Ash from a pulp mill boiler—Characterisation and vitrification

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ABSTRACT

The physical, chemical and mineralogical characterisation of the ash resulting from a pulp mill boiler was performed in order to investigate the valorisation of this waste material through the production of added-value glassy materials. The ash had a particle size distribution in the range 0.06–53 μm, and a high amount of SiO_2 ($\sim$82 wt%), which was present as quartz. To favour the vitrification of the ash and to obtain a melt with an adequate viscosity to cast into a mould, different amounts of Na_2O were added to act as fluxing agent. A batch with 80 wt% waste load melted at 1350 °C resulting in a homogeneous transparent green-coloured glass with good workability. The characterisation of the produced glass by differential thermal analysis and dilatometry showed that this glass presents a stable thermal behaviour. Standard leaching tests revealed that the concentration of heavy metals in the leaching solution was lower than those allowed by the Normative. As a conclusion, by vitrification of batch compositions with adequate waste load and additive content it is possible to produce an ash-based glass that may be used in similar applications as a conventional silicate glass inclusively as a building ecomaterial.

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1. Introduction

One of the biggest concerns in developed countries both from the environmental and economical point of view is the treatment of the increasingly amounts of waste materials either from industrial or urban sources. Therefore, the search for valorisation and recycling methodologies that must be economically viable is of utmost importance in order to contribute for a sustainable development. This fact is also supported by several factors such as the scarceness of raw materials sources, the lack of available space for landfill disposal of the residues, the high cost of landfilling and the regulations designed to protect the environment, which have become more stringent in a large number of countries [1–3].

Pulp and paper making industry generates important amounts of by-products and residues [4]. These include various types of inorganic solid wastes as well as organic wastes that are managed using several approaches such as landfilling, incineration, use in cement, mortars and bricks for construction applications, agricultural use and composting, anaerobic treatment, recycling and others [3–9]. Due to the high organic content and calorific values of some of these residues, treatment by incineration has been favoured [4,9].

The waste material studied in the present work is an inorganic by-product that results from the biomass boiler of a pulp mill "Cellulose do Caima, S.G.P.S., S.A.", situated in the central part of

Portugal, which produces monthly about 70 ton of this type of waste that is directly discharged into landfill. The main objective of this study is to characterise this ash from the pulp mill boiler and to determine its usability in the production of glass.

Pulp and paper fabrication commonly involves wood preparation, pulp production, pulp bleaching and paper manufacturing [10]. The use of wood as the main raw material to make pulp for paper began with the development of mechanical pulping in the mid of the 19th century. Pine has been a common source of timber for pulping [3], but in Portugal, since the 1960s, eucalyptus has become the principal source of fibre for pulp industry. Nowadays, another important source of fibre for papermaking is recovered paper, which is rewetted and reduced to pulp after removing inks, adhesives and other contaminants [10].

In a pulp mill, wood handling comprises debarking and chipping of wood. Bark contains relatively few usable fibres and, after being removed, is burned as fuel in a boiler, together with other wood residues, to produce steam and to generate electrical energy to run the mill. The ash resulting from the biomass fluidised bed boiler, which is undesirable by the producer, may have different uses such as mixing with sludge as soil improver [3], road construction as sub-base material, inertization of wastewater sludge or simply landfill disposal. The development of methodologies for the production of added-value materials from this ash presents a great challenge for the researchers.

Taking into account that the ash from the boiler of a pulp mill is very rich in silica (SiO_2), a network glass former oxide, vitrification is considered a promising solution for the treatment and

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valorisation of this type of waste material. There have been several studies focused on the melting behaviour of different types of ashes, e.g. fly ashes resulting from the combustion of coal in thermal power plants [11–13], municipal solid waste incineration (MSWI) fly ashes [14–17] and MSWI bottom ashes [18,19], however no research studies have been found on the melting of pulp mill boiler ash. Vitrification is a well-established technology that involves the conversion of a waste material in a stable and homogeneous silicate glass through a thermal treatment of fusion, with the possible additional modification of the starting composition with glass-forming additives [20]. Vitrification is widely accepted as the safest process for treating hazardous wastes and converting them into leach-resistant materials. Vitrification enables the decomposition of hazardous organic components, immobilizes the heavy metals into the glass network and promotes a drastic volume reduction that attains a value between 70% and 90% [18–20]. One of the drawbacks with vitrification is the high consumption of energy during the melting process. The key to reduce the overall cost is, on one hand, to improve the melting technology through the optimisation of the fusion process, i.e., lowering the melting temperature by the addition of adequate additives and, on the other hand, to convert the glass obtained by vitrification into a final added-value marketable glass product [18–20].

It is essential to know the physical, chemical, mineralogical and thermal characteristics of the waste materials in order to tailor a batch composition that might be vitrified and to optimise the final properties of the produced glasses. Particle size distribution, X-ray fluorescence (XRF), X-ray diffraction (XRD) and thermogravimetric and differential thermal analyses (TGA/DTA) were used for the characterisation of the ash investigated in this work. This waste is mainly composed of a glass network former oxide (SiO_2), together with small amounts of some modifier oxides (K_2O, Na_2O, CaO, MgO) and other ceramic oxides (Al_2O_3, Fe_2O_3), which are responsible for the physico-chemical properties of the final produced glass. The observed properties support the suggestion that the ash from a pulp mill boiler appears as an interesting eco raw material since it can replace the traditional natural sand in the glass manufacturing.

2. Materials and methods

2.1. Preparation and characterisation of the pulp mill boiler ash

The as-received waste material was dried overnight in an oven at 120 °C and then after cooling, the agglomerates were hand crushed in a porcelain mortar. The dried waste, a dark gray coloured powder consisting of a mixture of particles with variable size and morphology, was sampled according to standard procedures in order to obtain representative samples of the starting material [21]. This experimental procedure is widely used in powder technology, specifically in the processing of glass and ceramic materials, and it has the advantage that in addition to the reduction of the particle size it also produces more homogenous powder samples suitable for pursuing subsequent experimental work.

The physical characteristics of the ash such as density, particle size distribution and specific surface area were determined. Density was measured in a helium pycnometer QuantaChrome, using 6.7 g samples. Particle size distribution was determined in the range 0.040–2000 μm using a Coulter equipment (LS230 model). This method is not sensitive to the particle morphology and the obtained results are expressed in terms of mean equivalent diameter of a spherical particle. Specific surface area was determined by gas adsorption according to the model proposed by Braunauer, Emmet and Teller (B.E.T.) using a QuantaChrome equipment, Quantasorb model.

The chemical characterisation of the ash was performed by X-ray fluorescence (XRF) in order to determine the composition in terms of oxides and metallic elements. A Philips Pw1400 spectrometer with Rh kα radiation was used, at 40 kV and 70 mA, or at 60 kV and 40 mA, for the determination of the oxides and metallic elements, respectively.

The mineralogical phases present in the ash were identified by X-ray diffraction (XRD) using a Rigaku "Geigerflex" D/Max-SerieC diffractometer. The experimental tests were run at a scan speed of 0.5° min⁻¹ between 8° and 70° (2θ), using nickel filtered Cu Kα (λ = 1.5405 Å) radiation.

The thermal characteristics of the ash were determined by thermogravimetric and differential thermal analyses (TGA/DTA) using a simultaneous TGA/DTA equipment (Linseis, L81 model) operating in air at a heating rate of 5 °C min⁻¹ from room temperature until a maximum temperature of 1000 °C, using a 25 mg sample and calcined alumina (Al_2O_3) as reference material.

2.2. Preparation and characterisation of the glass

Batches of ~50 g were placed in sillimanite crucibles and heated in air using an electric furnace (Thermolab) at 10 °C min⁻¹. Taking into account the XRD and thermal analysis results obtained for the ash, which indicated the presence of some carbonate compounds, it was decided to heat the powders up to 1150 °C for a period of 2 h, to allow the dissociation of such compounds, and then submit the batch to a heat treatment up to the selected vitrification temperature. In order to obtain a homogeneous melt with an adequate viscosity to be poured out of the crucible, it was necessary to add a fluxing agent, which was mixed with the ash in several proportions. Sodium oxide (Na_2O) was the selected additive, and soda Solvay® was chosen as source of this modifier oxide because it is a cheap raw material generally used by the glass manufacturing industry. Three different batch compositions with a waste loading from 80% to 100% were prepared. Depending on the amount of additive, full melting of the batches was achieved at a temperature within the range 1350–1450 °C that was held for 2 h to ensure good compositional homogenisation of the melt. After that, the melt was quenched on a brass plate to allow fast cooling and to obtain an amorphous (glassy) bulk material. Alternatively, the melt could be quenched directly into water to obtain a frit that, after drying and milling, was analysed by XRD in order to assess its amorphous state.

The glasses were analysed by differential thermal analysis (DTA) to determine the glass transition temperature (Tg) and to evaluate the temperature of glass crystallization. DTA experiments were performed in powdered glass samples with a particle size <63 μm, at a heating rate of 5 °C min⁻¹, from room temperature up to 1000 °C, using alumina crucibles and calcined alumina as reference material. DTA tests with glass samples were carried out in laboratorial equipment having a tubular furnace connected to a linear variation temperature controller (Shimaden SR-53) and to a Kipp and Zonen recorder.

The dilatometric behaviour of the glasses was analysed using prismatic glass samples with dimensions of about $15 \times 4.5 \times 4.5 \, mm^3$. A dilatometer (Bahr Dil 801L) working at a heating rate of 10 °C min⁻¹ was used and from the dilatometric data the coefficient of thermal expansion (α) of the glass was determined.

2.3. Leaching tests

The pulp mill boiler ash and the ash-based glass were subjected to a leaching characterisation procedure according to the standard test EN 12457-1:2002(E), corresponding to leaching of granular waste materials and sludges at room temperature. Dry samples of ash and of ash-based glass (finely ground and screened into

Table 1
Physical properties of the ash.

Property	
Density ($g\,cm^{-3}$)	2.51
Mean particle size (μm)	11.92
Specific surface area ($m^2\,g^{-1}$)	2.40

less than 4 mm), with a mass of 0.175 kg, were placed into 500 ml high density polyethylene/polypropylene bottles and mixed with de-mineralized water, establishing a liquid to solid ratio (L/S) of 2 L/kg. Good mixing of solid and liquid was ensured by placing the bottles in a roller-table device, where they were submitted to a rotation of about 10 rpm during an extraction time of 24 h. Then, the suspended solids were allowed to settle for ~15 min and the eluate was filtered over a 0.45 μm membrane filter using a vacuum filtration device. The concentrations of the constituents in the eluates were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES), performed in a Jobin Yvon-JY 70 Plus equipment.

Additionally, standard test method DIN 38414-S4 was used to evaluate the leachability of heavy metals by water both in unprocessed boiler ash and in ash-based glass. According to this method [22], the water resistance was evaluated after 24 h of contact with deionised water at room temperature, using a powder sample of 0.16–1 mm. Each sample was weighed, placed in a bottle of appropriate volume, where it was mixed with dionised water in the ratio 1/10 and submitted to magnetic stirring. After the leaching period, the undissolved residue was separated by filtration and the concentrations of heavy metals in the filtrate were determined by ICP-AES.

The chemical durability of the ash-based glass was determined by weight loss per surface unit, using aqueous solutions (5%) of NaOH and HCl at boiling temperature, following the methodology reported by Romero et al. [22].

3. Results and discussion

3.1. Characteristics of pulp mill boiler ash

The value determined for the density of the dried and milled ash was 2.51 g cm^{-3} (Table 1). Values for other physical properties such as mean particle size and specific surface area, also included in Table 1, suggest that this waste has a good capacity for homogenisation and mixing with other materials. This is also helped by the bimodal distribution of the particle size and the particle size range, between 0.06 and 53 μm (see Fig. 1). The fact that the ash presents a reduced mean particle size (11.92 μm) and a high specific surface area (2.40 m^2 g^{-1}) explains its good reactivity when mixed with other components.

The chemical characterisation of the ash revealed the presence of oxides potentially valuable to obtain glasses. The data, presented in Table 2, show that the main components are silica (SiO$_2$), alumina (Al$_2$O$_3$) and lime (CaO) that together sum ~93 wt%. It is also
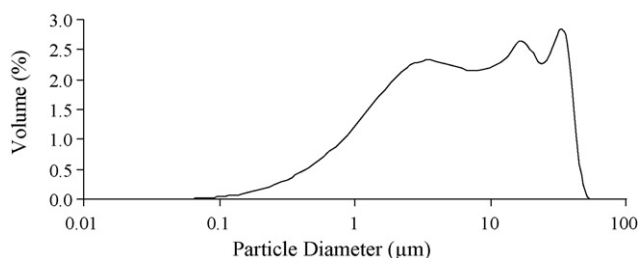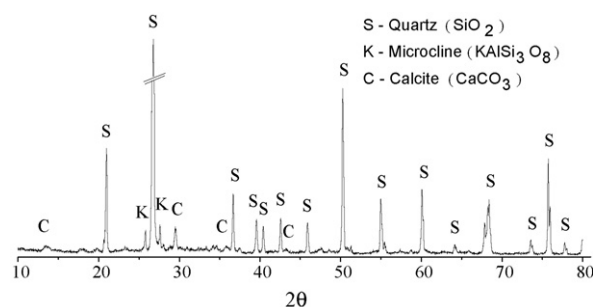
Fig. 2. XRD results for the ash.

observed the presence of small amounts of glass network modifier oxides (K$_2$O, Na$_2$O) as well as other minor oxides, Fe$_2$O$_3$, TiO$_2$ and P$_2$O$_5$, which may act as nucleating agents if a further thermal treatment is applied to the glass obtained from ash vitrification in order to achieve a controlled crystallization of the glass [23,24]. The total amount of metallic elements present in the ash (Table 3) is lower than 0.17 wt%.

The XRD data obtained for the ash (Fig. 2) show that its mineralogical composition is mostly quartz (SiO$_2$), together with a slight presence of calcite (CaCO$_3$) and of an aluminium and potassium silicate, microcline (KAlSiO$_3$O$_8$). The identification of quartz as major component explains the value obtained for the density of the ash that is similar to that quoted in literature for crystalline quartz, 2.53 g cm^{-3} [25]. Among the minerals identified by XRD, only calcite will dissociate during the heat treatment of the ash, contributing to the loss on ignition (LOI) detected by XRF analysis (Table 2).

From the study of the thermal behaviour of the ash, investigated by thermogravimetry and differential thermal analysis, the TGA and DTA curves presented in Fig. 3 were obtained. TGA curve shows a very slight weight loss at around 100 °C, due to moisture removal, and a sharp weight loss when the sample is heated between 700 and 800 °C, which is indicative that a decomposition reaction took place in this temperature range. Considering the mineralogical composition of the ash, this weight loss is mainly attributed to the decomposition of calcite (CaCO$_3$), which is quoted in literature as decomposing into CaO at above 700 °C [26]. The total weight loss determined by TGA is approximately 4.2 wt%, being higher than the value obtained for loss on ignition detected by XRF analysis (Table 2). This difference may be attributed to the different experimental methods and amounts of sample used in both procedures.

The fundamental aspects of the thermal behaviour of this ash, revealed by the DTA curve, are two endothermic peaks (see Fig. 3). The first one, situated at ~570 °C, is associated with the allotropic transformation of quartz-α into quartz-β [25], and the second one, situated at ~790 °C, is due to the calcium carbonate decomposition [26], associated with the weight loss that was detected by TGA. Taking into account the thermal behaviour of the ash, and

Fig. 1. Particle size distribution for the ash.
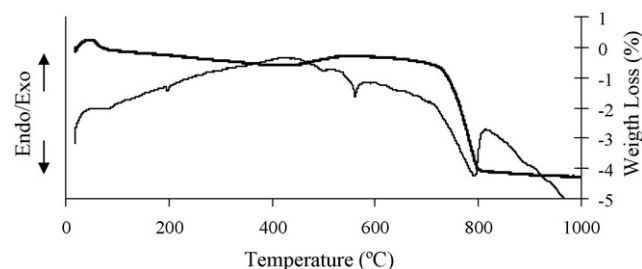
Fig. 3. TGA and DTA curves for the ash.

Table 2
Chemical composition of the ash in terms of oxides (wt%) and loss on ignition (LOI).

SiO_2	Al_2O_3	CaO	K_2O	Fe_2O_3	MgO	Na_2O	TiO_2	P_2O_5	LOI
81.84	5.92	5.45	2.87	2.19	0.69	0.61	0.30	0.13	1.81

Table 3
Metallic elements in the ash (wt%) $\times 10^{-2}$.

| Ba	Sn	Zr	Nb	Y	Sr	Rb	As	Pb	Zn	W	Cu	Ni	Co	Cr	V
4.81	0.07	1.15	0.15	0.22	2.36	0.91	<0.05[*]	0.84	3.15	0.12	0.61	0.27	<0.05[*]	0.72	0.58

[*] Below the detection capacity of the equipment.

in order to guarantee the integral dissociation of its components, it was decided to perform a calcination process at 1150 °C before the melting process, which was carried out by heating the batches for 2 h at a temperature between 1350 and 1450 °C.

3.2. Characteristics of ash-based glasses

As mentioned before, three different batch compositions were prepared for melting, which were named as 100S, 90S10N and 80S20N. The numbers included in the batch designation correspond to the weight percentages of ash (S) and of Na_2O (N).

A non-homogeneous and high viscous melt was obtained when batch 100S was heated at 1450 °C for 2 h. The high viscosity of such melt is due to the fact that the batch with 100% ash is very rich in silica (~82 wt%, cf. Table 2). This experimental observation indicated the necessity for the addition of alkali metal oxides, which act as a modifier oxide and are essential to obtain a glass with low melting point and a good workability [17,27–29]. When batch 90S10N was melted under the same conditions, pouring of the melt was still difficult. On the contrary, full vitrification of batch 80S20N was achieved after heating for 2 h at 1350 °C, and the resulting homogeneous melt exhibited an adequate viscosity to be easily poured out of the crucible, indicating a satisfactory workability for the production of glass products. Moreover, the fusion point of the ash was lowered in approximately 100 °C by adding 20 wt% Na_2O, turning the melting process more economic from the point of view of energy consumption, which is also of great significance in practical engineering. After quenching the melt obtained from batch 80S20N, a homogeneous green-coloured glass was obtained, as illustrated in Fig. 4, showing a photograph of a sample of the produced glass. The presence of iron oxide in the boiler ash composition (see Table 2) is responsible by the colouring of the resultant glass [28].
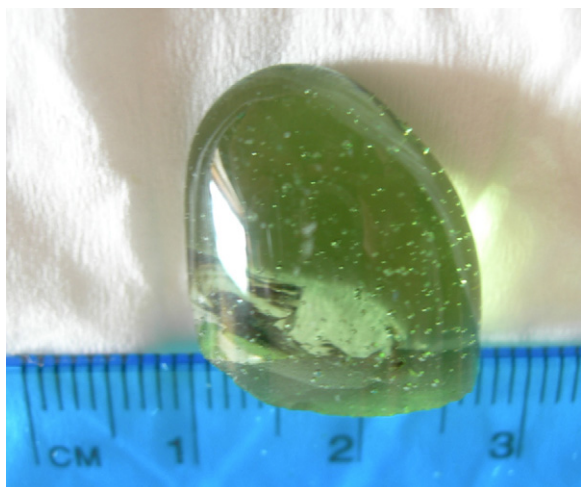
Fig. 4. Glass obtained from a composition with 80 wt% ash.
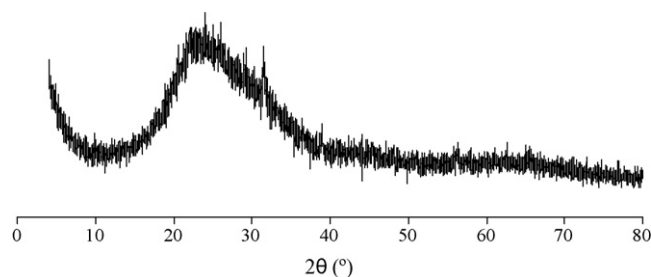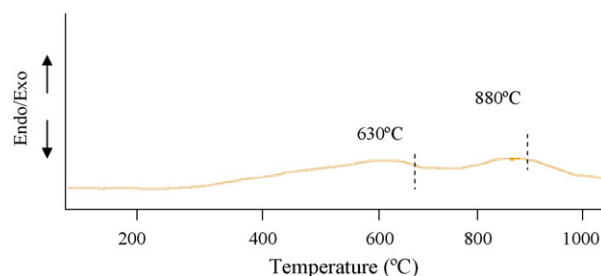
Fig. 5. XRD data for the glass obtained from a batch with 80 wt% ash.

The results from the XRD analysis of a powdered glass sample obtained from melting a batch 80S20N demonstrated that the initial crystalline structure of ash (Fig. 2) has been transformed by the melting process into a totally glassy structure, as shown in Fig. 5.

The density of the glass produced from batch 80S20N was 2.42 g cm^{-3}, which is similar to the density value quoted in literature for sodium calcium silicate glass, 2.48 g cm^{-3} [30], and lower than the density value for a glass obtained from coal fly ash, 2.66 g cm^{-3} [31], and from MSWI bottom ash, 2.69 g cm^{-3} [18].

DTA curves obtained for the glass prepared from batch 80S20N exhibited poorly defined peaks, as shown in Fig. 6. It is known that the shape of crystallization peak and the temperature of the maximum of the exothermic peak (Tc) depend on the glass particle size and on the heating rate [32]. From the curve presented in Fig. 6, a value of ~630 °C for the glass transition temperature (Tg) and a value of ~880 °C for Tc could be indicated. However, it was observed that, independently of the particle size of the powdered glass sample used in the DTA experiments, the exothermic peak of crystallization was poorly defined. The determination of Tg and Tc values is of great interest, specifically when the transformation of the glass by subsequent controlled heat treatment into a glass–ceramic material is envisaged. Some glass compositions are self-nucleating, but others need the addition of specific components to provide internal nucleation [23,24]. In the present case, DTA results indicate that the ash-based glass is thermally stable, and consequently, it will be difficult any further transformation into a glass–ceramic material by the application of a controlled

Fig. 6. DTA results for the glass obtained from a batch with 80 wt% ash, using a particle size fraction <0.63 μm and a heating rate of 5 °C min^{-1}

Table 4
Concentration of heavy metal ions in leachates after 24 h of contact with deionised water, µg/L, determined according to: (a) standard test DIN 38414-S4; (b) standard test EN 12457-1:2002(E).

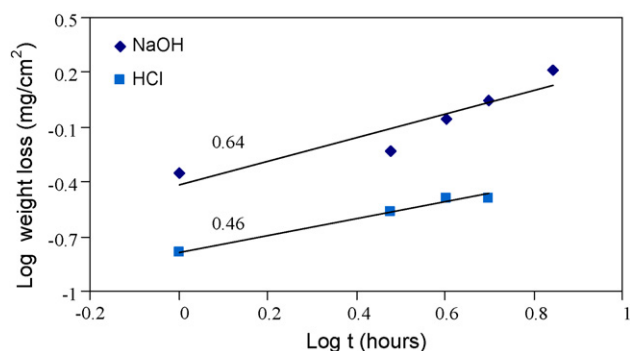|		As	Cd	Cr	Cu	Ni	Pb	Zn
Ash	(a)	<10.0	<3.0	98.8	30.5	<3.0	<3.0	<3.0
	(b)	nd	nd	150	20	<0.2	<5	10
Glass	(a)	<10.0	<3.0	3.52	7.61	9.42	10.2	14.1
	(b)	nd	nd	0.2	70	36	5	30
USEPA limit (µg/L) [22]		5×10^3	1×10^3	5×10^3	5×10^3	5×10^3	5×10^3	5×10^3

nd, not detected.

heat treatment, unless an appropriate amount of nucleating agent is added to the starting glass batch. Chemical analyses of the ash (Table 2) have revealed small amounts of Fe_2O_3, TiO_2 and P_2O_5, which may act as nucleating agents, but their presence in the processed glass is obviously too small to promote bulk crystallization.

The value for the coefficient of thermal expansion (α), determined by dilatometric analysis, was $13.69 \times 10^{-6} K^{-1}$. The high percentage ($\sim$20 wt%) of Na_2O, a modifier oxide, may explain the higher value for α than the typical values (9–$10 \times 10^{-6} K^{-1}$) observed for normal commercial sodium calcium silicate glasses and for glasses obtained from silicate wastes from different source [18,19]. The presence of this modifier may cause the increase of discontinuity points in the glass network, and so, it causes the rupture of Si–O–Si bonds, and consequently, the presence of non-bridging oxygen atoms [27,28], which explains the high value of α.

A comparison between the experimental results regarding the leaching behaviour in water of the starting pulp mill boiler ash and of the glass obtained from 80S20N batch has been performed. Table 4 shows the results of the analysis of heavy metal ions extracted in the leachates obtained according to the standard tests DIN 38414-S4 and EN 12457-1:2002(E). For each material, the differences between the results obtained from both methods are attributed to the different experimental conditions. It is clearly observed that in all cases the concentration of every leached heavy metal is far below the allowable regulatory limits imposed by the US Environmental Protection Agency (USEPA) also included in Table 4.

According to some authors [22,33], the interaction of the leaching medium (aggressive alkaline and acid solutions) with a glass can be expressed as weight loss as a function of time. It has been observed that in the initial stage (approx. first 10 h) of the corrosion process of some waste derived glasses, the weight loss w quickly increases with time t ($w \alpha t^n$, with $n = 1/2$, if diffusion is relevant) [22].

For the ash-based glass of the present study, the change in weight loss with time in the initial stage of corrosion in both NaOH and HCl solutions at boiling temperature is shown in Fig. 7. The value of n parameter, determined from the slope of the linear fits, was 0.46 for the acidic dissolution and 0.64 for the alkaline disso-

lution. The values referred for a typical window glass are $n = 0.76$ in basic conditions and $n = 0.44$ in acidic medium [22]. Further investigation should be carried out in order to draw reliable conclusions on the corrosion mechanism of the ash-based glass under study.

The overall characterisation and vitrification results presented in this paper have shown that the use of pulp mill boiler ash in replacement of sand in glass production constitutes a valorisation methodology of this waste material, as it contributes for the eco preservation of natural sand and allows the preparation of a glass with potential applications as an ecomaterial in building construction.

4. Conclusions

The chemical analysis revealed that the ash resulting from a biomass boiler of a pulp plant has a complex composition, with SiO_2 as the main component that, together with Al_2O_3 and CaO, totalise $\sim$93 wt%. These results indicated that it was necessary to use additional raw materials to favour the melting of the ash and the casting of the produced melt. It was possible to obtain glasses from this type of waste with an adequate adjustment of the chemical composition through the addition to the ash of soda Solvay®. The optimisation of the waste melting process was achieved at 1350 °C with a composition containing 20 wt% additive. A homogeneous green coloured glass was obtained, with suitable viscosity to be moulded. The produced glass was thermally stable and exhibited a satisfactory leaching behaviour. The results demonstrated the possibility of using the ash resulting from a biomass boiler of a pulp plant to substitute partially the sand used traditionally as raw material in the production of coloured vitreous products.

Fig. 7. Plot of log weight loss versus time in initial stage of corrosion (first 7 h), n values are indicated.

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