



## Reuse of woody biomass fly ash in cement-based materials



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### H I G H L I G H T S

- Physico-chemical and mineralogical characterisation of pure woody biomass fly ash (WBFA).
- Treatments of WBFA to reduce detrimental effects on the technological properties of cement mixes.
- Technological feasibility of WBFA reuse as partial cement replacement material in cement mixes.
- Technological feasibility of WBFA reuse as a filler/partial sand replacement material in concrete.
- Hydraulic and pozzolanic activity of WBFA.

### A R T I C L E I N F O

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### A B S T R A C T

The reuse of woody biomass fly ash (WBFA) as a mineral admixture or as a filler/partial sand replacement material in cementitious mixes was investigated. Three different WBFA were used, two coming from virgin wood and one from treated wood combustion. The physical and chemical characteristics of these ashes and the technological properties (workability, setting, compressive strength) of cementitious mixes incorporating WBFA were evaluated. It was found that, in spite of the satisfactory technological properties exhibited by most related blended cements, the studied WBFA did not meet the UNI EN 450-1 requirements for reuse as mineral admixtures, even if they were subjected to a preliminary water-washing treatment. The reuse of raw wood fly ash as a filler/partial sand replacement material was found to be satisfactory and possible for low-quality concrete.

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### 1. Introduction

The use of biomasses in place of traditional fuels represents a suitable way of reducing greenhouse gas emissions, in the general policy towards a highly energy-efficient, low-carbon economy.

The most important biomasses are the residues from wood-working or forest activities, the wastes from farms and agro-business, the organic fraction of municipal solid wastes, and the plants deliberately grown for energetic purposes. They represent a high potential of burnable biomass and their fast increasing use in biomass-based thermal plants has called for the disposal problems associated with the ash production.

According to the European Waste Catalogue and hazardous residues list [1], both bottom ash and fly ash coming from the

combustion of untreated wood are classified as non-hazardous wastes.

Woody biomass bottom ash may be reused as a building material for replacing granular material in geotechnical works, like road foundations [2]. Its application to agricultural or forests soils has also been proposed [3,4].

Reuse of Woody Biomass Fly Ash (WBFA) in agricultural and/or industrial applications could pose environmental problems related to higher content and higher leachability of heavy metals of this fly ash [5–8], as compared to bottom ash.

Published work [7,8] has shown that certain types of WBFA do not meet the limit concentrations of heavy metals established by Dutch or Austrian regulations for reuse of biomass ashes as mineral fertilisers. Leaching tests on WBFA samples [6] have shown that there is a leachant pH range (below 7.5) where the release of heavy metals of particular environmental concern is above the limits for disposal of WBFA into non-hazardous waste landfills. This leaching behaviour could be incompatible with the reuse of WBFA in agricultural applications, while it would be compatible with a safe

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reuse of this ash in cement-based materials, as a mineral admixture (partial cement replacement material) and/or as a filler material.

From the environmental point of view, the reuse of WBFA as a mineral admixture would produce several beneficial effects such as (1) a significant reduction of CO<sub>2</sub> emission related to industrial cement production from traditional raw materials (limestone and clay), (2) the preservation of the natural resources involved in cement production, and (3) the solution of the environmental problem related to the WBFA disposal. The last two beneficial effects would also be attained by using WBFA as a filler in concrete.

However, the reuse of WBFA as a partial cement replacement material is not allowed by ASTM C 618 [9] and UNI EN 450-1 [10], that are the current standards governing the use of fly ashes as mineral admixtures in concrete. Indeed, such regulations preclude the use of any material not derived from coal combustion. It is reasonable to think that a future extension of the current regulations to the reuse of fly ash from pure biomass combustion in concrete should be limited to those samples capable of meeting the physical and chemical requirements as specified in the ASTM C 618 or UNI EN 450-1 standards.

This may be the reason for which the research on the reuse of biomass fly ashes in cement-based materials has been mostly focused on co-fired fly ashes (fly ashes coming from combustion of coal and biomass blends) and, only in minor part, on pure biomass fly ashes.

At present, a conspicuous number of papers dealing with the reuse of woody biomass fly ashes in concrete or mortar is, however, available in the literature [11–42]. Most of these papers are focused on the reuse of WBFA as a partial cement replacement material, while only a few papers deal with the reuse of biomass fly ash as a filler [11,13,33,36].

Literature survey [27,30,33] has shown that the performance of woody biomass fly ash as mineral admixture is strongly dependent on its physico-chemical characteristics that, in turn, depend on the type of woody biomass and the type of combustion adopted in the thermal plant [43]. The content of unburned carbon and inorganic compounds in the WBFA samples could significantly affect the concrete properties (workability, setting, mechanical strength), as well as the presence of a considerable amount of heavy metals could pose severe limitations to reuse of this waste in cementitious mixes (excessive delay of cement hydration and/or excessive heavy metal leaching).

The feasibility of using biomass fly ash as a filler has been recently demonstrated by Cuenca et al. [36] in their experimental study on the performance of self-compacting concrete.

The present study was undertaken in order to achieve the following three objectives: (1) to evaluate the suitability of three different types of WBFA coming from the electrostatic precipitators of Italian wood burning plants as partial cement replacement materials; (2) to assess the feasibility of a preliminary washing treatment of WBFA with deionised water as a means of improving the chemical characteristics of such wastes; and (3) to evaluate the suitability of WBFA for reuse as a filler/partial sand replacement material in concrete.

The first two objectives were accomplished by evaluating the physical and chemical characteristics of raw and washed fly ashes, and the technological properties (workability, setting, pozzolanic activity, and mechanical strength) of blended cements prepared at different replacement levels of Portland cement with unwashed or washed WBFA.

The third objective was attained through measurements of workability and mechanical strength on concrete mixes containing one type of the studied fly ashes. This ash was selected on the basis of the results collected in the first phase of experimentation.

## 2. Materials and methods

### 2.1. WBFA characterisation and washing treatment

The three types of wood fly ash used in this study were labelled as WBFA1, WBFA2 and WBFA3. Samples WBFA1 and WBFA2 were obtained from the combustion of chestnut or poplar virgin wood chips, respectively. Sample WBFA3 resulted from the combustion of production scraps of treated wood.

An aliquot of as received fly ashes (raw ashes) was first dried in a laboratory oven at 80 °C and then analysed for particle size distribution through dry sieving and laser diffraction technique. The real density of each ash (dry mass per unit solid volume excluding open porosity) was determined by a pycnometer for solids. The chemical composition was determined by X-ray fluorescence (XRF) for major elements and by atomic absorption spectrophotometry (AAS) for trace metals. The latter analysis was performed on the liquid phase resulting from nitric acid/hydrogen peroxide hot digestion of each sample of WBFA. The same solution was analysed also for sulphate and chloride contents by ionic chromatography (HPLC). The contents of unburned carbon and inorganic carbon of fly ash were evaluated by simultaneous thermo-gravimetric analysis/differential scanning calorimetry (TGA/DSC) with a thermo-analyser operating under static air at a heating rate of 10 °C/min over a temperature range from 25 °C to 1100 °C. The crystalline phases of each WBFA were identified by X-ray diffraction (XRD) analysis by using a Ni-filtered Cu K $\alpha$  radiation (40 kV, 30 mA).

Prior to use of WBFA as a mineral admixture in blended cements, each type of raw fly ash was dried and then sieved on 150  $\mu$ m sieve. The retained portion on 150  $\mu$ m sieve (30, 15 and 47 wt.% for WBFA1, WBFA2 and WBFA3, respectively) was ground to fineness below 45  $\mu$ m and then mixed with the other portion of ash (combined WBFA). Thus, the retained portion of the combined WBFA did not exceed 30 wt.% when wet sieved on 45  $\mu$ m sieve.

An aliquot of each combined WBFA was also subjected to a two-step washing treatment with deionised water (liquid/solid ratio = 25 L/kg; contact time = 30 min/step). After each step, the suspension was filtered and the two filtrates were combined and analysed for chloride and sulphate ions by HPLC and for sodium, potassium and calcium ions by AAS. The overall weight loss of fly ash, L.O.W. (Loss On Washing), was also determined after drying of the solid residue to a constant weight at 80 °C. The combined WBFA after washing treatment was referred to as washed WBFA, while the combined WBFA not subjected to washing was indicated as unwashed WBFA.

### 2.2. Preparation and testing of blended cements

The ash-cement blends (blended cements) were made using unwashed or washed WBFA and Portland cement, CEM I 42.5R, the latter being also referred to as PC. The chemical and mineralogical compositions of Portland cement are given in Table 1. The blended cements, also indicated as WBFA-PC cements, were made at Portland cement replacement levels of 15 and 30 wt.% and were identified with the wt.% content of WBFA. These cements were characterised for their pozzolanic activity and technological properties.

#### 2.2.1. Pozzolanicity tests

Each blended cement was tested for its pozzolanic activity by using the UNI EN 196-5 test method [44].

According to this method, the pozzolanic activity is assessed on an aqueous suspension of the test cement (water/cement ratio of 5 ml/g) by comparing the concentration of calcium hydroxide (expressed as CaO) in the aqueous solution in contact with the hydrated cement, after a fixed period of curing at 40 °C (14 days), with the concentration of calcium hydroxide capable of saturating a solution of the same alkalinity, the latter being expressed as OH<sup>-</sup> ion concentration. The test cement is classified as a pozzolanic cement if the concentration of calcium hydroxide in the solution is lower than its saturation concentration.

#### 2.2.2. Physical tests on fresh cement pastes

The water demand of the blended cements was evaluated through workability measurements on cement pastes made with blended cement or Portland cement (control) as a binder and deionised water as mixing water. The water/binder weight ratio (w/b) was varied over the range from 0.45 to 0.75, and the workability of these pastes was evaluated through the use of a mini-slump test [45]. With this test, the mix workability was expressed in terms of the area  $A_{cp}$  (cm<sup>2</sup>) of the paste collapsed without shocking from a truncated cone open at both ends (upper diameter = 20 mm; base diameter = 40 mm; height = 60 mm) and preliminarily filled with the test sample.

The setting behaviour of blended and Portland cements was evaluated by measuring the initial and final setting times of pastes made with normal consistency (w/b ratio from 0.35 to 0.38, depending on the type and content of WBFA), according to UNI EN 196-3 test method (Vicat apparatus) [46].

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