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Preparation of clinker from paper pulp industry wastes

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HIGHLIGHTS

- Valorization of the pulp paper industry wastes (lime mud, biological sludge and fly ash).
- Despite the fly ash constrains (high chloride content) an application for it was found.
- Development of eco-clinkers (betilic and Portland) only from industrial wastes.
- Decrease (of about 60 °C) of the eco-Portland clinker processing temperature.

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ABSTRACT

The production of paper pulp by the Kraft method generates considerable amounts of wastes. Namely, lime mud generated in the recovery circuit of chemical reagents, biological sludge from the wastewater treatment of wood digestion process and fly ash collected in the fluidized bed combustor used to generate electricity from biomass burning. The final destination of such wastes is an important concern, since environmental regulations are becoming stricter regarding their landfill. Driven by this fact, industries are looking for more sustainable solutions, such as the recycling in distinct products.

This work tested these wastes as secondary raw materials to produce clinker/cement that was then experienced in mortar formulations. The first step involved the residues detailed characterization and a generated amounts survey. Then, specific but simple steps were suggested, aiming to facilitate transport and manipulation. Distinct blends were prepared and fired in order to get belitic and Portland clinkers. The Portland clinkers were processed at lower temperatures than the normally used in the industry due to the presence of mineralizing impurities in some wastes. Belite-based cements were used to produce mortars that developed satisfactory mechanical strength and did not reveal signs of deterioration or durability weaknesses.

1. Introduction

Paper and pulp paper production is one of the most important industrial activities in Portugal, which is ranked in third place among European countries, accounting for about 7% of all the produced cellulose in the EU [1]. The Kraft or sulphate method of wood digestion generates a considerable amount of solid wastes. Those residues are formed from: (i) the process used to recover chemical reagents ($NaOH + Na_2S$ liquor), consisting of inorganic components (dregs, grits and calcareous mud); (ii) the energy generation by burning the biomass by-products (fly and bottom ashes, and exhaust sand from the bubbling fluidized bed), and (iii) the wastewater treatment, resulting in two types of organic sludge: primary, resulting from flocculation/sedimentation operations; and secondary (or biological) when part of the primary sludge is decomposed by microorganisms [2,3]. Of these two, the biological sludge shows stronger compositional variability and much higher moisture content. Additionally, it may also contain hazardous elements, such as organic chloride compounds and heavy metals, requiring accurate control of conditioning and treating/manipulation conditions, and also adds difficulty to any potential recycling routes [4].

Nowadays, the final destination for industrial wastes in becoming critical, since legislation and environmental constraints are more severe. Those aspects need to be linked with economic vectors in order to achieve viable solutions for waste recycling. Clearly, the common landfilling practice is not recommended and increasing taxes are being applied as a way to discourage it. This offers an opportunity to develop better sustainable practices, involving the valorization of wastes and by-products as raw materials for distinct industrial sectors [5].

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The pulp paper wastes are mainly used in agriculture [6–11], for energy production [4] and in building materials [12–24]. According to the literature [6–11], the sludge improves the physical, chemical, and biological properties of the soil, being considered as a substitute for fertilizers. The building materials are an ideal target for wastes recycling, due to the huge amount of primary and non-renewable resources that are consumed, as well as the flexibility/variety of available products (cement, concrete, aggregates, ceramics, etc.). For example, the literature reports that the incorporation of sewage sludge in ceramic products has technical [13–16] and economic [12] advantages. The substitution of natural aggregates or cement in mortars and concrete by fly and biomass ash was also reported [17–23]. Previous studies suggest the use of ash and wastewater sludge as partial substitutes for natural components of clinker/cement [17,24]. Upon clinkering, organic and volatile compounds are completely destroyed while the inorganic fraction (e.g. heavy metals) is immobilized in the clinker ceramic matrix, mostly made up of calcium silicates [25]. The burning of organic matter will generate heat, thus contributing to minimize the energy demand for the calcination. To be effective, the moisture in the waste should be eliminated, for instance by using the excess heat from the furnace. Actual systems to treat the gaseous emissions are already rather effective, but the strong alkaline character of the atmosphere of a clinker furnace assures, a priori, a strong cleaning effect [26].

This work aims to find solutions for the huge amounts of wastes generated in the manufacture of paper pulp by the Kraft method. According to the literature [4,17,24,27], the fly ash from the biomass combustion are rich in SiO_2 (28–41 wt.%) and have small quantities of Fe_2O_3 (2.2–2.6 wt.%) and Al_2O_3 (6.2–9.3 wt.%). The limestone mud is mainly constituted by calcium carbonate, whereas the biological sludge can be regarded, due to its high organic matter content, as a secondary fuel. This sludge also contains small amounts of the required oxides (SiO_2, Al_2O_3, $CaCO_3$ and Fe_2O_3) for the clinker production. Consequently, this work studied the biological sludge, the lime mud and the fly ash, as secondary raw materials, to produce clinkers/cements which were subsequently tested in the preparation of mortars.

2. Materials and methods

2.1. Materials

The wastes studied in this work were produced by Portucel/Soporcel (gPS) group and include: (i) lime mud (LM), generated in the recovery circuit of chemical reagents; (ii) biological sludge (BS), formed in the last step of the wastewater treatment from the main wood digestion operation; and (iii) fly ash (FA) from the biomass burning in bubbling fluidized combustor.

For the cement preparation it was used the prepared clinker (<63 μm), gypsum (<63 μm) and LM (as-received). In the mortars it was used a calibrated sand (D_{50} = 1·15 mm; D_{max} < 2.0 mm) and a limestone filler (D_{50} = 3.184 μm; D_{max} < 50 μm).

2.2. Clinker preparation

Mixtures of the raw wastes were prepared by using BS and LM in the as-received condition, while FA was previously sieved at 63 μm. A porcelain jar mill (500 mL) containing alumina balls was used to get homogeneous mixtures of fine powders. The proportions of the mixtures are presented in Table 1 and were guided by the following objectives: (i) achieving a desirable clinker composition (belite-rich or Portland-type), defined from the wastes chemical composition and by using Bogue equations and the lime saturation factor (LSF) [28]; (ii) attempting to consume the highest amount of BS and (iii) minimizing the moisture content to facilitate indoor manipulation and transportation.

Table 1
Composition and moisture content of the mixtures.

FORMULATION	BS (wt.%)	LM (wt.%)	FA (wt.%)	Moisture content (%)
F_1	1.75	65.5	32.8	11.1
F_2	15.1	47.8	37.1	30.4
F_3 [a]	55.1	22.8	22.1	54.0
F_4	30.6	49.0	20.4	43.8
F_5	25.0	59.8	15.4	38.6
F_6	9.51	67.4	23.1	21.1
F_7	57.3	29.3	13.4	69.0
F_8	41.0	46.0	13.0	50.8
F_9	43.6	41.0	15.4	51.9
F_{10}	42.0	45.0	13.0	52.0
F_{11}	43.0	47.0	10.0	60.0

[a] F_3 corresponds to the balanced amounts of generated wastes in the production unit.

Table 2
Maximum firing temperature and dwell time of the clinkering treatments.

Formulation	Temperature (°C)	Dwell (min.)
F_1, F_2, F_4, F_7	1350	30, 180
F_3	1300, 1350	30
F_5, F_6	1350, 1390	30, 180
F_8	1455	60
F_9–F_{11}	1455	120

The mixed powders were then fired in an electrical lab-furnace. The firing cycle to obtain the clinker involved the following steps: (i) heating at 5 °C/min up to 1000 °C; (ii) 120 min dwell time at 1000 °C to promote full decarbonation/decomposition; (iii) heating at 10 °C/min. up to the maximum temperature, which changed (along with the dwell time) according to the formulation (Table 2); and (iv) quenching in air.

2.3. Mortars preparation

Due to experimental limitations in generating large amounts of clinker, it was chosen a belite-based formulation (F_4) to compose the cement. According to EN197-1:2011 there are two main types of Portland cement: CEM I and CEM II. The CEM I (ordinary Portland cement) is constituted mainly by clinker (95–100 wt.%) and 0–5 wt.% of minor additional constituents (e.g., gypsum). In CEM II (Portland-composite cement) the clinker percentage varies from 65 to 94 wt.% and are used, depending on the cement type, several other constituents (e.g., limestone, FA, silica fume). In this work it was prepared the CEM II A-L that must have 80–94 wt.% of clinker, 6–20 wt.% of limestone and 0–5 wt.% of additional constituents.

First, the fired powder (clinker) was milled and sieved at 63 μm and then, in order to get the CEM II A-L cement, 16 wt.% of LM and 4 wt.% of gypsum were added. The mortars, whose composition is given in Table 3, were prepared with CEM II A-L, calibrated sand, and limestone filler. The amount of water (11.6 wt.%) was the minimum necessary to ensure a good homogeneity and consistency in the fresh state.

For the manufacture of mortar test bodies all the solid components (cement, calibrated sand and limestone filler) were dry mixed

Table 3
Composition of the prepared mortars.

Components	wt.%
Eco-cement CEM II/A-L	14.3
Calibrated sand(D_{50} = 1.15 mm; D_{max} = 2.0 mm)	71.4
Limestone filler	14.3
Water	11.6