

Mineral phases synthesized by hydrothermal treatment from biomass ashes



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ABSTRACT

The development of mineral phases, analcime, tobermorite and cancrinite, from the valorisation of a waste, is the main objective of this work. The waste considered is a biomass ash (BA) obtained from a fluidized bed forest combustor powered principally by eucalyptus bark residue in a paper company. BA is valorised positively by a hydrothermal treatment (HT) in an alkaline solution. This treatment is an eco-efficient process because it employs low temperatures to activate the BA and implies no emission of CO₂ to the atmosphere. Through this HT process, the synthesis of tobermorite is optimized considering the results from different characterization techniques. In addition, the dissolution of chlorides through HT is observed, improving the reutilization of BA in cement-based materials. The results promote the reuse of BA waste and assess its incorporation in cement-based materials due to the high pozzolanic activity shown by the synthesized tobermorite phase (98% of fixed lime at 28 days).

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1. Introduction

The continuous industrial development is associated with an increase in waste generation that creates important environmental problems, such as the generation of tons of ashes from different industrial processes. Within this context, hydrothermal treatment (HT) may be noted as an interesting eco-efficient method increasingly used in the recycling and reuse of industrial waste (Jha and Singh, 2014; Jing et al., 2008; Quina et al., 2008; Wang et al., 2012; Zhou et al., 2014).

Bioenergy is a renewable energy considered as having CO₂ negative emission that can be generated from wood or biomass waste, among others. This is the fastest growing renewable energy, representing 10% of the global primary energy supply (Eisentraut and Brown, 2014) but also creates ash generation problems. Some biomass ashes have been studied to compare their composition with the better known carbon ashes (Vassilev et al., 2013a, 2013b) and, although their high content of alkalis and chlorides may limit their reutilization, the viability of their incorporation into cementitious materials has been studied (Carrasco et al., 2014; Rajamma et al., 2009; Vassilev et al., 2013a; Wang et al., 2008).

In order to enhance the possibility of biomass ashes reutilization, HT processes are employed in this work to obtain new materials with potential new applications. The biomass ash (BA) considered is the inorganic fraction of the ashes studied by Girón et al. (2012). This paper analyses the principal solid phases synthesized and the dissolution of

chlorides through the HT at different concentration of an activating solution. The viability of BA reutilization as a pozzolanic addition to cement-based materials is also studied.

2. Material and experimental procedures

The biomass ash (BA) from a fluidized bed forest combustor was provided by the CEASA Company in Spain and comes principally from the eucalyptus bark residue. BA is the inorganic fraction of the ash with a particle size below 500 μm. Table 1 shows its principal oxides composition (>2% of mass) determined by X-ray fluorescence (XRF) and the loss on ignition determined previous to XRF analysis. The ash is mainly composed of oxides of Si, Ca and Al which are important for many applications, particularly for construction materials. However the presence of Cl⁻ may limit the applications especially concerning to cement-based composites due to potential durability problems.

The BA was submitted to a hydrothermal treatment (HT) where the ash is kept in contact with an activating solution (liquid/solid ratio of 10) during 4 h at 200 °C. Alkali activating solution of 0.5 M, 1.0 M, 1.5 M and 3.0 M of NaOH were used to favour the stability of zeolitic compounds. The HT processes were performed in a Parr equipment, model 4522 with a PID temperature controller, model 4842. After the treatment the solid phase was filtered and dried at 50 °C during 24 h.

Changes in the solid phase obtained from HT in different conditions were evaluated by several characterization techniques. X-ray diffraction (XRD) was performed with Philips PW 1730 equipment, with a graphite monochromator and Cu Kα1 radiation. The Fourier Transform Infrared Spectroscopy (FTIR) characterization was carried out on a Nicolet

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Table 1
Chemical Composition of BA. (LOI: Loss on Ignition UNE-EN ISO 8015).

% weight	CaO	SiO ₂	K ₂ O	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Cl ⁻	MnO	P ₂ O ₅	Na ₂ O	TiO ₂	LOI
BA	39.9	18.0	6.2	6.0	4.5	3.4	3.0	2.8	1.3	1.2	0.8	0.7	11.7

6700 equipment and KBr pellets containing 1 mg of sample per 300 mg of KBr. The thermogravimetric analysis (TG/DTA) was performed with a Netzsch STA 409. Also, morphological information was obtained by the Scanning Electron Microscope (SEM) HITACHI S-4800 and a compositional microanalysis was performed by Energy Dispersive X-ray Spectroscopy (EDX) with a BRUKER X-Flash 5030 Si-Li detector and X-Ray DX4i analyzer. Measurements of adsorption-desorption isotherms were made in an ASAP 2010 analyzer (Micromeritics Instrument Corp. Norcross, GA), using N₂-77K gas as the adsorptive and the specific surface area was obtained through the BET method (Brunauer et al., 1938).

In order to determine the pozzolanic activity of selected materials, an accelerated chemical method optimized at the Institute of Construction Science “Eduardo Torroja” (Sanchez de Rojas, 1986; Sánchez de Rojas and Frías, 1996; Sánchez de Rojas et al., 2000) was used. This method consists in the addition of the analyzed solid to a saturated lime solution at 40 °C to determine the amount of fixed lime at different reaction times.

3. Results and discussions

3.1. Hydrothermal treatment

The crystalline phases in the BA and the hydrothermally treated ashes at 200 °C in different molar concentrations of NaOH during 4 h (BA-HT) were analyzed from the X-ray diffraction data shown in Fig. 1.

The main crystalline phases found in the BA are quartz (SiO₂), calcite (CaCO₃), sylvite (KCl) and portlandite (Ca(OH)₂). The XRD patterns of the biomass ash after the HT in different conditions show the disappearance of the portlandite, sylvite and a clear decrease in the intensity of the peaks corresponding to quartz and calcite phases, even almost disappearing at high concentrations (1.5 and 3.0 M). The dissolution of these two phases of the initial ash, leads to the formation of different minerals.

After the HT at 0.5 M NaOH, analcime (Na(AlSi₂O₆)(H₂O)) with greater intensity in the main reflections of 25.9° 2θ and 15.8° 2θ was obtained, while with 1.0 and 1.5 M NaOH the tobermorite

(Ca_{2.25}(Si₃O_{7.5}(OH)_{1.5})(H₂O)) becomes more clear in the main reflections of 7.8° 2θ and 29° 2θ. Analcime peaks decrease at higher concentrations until 1.5 and 3.0 M, where the peaks corresponding to this phase disappear and a new zeolitic phase arises, cancrinite (Na₈(Al₆Si₆O₂₄)(OH)_{2.04}(H₂O)_{2.66}). The cancrinite peaks intensity is higher for the solid after HT at 3.0 M suggesting a higher crystalline degree. Hydrothermal treatment at 3.0 M NaOH gives rise to other crystalline phases in the solid, as sodium calcium hydrogen silicate (NaCaHSiO₄) and sodium carbonate (Na₂CO₃).

The presence of portlandite in BA, detected by XRD, may be confirmed through Fourier Transform Infrared Spectroscopy (FTIR) by the narrow absorption peak centred at 3642 cm⁻¹ in Fig. 2, associated with the O—H bond stretching in hydroxyl groups (Myneni et al., 1998). A broad band at 3430 cm⁻¹, together with the shoulder observed at 1625 cm⁻¹, confirm the presence of water, since they correspond to the O—H bond stretching and O—H—O bond bending in the water molecule, respectively (Myneni et al., 1998). A pronounced absorption band at 1427 cm⁻¹ can be observed that together with the peaks at 875 and 714 cm⁻¹ are associated with the C—O bond vibrations in carbonate groups [CO₃]²⁻ due to the presence of calcite as detected by XRD. On the other hand, the stretching vibrations of Si—O bonds corresponding to quartz may be associated to the band with minimum transmission at 1116 cm⁻¹ (Ramachandran and Beaudoin, 2001).

The infrared absorption peak due to the portlandite phase disappears after the treatment, as detected by XRD. The 3430 and 1625 cm⁻¹ bands, related to O—H and O—H—O bonds, are more pronounced in lower concentrations maybe due to the appearance of hydrated phases analcime and tobermorite in the solid. At 3.0 M, those bands are weaker maybe due the almost disappearance of analcime and tobermorite, and the appearance of new non-hydrated phases as sodium calcium hydrogen silicate and sodium carbonate.

The carbonate absorption, specially the band at 1427 cm⁻¹, is clearly modified by the processes in different molar concentrations. At lower concentrations, 0.5 and 1.0 M, this band is less intense maybe due to the decrease of calcite content of the solid as observed by XRD. However, at higher concentrations, especially at 3.0 M, the band is more pronounced and shifted to 1450 cm⁻¹ due to the presence of sodium carbonate.

The infrared spectrum presents important changes in the silicate band (between 1200 and 800 cm⁻¹) where the quartz contribution at

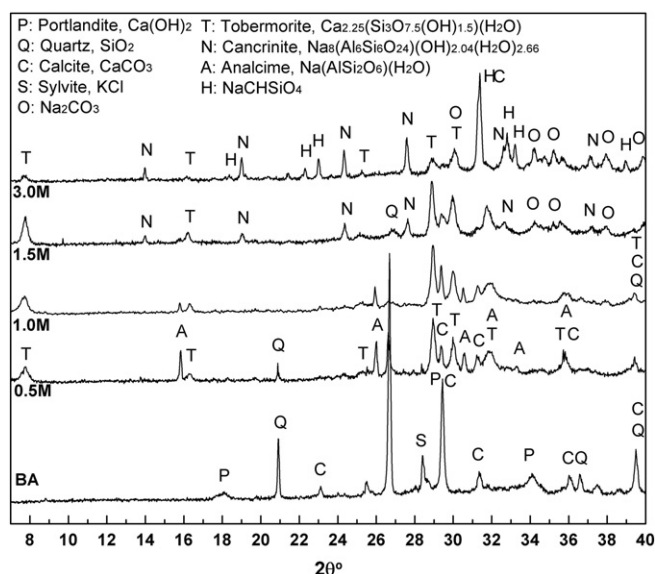


Fig. 1. XRD patterns of BA and BA-HT in different NaOH concentrations.

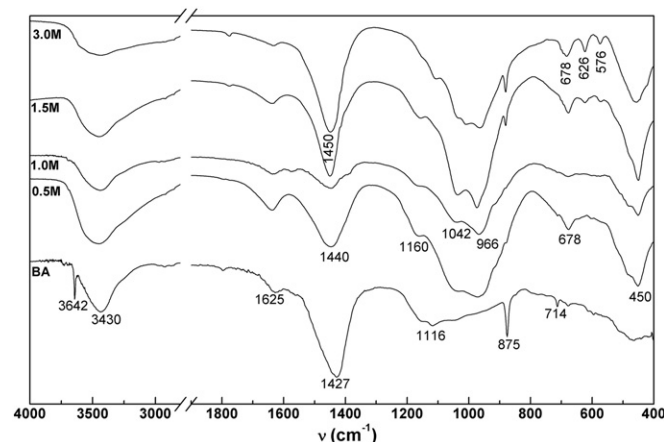


Fig. 2. Fourier Transform Infrared Spectroscopy (FTIR) of BA and BA hydrothermally treated.

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