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Valorisation of woody biomass bottom ash in Portland cement: A characterization and hydration study

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ABSTRACT

In the present research work, a characterization of a bottom ash derived from olive plants trimmings combustion was carried out in order to examine its suitability as a substitute in the production of composite cements. For that purpose six different mixtures were prepared: a reference one, containing only ordinary raw materials and five others, substituting Portland cement for 2, 3, 5, 7 and 10 wt%. The woody bottom ash (WBA) characterization was carried out by using particle size distribution analysis, chemical analysis and X-ray diffraction (XRD), whereas its microstructure and morphological characteristics were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The physicochemical and mechanical properties of the produced cements mixtures were examined by means of their initial and final setting times, standard consistency, flow of normal mortar, soundness and compressive strength at 1, 2, 7 and 28 days. Their hydration progress was attested by X-ray diffraction, thermogravimetric/differential thermal analysis (TG/DTG), whereas the microstructure of the hardened cement pastes was examined by SEM. According to the results, the WBA could be used as a substitute for Portland cement, in the production of composite cements of the strength classes 42.5 and 32.5 of EN 197-1.

1. Introduction

In recent years, an increased demand on alternative renewable energy resources has been raised, due to the strict environmental laws and the corresponding energy preservation strategies. An alternative non-fossil source, today used in co-combustion with hard coal power plants for electrical energy and heat generation, is woody biomass, whose valorization presents not only the benefit of the economical cost decrement but also reduces the environmental impact [1,2]. Woody biomass has become one of the highest-growth renewable energy in Europe, as its contribution has increased substantially and it is expected to increase up to 200% by the end of 2030 [3,4].

However, the use of such energy substitutes could also lead to a relative increase of the bottom and fly ash produced, during the incineration process, in relation with traditional energy resources and therefore they should be treated according to federal and local legislation. Bottom ash, which is often mixed with other impurities, such as sand or stone, is produced in the boiler first combustion chamber, whereas fly ash is collected primarily in cyclones, which are located behind the combustion unit, and in electrostatic and bag filters, which are usually placed behind the cyclones [4,5].

The main part of the ash generated in fixed-bed furnaces is the bottom ash, which comprises about the 80% of the total. Its quantity and chemical composition may vary considerably according to the biomass quality used and the technology applied, especially the temperatures to which the source is subjected during the combustion process [2,6]. The bottom ash examined in the present work is a combustion by-product of olive plants trimmings in fixed-bed combustion systems, used in various wood burning facilities, and it generally consists of 5–60 wt% SiO_2, 5–40 wt% CaO, 5–20 wt% Al_2O_3 and 0.5–5 wt% MgO. It may be rich in potassium, whereas residual carbon may also be present. Higher

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combustion temperatures can lead to the decrease of alkalis (potassium, sodium) and carbonate content, whereas the other major elements remained almost constant or increased [7,8]. Although it has been classified as non hazardous wastes, according to the European Catalogue for Hazardous Wastes, due to its relatively high alkalinity and its fine grain size, its disposal is a growing problem.

Today, the increasing number of environmental regulations has led the waste producers in Europe to the choice of recycling and reuse, as the disposal cost is very high and in some cases it may require controlled landfills, especially for fly ashes, which may be rich in heavy metal contaminants, such as Cd [9]. Finding utilization pathways for this type of residue is an important aspect, because processes that would convert the oxide content of the combustion wastes to value-added products are necessary for the profitability of the recycling process.

As biomass ashes contain significant amounts of nutritious ingredients (calcium, potassium, phosphorus), traditionally they have been used in agriculture as mineral soil supplement and fertilizer, aiming to the improvement of soil qualitative characteristics and to the consequent crop performance [4,10]. Furthermore, due to their highly alkalinity (pH: 9–13) decreases the soil acidification and counteracting the loss of nutrients from forest soil [2,7]. Currently, European countries, which have promoted the use of biomass for energy production, have also proceeded to the corresponding sustainable legislation that exploits the returning of the produced ashes to the locations (forests and agricultural areas) from where the biomass had been harvested.

Wood ashes valorization has been also examined as raw material in ceramic industry [11,12], as a filler material in road bases construction [13], as neutralize agent for wastes with high acidity, as glazing material [4,6] or as a filler material in concrete [2,14]. Although there are several studies [1,4,15] that aim to the partial incorporation of the fine wood fly ash in cement, the so far published literature has given little attention to the wood bottom ash possible utilization in cement-based materials, mainly because of its high alkali content [16].

Portland cement is one of the most widely used construction material and it accounts for approximately 4–5 wt% of greenhouse gas emissions [17]. Thus, in view of the growing environmental concern of WBA management and taking into account that 70% of the total world olive oil and table olives production is accomplished in Spain, Italy, Greece and Portugal, producing significant amount of residual biomass (three tones of trimming residues are generated per hectare of olive trees) [2], the partial addition of wood ash from combustion in cement mixtures could lead not only to the reduction of the atmospheric emissions, but also to energy cost savings.

The aim of the present research work was to investigate the possibility of using WBA as a constituent of composite cements blends. For that reason different mixtures were prepared substituting Portland cement up to 10 wt%. All mixtures were tested for water demand, setting times, compressive strengths, and soundness, whereas XRD, TG/DTG and SEM were applied in order to study the hydration products at various ages.

2. Experimental

2.1. Materials

The cement used in all mixtures was a CEM I 52.5N Ordinary Portland Cement (OPC), produced by Titan Cement Company of Greece. The bottom ash under investigation had been generated after the combustion of olive plants trimmings in a fixed-bed combustion system, with underfeed stokers. Its particle size distribution was determined by a laser scattering particle size distribution analyzer (Mastersizer 2000, Malvern) after dispersion treatment with ultrasonic. Chemical analyses were carried out with X-ray Fluorescence (Spectro–Xepos) and Atomic Absorption Spectrophotometry (Perkin Elmer 4100). The crystalline phases of both WBA and CEM I 52.5N were determined by XRD analysis, using a Bruker D8-Focus diffractometer with nickel-filtered CuKa radiation ($\lambda = 1.5406$ Å), at 40 kV and 40 mA. Semi-quantitative phases analysis was carried out by TOPAS software (Bruker-AXS), based on Rietveld algorithm. The morphology of WBA was examined by scanning electron microscopy (SEM) using a Jeol 6380LV Scanning Electron Microscope. Spot chemical analysis of samples particles was carried out by an Oxford INCA Energy Dispersive Spectrometer (EDS) connected to the SEM. Finally, TEM measurement was conducted with a high resolution JEOL JEM-2100, operating at 200 kV, equipped with an Oxford X-Max 100 EDS detector.

2.2. Blended cements

The cements mixtures were produced by mixing the WBA and Portland cement, in a laboratory ball mill with further grinding, in order to the final blended cement present homogenous particle size distribution. The mixing ratios, as well as the physical characteristics of the final cements produced are presented in Table 1.

Vicat apparatus was used for the determination of the cement pastes standard consistency and setting times, according to the European Standard EN 196-3 [18]. The determination of the normal mortar flow was carried out according to ASTM C1437 [19], whereas the Le Chatelier method was used for expansions measurements of the cement pastes [18]. Compressive strength measurements were conducted at the ages of 1, 2, 7 and 28 days on mortar specimens (dimensions 40 mm × 40 mm × 160 mm), prepared and tested in accordance with European Standard EN 196-1 [20].

The hydration products were mineralogically determined by X-ray diffraction, using a Bruker D8-Focus diffractometer. Thermal Gravimetric Analysis (TGA) was carried out to evaluate hydration rate using a Mettler-Toledo TGA 851 instrument (25–900 °C, 10 °C/min and nitrogen under static condition). The exact boundaries for the temperature intervals were defined from the derivative curve (DTG). Finally, morphological analysis and observation of hydration products were performed by Scanning Electron Microscopy.

Table 1
Composition and characteristics of cement mixtures.

Code	CEM I 52.5N (wt%)	WBA (wt%)	Specific Surface Area (cm^2/g)	Specific Gravity (g/cm^3)
C_{Ref}	100	0	3870	3.14
C_2	98	2	3870	3.13
C_3	97	3	3870	3.12
C_5	95	5	3875	3.10
C_7	93	7	3875	3.08
C_{10}	90	10	3880	3.06