Construction and Building Materials 184 (2018) 464–472

Contents lists available at ScienceDirect

Construction and Building Materials

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

Upcycling unexplored dregs and biomass fly ash from the paper and pulp industry in the production of eco-friendly geopolymer mortars: A preliminary assessment

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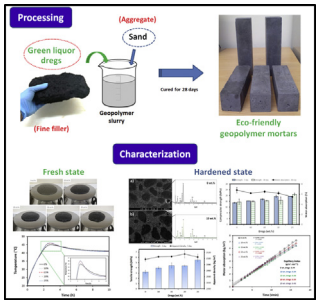
HIGHLIGHTS

- Two unexplored waste streams from pulp and paper industry were investigated.
- Dregs were used for the first time as filler in geopolymeric mortars production.
- Biomass fly ash was used as main aluminosilicate source (75 wt%).
- Dregs enhanced mortars' tensile (up to 71%) and compressive strength (up to 34%).
- Using dregs as additives in geopolymers is an effective waste recycling strategy.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 January 2018
Received in revised form 2 July 2018
Accepted 5 July 2018

Keywords:
Green liquor dregs
Biomass fly ash
Inorganic polymer
Calorimetry
Mechanical resistance

ABSTRACT

Green liquor dregs wastes coming from pulp and paper production are currently disposed in landfills at a huge cost for industry and the environment. In this work, a novel and more sustainable waste management strategy is proposed. Dregs were used for the first time as fine filler in the production of biomass fly ash-based geopolymeric mortars. The influence of the dregs incorporation amount on the fresh (geopolymer kinetics and mortars workability) and hardened-state (mechanical resistance, water absorption and capillary water absorption) properties of the mortars was evaluated. Although dregs incorporation reduce the flow workability (up to 19%), their presence and amount did not significantly alter the geopolymerization kinetics. Additionally dregs-containing mortars exhibited enhanced tensile (up to 71%) and compressive strength (up to 34%), and lower water absorption in comparison with the reference mortar. These results demonstrate the feasibility of using dregs as fine filler in geopolymers production. Moreover the mortars were produced using mainly biomass fly ash waste as aluminosilicate source which further reduces the environmental impact of the pulp and paper industry.

1. Introduction

The pulp and paper production is one of the most vital industrial activities in Portugal, which is ranked in third place amongst European countries, accounting for ~7% of all EU pulp production [1]. However this industry is also responsible for a distressing amount of residues (11 million tons generated in Europe) [2], the most abundant being dregs, grits and biomass ash. Among these, dregs are the most challenging residue since there is currently no viable solution for their recycling. Dregs worldwide production is unknown. However an estimated production of 0.5 and 1.3 million

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https://doi.org/10.1016/j.conbuildmat.2018.07.017
0950-0618/

tons was reported by Kinnarinen et al. [3], considering a global production of 117 million tons of Kraft pulp. Recent data shows an even higher amount (178.8 million tons) [1], which raises the dregs annual production to values ranging from 0.7 to 2.0 million tons. Dregs are usually dumped in landfills [4], which is environmentally unsustainable. In addition over the past years landfill tax has been increasing [5], while existing landfills are progressively reaching exhaustion. These environmental and economic concerns exert pressure on the paper and pulp industry to change the paradigm from conventional linear concept to the circular economy. Indeed the increasing public awareness regarding environmental issues is an important driver for the development of new and more sustainable waste management strategies.

Dregs are produced during the clarification of the green liquor and consist of insoluble residue of the smelt (which is a flux of inorganics coming from the recuperation boiler) dissolver. Typically dregs contain sodium and calcium carbonates, sulphides, and an organic fraction due to incomplete burning in the recuperation biomass boiler [6]. This waste is strongly alkaline (pH typically ranging from 10 to 12.8 [4]), contains high alkaline and earth-alkaline oxides content and chlorine, which hinders their recycling in common application, such as their incorporation in cement or concrete. The latter is possibly the reason for the surprisingly low number of studies in this field. Nevertheless recent studies evaluated the feasibility of using dregs as aggregate in road pavement construction [7] and as cement replacement in concretes and mortars [8]. Pasandín et al. [7] observed poor water resistance for the dregs-containing hot-mix asphalt, which was attributed to the high water content of the dregs and their fineness, but also due to their chemical composition and the increase in the mastic viscosity. Martínez-Lage et al. [8] reported similar compressive and flexural strength of the mortars in which 10% cement was replaced by dregs, while a decrease was observed for higher replacement values. Still a severe fall in compressive strength for the dregs-containing concretes was observed, and for that reason the authors have concluded that the use of dregs as replacement of cement in concretes is unsuitable. In this context novel management strategies that ensure valorisation of substantial amounts of dregs are a pressing matter.

Geopolymers have attracted a lot of attention over the past years since they are considered an environmentally friendlier alternative to Portland cement [9]. This technology allows the use of distinct waste streams as raw materials [10–12], which further decrease their carbon footprint. Additionally, hazardous materials can be immobilized in the geopolymer network [13,14]. Geopolymer synthesis involves mixing aluminosilicate precursors (e.g. fly ash, metakaolin) with alkaline activators. Considering that dregs contain very low SiO_2 and Al_2O_3 content they cannot be used as a precursor in geopolymer preparation. Nevertheless they could be used as filler in geopolymeric mortars. Yet surprisingly this strategy has never been exploited, up to now.

The present work evaluates the feasibility of using dregs as filler in the production of biomass fly ash (FA)-based geopolymer mortars. This is the first ever report considering the incorporation of dregs in geopolymeric mortars. In this investigation, the influence of dregs incorporation content on the fresh (geopolymer kinetics and mortars workability) and hardened-state properties (compressive strength and water absorption) of the mortars was evaluated.

This investigation aims to provide a sustainable management methodology for this unexplored waste stream, while simultaneously decrease the knowledge gap regarding the influence of dregs incorporation in geopolymeric mortars properties. Moreover the geopolymers were prepared using 75 wt% biomass FA as aluminosilicate source, whose recycling is still insipient, which further mitigates the pulp and paper industry wastes environmental impact.

2. Experimental conditions

2.1. Materials

In this investigation biomass FA and dregs wastes, produced by a Portuguese paper pulp plant, were used as main aluminosilicate source (75 wt%) and as fine filler, respectively. The FA was used without any pre-treatment step, albeit their coarse particle size distribution that will negatively affect the geopolymerization extension. Nevertheless milling or sieving was avoided to reduce the geopolymer production cost. As for the dregs they were supplied as very large solid blocks containing ~46 wt% water. The dregs were dried, crushed in a mortar and then sieved through a 75 μm mesh prior to mixing.

Benchmark metakaolin (MK) (Argical™ M1200S; Univar) was also used in the compositions (25 wt%) to ensure suitable molar ratios. To promote alkaline activation a mixture of sodium silicate (H_2O = 62.1 wt%; SiO_2/Na_2O = 3.15; Quimialmel) and 10 M sodium hydroxide solution (ACS reagent, 97%; Sigma Aldrich) was used.

The sand employed as an aggregate was composed by particles ranging from 0.125 to 2 mm.

2.2. Geopolymer mortars preparation

To evaluate the influence of dregs incorporation content on the geopolymer mortars' physical properties five formulations containing distinct dregs content (0, 10, 15, 20 and 25 wt%) were produced (Table 1). In this study dregs were used as additives, amount depending on the composition but considering the total aluminosilicate mass (MK and FA mixture).

The preparation of the blends involved: i) mixing MK and FA in a plastic bag for 1 min; ii) homogenisation of the alkaline solution during 5 min; iii) mixture of the aluminosilicate sources with the alkaline solution for 10 min; and iv) addition of sand and dregs to the blend and mixture. Afterwards, the slurry was casted in metallic moulds and covered with a plastic film. The mortars were cured at 40 °C and 65% relative humidity for 24 h. afterwards the samples were demoulded and left at ambient conditions until the 28th curing day.

2.3. Materials characterisation

X-ray powder diffraction (XRD) was used to evaluate the mineralogical compositions of the precursors and of the produced geopolymers using a Rigaku Geigerflex D/max-Series instrument (Cu K_α radiation, 10–80° 2θ, 0.02° 2θ step-scan and 10 s per step), and phase identification by PANalytical X'Pert HighScore Plus software.

X-ray fluorescence (Philips X'Pert PRO MPD spectrometer) was used to study the chemical composition of MK, FA and dregs. The loss on ignition (LOI) at 1000 °C was also determined.

Particle size distribution was determined by laser diffraction (Coulter LS230 analyzer). The determination was performed by a laser diffraction technique (Fraunhofer method) for particles with a particle size from 0.4 μm to 2000 μm, and simultaneously by PIDS (Polarization Intensity Differential Scattering) to lower particle sizes (between 0.4 μm and 0.04 μm).

The microstructure of the precursors and of cured geopolymeric mortars was evaluated using scanning electron microscopy (SEM – Hitachi S4100 equipped with energy dispersion spectroscopy, EDS – Rontec).

In the fresh state, the influence of fine dregs on mortars was evaluated by flow table test after mechanical mixing EN 1015-3 [15], while the temperature evolution of geopolymeric pastes upon curing was monitored in the first 10 h in a quasi-adiabatic calorimeter under controlled relative humidity (65%) and temperature (40 °C). The acquisition period was selected considering a previous work by the authors [16].

In the hardened state, the tensile strength of mortars was evaluated after 24 h curing and then the compressive strength of specimens cured for 7 and 28 days was determined EN 1015-11:1999 [17], using a Universal Testing Machine (Shimadzu, model AG-25 TA) running at a displacement rate of 0.5 mm/min and the water absorption of the geopolymer mortars was determined by using the Archimedes Principle. Three specimens of each formulation were tested and the average data reported.

Table 1
Geopolymer preparation: mixture composition and NaOH molarity.

Sample name	Mixture proportion (g)						Spread on table (SD)
	MK	FA	Dregs	Sodium silicate	NaOH	Sand	
M0	100	300	0	200	200	1200	203 ± 4
M10			40				188 ± 4
M15			60				174 ± 6
M20			80				170 ± 7
M25			100				165 ± 7