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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 SiO₂ content of biomass ash does not imply a pozzolanic material with a high efficiency factor.

• Concentration of other compounds, even for high SiO₂ content is responsible for low *k*-values.

• Biomass ash from agro-industrial by-products can be used as pozzolanic material in concrete.

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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.

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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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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 cofiring 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 SiO₂ 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 μ m). 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 SiO₂. (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 SiO₂, Al₂O₃, and Fe₂O₃ are higher than or close to 70%, SO₃ 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 SiO₂, Al₂O₃, and Fe₂O₃ 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 SiO₂ 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 SiO₂ 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.

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