An investigation of the effectiveness of the utilization of biomass ashes as pozzolanic materials

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HIGHLIGHTS

- Evaluation of biomass ashes as SCMs, for concrete strength and chloride penetration.
- High SiO_2 content of biomass ash does not imply a pozzolanic material with a high efficiency factor.
- Concentration of other compounds, even for high SiO_2 content is responsible for low k-values.
- Biomass ash from agro-industrial by-products can be used as pozzolanic material in concrete.

ARTICLE INFO

ABSTRACT

Utilization of biomass ash from agro-industrial by-products (containing large amounts of silica in amorphous form) in cement manufacturing and/or concrete production can be an alternative solution to the incorporation of the traditionally used supplementary cementing materials (SCMs). An evaluation of biomass ashes, identified in the literature, with varying SiO_2 contents in terms of concrete strength and performance in chloride exposure is the focus of this study. Results indicate that these materials are effective on concrete strength development and extremely efficient in reducing the concrete permeability. The dependency of this behavior on the level of SiO_2 of the ash content was examined in depth and was concluded that it is affected by the composition of other components of the biomass ash.

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1. Introduction

Ordinary Portland cement is well recognized as the major construction material throughout the world. Given its known environmental issues (in terms of energy and raw materials required for its production), direct reduction of its clinker content through utilization of industrial by-products as supplementary cementing materials (SCM), is a very promising first step in reducing considerably the associated environmental burden. Just to reinforce this observation, it has been estimated [1] that 18% replacement of Portland cement would result in a 17% reduction of CO_2 emissions and that, if just 30% of cement used globally were replaced with SCM, the rise in CO_2 emissions from cement production could be reversed.

Industrial by-products, such as blast furnace slag, fly ash and silica fume have been used as traditionally supplementary cement replacement materials (both in the production of clinker and in partial replacement of Portland cement in mortars and concrete) for the last 25 years. A number of investigations have demonstrated the validity of using these materials from both technical, environmental reasons and, at times, even economical [2–4]. Today, research studies [5–8] are indicating the feasibility of using pozzolans originating from the agricultural industry, through biomass utilization. Biomass in general, considered as one of the major renewable energy sources (in absolute terms), accounts for more than 4% of the total energy consumption in the European Union (EU) [9]. However, despite its wide use as energy source much of the waste produced remain unprocessed [10]. Various types of biomass, from agro-industrial processes, produces ash (as rice husk ash, palm oil fuel ash, sugar cane bagasse ash, etc.) which under certain conditions (chemical configuration, level of fineness) can have a similar pozzolanic activity to coal fly ash [5–8,11]. These agro-waste ashes, containing a large amount of

silica in amorphous form, have potential for use as pozzolanic materials replacing cement [12].

Strict interpretation of ASTM C618 [13] (and of most standards in other countries addressing a similar issue) precludes the use of any material (including biomass ash) not derived from coal combustion, in cement and concrete utilization. The fraction of fly ash that qualifies under this strict interpretation for use in concrete is in rapid decline due to issues such as co-firing fuels with coal and injecting a variety of materials for emission control [11]. This observation is essential, due to the fact that biomass ash can be originated through a number of processes including pure solid biomass combustion or co-firing (of a less than 10% biomass by energy content) with coal. In terms of the latter, even though biomass co-firing is a way of producing cost effective and efficient renewable power, the relatively low amounts of biomass in the co-firing process leads in general to low contents of the biomass derived ass. Solid biomass combustion is a proven technology for heat and power production, where the technologies of fluidised bed and grate furnace combustion are mainly used [14,15]. The quantity and quality of ashes produced in a biomass power plant are strongly influenced by the characteristics of the biomass used: agriculture wastes or herbaceous biomass, wood or bark [14,16]. Combustion of wood, for example, generates fewer amounts of ashes to be managed, because herbaceous biomass, agriculture wastes and bark have higher ash content when compared to wood [12]. Biomass ashes differ from coal ashes, in terms of chemistry and mineralogy. The characteristics of ashes from biomass combustion vary widely and are influenced by: (i) biomass characteristics (for example, herbaceous material, wood or bark), (ii) combustion technology (for example, fixed bed or fluidized bed), (iii) the location where the ashes are collected (for example, bottom ashes or fly ashes) [14,15,17]. Typically, fly ash from neat biomass combustion has more alkali (Na and K) and less alumina (Al_2O_3) than coal fly ash [18,19].

Most of the biomass ash produced in thermal power plants is either disposed of in landfill or recycled on agricultural fields or forest [14]. Considering that the disposal cost of biomass ashes and biomass ash volumes are increasing (worldwide), a sustainable ash management has to be established. In addition, exploitation of the cement/concrete industry of agro-industrial ashes can be an attractive activity for several countries which use great volumes of rice husk, palm oil fuels and sugar cane bagasse as biomass in processes of energy cogeneration (such as China, India, Brazil and Thailand).

Considerable amount of work on developing analytical models for the evaluation of (traditional) SCM in concrete using the concept of efficiency factors (or k-values, to compare the relative performance of supplementary cementing materials on concrete durability) by Papadakis [2–4] has identified the high-added value of certain types of these materials and their pozzolanic properties on cement and mortar and their effects they entail on early concrete strength and volume stability [20–22].

The same principle can be applied to biomass ashes, as presented in this study. By selecting data from representative biomass ashes from the literature, the feasibility of their utilization in cement manufacturing, as pozzolanic materials is investigated. An evaluation of the ashes in terms of the derived efficiency factors for 28 days compressive strength (as calculated based on the analytical models of strength prediction developed and validated by some of the authors of this study), further enhanced by their performance in chloride penetration (as defined in ASTM C 1202 [23]) is presented in this study. The main aim is to try to shed some light on the specific influence of the main characteristics of biomass ashes on concrete strength development and performance in chloride exposure, exploring in this way their future utilization in cement manufacturing.

2. Types of biomass ashes investigated

Based on data from the literature, a range of characteristic types of biomass (and other) ashes was selected, including rice husk ash and mixtures (RHA), palm oil fuel ash (POFA), sugar cane bagasse ashes (SCBA) and wood ashes (WA). Their origin and main points concerning their chemical composition is briefly discussed bellow and presented in Table 1.

Rice husk ash (RHA), an agricultural waste material, produced by controlled burning of rice husk has shown to contain highly reactive silica which could contribute chemically to Portland cement ingredients. Typical highly reactive RHA ashes [24–26] with SiO_2 content of more than 90% were selected. Their reactivity is attributed to the high content of amorphous silica, and to the very large surface area governed by the porous structure of the particles. Generally, the reactivity is also favored by increasing the fineness of the RHA (expressed in this study as the median size d_{50} in μm). In addition certain RHA mixtures, utilizing eucalyptus bark (RHBA) and chop wood (BRWA) were also selected. Rice husk–bark ash [27] is a by-product produced from burning a mixture of rice husk (65%) and eucalyptus bark (35%) by fluidized bed combustion process in a biomass power plant (used as fuel). The level of SiO_2, (of more than 74%) indicates a high potential for pozzolanic reactivity. According to ASTM C 618, this particular type of biomass ash can be said to be Class N pozzolan since the sum of SiO_2, Al_2O_3, and Fe_2O_3 are higher than or close to 70%, SO_3 content is not higher than 4%, and loss of ignition (LOI) is close to 10%. Bagasse-rice husk-wood ash (BRWA) [28] is a by-product obtained from biomass power plants that use bagasse (82.5%), rice husk (15%) and chop wood (2.5%) co-burning in producing steam for generating electricity to supply the sugar mills. It should be noted that most of the BRWA is disposed of as waste in landfill which causes environmental problems such as air pollution as well as groundwater quality problem owing to the leaching of metals from the ashes. In terms of chemical composition, the sum of SiO_2, Al_2O_3, and Fe_2O_3 was 82.7% and the LOI was 3.6% (<10%) complying with ASTM C618 requirement as a natural pozzolan.

Palm oil fuel ash (POFA) is a by-product of the palm oil industry. It is a waste obtained from burning palm oil fibers, shells, and empty fruit bunches as fuel in producing steam to generate electricity for the palm oil extraction process. In general, it contains high amounts of silicon and aluminum oxides (in the amorphous state) and was recently accepted as a pozzolanic material [7]. According to the chemical composition of the types of POFA selected in this study [7,29–31], of an average SiO_2 composition from 55% to 65% and LOI in the region of 10%, it can be said that, although POFA is not a natural pozzolan, it may be classified as Class N (natural) pozzolan according to ASTM C618 [13].

Sugar Cane Bagasse Ash (SCBA) is a by-product of the industry involved with sugar cane and alcohol production. The bagasse is usually burned in boilers at temperatures varying from 700 to 900 °C. Preliminary investigations on SCBA have demonstrated that it presents the appropriate chemical composition for application as a pozzolan, mainly in regard to its high silica content and presence of amorphous silica [32]. However, it is important to note that the SiO_2 content (78.3%) covers amorphous and crystalline silica (from SCBA) and some sand contamination has been observed, identified by the presence of quartz and cristobalite phases in the diffraction patterns of SCBA. This high content of quartz is ultimately due to sand adhered to the sugar cane, which is harvested along with it. Even after washing the sugar cane, sand can represent as much as 2% in weight of the material that is processed [32]. After the loss of organic matter during bagasse burning, this proportion increases significantly. The presence of cristobalite, previously mentioned, can be associated to the high temperature in the boiler.

Table 1
Chemical composition and characterization of ashes.

Type	Ref.	SiO$_2$ (%)	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)	CaO (%)	SO$_3$ (%)	Na$_2$O$_3$ (%)	K$_2$O (%)	LOI	d_{50} (mm)	Density (kg/m^3)	[h]
Rice	GRHBA[a]	[27]	87.0	1.08	2.58	1.25	0.09	0.08	1.0	5.71	10.8	2150	k
Husk	GRHBA	[29]	74.8	0.20	0.80	5.90	0.50	0.20	2.0	11.2	10.8	2150	k
Ash	BRWA[b]	[28]	78.4	2.60	1.70	7.40	1.10	0.20	3.7	3.60	15.5	2100	k
	RHA	[24]	91.0	0.35	0.41	1.95	1.21	0.08	3.21	8.50	12.0	2060	k
	RHA	[26]	87.3	0.22	0.28	0.48	–	1.02	3.14	2.10	3.80	2060	k, RCPT
	RHA	[25]	92.9	0.31	0.26	0.53	–	0.08	2.06	1.97	–	–	RCPT
	RHA	[31]	91.6	0.35	0.40	0.60	–	0.30	1.60	3.70	7.41	2050	RCPT
Palm	GPOFA[c]	[7]	65.3	2.50	1.90	6.40	0.40	0.30	5.70	10.0	19.9	2170	k
Oil	GPOFA[d]	[7]	65.3	2.50	1.90	6.40	0.40	0.30	5.70	10.0	10.1	2330	k
Fuel	GPOFA	[29]	65.3	2.60	2.00	6.40	0.50	0.30	5.70	10.1	10.1	2330	k
Ash	POFA	[30]	55.5	9.20	5.60	12.4	2.30	–	–	7.90	10.7	2530	k
	POFA	[31]	63.6	1.60	1.40	7.60	0.20	0.10	6.90	9.60	7.20	2250	RCPT
Sugar	SCBA[e]	[34]	78.3	8.90	3.60	2.20	–	0.10	3.50	–	2.70	2530	k
Cane	SCBA	[5]	64.2	9.05	5.52	8.14	–	0.92	1.35	4.90	5.40	1850	k, RCPT
	SCBA	[32]	78.4	8.55	3.61	2.15	–	0.12	3.46	0.42	–	2530	k, RCPT
Wood	W(S)A[f]	[33]	31.8	28.0	2.64	10.5	0.45	6.50	10.4	27.0	–	2130	k
Ash	HCWA[g]	[35]	28.0	4.10	2.50	39.0	1.00	1.00	7.40	7.22	5.16	2520	k

[a] GRHBA: Ground rice husk bark ash, 65% rice husk and 35% eucalyptus bark.
[b] BRWA: Bagasse rice husk wood ash, 15% rice husk, 82.5% bagasse ash and 2.5% chop wood.
[c] GPOFA: Ground palm oil fuel ash, coarse ground.
[d] GPOFA: Ground palm oil fuel ash, fine ground.
[e] SCBA: Sugar cane bagasse ash.
[f] W(S)A: Wood (sawdust) ash.
[g] HCWA: High calcium wood ash.
[h] Denotes if the particular type of ash was used for strength (k) of for Rapid Chloride Permeability Test (RCPT) assessment.

Wood ash (*WA*) is the inorganic and organic residue generated due to combustion of wood and wood products (chips, saw dust, bark, etc.). Typically wood burned for fuel at pulp/paper mills or at wood products industries, consist of saw dust, wood chips, bark, saw mill scraps, hard chips rejected from pulping and excess screenings sheaves [33]. In a sense it can be related to fly ash since fly ash is obtained from coal, which is a fossilized wood. The chemical composition of the selected types of WA indicates very high LOI, high alkali content and very low SiO$_2$ values. Overall, these particular types of WA do not satisfy the requirements prescribed in ASTM Standard C618 [13] to be classified as a Class N pozzolan. It should also be noted that the high loss of ignition means that the wood ash contain appreciable amount of un-burnt carbon which reduces its pozzolanic activity. The un-burnt carbon is not pozzolanic and its presence serves as filler to the mixture.

2.1. Methodology followed for the evaluation of biomass ashes as cementitious materials

According to the chemical configuration of these types of ashes, the mix design (*w/c* ratio, cement content, SCM replacement level, aggregate size) used in each particular study and based on the compressive strength data available from the literature (noted as experimental), estimation of the compressive strength for a range of *k*-values, took place. Such calculations were possible using an analytical tool for the estimation of concrete strength and service life, well published, developed and validated by some of the authors of this study. For each type of biomass ash used in this study, different sets of compressive strength data were estimated for a range of *k*-values (from the very low value of 0.2 to higher values of 1.7). Each set of strength data, was evaluated in terms of statistical proximity to the experimental strength values, based on the principles of the least squares method (Table 2 and Fig. 1). The *k*-value of the set of data that provided the best fit was assumed to be the efficiency factor (for 28 days compressive strength) of the biomass ash.

In addition, where data were available, the performance of biomass ashes in terms of chloride ion penetration, expressed as the total charge passed through biomass ash blended concrete specimens (measured according to ASTM C 1202), were evaluated. Based on the values of charge (Coulombs) passed through each individual biomass ash concrete investigated, with increasing SCM content, the difference (%) to control (no SCM) was calculated, as it is illustrated in Section 3.2 of this study.

3. Results

In terms of compressive strength development it should be noted that, a common observation from the literature (as indicated in Fig. 1) is that there is an optimum level of cement replacement by biomass ashes. After a certain percentage of biomass ash, the derived strength values are reducing (in some cases being higher than control). This can be attributed to the initial fast rate of the pozzolanic reaction, which at high replacement levels this rate drops at values bellow one and the filler effect becomes more pronounced.

Overall, in most of the RHA mixtures the high levels of amorphous silica and the fine particle size of RHA are the principle reasons for the excellent pozzolanic activity and the increase in compressive strength observed.

Utilization of Palm oil fuel ashes (with SiO$_2$ content on average in the region of 65%, less than that of the RHA types of ashes) in the concrete mix contributed to the compressive strength, via a fast pozzolanic reaction, depending on the level of fineness of the POFA. The compressive strength of concrete with 20% POFA [29] was found to be higher than those of 10% and 30% (Fig. 1b). At another study [7] for the same percentage of POFA (20%) of the same chemical composition but of different level of fineness (of median size 19.9 mm and 10.1 mm) the one with the lower median size resulted in higher compressive strength (33 MPa, for d_{50} of 10.1 μm, compared to 27 MPa for d_{50} of 19.1 μm) at 28 days.

The same was noticed on SCBA mixes [5]. Up to 20% replacement level the compressive strength was higher compared to control specimens, while at higher levels the strength was decreased. As far as WA is concerned, results from the literature [33,35] showed in general the increase in the levels of cement replacement

Table 2
Regression analysis for the calculation of *k*-value of ashes based on the estimation of compressive strength.

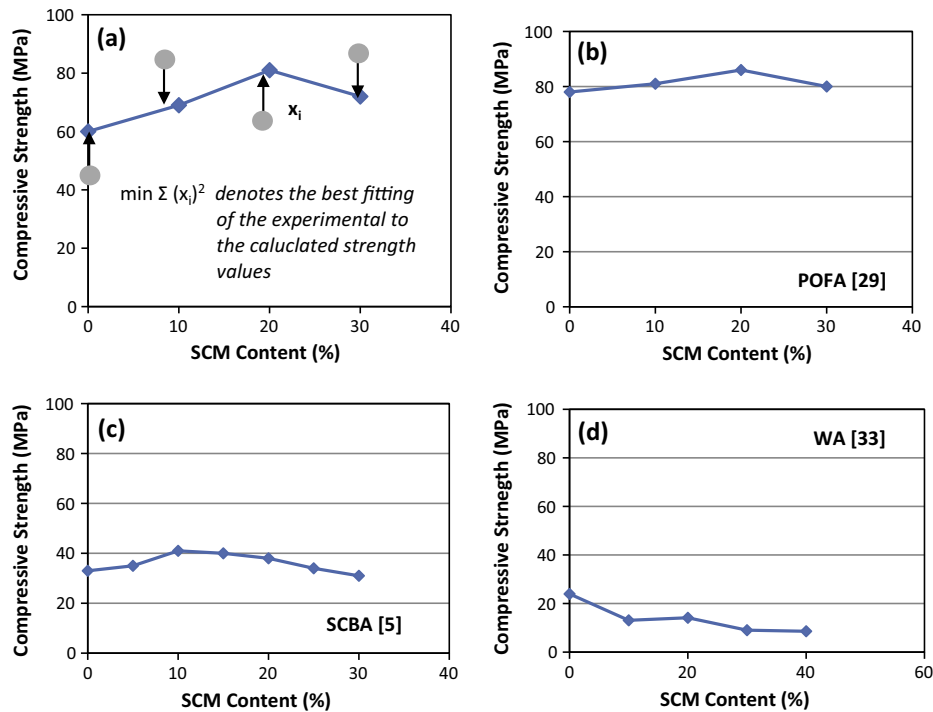| SCM		Experimental compressive strength (MPa)	Calculated compressive strength (MPa)			
			k factor for 28 days compressive strength			
Type	(%)		1.0	1.2	1.4	1.6
RHBA	0	78	80.1	80.1	80.1	80.1
[29]	10	86	80.1	81.8	83.4	85.0
	20	88	80.3	83.6	86.7	89.9
	30	85	71.0	74.0	77.1	82.0
		SLSQ	294.5	162.4	75.3	18.0

Fig. 1. Estimation of *k*-factor using regression analysis, (a) schematic overview, (b) POFA [29], (c) SCBA [5], and (d) WA [33].

resulted in a gradual decrease in the compressive strength. Despite the subsequent strength reduction per increasing level of WA incorporation, the mix containing 20% wood ash had higher strength than that containing 10% wood ash at 28 days. This was due to the fact that the silica provided by 10% wood ash was inadequate to react with the calcium hydroxide produced by the hydration of cement. Increase in wood ash content beyond 20% resulted in a reduction in strength. In this case the silica present in the mix was in excess of the amount required to combine with the calcium hydroxide from the hydrating cement. The excess silica had no pozzolanic value but only served as filler.

3.1. Efficiency factors

An overview of the calculated *k*-factors, per group category of the biomass ashes investigated, is illustrated in Fig. 2 and given in Table 3. A first observation is that the different origins and chemical configurations of the individual ashes resulted in different *k*-values. Overall, on average, a *k*-value of 1.38 was calculated for rice husk (and mixtures) ashes, while for palm oil fuel and sugar cane bagasse ashes the corresponding efficiency factors were found to be 1.2 and 0.5 (respectively). As it was expected wood contained ashes gave *k*-values bellow 0.2.

In particular the following main observations can be made:

- RHA and mixtures (rich in rice husk ash) produced *k*-values of above 1.3, up to 1.6 (except BRWA [28] with a RHA participation of 15%, which gave a *k*-value of 1.0).
- The low level of fineness (expressed as d_{50} from 3.8 μm to 10.8 μm, does not seem to have a profound effect on the derived *k*-factors, since RHA of similar compositions produced values of 1.5–1.6. However, for a median size of 12 μm, the derived efficiency factor was slightly lower (1.3).
- These inconsistencies with the level of fineness were also observed in the case of sugar cane bagasse ash (SCBA), but for similar (low) d_{50} values. A particular type of SCBA with a d_{50} of 2.70 μm, produced a *k*-value of 0.5 [34], while a similar type of SCBA with larger d_{50} value of 5.4 μm, produced a *k*-value of 0.8 [5]. This difference however can be attributed on the fact that the SCBA with the low *k*-value was rich in crystalline silica.
- Palm oil fuel ashes (POFA) with less SiO_2 content than RHA produced in certain cases similar *k*-factors (1.3 [29], 1.5 [7]).
- The level of fineness appears to have some effect on POFA mixtures [7,29–30]. For the same chemical composition of POFA reduction of the d_{50} from 19.1 μm to 10.1 μm [7] was translated as an increase of the *k*-values (from 1.2 to 1.5). However, another type of POFA with a similar level of fineness to 10.1 μm (10.7 μm) [30] produced a *k*-value of 1.0 (much lower than 1.5).
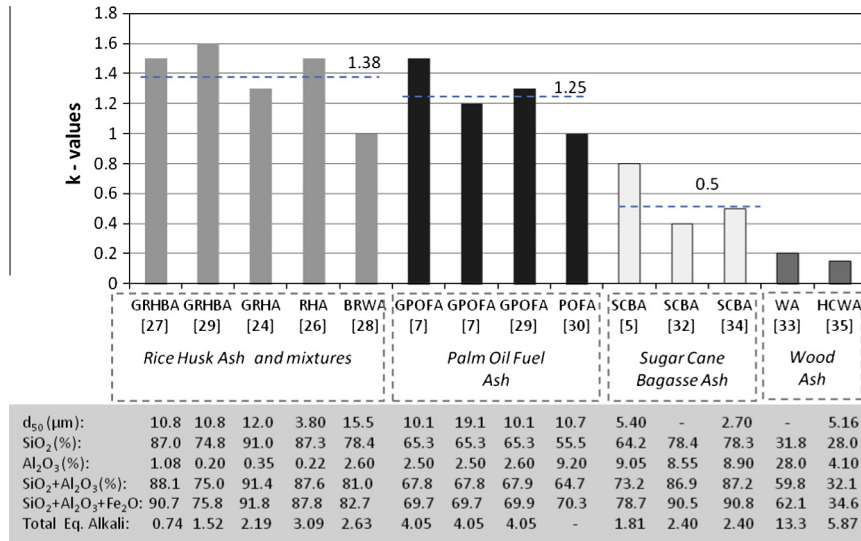
Fig. 2. Estimation of k-values of various biomass ashes.

Table 3
k-Values of ashes investigated in this study.

SCM type	SiO$_2$ (%)	Al$_2$O$_3$ (%)	Fe$_2$O$_3$ (%)	SiO$_2$ + Al$_2$O$_3$ (%)	SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$ (%)	CaO (%)	SO$_3$ (%)	Na$_2$O$_3$ (%)	K$_2$O (%)	LOI (%)	d$_{50}$ (mm)	k
GRHBA [27]	87.0	1.08	2.58	88.1	90.7	1.25	0.09	0.08	1.00	5.71	10.8	1.5
GRHBA [29]	74.8	0.20	0.80	75.0	75.8	5.90	0.50	0.20	2.00	11.2	10.8	1.6
RHA [24]	91.0	0.35	0.41	91.3	91.8	1.95	1.21	0.08	3.21	8.50	12.0	1.3
RHA [26]	87.3	0.22	0.28	87.5	87.8	0.48	–	1.02	3.14	2.10	3.80	1.5
BRWA [28]	78.4	2.60	1.70	81.0	82.7	7.40	1.10	0.20	3.70	3.60	15.5	1.0
GPOFA [7]	65.3	2.50	1.90	67.8	69.7	6.40	0.40	0.30	5.70	10.0	10.1	1.5
GPOFA [7]	65.3	2.50	1.90	67.8	69.7	6.40	0.40	0.30	5.70	19.1	10.1	1.2
GPOFA [29]	65.3	2.60	2.00	67.9	69.9	6.40	0.50	0.30	5.70	10.1	10.1	1.3
POFA [30]	55.5	9.20	5.60	64.7	70.3	12.4	2.30	–	–	7.90	10.7	1.0
SCBA [5]	64.2	9.05	5.52	73.2	78.7	8.14	–	0.92	1.35	4.90	5.40	0.8
SCBA [32]	78.3	8.55	3.61	86.9	90.5	2.15	–	0.12	3.46	0.42	–	0.4
SCBA [34]	78.3	8.90	3.60	87.2	90.8	2.20	–	0.10	3.50	–	2.70	0.5
W(S)A [33]	31.8	28.0	2.64	59.8	62.1	10.5	0.45	6.50	10.4	27.0	–	0.2
HCWA [35]	28.0	4.10	2.50	32.1	34.6	39.0	1.00	1.00	7.40	7.22	5.16	0.15

3.2. Chloride penetration

As it was previously mentioned, where data were available, the performance of biomass ashes in terms of chloride ion penetration, (measured according to ASTM C 1202), were evaluated. The difference (%) to control (no SCM) in terms of charge passed per increasing SCM content is given in Table 4.

Overall, the charge passed was substantially reduced with incorporation of biomass ashes into the concrete mix. Cement replacement by rice husk ash drastically reduced the (per ASTM C1202) rapid chloride penetrability of concrete from a low (charge ranging from 1000 to 2000 C) to very low (charge ranging from 100 to 1000 C) ratings (per ASTM C1202). In general RHA was found to be more drastic in that sense, than SCBA and POFA. Incorporation

Table 4
Performance in RCPT in terms of reduction in electrical charge passed.

SCM (%)	SCBA [5]		SCBA [32]		RHA [25]		RHA [31]		RHA [26]		POFA [31]	
	(C)	D (%)	(C)	D (%)	(C)	D (%)	(C)	D (%)	(C)	D (%)	(C)	D (%)
0	2780	0	1179	0	1161	0	7450	0	2870	0	7450	0
5	2045	26.4	783	33.6	1108	4.57	–	–	2200	23.3	–	–
10	1850	33.5	774	34.4	653	43.8	–	–	1500	47.7	–	–
15	1300	53.3	882	25.2	309	73.4	–	–	1250	56.5	–	–
20	1200	56.8	–	–	265	77.2	750	89.9	1000	65.2	1950	73.8
25	1050	62.2	–	–	213	81.7	–	–	850	70.4	–	–
30	2090	24.8	–	–	273	76.5	–	–	780	72.8	–	–
35	–	–	–	–	–	–	–	–	950	66.9	–	–
40	–	–	–	–	–	–	250	96.6	–	–	1000	86.6

(C) Charge passed (in Coulombs), (D) Difference to the control value (%).
Charge ranging from 1000 to 2000 C: low permeability, while from 100 to 1000 C: very low permeability.
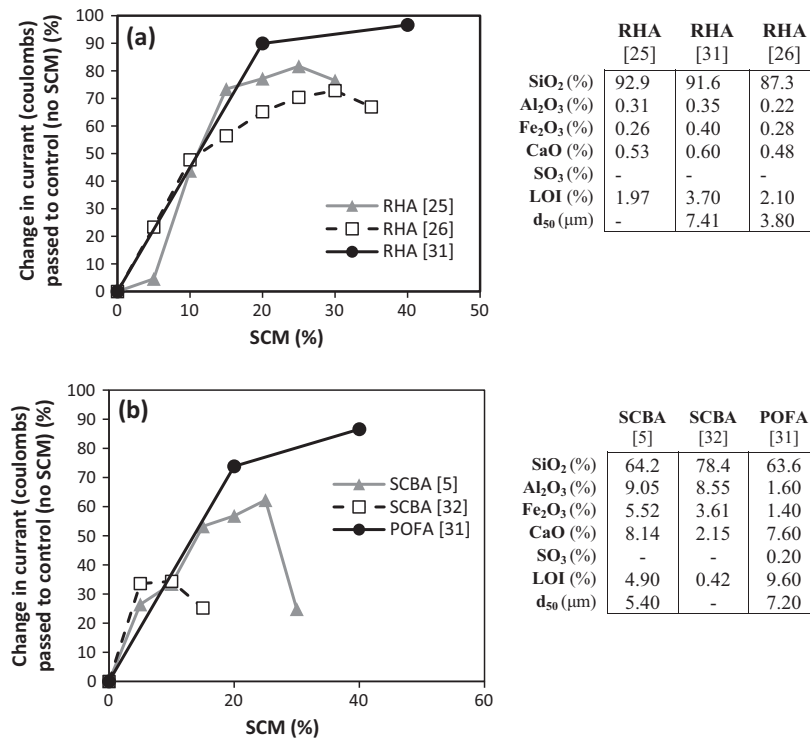
	RHA [25]	RHA [31]	RHA [26]
SiO_2 (%)	92.9	91.6	87.3
Al_2O_3 (%)	0.31	0.35	0.22
Fe_2O_3 (%)	0.26	0.40	0.28
CaO (%)	0.53	0.60	0.48
SO_3 (%)	-	-	-
LOI (%)	1.97	3.70	2.10
d_{50} (µm)	-	7.41	3.80

	SCBA [5]	SCBA [32]	POFA [31]
SiO_2 (%)	64.2	78.4	63.6
Al_2O_3 (%)	9.05	8.55	1.60
Fe_2O_3 (%)	5.52	3.61	1.40
CaO (%)	8.14	2.15	7.60
SO_3 (%)	-	-	0.20
LOI (%)	4.90	0.42	9.60
d_{50} (µm)	5.40	-	7.20

Fig. 3. Performance of representative biomass ashes in RCPT.

of 20% (Fig. 3a) produced a reduction in the charge passed of more than 60% (and up to 90%), while at lower biomass ash quantities (10%) a steady reduction (for all RHA investigated) of 43% on average was noticed.

4. Discussion

Trying to identify the specific influence of the main characteristics of the biomass ashes on the efficiency factors, it can be noted that

- Overall RHAs, rich in SiO_2 content (>85%), produced high k-values.
- Wood containing ashes, with very low SiO_2 content (<30%) produced the lowest k-values.

Hence, it appears that the influence of SiO_2 should be quite significant on the derived k-value of the ash. However, considering that SCBA with higher SiO_2 content than that of POFA produced smaller k-values than the latter type of ash, the influence of SiO_2 content is not straight forward.

In the literature [2,4,36] there is a consensus that the activity of SCMs, in general (including biomass ashes), is mainly attributed to the fact the they possess significant contents of active constituents (active silica) that combine with Ca(OH)$_2$ produced from cement hydration to form hydration products with binding properties. It is the active silica (non-crystalline silica glass, present in the amorphous and mostly vitreous part of the SCM), which is part of the total silica content of the SCM that is involved in the hydration reactions producing CSH to which the strengthening of cement is attributed. However, for the variety of biomass ashes investigated in this study, information on the active silica content were unavailable. On this note, benchmarking of the different types of ashes used in this project in terms of the influence of SiO_2 content and of the added influence of SiO_2 with the other primary oxides

(Al_2O_3, Fe_2O_3), on the derived efficiency factors, is given in Table 5 and illustrated in Fig. 4.

Although a trend, that with reducing SiO_2 content smaller derived k-values are derived, is slightly evident (Fig. 4a), certain "abnormalities" (points 4, 5, 6 and 11 illustrated in Fig. 4a and highlighted in Table 5a) distort this image.

A closer look reveals that ashes with high SiO_2 content and low (up to 2.6%) Al_2O_3 and Fe_2O_3 contents produced higher than 1.0 k-values. On the other hand ashes with high Al_2O_3 (more than 8%) and Fe_2O_3 (above 2.6%) even if they are rich in SiO_2 (78%), they produced k-values bellow 0.8. The previously mentioned "abnormalities" refer to such types of ashes, namely sugar cane bagasse ashes (points 5 [32], 6 [34], 11 [5] in Fig. 4a).

In addition to the above, two further points strike out. A type of POFA [30] (point 12) with high Al_2O_3 and Fe_2O_3 contents but also rich in CaO (12.4%) and a mixture type of ash, BRWA [28] (point 4) containing a very small portion (15%) of rice husk wood ash, being low in Al_2O_3 and Fe_2O_3 contents but high in CaO (7.4%).

Hence the influence of the level of SiO_2 in the ash does carry a certain validity on the derived value of the efficiency factor, but is also affected by the composition of the ash in other oxides. On that note, the influence SiO_2 in connection to the other major oxides (Al_2O_3 and Fe_2O_3) is examined. By investigating the combined effect of $SiO_2 + Al_2O_3$ content, a similar behavior is observed (Table 5bc, Fig. 4b and c). The same trend/mishaps is observed as in the case of the effect of SiO_2 content, with the same types of ashes and their particularities as previously explained (in primary oxides and CaO composition) deviating to a great extend. Such a deviation becomes even clearer when the combined effect of all three major oxides on the derived k-values is investigated (Table 5c and Fig. 4c).

A common observation of all of the above mentioned ash classifications (in terms of their primary oxide contents) is that certain types of rice husk ash by producing high k-values, appear at the top of these classifications, while, wood containing type of ashes

Table 5
Biomass ash results categorized by primary oxide contents.

	a/a	SCM Type	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	$SiO_2 + Al_2O_3$ (%)	$SiO_2 + Al_2O_3 + Fe_2O_3$ (%)	CaO (%)	SO_3 (%)	Eq. Alk. (%)	LOI (%)	d_{50} (μm)	k
[a]	1	[24] GRHA	91.0	0.35	0.41	91.4	91.8	1.95	1.21	2.19	8.50	12.0	1.3
	2	[26] RHA	87.3	0.22	0.28	87.5	87.8	0.48	–	3.09	2.10	3.80	1.5
	3	[27] GRHBA	87.0	1.08	2.58	88.1	90.7	1.25	0.09	0.74	5.71	10.8	1.5
	4	[28] BRWA	78.4	2.60	1.70	81.0	82.7	7.40	1.10	2.63	3.60	15.5	1
	5	[32] SCBA	78.3	8.55	3.61	86.9	90.5	2.15	–	2.40	0.42	–	0.4
	6	[34] SCBA	78.3	8.90	3.60	87.2	90.8	8.14	–	1.81	4.90	5.40	0.5
	7	[29] GRHBA	74.8	0.20	0.80	75.0	75.8	5.90	0.50	1.52	11.2	10.8	1.6
	8	[29] GPOFA	65.3	2.60	2.00	67.9	69.9	6.40	0.50	4.05	10.1	10.1	1.3
	9	[7] GPOFA	65.3	2.50	1.90	67.8	69.7	6.40	0.40	4.05	10.0	10.1	1.5
	10	[7] GPOFA	65.3	2.50	1.90	67.8	69.7	6.40	0.40	4.05	10.0	19.1	1.2
	11	[5] SCBA	64.1	9.05	5.52	73.2	78.7	8.14	–	1.81	4.90	5.40	0.8
	12	[30] POFA	55.5	9.20	5.60	64.7	70.3	12.40	2.30	0.00	7.90	10.7	1
	13	[33] WA	31.8	28.0	2.34	59.8	62.1	10.53	0.45	13.3	27.0	–	0.2
	14	[35] HCWA	28.0	4.10	2.50	32.1	34.6	39.0	1.00	5.87	7.22	5.16	0.15
[b]	1	[24] GRHA	91.0	0.35	0.41	91.4	91.8	1.95	1.21	2.19	8.50	12.0	1.3
	2	[27] GRHBA	87.0	1.08	2.58	88.1	90.7	1.25	0.09	0.74	5.71	10.8	1.5
	3	[26] RHA	87.3	0.22	0.28	87.5	87.8	0.48	–	3.09	2.10	3.80	1.5
	4	[34] SCBA	78.3	8.90	3.60	87.2	90.8	8.14	–	1.81	4.90	5.40	0.5
	5	[32] SCBA	78.3	8.55	3.61	86.9	90.5	2.15	–	2.40	0.42	–	0.4
	6	[28] BRWA	78.4	2.60	1.70	81.0	82.7	7.40	1.10	2.63	3.60	15.5	1
	7	[29] GRHBA	74.8	0.20	0.80	75.0	75.8	5.90	0.50	1.52	11.2	10.8	1.6
	8	[5] SCBA	64.2	9.05	5.52	73.2	78.7	8.14	–	1.81	4.90	5.40	0.8
	9	[29] GPOFA	65.3	2.60	2.00	67.9	69.9	6.40	0.50	4.05	10.1	10.1	1.3
	10	[7] GPOFA	65.3	2.50	1.90	67.8	69.7	6.40	0.40	4.05	10.0	10.1	1.5
	11	[7] GPOFA	65.3	2.50	1.90	67.8	69.7	6.40	0.40	4.05	10.0	19.1	1.2
	12	[30] POFA	55.5	9.20	5.60	64.7	70.3	12.4	2.30	0.00	7.90	10.7	1
	13	[33] WA	31.8	28.0	2.34	59.8	62.1	10.5	0.45	13.3	27.0	–	0.2
	14	[35] HCWA	28.0	4.10	2.50	32.1	34.6	39.0	1.00	5.87	7.22	5.16	0.15
[c]	1	[24] GRHA	91.0	0.35	0.41	91.8	91.4	1.95	1.21	2.19	8.50	12.0	1.3
	2	[34] SCBA	78.3	8.90	3.60	90.8	87.2	8.14	–	1.81	4.90	5.40	0.5
	3	[35] GRHBA	87.0	1.08	2.58	90.7	88.1	1.25	0.09	0.74	5.71	10.8	1.5
	4	[32] SCBA	78.3	8.55	3.61	90.5	86.9	2.15	–	2.40	0.42	–	0.4
	5	[26] RHA	87.3	0.22	0.28	87.8	87.5	0.48	–	3.09	2.10	3.80	1.5
	6	[28] BRWA	78.4	2.60	1.70	82.7	81.0	7.40	1.10	2.63	3.60	15.5	1
	7	[5] SCBA	64.2	9.05	5.52	78.7	73.2	8.14	–	1.81	4.90	5.40	0.8
	8	[29] GRHBA	74.8	0.20	0.80	75.8	75.0	5.90	0.50	1.52	11.2	10.8	1.6
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	10	[29] GPOFA	65.3	2.60	2.00	69.9	67.9	6.40	0.50	4.05	10.1	10.1	1.3
	11	[7] GPOFA	65.3	2.50	1.90	69.7	67.8	6.40	0.40	4.05	10.0	10.1	1.5
	12	[7] GPOFA	65.3	2.50	1.90	69.7	67.8	6.40	0.40	4.05	10.0	19.1	1.2
	13	[33] WA	31.8	28.0	2.34	62.1	59.8	10.5	0.45	13.33	27.0	–	0.2
	14	[35] HCWA	28.0	4.10	2.50	34.6	32.1	39.0	1.00	5.87	7.22	5.16	0.15

(a) SiO_2 (%), (b) $SiO_2 + Al_2O_3$ (%) and (c) $SiO_2 + Al_2O_3 + Fe_2O_3$ (%) contents.

(WA[33], HCWA[35]), with very low derived efficiency factors (<0.2), appear at the bottom. This is not surprising since wood ashes, usually have very low contents in SiO_2 and contain appreciable amounts of un-burnt carbon (up to 27% in a particular WA [33] investigated in this study) which reduces their pozzolanic activity to a great extend. Unburned carbon is not pozzolanic and its presence serves as filler to the mixture. High unburned carbon contents, the main form of LOI (loss of ignition) in the ash, are known to be responsible for strength development and durability associated problems (increased water demand, increased permeability [24,34,37].

It should be noted at this stage, that when the ash is produced in industrial combustion systems (as the majority of the ashes investigated in this study), the temperature of combustion, the cleanliness of the biomass fuel and the technology used can have profound effects on the characteristics of the ash, especially on the unburned carbon content. Controlled burning at 800 °C, through a fluidized bed combustion process resulted in considerably higher values of LOI, compared to burning at 1300 °C [29]. However, it has also been reported that smaller LOI values (or residual carbon contents) of up to 12%, exhibited by every type of biomass ash investigated in this study, except wood ash, did not have any detrimental effect on the strength and microstructure of cement and concrete [38].

Overall, at this point, it can be concluded that upon a certain percentage in Al_2O_3, Fe_2O_3 and CaO contents, high SiO_2 content translates into a high k-value. However, at high compositions of CaO (even for low Al_2O_3, Fe_2O_3 contents) and/or at high contents of Al_2O_3, Fe_2O_3, the derived k-values are not "linear" with that high SiO_2 content. The way Al_2O_3, Fe_2O_3 and CaO contents influence the level of the derived k-value, (even for a high contained percentage of SiO_2 in the ash) is evident into the following Fig. 5.

On the range of biomass ashes investigated in this study, of similar particle median size (d_{50}) and LOI, concentration in Al_2O_3 of more than 4.1% produced efficiency factors bellow 1.0, even for high SiO_2 content (more than 78%), as it illustrated at points 1 [32] and 2 [34] in Fig. 5a. In terms of Fe_2O_3 (Fig. 5b) and Cao (Fig. 5c) contents, concentration of more than 3.0% and 8.0% respectively, produced efficiency factors well bellow 1.0. Overall, based on their combined influence, it appears that as their percentages in the ash increase, the derived k-values drop bellow 1.0, well even bellow 0.5 (Fig. 5d).

In terms of the influence of CaO results are contradictory. In theory, high CaO contents in the ash, are expected to contribute to hydraulic activity [39]. The pozzolanic activity of the ash in a cement matrix enhances the formation of C–S–H gel, through the reaction of amorphous silica content of the ash with the free lime from cement hydration. On that note, high CaO contents have been
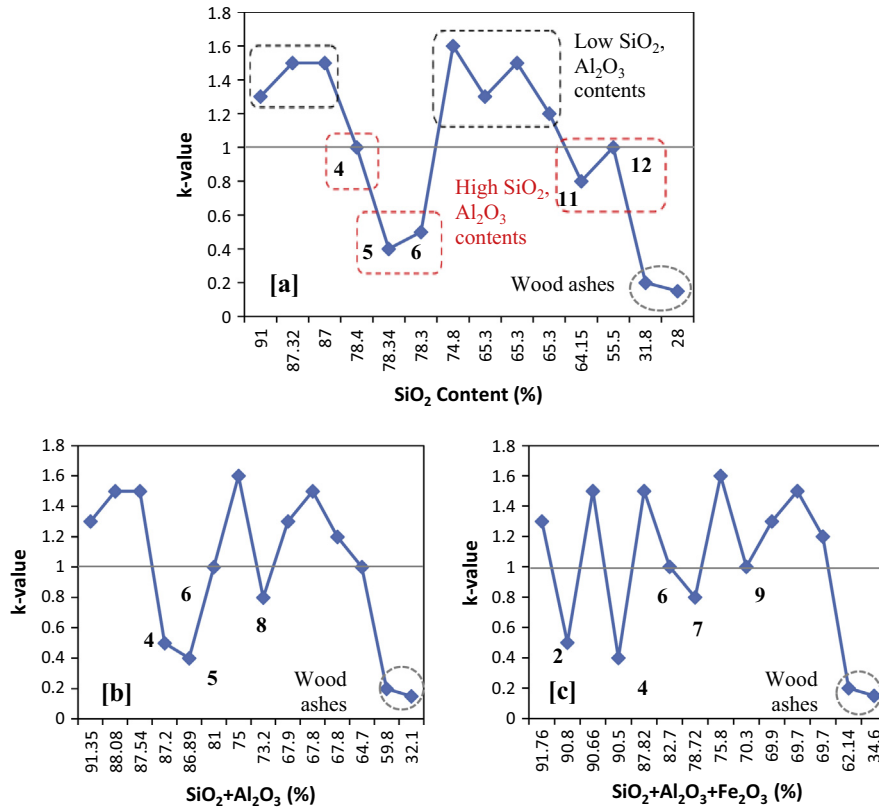
Fig. 4. Effect of primary oxide contents on k-values of biomass ashes; (a) SiO_2 (%), (b) $SiO_2 + Al_2O_3$ (%) and (c) $SiO_2 + Al_2O_3 + Fe_2O_3$ (%) content.
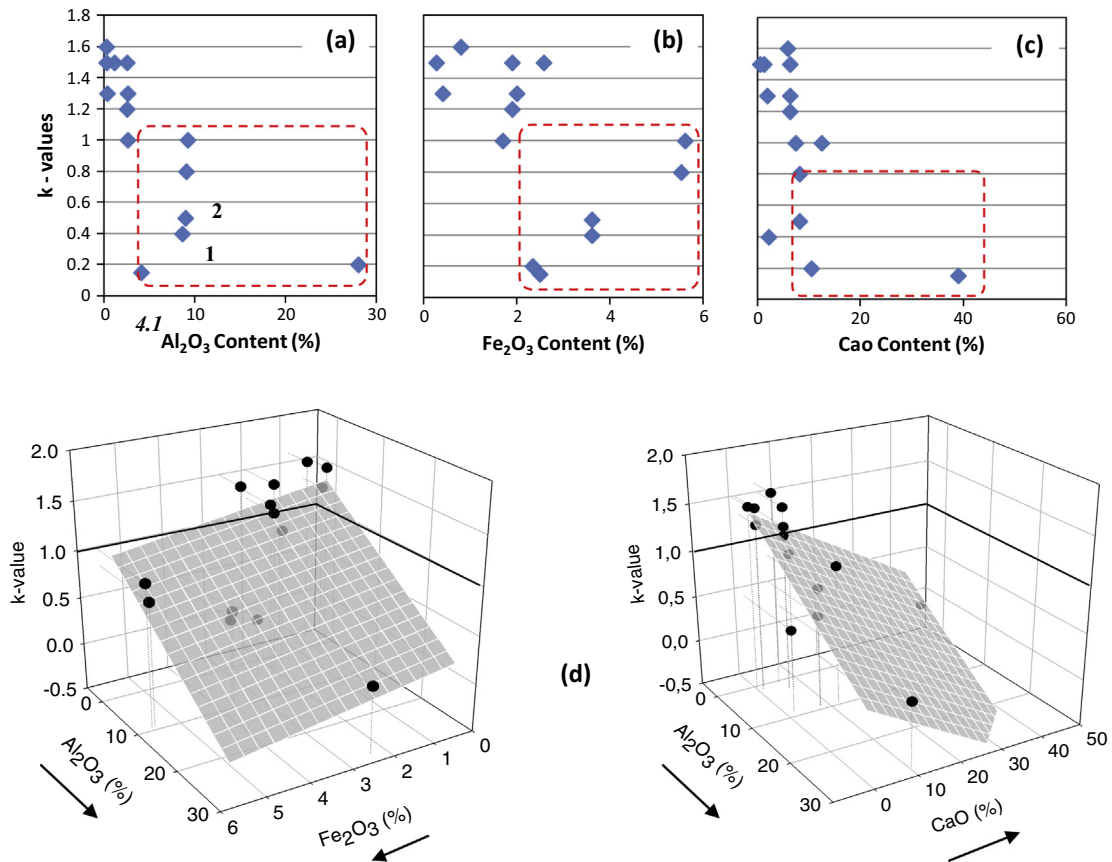

Fig. 5. Effect of high quantities of Al_2O_3 (%) (a), Fe_2O_3 (%) (b) and CaO (%) (c) contents on k-values of ashes.

found to further aid this particular process by reacting with the SiO$_2$ content of the ash [5]. However, it has been reported that high carbon contents led to increased water demand of the concrete mix [24,29].

Although, relatively high alumina contents (and iron oxide) in cement in the form of C$_3$A (3·CaO·Al$_2$O$_3$) or C$_4$AF (4·CaO·Al$_2$O$_3$·Fe$_2$O$_3$) phases, are known for their small contribution to early strength development, their influence in the chloride binding capacity of the cement mix is crucial. High alumina contents can increase cement's potential for Friedel's salt production. The latter is formed as a result of the chloride binding by cementitious components (C$_3$A, C$_4$AF phases). This process is beneficial, as far as the permeability of chlorides is concerned, since formation of Friedel's salt results in a less porous structure, hence to reduced "transport" of chlorides into the concrete mix.

Such a less porous structure, was observed on a variety of the biomass ashes (RHA, POFA and in some SCBA) investigated in this study, based on the change of the reduction of chloride permeability from "low" to "very low" rating (according to ASTM C1202), as it was discussed in the previous section. Rapid Chloride Permeability Test (RCPT) indicated that the total charge passed on biomass ash concrete samples, was considerably reduced (compared to control samples), up to almost 90% (as it was indicated in Fig. 3) for a 20% replacement by RHA. Considerable reductions were also notices for other types of biomass ashes (73.8% for 20% POFA incorporation and 56.8% for SCBA).

In general, the transport of chloride ions (and the consequent electrochemical processes) through biomass ash blended concretes depends on the pore structure of the concrete, while the electrical conduction depends on both pore structure characteristics and electrical conductivity of the pore solution [26]. Overall, the finer particles of ashes develop discontinuous and tortuous pore in concrete structure and the pores present in the concrete are completely filled up by finer particles.

Since the total charge passed through the concrete depends on the electrical conductance, low unburnt carbon content present in some types of biomass ashes is known to contribute to the significant reduction in the electrical charge passed. In general, a reduction in the unburnt carbon content may be beneficial from the chloride permeability point of view. For example, when rice husk ash which has a lower loss on ignition value compared to OPC is used to partially replace OPC, resistance to chloride permeation is substantially improved. This may be probably due to a decrease in electrical conductivity of concrete due to lowering of unburnt carbon content in RHA, in addition to pore structure refinement and conductivity of pore solution. Such an observation is further reinforced considering the substantial reductions in charge passed achieved when RHA was utilized (Fig. 3) with low LOI values from 1.97% to 3.7%.

Overall, the chloride-ion penetration results suggest pore refinement due to the pozzolanic reaction of ultrafine biomass ash and demonstrate the significant potential of these types of ashes as mineral admixtures in concrete, as long as an appropriate grinding strategy is used and product fineness is achieved.

5. Conclusions

In the current study by investigating the efficiency of a range of biomass ashes, identified in the literature, as cementitious materials, in terms of efficiency factors for concrete strength and chloride penetration, it can be concluded that:

- Variations in the operating conditions (temperature of combustion, technology used) and source of the biomass can influence to a great extend the chemical characteristics of the biomass ashes, even of the same group.

- High SiO$_2$ content in the biomass ash, does not automatically implies an effective pozzolanic material with a high efficiency factor.
- It appears that after certain percentages in the concentration of the ash in Al$_2$O$_3$, Fe$_2$O$_3$ and CaO, even for high SiO$_2$ content, high level of fineness, and low values of LOI, the derived efficiency factors drop bellow 1.0.
- Biomass ashes (except wood related aches) from a variety of agro-industrial by products can be used as cement replacement materials with beneficial results in strength development and performance in chloride penetration.
- Utilization of RHA drastically reduced the Coulomb values and subsequently the corresponding chloride penetration.
- Overall, utilization of agro-industrial by-products for biomass ash production can be a valid source of a future pozzolanic material in concrete production.

It is hoped that the results of this study will pave the way for a more in depth evaluation of a wider range of biomass ashes on cement and concrete production.

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