### ARTICLE IN PRESS

Journal of Environmental Management xxx (2016) 1-11



Contents lists available at ScienceDirect

## Journal of Environmental Management



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

**Research article** 

# Concretes and mortars with waste paper industry: Biomass ash and dregs

Isabel Martínez-Lage <sup>a, \*</sup>, Miriam Velay-Lizancos <sup>a</sup>, Pablo Vázquez-Burgo <sup>a</sup>, Marcos Rivas-Fernández <sup>a</sup>, Cristina Vázquez-Herrero <sup>a</sup>, Antonio Ramírez-Rodríguez <sup>b</sup>, Miguel Martín-Cano <sup>b</sup>

<sup>a</sup> Grupo de Construcción, Centro de Innovación Tecnológica en Edificación e Ingeniería Civil (CITEEC), E.T.S. Ingenieros de Caminos, Canales y Puertos.
Universidade da Coruña, Campus de A Coruña, s/n, 15071, A Coruña, Spain
<sup>b</sup> SACYR Construcción S.A., Departamento I + D + i, Grupo SACYR, Paseo de la Castellana 83-85, 5<sup>a</sup> planta, 28046, Madrid, Spain

#### ARTICLE INFO

Article history: Received 13 January 2016 Received in revised form 10 June 2016 Accepted 25 June 2016 Available online xxx

Keywords: Paper industry waste Biomass ash Mortar Concrete Mechanical properties Depth of penetration of water under pressure

#### ABSTRACT

This article describes a study on the viability of using waste from the paper industry: biomass boiler ash and green liquor dregs to fabricate mortars and concretes. Both types of ash were characterized by obtaining their chemical and mineralogical composition, their organic matter content, granulometry, adsorption and other common tests for construction materials. Seven different mortars were fabricated, one for reference made up of cement, sand, and water, three in which 10, 20, or 30% of the cement was replaced by biomass ash, and three others in which 10, 20, or 30% of the cement was replaced with dregs. Test specimens were fabricated with these mortars to conduct flexural and compression tests. Flexural strength is reduced for all the mortars studied. Compressive strength increases for the mortars fabricated with biomass ash and decreases for the mortar with dregs. Finally, 5 concretes were made, one of them as a reference (neither biomass ash nor dregs added), two of them with replacements of 10 and 20% of biomass ash instead of cement and another two with replacements of 10 and 20% of dregs instead of cement. The compressive and tensile splitting strength increase when a 10% of ash is replaced and decrease in all the other cases. The modulus of elasticity always decreases.

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#### 1. Introduction

The paper and woodpulp industry generates different wastes, with water treatment sludge, lime sludge, sands or lime grits, green liquor dregs, and biomass ash being the most significant. Their composition depends on the raw materials used and the configuration and operation of the plant, but in Spain, more than 95% of these wastes can be considered non-hazardous according to the European Waste Catalogue.

Currently, at the paper industry, the main wastes are dregs, biomass ash, and secondary treatment bio sludge. Management of the latter is internal, but the other two are sent to a dump because of the lack of studies validating their possible recycling value. This study is conducted to avoid this poor management of biomass ash and dregs. Once these wastes were analyzed, it was decided to

\* Corresponding author.

E-mail address: isabel.martinez@udc.es (I. Martínez-Lage).

http://dx.doi.org/10.1016/j.jenvman.2016.06.052 0301-4797/© 2016 Elsevier Ltd. All rights reserved. perform a study on the viability of mortar fabrication, the results of which would help decide if another subsequent study should be performed on their use in concrete.

The first thing that needs to be highlighted is that the chemical composition of biomass ash varies greatly (Tkaczewska et al., 2012; Vassilev et al., 2010), not only between ashes of different groups but even within the same group. Several studies found in the current literature utilize biomass fly ash or bottom ash in cement based materials, and it has also been proved that the chemical composition of the biomass ash utilized is very different. So, in some of them the sum of the contents of silicon dioxide SiO<sub>2</sub>, aluminum oxide Al<sub>2</sub>O<sub>3</sub> and iron oxide Fe<sub>2</sub>O<sub>3</sub> is higher than 70% and calcium oxide CaO lower than10% (García and Sousa, 2013; Ramos et al., 2013; Tkaczewska et al., 2012; Wang and Baxter, 2007). In others, the sum of  $SiO_2$ ,  $Al_2O_3$  y  $Fe_2O_3$  is between 50 and 70%, and the content of CaO is between 10 and 20% (Johnson et al., 2010; Wang and Baxter, 2007) and in others the sum of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> y Fe<sub>2</sub>O<sub>3</sub> is lower than 50% and the content of CaO is higher than 20% (García Calvo et al., 2010; Rajamma et al., 2009; Esteves et al., 2012;

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Tkaczewska et al., 2012; Carrasco et al., 2014; Cuenca et al., 2013; Berra et al., 2015). It should also be noted that in many cases, the content of magnesium oxide is higher than the amount allowed by the EN 450-1 Standard and by the ASTM C618 Standard (García Calvo et al., 2010; Rajamma et al., 2009; Esteves et al., 2012; Tkaczewska et al., 2012; Wang and Baxter, 2007; Carrasco et al., 2014; Cuenca et al., 2013) and that almost all cases comply with the content of sulfuric anhydride.

In some studies, mortars were made replacing part of the cement with biomass ash. With regard to the flexural strength, García and Sousa (2013) and Ramos et al. (2013) found that it is similar to that of the reference mortar, but Rajamma et al. (2009) found that it diminishes. Concerning the compressive strength, García and Sousa (2013) found that it is lower at 28 days but increases at 90 days; Rajamma et al. (2009) found that it increases when 10% of cement is replaced but decreases for higher replacement levels; and Ramos et al. (2013) and Johnson et al. (2010) found that it is similar to that of the reference mortar; García and Sousa (2013) notice that the chloride permeability increases as the content of biomass ash raises. Johnson et al. (2010) observe that the content of biomass ash does not have an effect on the behavior of frost/thaw cycles; and Esteves et al. (2012) and Ramos et al. (2013) notice that biomass ashes mitigate the expansion in the alkali-silica test

Barbosa et al. (2013) used two biomass ashes, fly ash and bottom ash, to fabricate concrete and they concluded that for 10% substitution of cement with fly ash, compressive strength was similar to the reference concrete, while concretes with 30% substitution yielded lower compression strength than the reference concrete.

Wang and Baxter (2007), Wang et al. (2008a, 2008b) fabricated concrete replacing 25% of cement with biomass ash. The main results obtained were as follows: (1) compressive strength was similar for any type of ash at 7, 28, 91 and 365 days, and for 28, 91 and 365 days they were also similar to the concrete without ash, (2) mixed biomass exhibited better behavior in mitigating alkali-silica expansion than C ash, (3) flexural strength for the concrete with biomass ash at 56 days was lower than for the rest of the concretes, (4) biomass ash had no impact on freeze-thaw stresses and (5) biomass ash specimen exhibited higher chloride permeability, which was similar to the case without ash, almost certainly due to the higher particle size.

Carrasco et al. (2014) investigated the substitution of cement for bottom ash from a biomass plant, using proportions of 10%–90%, fabricating concrete blocks with compressive strengths of 20 MPa. They determined that as the substitution percentage was increased, the porosity also increased, leading to decrease thermal conductivity, which is beneficial. They also found that the apparent density decreases, which increases water absorption, confirming that compressive strength is also reduced.

Analyzing the chemical composition of the biomass ash and dregs from the paper industry studied, it may be concluded that it is not possible to assimilate it to any of the previous studies so, to decide on its feasibility as a substitute of concrete to produce mortars and concretes it is necessary to conduct a specific study with these materials.

In the study of the mortars, flexural and compressive strength will be analyzed and compared with the studies performed with another kind of biomass ash. In the case of concrete, the compressive stenght, tensile splitting strength, modulus of elasticity and permeability will be studied. It should be highlighted that studies with results of these last three properties have not been found. Although there are some studies in which compressive strength is studied, the composition is so different that they cannot be compared with these ashes.

#### 2. Materials and methods

#### 2.1. Biomass ash and dregs

Biomass ash utilized in this study is a waste produced in the process of obtaining energy through the biomass combustion. This biomass comes from eucalyptus wood, both the bark and forest residues, and the black liquor from the wood baking process. Dregs are the heaviest solids "unburned" included in the ashes of green bleaches produced from the burning of the obtained black liquor. Both residues are listed as non-hazardous wastes according to the European List of Waste.

Table 1 shows the chemical analysis performed using X-ray fluorescence, which also shows the loss of ignition (LOI) at 975  $^{\circ}$ C.

In light of the chemical composition results, it is confirmed that both biomass ash and dregs are of limestone origin, so clearly none of them comply with the requirement regarding the sum of silicon dioxide, aluminum oxide, and iron contents specified in EN 450-1 (CEN, 2005a) or ASTM C618 (2008), as these standards are oriented towards silicon-based fly ash.

The mineralogical composition was obtained using X-ray diffraction, including the diffractogram of the biomass ashes shown in Fig. 1 and of the dregs shown in Fig. 2. From these figures, it is possible to conclude that the dregs are basically made up of calcite, very little dolomite, and possible traces of sodium sulfate and sodium calcium sulfate and that the biomass ashes exhibit greater variation in sodium chloride, calcium chloride, anhydrite, calcite, dolomite and porlandite, with the most intense peak being that of quartz but the majority phase being calcite.

The granulometry of the biomass ashes as well as of the dregs was obtained using laser techniques. Fig. 3 shows the accumulated distribution of ashes and the accumulated distribution of dregs. Analysis of this distribution reveals that the maximum size of the ash particles is 200  $\mu$ m and of the dreg particles is 125  $\mu$ m. In addition, there are almost no ash or dreg particles with sizes between 0.15 and 5  $\mu$ m, although in the case of the ashes, the percentage of particles smaller than 0.15  $\mu$ m is 15%, and in the case of the dregs, that percentage is 50%. In both cases, the amount retained by the 45  $\mu$ m sieve is lower than 40% (requirement in EN 450-1 (CEN, 2005a) and 34% (requirement in ASTM C618 (2008)).

Table 1	
Chemical	composition

Component	Biomass ash (wt%)	Dregs (wt%)
CaO	34.9	46.2
SiO <sub>2</sub>	11.6	1.3
SO <sub>3</sub>	11.4	1.4
K <sub>2</sub> O	6.5	0.28
MgO	4.4	3.3
$Al_2O_3$	4.4	0.43
Cl	2.7	0.099
Fe <sub>2</sub> O <sub>3</sub>	2.6	0.8
$P_2O_5$	1.6	3.3
Na <sub>2</sub> O	1.4	3.4
MnO	1.4	0.41
TiO <sub>2</sub>	0.25	< 0.03
SrO	0.21	0.14
V <sub>2</sub> O <sub>5</sub>	0.18	< 0.03
ZnO	0.057	0.15
NiO	0.040	0.015
Rb <sub>2</sub> O	0.037	< 0.03
CuO	0.022	0.023
ZrO <sub>2</sub>	0.020	0.007
Br	0.007	<0.03
LOI	15.8	38.5

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