</sup>	FL <sup>b</sup>	SF <sup>b</sup>
Strength, 2 days	0.5	0.5	0.8	–	–
Strength, 7 days	0.7	0.8	0.9	–	–
Strength, 28 days	0.7	0.8	0.9	0.5	3.0
Strength, 90 days	0.8	0.9	0.9	0.7	2.4

<sup>a</sup> This work.

<sup>b</sup> Earlier works [23–25]. HCFA: High-calcium fly ash, FL: anthracite fly ash of almost zero calcium content, SF: silica fume.

38.1 MPa. Using the mean measured values of the compressive strength of the control specimen,  $a$  is estimated as 1.06, 0.8, 0.5, and 0.3, for 2, 7, 28, and 90 days, respectively.

In the case of SCM-concrete, the following expression for compressive strength can be used which involves the concept of k-value:

$$f_c = K \left( \frac{1}{W/(C + kP)} - a \right) \quad (4)$$

where  $P$  is the SCM content in the concrete ( $\text{kg}/\text{m}^3$ ). The efficiency factor (or k-value) is defined as the part of the SCM in a pozzolanic concrete which can be considered as equivalent to Portland cement, having the same properties as the concrete without SCM (obviously  $k = 1$  for Portland cement). The quantity of the SCM in the mixture can be multiplied by the k-value to estimate the equivalent cement content, which can be added to the cement content for the determination of the water-to-cement ratio, minimum required cement content, etc. The compressive strength was so far used as the property for the estimation of k-values. Using Eq. (4), the measured values of the compressive strength given in Fig. 6, and the  $W$ ,  $C$  and  $P$  contents given in Table 3, the k-values for the SCMs of the present work (RHA8 and RHA12) were calculated and are given in Table 7. In general, RHA exhibits adequate strengths resulting at moderate k-values, about 0.8 at 28 days. This behaviour is better than low-calcium fly ash (FL where  $k = 0.5$ – $0.7$ ) and almost equivalent to high-calcium fly ash, but much worse compared to silica fume (SF, where  $k = 2.5$ – $3$ ). RHA exhibits these k-values due to high silica content, higher than FL, and lower than SF; whereas in addition with the later, RHA is much coarser than SF contributing in lower k-values. A more comprehensive correlation among k-values and silica content is given elsewhere [26].

### 3.5.3. Chloride resistance

Data in Table 8 reveal the very good resistance of RHA-based concrete in chloride penetration test with respect to the no-RHA mixture. The curing time applied here (almost two months) allowed the development of the RHA pozzolanicity, however – as shown by reaction degree results – this has not been completed at the time of testing.

It is obvious that the grinding process before usage led to the creation of finer particles than those of cement. It is a consensus that – in concrete level – the smaller particles of several ashes (through filler effect) are strengthening the packing between aggregates and cement grains, thereby reducing the porosity of the hardened product and ultimately its permeability. The P-level ground RHAs were used and even with this lower level of grinding RHA-concretes exhibit a

lower (for cement replacement) and significantly lower (for aggregate replacement) permeability to chloride ingress. Reference concrete at the same time exhibits a rather moderate performance under this attack.

Again, the chemical reactivity effect of RHA cannot be neglected since it becomes clear that concrete with more reactive RHA12 for the respective replacement type and levels outperforms the concretes that incorporated RHA8. Obviously, pore refining [27,28] is enhanced by the additional creation of C–S–H gel (“secondary”) which is due to the pozzolanic reaction of more reactive siliceous RHA12. The higher C–S–H content especially that with lower C/S ratio, can bind more  $\text{Na}^+$  ions and, therefore, the accompanying  $\text{Cl}^-$ . On the other hand, the pore restructuring due to pozzolanic products may decrease intrinsic diffusivity as well [27].

## 4. Conclusions

For recording the effect of RHA chemical reactivity and fineness on mortar and concrete, two RHA of different reactive silica contents were utilized after ground to similar PSD. The fineness effect was monitored by grinding RHA to two different levels ( $P$  and  $U$  as explained in the main body of this work).

Major conclusions drawn are;

1. RHA activity is governed by its content in amorphous silica and size. Best results were achieved when the more reactive RHA was ground to  $7000 \text{ cm}^2/\text{g}$ . Under similar fineness level, less reactive ash failed to provide similar strength (in mortar and concrete) for a good range of cement replacement levels (10–30% b.w.).
2. Supplementary grinding increases the percentage of RHA that can be rated equal to Portland cement. Its beneficial effect is primarily located at 28 days, while it remains marginal at early ages.
3. A good ability of RHA to consume available lime is recorded; this is comparable or even higher than the respective ability of fly ash (high or low calcium ones) but lower than very active by-products such as spent catalyst from oil cracking processes. Part of this ability should be attributed to its relatively quick reaction rate (approximately 55% after 90 days), a result of its high amorphousness.
4. RHA addition in concrete is feasible since slump can be retained at target with the small addition of a superplasticizer, strength profile remains competitive (and can be improved with aggregate replacement) and chloride resistance is significantly improved. Assuming workability will not deteriorate, further grinding can have a significant benefit both for mechanical and durability performance of RHA concrete.
5. RHA exhibits adequate reactivity resulting at moderate concrete k-values, about 0.8 at 28 days. This behaviour is better than low-calcium fly ash (FL where  $k = 0.5$ – $0.7$ ) but worse compared to silica fume (SF, where  $k = 2.5$ – $3$ ).
6. Practically, even in countries with limited production, RHA can be a valuable addition in special products such as high strength concrete and repair mortars. The notable improvement through a controlled grinding (to keep energy cost as low as possible) was verified in this work and indicates that its potential can be furthered improved even at same cost (e.g. intergrinding during cement milling).

**Table 8**  
Concrete mix designs with workability and chloride resistance results.

Components in $\text{kg}/\text{m}^3$	REF	Cement replacement				Aggregate replacement			
		10RHA8	20RHA8	10RHA12	20RHA12	10RHA8	20RHA8	10RHA12	20RHA12
Charge passed (Cbs)	3135	3896	1962	2962	996	1842	490	287	1049
Adjusted charge passed (Cbs)	2719	3380	1702	2569	864	1598	425	249	910
Permeability class	Moderate	Moderate	Low	Moderate	Very low	Low	Very low	Very low	Very low

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