Construction and Building Materials 136 (2017) 73–80

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

# Advances on the development of ternary cements elaborated with biomass ashes coming from different activation process

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## HIGHLIGHTS

- Advances on the sugarcane bagasse-leaf mix as pozzolan.
- Behaviour differences between industrial ash and laboratory ash.
- The industrial ash shows a soil contamination.
- The reaction kinetics of the cogeneration ash differed from the lab ash.
- The mixture of bagasse and leaf waste complied with the existing standards.

## ARTICLE INFO

*Article history:*
Received 20 June 2016
Received in revised form 19 December 2016
Accepted 6 January 2017

*Keywords:*
Sugar cane cogeneration ash
Characterization
Pozzolanic behavior
Blended cement
Performances

## ABSTRACT

Due to economical and sustainable issues there is growing interest in investigating agro-industrial wastes as alternative route for future eco-efficient and sustainable pozzolans. The generation of ashes from cogeneration processes in which sugar cane wastes are used as biomass, involves significant environmental, social and health problems when they are accumulated in dumps. This paper explores the scientific and technical aspects of two Brazilian sugar cane ashes from different processes of production: one from an industrial cogeneration process and another from laboratory scale, maintaining the same proportions of mixture (50% mixture of bagasse and leaf). Subsequently, their behavior in ordinary Portland cement matrices made with 20% ashes substitution was analyzed. The results show that the industrial ashes presented variations on the chemical and mineralogical compositions, pozzolanic reaction rate and different formation of hydrated phases with respect to the laboratory ashes. The 20% blended cements complied with the chemical, physical and mechanical requirements set out in the existing Standards, maintaining the mechanical performance with respect to the control mortar at 60 days of curing.



## 1. Introduction

For decades, ordinary Portland cement is one of the materials commonly used in the construction sector with important benefits in socio-economic development of a country. However, fabrication of this artificial product is associated with the release of greenhouse gases, mainly $CO_2$ from the decarbonation of limestone and fossil fuels, which represents about 5–7% of global emissions of carbon dioxide, the main cause of global warming [1]. In 2013, world production of cement was 4 billion of tons [2], releasing to the atmosphere 800 kg of $CO_2$ per ton of cement produced. Two of the three main strategies to reduce $CO_2$ emissions from the cement industry are related to: replace fossil fuels by alternative ones mainly biofuels [3–5] and the partial replacement of cement by supplementary cementing materials (pozzolans) [6–10]. The second alternative is the focus of the researchers to get future eco-efficient cements.

The use of waste materials with pozzolanic properties (such as silica fume and fly ash) and blast furnace slag in cement mortar and concrete is a worldwide practise [11], which is included in different regulations. During the last decade, the investigations are entering a new range of wastes from the agro-industrial sector [12–15], which is an inexhaustible source of alternative pozzolans, mainly in Asian and Latin American countries, which do not have the local production, at least at affordable costs, of traditional poz-

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http://dx.doi.org/10.1016/j.conbuildmat.2017.01.018
0950-0618/

zolans. These wastes are generating serious environmental, technical and social problems, by their accumulation in landfills and uncontrolled burning. However, due to their chemical and mineralogical composition, once thermally activated between 600 and 800 °C, they achieve excellent properties as supplementary cementing materials, improving the mortars and concretes performances [8,16,17].

Nowadays, among the wide range of agro-industrial residues, the sugar cane wastes are getting particular attention of researchers worldwide, as they comprise high volume of solid wastes (bagasse and straw). According to the available data, in 2011 more than 1800 million tons of sugar cane were generated in the world, being Brazil the biggest sugar producer (568 million tons) with an estimated production of 1000 million tons for 2020. The generation of bagasse wastes during the industrial (sugar and bioethanol) process is estimated about 25% by mass of sugar cane and with consequent production of 4 million tons of bagasse ash only in this country.

Due to the energy properties, these sugar cane wastes are being used as main alternative biofuel (1 ton of bagasse is equal to 1.6 barrels of fuel oil) [4]. However, the ashes produced during the cogeneration process can perform significantly different from the ashes obtained at laboratory scale, due to their dependence with factors such as agriculture variables, raw fuels (alone or mix), boiler temperature and, contamination of soils [18].

In view of that, the published research works are still scanty and mainly based on technical studies with (bottom and filter) boiler bagasse ashes [19–22]. At present, the Brazilian cogeneration companies are using, in function of season, a mix of sugar cane bagasse and straw wastes as biomass, whose characteristics are still unknown to the scientific community.

In view of the limited information, the main goal of the present work is to deepen the scientific aspects of cogenerated bagasse-straw ashes obtained in a sugar factory (BIOI), as well as the corresponding ashes produced at laboratory scale (BIOL), with burning temperature and mix of bagasse /leaf similar to the conditions used in the industrial process, and the subsequent effect on the chemical, physical and mechanical properties of the 20% blended cements. The expected results are fundamental for the establishment of an action protocol in this kind of industry, for the commercialization of these ashes as pozzolans in the manufacture of future eco-efficient and innovative Portland cements.

## 2. Experimental

### 2.1. Materials

Two bio-ashes were used in this research work with different production sources: 1) An industrial bottom ash (BIOI) from a Brazilian sugar cane mill, which uses a mix of sugar cane bagasse and leaf wastes as biomass (around 40–50% of mix) for cogeneration processes. These ashes reached boiler temperature between 700 and 800 °C; 2) An ash produced in laboratory (BIOL) formed by a mixture (1:1 ratio by weight) of sugar cane bagasse and sugar cane leaf ashes, which were separately obtained in an electric furnace with a 10 °C/min heating rate, and then at 700 °C for 90 min. The starting sugarcane bagasse and sugarcane leaf wastes for laboratory tests were collected in an area next to crop fields of sugar industry (BIOI ash).

Both ashes were ground and sized in order to obtain particles below 63 μm, the same order to the commercial Portland cement.

### 2.2. Blended cements

CEM I 42.5 R Ordinary Portland Cement (OPC) was supplied from the Lafarge Cement Company's plant at Villaluenga de la Sagra (Toledo, Spain) was used. The 90% of cement particles were under 42.90 μm. The mineralogical composition of OPC was of alite (67.58%), belite (8.11%), aluminate (4.96%) and ferrite (8.85%).

The blended cements were prepared in a high-speed powder mixer to guarantee homogeneity. The blends were calculated by weight, with bio-ash/OPC ratios of 0/100 and 20/80. This replacement level corresponds to the standardized maximum ratio for type II/A cements (6–20%).The chemical composition of the OPC is given in Table 1.

### 2.3. Methods

#### 2.3.1. Pozzolanic method

The pozzolanic activity of ashes was studied by using an accelerated chemical method. The test consists in placing the bagasse ash (1 g) in a lime-saturated solution (75 ml) at 40 °C for 1, 7, 28 and 90 days. The CaO concentration in the solution was analyzed at the end of each period. The combined CaO (mmol/l) was obtained as the difference between the concentration in the control lime-saturated solution (17.68 mmol/l) and the CaO content in the solution in contact with the sample.

The pozzolanicity of pozzolanic cements was evaluated according to the current regulations 196-5 [23], in cement pastes elaborated with 20% of bio-ashes. The calcium ions values, expressed as calcium hydroxide, were determined at 8 and 15 days of reaction.

#### 2.3.2. Kinetic-diffusive mathematic model

For the quantitative characterization of the pozzolanic activity (computing of the kinetic parameters of the pozzolanic reaction) in a pozzolan/lime solution system a kinetic–diffusive model published by Villar-Cociña et al. [24–26] is used. The model is:

$$C_t = \frac{0,23 \cdot Exp\left(\frac{-3t}{\tau}\right) \cdot \left(-1 + Exp\left(\frac{t}{\tau}\right)\right) \cdot \frac{1}{\tau}}{D_e\, r_s} + \frac{0,23 \cdot Exp\left(-\frac{t}{\tau}\right) \cdot \frac{1}{\tau}}{K\, r_s^2} + C_{corr} \quad (1)$$

where, De is the effective diffusion coefficient, K is the reaction rate constant, $\tau$ is a time constant (the time interval during which the pozzolan radius diminishes until a 37% of its initial radio $r_s$). $C_t$ represents the absolute loss of CH concentration with time for pozzolan/lime system and $C_{corr}$ is a correction parameter that takes into account the concentration remainder of CH that is not consumed in the reaction. In some systems the CH is not totally consumed.

It is known that the pozzolanic reaction develops by stages. The resistances of these stages are usually very different and the stages presenting the greatest resistances (i.e. the stages that lapses more slowly) control the process. Accordingly, it is possible in certain cases to have different behaviors: diffusive (described by the first term of Eq. (1)), kinetic (second term) and kinetic–diffusive (both terms). Further explanations about the model can be found in Villar-Cociña et al. [25,26].

#### 2.3.3. Experimental techniques of characterization

Different techniques were used for the chemical, physical, mineralogical and morphological characterization.

Chemical characterization was carried out by X- ray fluorescence (XRF), using a Philips PW 780 equipment, with an anticathode tube of rhodium of 4 kW.

Mineralogical characterization was studied by X-ray diffraction (XRD) by using the random powder method for the bulk sample and the oriented slides method for the <2 μm fraction. The X-ray diffractometer is a SIEMENS D-500 with a Cu anode, operated at 30 mA and 40 kV using divergence and reception slits of 2 and