

Incorporation of the ash from cellulignin into vitrified ceramic tiles

D.G. Pinatti^a, R.A. Conte^a, M.C. Borlini^c, B.C. Santos^a, I. Oliveira^b,
C.M.F. Vieira^{c,*}, S.N. Monteiro^c

^a Chemical Engineering College of Lorena-FAENQUIL, Department of Materials Engineering-DEMAR,
Pólo Urbo-Industrial Gleba AI-6, 12600-970 Lorena-SP, Brazil

^b RM Materiais Refratários Ltda, Av. Dr Leo de Affonseca Netto 750, 12600-000 Lorena-SP, Brazil

^c State University of the North Fluminense-UENF, Advanced Materials Laboratory-LAMAV,
Av. Alberto Lamego 2000, 28013-602 Campos dos Goytacazes-RJ, Brazil

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Abstract

The incorporation of the ash from cellulignin, a catalytic biofuel, into a clay/feldspar body was investigated. The cellulignin was obtained by acidic prehydrolysis and was then burnt in boilers leaving behind the ash as a solid residue. Characterization tests of the ash employed X-ray diffraction, particle size distribution, mercury porosimetry, chemical analysis, thermal analysis and high-resolution scanning electron microscopy. The ash/clay/feldspar compositions were fired at 1200 °C and the linear shrinkage, water absorption and flexural strength were determined. Solution and leaching tests were conducted to evaluate the environmental safety of the final ceramics. The results showed that the ash is mainly composed of quartz with partially nanometric particle size, high surface area and high content of alkaline and alkaline earth oxides. These are advantages for a potential use of this ash as a flux. The partial replacement of feldspar by ash promoted a better vitrification decreasing the open porosity and increasing the mechanical strength. Heavy metals present in the ash became inert after the firing stage.

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1. Introduction

The Biomass Refinery is a pollution-free thermochemical sequential cracking operation to process any biomass and some petrochemical products. It is composed of six basic technologies: (a) acidic prehydrolysis; (b) furfural reactor and distillery; (c) closed cycle affluent treatment; (d) low temperature conversion of sludge; (e) thermoelectric plant, and (f) ceramic vitrification of toxic metals.¹ In the acidic prehydrolysis operation, the biomass is cracked into a sugar solution and a powder catalytic biofuel known as cellulignin.

The cellulignin can be obtained from any cellulose-containing biomass. This includes wood, sugarcane bagasse, agricultural leftovers, grass and straw. Moreover, waste materials such as the organic matter of municipal solid waste,

organic sludge and petrochemical polymer residues (tires and plastics) can also be transformed in cellulignin through acidic prehydrolysis. During combustion of the cellulignin for generation of thermoelectric energy an ash with high alkaline (Na + K) content is produced. This combustion in a recovery boiler occurs below 800 °C, which avoids sintering of the ash and produces a partially nanometric powder. The nanometric structure of the biomasses is preserved in the ash powder, even when submitted to temperatures higher than 800 °C. In this case, the sintering of the particles in crystalline forms with size above the micrometric range is promoted.

The incorporation of wastes, including ashes, from several industrial activities in clayey ceramic products is one technological alternative to reduce environmental impact caused by indiscriminate disposal. The firing stage during the ceramic fabrication can promote the elimination of potentially toxic materials through volatilization, chemical

* Corresponding author. Fax: +55 222726 1533.

E-mail address: vieira@uenf.br (C.M.F. Vieira).

changes and stabilization in the vitreous phase that is normally formed by the alumino-silicates and fluxes.^{2–5}

The incorporation of ashes into clayey ceramic materials has been widely investigated.^{5–10} In particular, the fly ash coming from coal-fed thermal power plants is the most studied and, in principle, one might consider it to serve as a basis for comparison with cellulignin ash. However, it will be shown that the cellulignin ash has a significantly smaller particle size than that of this type of fly ash, which varies from 5 to 200 μm .⁵ Moreover, due to the extreme variability of its physical–chemical characteristics, the incorporation of this type of fly ash in the ceramic process may result in widely variable quality for the product.⁵ Dondi et al.^{6–8} investigated the incorporation into clay bricks of up to 6 wt.% of a fly ash from orimulsion, a bitumen-in-water emulsion, combustion. The results showed that the orimulsion fly ash causes a series of effects on both unfired and fired products. The proper homogenizing of the clay–ash mixture was difficult due to the higroscopicity and water-solubilization of the waste. In the drying stage, the ash has a tolerable influence on the behavior of relatively coarse-grained bodies. However, some negative effects on fine-grained bodies were found. The ash addition of 1.5 wt.% apparently did not deteriorate the material performance, while percentages of 3 or 6 wt.% induced several changes in technological properties such as the firing shrinkage, mechanical resistance, porosity and bulk density. During the firing stage, the complete inertization of the ash was not attained and efflorescence was strongly increased. Finally, the maximum recommendable amount of ash to be incorporated into clay bricks was 1 wt.%. Prasad et al.^{9,10} investigated the incorporation of rice husk ash in the form of silica in whiteware compositions and found improvements in the properties with a reduction in the maturing temperature. This was attributed to sharp changes in the microstructural features as a result of a significant reduction in the quartz phase content and the simultaneous increase in glassy phase.

The objective of the present work was then to investigate the incorporation into a clayey body of the ash obtained from the burning of the cellulignin that results from acidic prehydrolysis of a mixture of 50 wt.% waste organic matter (WOM) and 50 wt.% wood. The idea was to have the ash acting as a flux material to improve the characteristics of vitrified ceramic tiles.

2. Experimental procedure

The ash investigated in this work was obtained as a solid residue formed after burning cellulignin at temperatures around 800 °C. The ash corresponds to 6% of the total weight of the cellulignin that results from acidic pre-hydrolysis of 50 wt.% WOM and 50 wt.% wood.

The ash was initially characterized in terms of its mineralogical and chemical composition. The chemical composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The qualitative

Table 1
Ceramic body compositions (wt.%)

	Raw materials (compositions)		
	Clay	Feldspar	Ash
C	100	–	–
C40F	60	40	0
C20F20A	60	20	20

phase identification in the ash was performed by X-ray diffraction (XRD). The XRD tests were conducted on powder samples using a Seifert model URD 65 diffractometer operating with Cu K α radiation and a scanning angle 2θ from 5 to 70°. The ash microstructure was characterized by high-resolution scanning electron microscopy SEM in a JEOL JSM-6330F equipment. The particle size distribution was measured by sedimentation technique with a Horiba model CAPA-700 laser sedigraph. The pore size distribution was determined by mercury porosimetry using a Micromeritics model 9310 apparatus. The thermogravimetric (TGA) and thermodifferential (DTA) analyses of the ash powder sample, 25 mg screened at 200 mesh (75 μm), were simultaneously conducted in a TA model SDT 2960 instrument operating under a flow of argon (100 mL/min) and heating rate of 10 °C/min until the maximum temperature of 1400 °C.

Three body compositions were prepared to evaluate the effect of the ash as a partial substitute for feldspar in vitrified ceramic tiles, according to Table 1.

The compositions were prepared by ball milling the mixture for 1 h, sieving at 200 mesh and humidified with 8% by water spraying. Test specimens (114.5 mm \times 2.54 mm \times 10 mm) were obtained by axial pressing at 18 MPa, dried for 24 h and then fired at 1200 °C in an electric furnace under a heating rate of 4 °C/min until 600 °C and 10 °C/min until the maximum temperature, followed by 1 h soaking. The water absorption was determined according to standard procedure.¹¹ The linear shrinkage was obtained by the measurement of the length of the samples before and after the firing stage using a paquimeter Mitutoyo (precision of ± 0.01 mm). The flexural strength of the fired test specimens was evaluated in a model 5582 Instron universal machine. The results obtained on 20 specimens for each condition were analyzed using the Weibull statistics.¹²

In order to verify the mobility of pollutant metals, solution and leaching tests^{13,14} were carried out on the pure clay and the ceramic materials obtained with ash addition. The content of potentially toxic metals such as Cd, Cr, Pb as well as other metals required by norms, was determined in the solution and leaching extracts by ICP-OES.

3. Results and discussion

3.1. Microstructure

Fig. 1 shows the microstructure of the cellulignin ash with a typical structure in the form of powder agglomerates. These

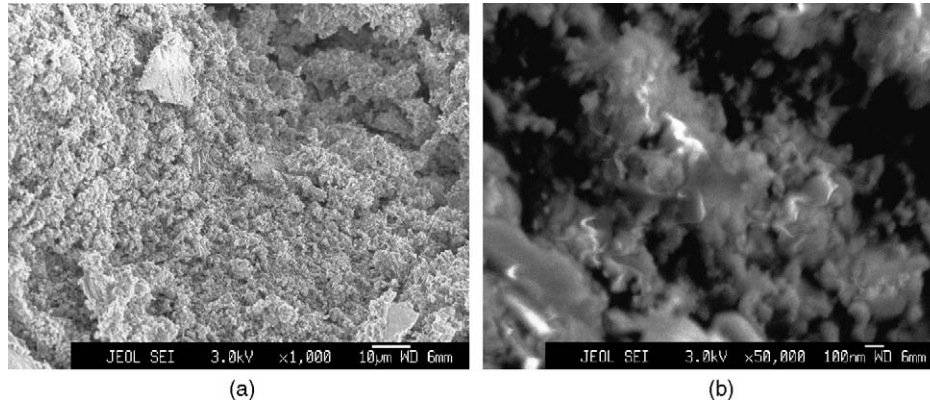


Fig. 1. SEM photomicrographs of the ash agglomerates. (a) 1000 \times ; (b) 50,000 \times .

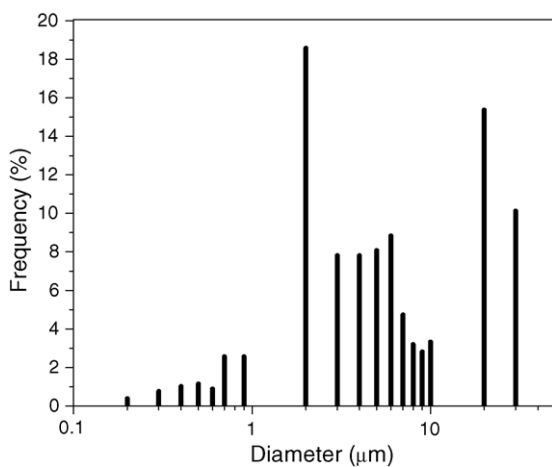


Fig. 2. Particle size distribution of the cellulignin ash agglomerates.

agglomerates have elementary particles with two sizes corresponding to 400 nm from the WOM, and 70 nm from the wood, both originally used in the prehydrolysis.

According to Fig. 2, the particle size distribution shows agglomerates with diameter between 0.1 and 30 μm , with a maximum frequency size of 2 μm . The mean value for the agglomerate diameter is 4.8 μm . The partially nanometric size of the ash agglomerate is confirmed by the presence of 9.34% of the agglomerate below 1 μm in equivalent spherical diameter. It is interesting to notice that the maximum frequency size of the ash, 2 μm , corresponds to the limit used to define a clay mineral.¹⁵ Therefore, one could suppose that, at the proper firing temperature, the added ash is highly reactive, which helps the ceramic sintering.

Fig. 3 shows the pore size distribution of the cellulignin ash. It can be observed that the pore diameter ranges from about 0.007 to 107 μm , the mean pore size being 0.51 μm .

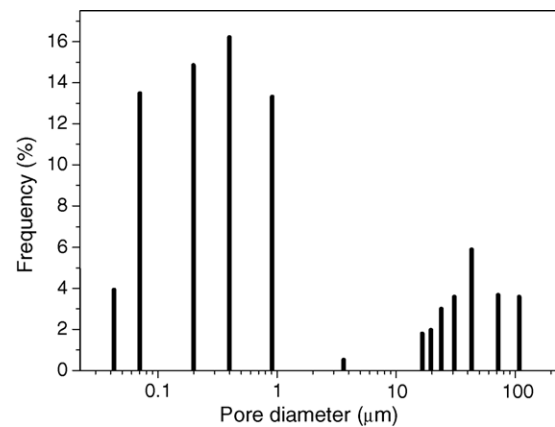


Fig. 3. Pore size distribution of the cellulignin ash.

The cellulignin ash presents a density, measured by mercury porosimetry, of 2.38 g/cm^3 and an open porosity of 56.8%. The measured surface area was 34.64 m^2/g . The relatively high porosity of the ash can facilitate the drying of the ceramics and the degassing during the initial stage of firing.

One should notice in Fig. 3 that the pore size distribution has two modes, the first with a maximum frequency around 0.4 μm and the second around 40 μm . Apparently, the first mode associated with smaller diameters corresponds to pores that are intrinsic to the ash agglomerates. By contrast, the second mode with pore diameters up to 100 μm , corresponds to the open spaces between ash agglomerates like the ones shown in Fig. 1.

3.2. Mineralogical and chemical composition

Table 2 shows the chemical composition of the cellulignin ash. The chemical composition is basically characterized by

Table 2
Chemical composition of the cellulignin ash (wt.%)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	MgO	CaO	MnO	PO ₄	CO ₃	SO ₄	LOI
49.6	6.9	1.7	0.6	2.2	1.4	0.5	11.7	0.06	3.0	1.7	7.4	10.9

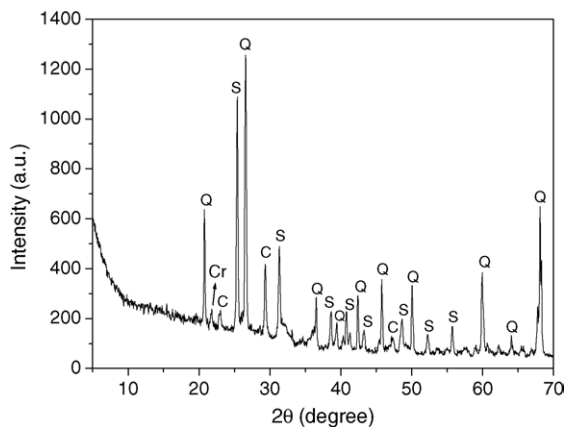


Fig. 4. X-ray patterns of cellulignin ash. C, calcium carbonate; Cr, cristobalite; Q, quartz; S, calcium sulfate.

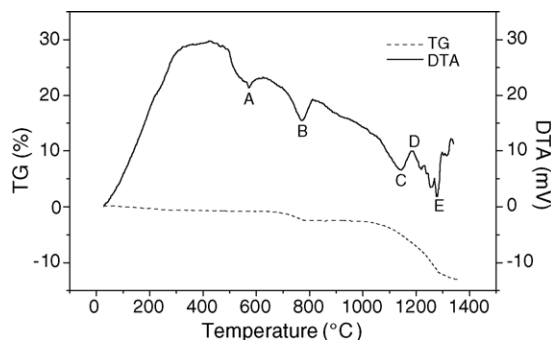


Fig. 5. Thermogravimetric (TG) and differential thermal analysis (DTA) curves for cellulignin ash.

high amounts of SiO_2 , CaO , SO_4 and Al_2O_3 . The large amount of SiO_2 is associated with two crystalline phases: quartz and cristobalite, as confirmed by the X-ray pattern in Fig. 4. The CaO is predominantly associated with sulfate and carbonate. The Al_2O_3 is probably associated with SiO_2 and alkaline and alkaline earth oxides that form feldspathic phases.

Fig. 4 shows the XRD pattern of the cellulignin ash. The major crystalline phases are quartz (SiO_2), cristobalite (SiO_2), calcium carbonate (CaCO_3) and calcium sulfate (CaSO_4). The relatively high percentage of alumina (Al_2O_3) suggests the presence of aluminum and alkali metals silicates undetected by XRD. Phosphates were also not detected by XRD. The relatively high amount of calcium sulfate can promote the appearance of efflorescence defects.¹⁶

Table 3
Chemical composition of the investigated bodies (wt.%)

	Compositions								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	LOI
C	56.5	23.6	3.9	0.9	1.7	–	0.1	0.4	12.9
C40F	54.6	24.5	2.4	1.1	5.5	0.2	0.1	0.5	7.9
C20F20A	56.9	19.3	2.7	0.7	3.9	0.9	2.4	0.3	10.0

Table 4
Fired technological properties of the body composition

Bodies	Fired properties		
	Linear shrinkage (%)	Water absorption (%)	Flexural strength (MPa)
C	10.0 ± 0.3	8.0 ± 1.0	34.0 ± 3.3
C40F	11.0 ± 0.4	2.0 ± 0.3	42.0 ± 2.5
C20F20A	11.0 ± 0.1	0.2 ± 0.1	49.0 ± 3.0

3.3. Thermal behavior

The thermal behavior of the ash was analyzed by thermogravimetry and thermodifferential analysis. Fig. 5 shows the TGA and DTA curves for the cellulignin ash. The fundamental aspects of the thermal behavior of this ash are the following, in association with points (letters) marked in Fig. 5:

- endothermic peak at 574°C associated with the allotropic transformation of quartz- α to quartz- β ;
- endothermic peak at 774°C due to the calcium carbonate decomposition, associated with a weight loss of 1.55%;
- endothermic peak at 1144°C probably due to the melting of alkali rich crystalline phases;
- exothermic peak at 1185°C due to the reduction of the hematite or recrystallization of amorphous phases;
- endothermic peak at 1278°C due to the calcium sulfate decomposition. The last three reactions (C, D and E) are associated with a weight loss of 10.2%.

3.4. Characteristics and fired properties of body compositions

The chemical analysis of the body compositions is presented in Table 3. Body C shows a high alumina and low alkaline oxides contents that are typical characteristic of kaolinitic clays. With incorporation of feldspar, C40F, an increase in the alkaline oxides and decrease in the loss on ignition clearly occurred. The partial replacement of feldspar by ash, body C20F20A, promoted a decrease in the Al_2O_3 content and an increase in the CaO . Decreasing the Al_2O_3 can reduce the refractoriness of the composition, while an increase in CaO will act as an energetic flux at high temperatures.

The fired technological properties determined for the bodies are presented in Table 4. With the incorporation of feldspar, C40F, the linear shrinkage and flexural strength increased and the water absorption decreased. This is due to the well-known flux action of the feldspar in clayey ceramics.¹⁷

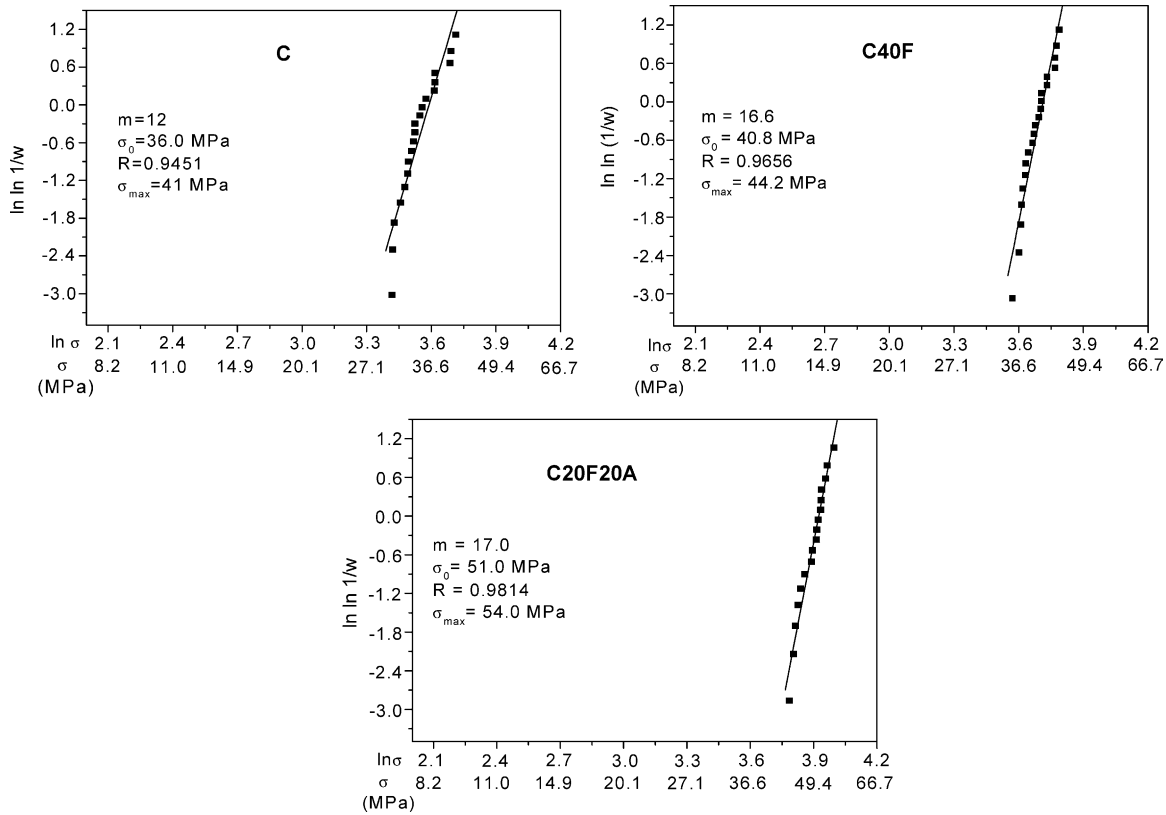


Fig. 6. Weibull diagram of the compositions.

The partial replacement of feldspar by ash promoted a decrease in the water absorption and an increase in the flexural strength. The better technological properties obtained by ash incorporation, C20F20A, in comparison with the clay–feldspar mixture, C40F, can be attributed to the increase in the dry bulk density of the tested specimens as well as the partial nanometric size of the ash and the increase in the CaO

content. A higher contact among the particles and lower size particles promote the sintering process. Moreover, at higher temperatures, normally $>1100\text{ }^{\circ}\text{C}$, the crystalline phases of calcium silicates melt to form a low viscous liquid, which also contributes to reduce the porosity.¹⁸

Fig. 6 shows Weibull diagrams for the mechanical strength of the investigated body compositions. A single

Table 5
Potentially toxic metals in the solution and leaching extracts of clay and vitrified ceramic

Element	Solution extracts (mg/L)		Solution test ^a (mg/L)	Leaching extracts (mg/L)		Leaching test ^a (mg/L)
	C	C20F20A		C	C20F20A	
Ag	<0.05	<0.05	0.05	<0.007	<0.005	5.0
Al	<0.05	<0.01	0.2	Not required	Not required	Not required
As	Not determined ^b	Not determined ^b	0.05	Not required	Not required	Not required
Ba	<0.007	<0.01	1.0	<0.005	<0.01	100.0
Cd	<0.005	<0.005	0.005	<0.004	<0.004	0.5
Cr (total)	<0.05	<0.05	0.05	<0.03	<0.06	5.0
Cu	<0.05	<0.05	1.0	Not required	Not required	Not required
Fe	<0.006	<0.02	0.3	Not required	Not required	Not required
Hg	Not determined ^b	Not determined ^b	0.001	Not required	Not required	Not required
Mn	<0.001	<0.001	0.1	Not required	Not required	Not required
Na	1.2	1.1	200.0	Not required	Not required	Not required
Pb	<0.1	<0.2	0.05	<0.1	<0.2	5.0
Se	Not determined ^b	Not determined ^b	0.01	Not required	Not required	Not required
Zn	<0.005	<0.02	5.0	Not required	Not required	Not required

^a Maximum allowed limits by NBR 10004 standard.

^b Elements not determined because their contents in the raw materials were already lower than the standard specifications.

mode distribution with satisfactory values for the module m was obtained. This indicates that the bodies are very homogeneous and that the processing was well accomplished. It can also be observed a displacement of the Weibull curve to the right with the incorporation of feldspar and, even further right, with the partial substitution for ash. This indicates a consistent increase in mechanical strength with feldspar and cellulignin ash additions to a ceramic body.

3.5. Solution and leaching tests

Results of the determination of potentially toxic metals in the solution and leaching extracts of bodies C and C20F20A are shown in Table 5. The analyzed ceramic bodies fulfill the requirements of the Brazilian environmental standards.^{13,14} This means that the cellulignin ash can be incorporated into ceramic products, accomplishing the pollution free processing cycle, technology (f), of the Biomass Refinery.¹ Some elements (Al, Cd and Pb), present in very low concentrations, have detection limits above their concentration requirements due to the low sensitivity of the emission lines used for the determination by ICP-OES. For these elements, analyses by more sensitive techniques are being carried out.

4. Conclusions

The ash resulting from the burnt of cellulignin, a biofuel produced by acidic prehydrolysis of any cellulose-containing biomass, can be incorporated into vitrified ceramics as a technologically advantageous and environmentally correct solution.

The ash presents partially nanometric particle size and forms agglomerates with coarse pores that can be associated with the porosity found in the incorporated ceramic body. During firing the ash acts as a flux and contributes to consolidate the ceramic structure. This promotes a reduction in water absorption and an increase in mechanical strength. Leaching tests showed that potentially toxic metals present in the ash become inert after the ceramic firing.

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