VALORISATION OF FIREWOOD ASH WASTE FOR FIRED CLAY CERAMICS PRODUCTION

Filipe Santos[*], **Fabrício Bagli Siqueira**[*], **José Nilson França Holanda**[*]

[*] State University of the North Fluminense Darcy Ribeiro, Group of Ceramic Materials, Campos dos Goytacazes - RJ, Brazil

corresponding author: José Nilson França Holanda, e-mail: holanda@uenf.br

ABSTRACT

The objective of this work was to investigate the valorisation of firewood ash waste as an alternative raw material for clay ceramic production, through replacement of industrial plastic clay up to 20 wt.%. For this purpose, clay ceramic pieces were produced by uniaxial pressing and fired at temperatures ranging from 800 °C to 1100 °C. The technical properties of the fired clay ceramic pieces have been determined. It was found that the technical properties of the clay ceramic pieces depend on the firewood ash waste amount and firing temperature. The fired pieces incorporated with up to 20 wt.% of firewood ash waste showed a water absorption level of 9.90 to 16.62 % and flexural strength of 4.12 to 12.02 MPa, indicating their conformity for clay ceramic production (bricks and roofing tiles). Obtained results confirmed the feasibility of valorisation of firewood ash waste in the production of fired clay ceramics.

Keywords: *waste utilization, firewood ash, valorisation, clay ceramic*

INTRODUCTION

Brazil stands out in the world in the production of renewable energy from biomass [1 - 3]. Despite the economic and social importance of biomass in the Brazilian energy matrix, large amounts of biomass ashes are produced every year [2, 3]. Such biomass ashes are solid waste materials that cause high environmental impact.

The clay ceramic industry in the Campos dos Goytacazes - RJ region, Brazil, which assembles about 100 plants, is mainly specialised in the production of bricks, ceramic blocks, and roofing tiles. In particular, the main fuel used in the firing step of the industrial clay ceramic processing is firewood, mainly eucalyptus [4]. Thus, large amount of firewood ash waste is produced. In addition, most of the firewood ash waste produced (~ 5,000 tonnes per year) is discarded in the environment without any treatment. Thus, an important issue for the local clay ceramic industry is to find an economical and ecological solution for the final disposal of the firewood ash waste.

The firewood ashes derived from forest biomass combustion (mainly eucalyptus) can

be characterized as a solid waste material with a high calcium amount [5 - 7]. This indicates that such firewood ashes have a high potential to be used as sources of low-cost renewable ceramic raw materials. In fact, previous studies [2, 4, 6 - 15] have shown the use of firewood ash waste in the production of clay bricks, cement, concrete, mortar and electrical porcelain. However, until now, the clay ceramic industry in Campos dos Goytacazes - RJ region has paid little attention to the possibility of use of the firewood ash waste generated in its kilns during the energy co-generation process. This situation is mainly caused by the lack of consistent technical and economic information on the replacement of local plastic clays with firewood ash waste. Thus, it is very important to perform a study on the characteristics and technical properties of clay ceramic incorporated with firewood ash waste in order to generate more knowledge, which can contribute to its sustainable valorisation.

In this work, the firewood ash waste generated in Campos dos Goytacazes - RJ region (Brazil) has been examined and its use as a partial replacement of industrial plastic clay to produce fired clay ceramics has been evaluated. The effects of the incorporation of the firewood ash waste and firing temperature on the technical properties have been shown.

EXPERIMENTAL

Materials and samples preparation

Industrial plastic clay and firewood ash waste were selected as raw materials. Both raw materials were supplied by a ceramic industry located in the Campos dos Goytacazes - RJ region, Brazil. The firewood ash waste used in this work is generated in the firing step during the industrial production of clay-based ceramic materials.

The plastic clay and firewood ash waste were dried at 110 °C for 24 h, disaggregated and passed through a 45-mesh sieve (< 355 μm ASTM). The firewood ash waste was used to

partially replace industrial plastic clay, as shown in Table 1.

Table 1. The proportions of the clayey compositions

Composition	Plastic clay, wt.%	Firewood ash waste, wt.%
MS1	100	0
MS2	95	5
MS3	90	10
MS4	85	15
MS5	80	20

Methods of characterization and processing

The chemical analyses of the raw materials were carried out using an energy-dispersive X-ray spectrometer (Shimadzu Instrument, EDX 700 model). The loss on ignition was obtained by calculating the wt.% difference between sample dried at 110 °C and the sample calcined at 1000 °C for 2 h. Mineral analysis of the samples was done by X-ray powder diffraction (Shimadzu Instrument, XRD-7000 model) using Cu-Kα radiation and 1.5° (2θ)/min scanning speed. The mineral phases were identified using ICDD-JCPDS cards. The particle size distribution was determined according to the NBR 7181-84 standard [16]. The plasticity index (PI) was obtained through the Atterberg consistency limits (PI = LL - PL, in which LL is the liquid limit and PL is the plastic limit) according to the NBR 6459-84 [17] and NBR 7180-84 [18] standards. The organic matter content was determined according to the Walker-Black method.

The compositions in the proportions shown in Table 1 were homogenized in a cylindrical blender for 30 min. The moisture content was adjusted to 7 % (moisture mass/dry mass). The clay ceramic pieces in form of cylindrical disk (25 mm in diameter) were prepared by uniaxial pressing at 25 MPa, and then dried at 110 °C for 24 h. The green pieces thus formed were fired at temperatures between 800 and 1100 °C for 2 h soaking time in a muffle kiln. Heating and cooling rates were controlled (24 h cold to cold).

The clay ceramic pieces produced were subjected to tests to characterize them in terms of linear shrinkage, water absorption, apparent density, apparent porosity and flexural strength. The experimental results from all the tests for each composition were calculated from the values of five test specimens (mean value ± standard deviation). Linear shrinkage values upon drying and firing were determined from variation of the diameter of the clay ceramic pieces. The water absorption, apparent porosity and apparent density of the fired pieces were determined according to the ASTM C373 standard [19]. In this work, due to the cylindrical geometry of the fired clay ceramic pieces, the flexural strength (FS) was determined from the expression given by $FS = 2.7 \cdot TS$ (MPa) [20], where $TS = 2P/\pi dh$ is the tensile strength determined by the diametrical compression method (P is the rupture load, d is the sample diameter and h is the sample thickness). The rupture load (P) was determined using a universal testing machine (Instron, model 5582) with a loading speed of 0.5 mm/min.

RESULTS AND DISCUSSION

The mineral phases identified by X-ray diffraction analysis of the raw materials are given in Table 2. The sample of the industrial plastic clay used is mainly composed of kaolinite $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$. However, quartz (SiO_2), gibbsite $(Al_2O_3 \cdot 3H_2O)$, goethite $(\alpha\text{-}Fe_2O_3 \cdot H_2O)$, and illite were also detected. This mineral composition is typical for the plastic clays of the Campos dos Goytacazes - RJ region, Brazil [21]. In the firewood ash waste sample, the major mineral phase is calcite $(CaCO_3)$. In addition, potassium carbonate (K_2CO_3), hydrated magnesium sulphate $((Mg(SO_4) \cdot 7H_2O)$, hematite (Fe_2O_3), portlandite $(Ca(OH)_2)$, gypsum $(CaSO_4))$, and quartz as accessory minerals were also detected.

The chemical analysis and loss on ignition of the plastic clay and firewood ash waste used in this work are given in Table 3. Both chemical compositions of the plastic clay and firewood ash waste are well correlated with the mineral composition data (Table 2). However, their chemical compositions are quite different. The clay sample is mainly composed by SiO_2 (41.19 wt.%) and Al_2O_3 (32.31 wt.%), and minor amount of Fe_2O_3 (8.25 wt.%). The amount of fluxing oxides $(CaO + MgO + K_2O + Na_2O)$ is low (2.31 wt.%). Traces of Mn, Ti, and S oxides were also detected. The SiO_2/Al_2O_3 ratio of $\cong 1.27$ indicates the presence of a high amount of kaolinite [21, 22] confirming the mineralogical analysis (Table 2). The loss on ignition (12.82 wt.%) is mainly due to the presence of clay minerals (kaolinite and illite) and hydroxides (gibbsite and goethite), as shown in Table 2. The presence of iron oxide (Fe_2O_3) is responsible for the reddish colour of the clay after firing. The firewood ash waste is mainly composed of CaO (40.77 wt.%), and smaller amounts of SiO_2 (9.55 wt.%), Al_2O_3 (6.63 wt.%), Fe_2O_3 (4.38 wt.%), MgO (10.79 wt.%) and K_2O (7.35 wt.%). Mn, Ti, and S-oxides were also detected. This result confirms that the firewood ash waste used in this work is typically a high calcium ash from forest wood [5 - 7], in this case eucalyptus. The loss on ignition was relatively high as of 17.30 wt.%, which may be related to the decomposition of mineral compounds and unburned organic matter present in the used firewood ash waste sample. In fact, the sample of firewood ash waste contains about 6.83 % of organic matter. These results indicate that the partial replacement of plastic clay with firewood ash waste tends to modify the overall chemical composition of the clayey compositions prepared in this work. Thus, an influence on the technical properties of clay ceramics can be expected.

Table 2. Mineral phase analysis of the raw materials

Raw material	Mineral phases
Plastic clay	[++]Kaolinite, illite, quartz, gibbsite, and goethite
Firewood ash waste	[++]Calcite, potassium carbonate, quartz, hydrated magnesium sulphate, hematite, portlandite, and gypsum

[++] main mineral phase

Table 3. Chemical compositions of the raw materials

Components	Plastic clay, wt.%	Firewood ash waste, wt.%
SiO_2	41.19	9.55
Al_2O_3	32.31	6.63
Fe_2O_3	8.25	4.38
CaO	0.60	40.77
MgO	0.05	10.79
K_2O	1.41	7.35
Na_2O	0.25	-
MnO	0.06	0.72
TiO_2	1.56	0.83
SO_3	1.50	1.68
Loss on ignition	12.82	17.30

The data on the particle size distribution and Atterberg consistency limits of the raw materials are presented in Table 4. The granulometric data show that the pure clay had high concentration of particles < 2 μm (39.7 %) and between 2 - 20 μm (37.8 %). The firewood ash waste sample, however, presents a high concentration of coarse particles above 20 μm (83.0 %). Such a difference in particle size distribution between the plastic clay and firewood ash waste reflects their mineral composition, as shown in Table 2. In terms of plastic properties, the pure clay sample had high plasticity (Atterberg plastic index = 25.6 %). This is due to the high concentration of the fine particles (< 2 μm), which is essentially composed of kaolinite. The firewood ash waste sample, however, had a non-plastic behaviour. In fact, the firewood ash waste is a material rich in non-plastic components, as shown in Table 2. For this reason, it acts as plasticity reducer in the prepared clayey compositions.

Table 4. Particle size distribution and Atterberg consistency limits of the raw materials

Raw materials	Particle size fraction [%]			Atterberg limits [%]		
	< 2 μm	2-20 μm	> 20 μm	LL	PL	PI
Clay	39.7	37.8	22.5	54.4	28.8	25.6
Ash	4.8	12.2	83.0	-	++NP	++NP

++NP – non plastic

Figure 1 shows the linear shrinkage of the fired clay ceramic pieces. It can be observed that the clay ceramic pieces show firing shrinkage values varying from 1.12 to 6.50 %, which is within the appropriate range for industrial production. Note also that both firewood ash waste addition and firing temperature have influenced the linear shrinkage behaviour. The effect of the firing temperature was to increase the linear shrinkage due to the higher degree of sintering of the clay ceramic pieces. However, two distinct linear shrinkage behaviours have been established. For temperatures between 800 and 900 °C, low linear shrinkage values were obtained. The ceramic pieces have not yet experienced high degree of sintering. In this case, weak solid sintering process due to particle-to-particle contact of the clay-firewood ash waste mixture components is dominant. When the firing temperature was increased (1000 °C and 1100 °C), higher values of linear shrinkage were obtained. As a result, the clay ceramic pieces have achieved a higher degree of sintering. This behaviour is due to the formation of glassy phase during firing, with likely predominance of viscous flow sintering. The results presented in Figure 1 also showed that the linear shrinkage increased with increasing firewood ash waste amount up to 10 wt.%. Then, the linear shrinkage tended to decrease when the amount of firewood ash waste was increased. This effect is primarily related to the mineralogical composition and non-plastic behaviour of the firewood ash waste, which tends to decrease the plasticity of the clay-firewood ash waste compositions.
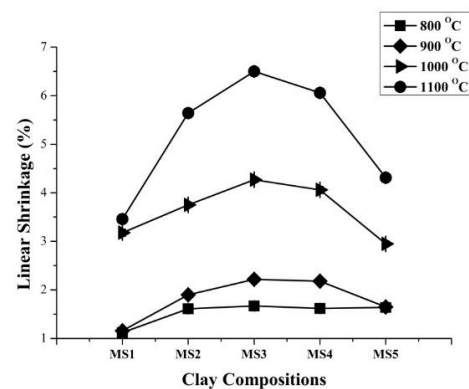

Figure 1. Linear shrinkage of the clay ceramic pieces

Figure 2 shows the apparent density of the fired clay ceramic pieces. For the studied conditions, the apparent density of the clay ceramic pieces was in the range of 1.82 to 2.24 g/cm^3. Similar to observed behaviour for the linear shrinkage, the apparent density of the clay brick pieces was influenced by both firing temperature and incorporation of the firewood ash waste. As expected, the effect of the firing temperature was to promote higher densification of the clay ceramic pieces mainly above 900 °C due to the formation of a glassy phase during the firing process [23]. The incorporation of the firewood ash waste influenced the densification behaviour of the pure plastic clay. For additions up to 10 wt.% of firewood ash waste (MS2 and MS3 compositions), the effect of the firewood ash waste on the pure clay was to increase the apparent density of the clay ceramic pieces. However, additions above 10 wt.% of firewood ash waste (MS4 and MS5 compositions) decreased the apparent density. This finding is related to the composition of the firewood ash waste, which presents high loss on ignition and not-plastic nature.
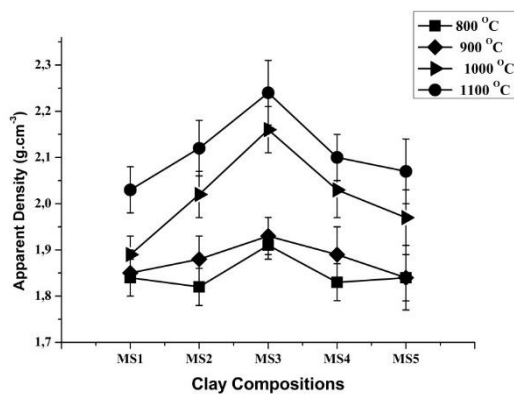
higher firing temperatures, vitrification is in progress with the open-pore partial closure. For compositions containing firewood ash waste, however, the water absorption decreased with additions up to 10 wt.%. A further increase of firewood ash waste up to 20 wt.% increased the water absorption. This finding is caused by a lower densification rate due to the composition of the firewood ash waste, as observed in the apparent density values (Figure 2).
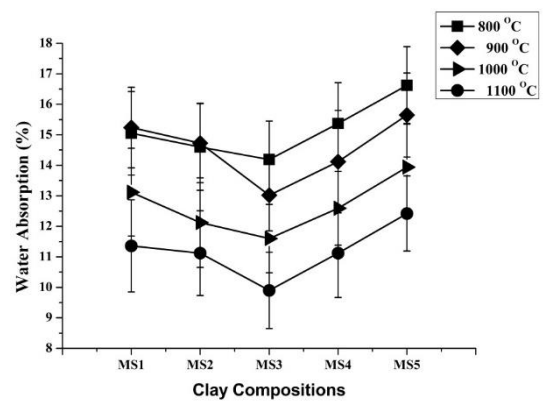

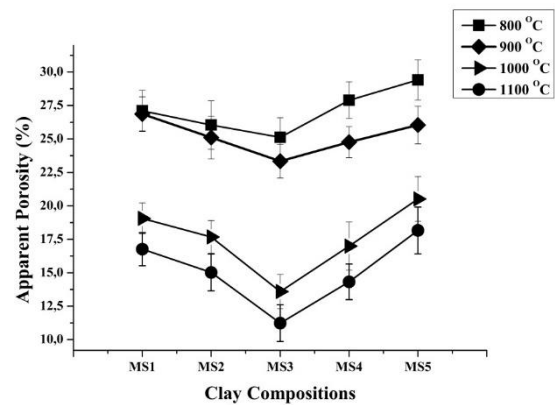Figure 3. Water absorption of the clay ceramic pieces

Figure 2. Apparent density of the clay ceramic pieces

Figure 4. Apparent porosity of the clay ceramic pieces

The water absorption behaviour of the fired clay ceramic pieces is shown in Figure 3. The results showed that the water absorption behaviour is quite correlated with the linear shrinkage (Figure 1), apparent density (Figure 2) and apparent porosity (Figure 4). The water absorption of the clay ceramic pieces varied of 9.90 to 16.62 %. It was found that the water absorption tends to decrease with increasing firing temperature mainly above 900 °C. At

Figure 5 shows the flexural strength of the fired clay ceramic pieces. It was found that the flexural strength of the clay ceramic pieces varied of 4.12 to 12.02 MPa. In addition, the effect of the firing temperature was to increase the flexural strength of the ceramic pieces. This behaviour is in line with the higher densification of the ceramic pieces, supporting the apparent density (Figure 2), water absorption (Figure 3) and apparent porosity

(Figure 4) data. The results also showed that higher concentrations of firewood ash waste (MS4 and MS5 compositions) negatively affect the mechanical strength of the clay ceramic pieces. This finding was observed for all the firing temperatures employed. The reasons for this behaviour are related to high loss on ignition and the presence of non-plastic minerals in the used firewood ash waste, such as free quartz particles. In particular, at higher temperatures, the presence of free quartz particles tends to induce flaws in the vitrified ceramic matrix. This means that incorporation of very high firewood ash waste concentrations into clay ceramics is quite problematic, because it decreases the mechanical strength of the fired pieces.
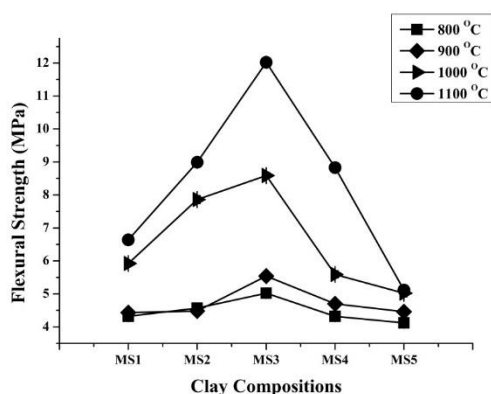

Figure 5 Flexural strength of the clay ceramic pieces

From the point of view of industrial application, the clay ceramic pieces are evaluated in terms of water absorption and mechanical strength. According to the literature [24], the reference values generally accepted in industrial practice for water absorption (WA) and flexural strength (FS) of clay ceramics (bricks and roofing tiles) are: optimal variation (WA = 12 – 24 % and FS = 12 - 22 MPa) and acceptable variation (WA = 10 – 30 % and FS = 4 - 30 MPa). In general, as shown in Figure 3, the clay ceramic pieces produced in this work presented optimal values of water absorption, indicating their conformity with bricks and roofing tiles. In terms of flexural strength (Figure 5), however, almost all of the clay ceramic pieces had acceptable values of mechanical strength. Thus, the results obtained in this work suggest that the incorporation of an adequate amount of firewood ash waste ($\leq$ 20 wt.%) could result in clay ceramic products of good technical quality.

CONCLUSION

This work demonstrates the feasibility of valorisation of firewood ash waste from Campos dos Goytacazes - RJ, Brazil, as low-cost alternative raw material for the clay ceramic industry. Such a valorisation approach can produce positive effects in terms of economic and environmental repercussions.

The firewood ash waste is a non-plastic material with complex mineral composition, and composed mainly of calcium-based minerals. Both firewood ash waste amount and firing temperature tend to influence the technical properties of the clay ceramic pieces. The results obtained in this work indicate that the partial replacement of industrial plastic clay with firewood ash waste, in the range up to 20 wt.%, enables the production of clay ceramics (fired bricks and roofing tiles) of good technical quality.

Finally, the results obtained here indicate that it could be advantageous for the clay ceramic industry to recycle the firewood ash waste in its own industrial production route.

REFERENCES

[1] T.A.S. Vieira, S.A.C. Carabineiro, P.F. Trugilho, Forest biomass as energy source in Brazil, International Journal of Environmental Sciences & Natural Resources 19(2019) 3, 75-79. http://doi.org/10.19080/IJESNR.2019.19.556013

[2] T.A. Cacuro, W.R. Waldman, Fly-ash from biomass burning: applications and opportunities, Revista Virtual de Química 7(2015) 6, 2154-2165. http://doi.org/10.5935/1984-6835.20150127

[3] A.K. James, R.W. Thring, S. Helle, H.S. Ghuman, Ash management review - applications of biomass bottom ash, Energies 5(2012) 10, 3856-3873. https://doi.org/10.3390/en5103856

[4] N.C. Coutinho, R.L. Loiola, H.R. Paes Junior, J.N.F. Holanda, Use of firewood ash waste in electrical siliceous porcelain, Materials Research 22(2019), 1-5. https://doi.org/10.1590/1980-5373-MR-2018-0860

[5] E. Serafinova, M. Mladenov, I. Mihailova, Y. Pelovski, Study on the characteristics of waste wood ash, Journal of the University of Chemical Technology and Metallurgy 46(2011) 1, 31-34.

[6] L.P. Villarejo, D.E. Quesada, F.J.I. Godino, C.M. García, F.A.C. Iglesias, Recycling of ash from biomass incineration in clay matrix to produce ceramic brick, Journal of Environmental Management 95(2012), S349-S354. https://doi.org/10.1016/j.jenvman.2010.10.022

[7] S.I. Pereira, M. Peterson, A. Zaccaron, V.S. Nandi, P. Fernandes, Incorporação de cinza de eucalipto em massa cerâmica vermelha, Revista Eletrônica de Materiais e Processos 11(2016) 2, 68-72.

[8] C.B. Cheah, M. Ranli, The implementation of wood waste ash as a partial cement replacement material in the production of structural grade concrete and mortar: An overview, Resources, Conservation and Recycling 55(2011) 7, 669-685. https://doi.org/10.1016/j.resconrec.2011.02.002

[9] R. Siddique, Utilization of wood ash in concrete manufacturing, Resources, Conservation and Recycling 67(2012), 27-33. https://doi.org/10.1016/j.resconrec.2012.07.004

[10] S.V. Vassilev, D. Baxter, L.K. Anderson, C.G. Vassileva, An overview of the composition and application of biomass ash. Part 2: potential utilization, technological and ecological advantages and challenges, Fuel 105(2013), 19-39.

https://doi.org/10.1016/j.fuel.2012.10.001

[11] R. Rajamma, R.J. Ball, L.A.C. Tarelho, G.C. Allen, J.A. Labrincha, V.M. Ferreira, Characterisation and use of biomass fly ash in cement-based material, Journal of Hazardous Materials 172(2009) 2-3, 1049-1060. https://doi.org/10.1016/j.jhazmat.2009.07.109

[12] O. Kizinievic, V. Kizinievic, Utilisation of wood ash from biomass for the production of ceramic products, Construction and Building Materials 127(2016), 264-273. https://doi.org/10.1016/j.conbuildmat.2016.09.124

[13] V.A.S. Shein, G. Conte, M.V. Folgueras, L.V.O.D. Valentina, M.R. Medeiros, Uses of ashes from biomass combustion as an aggregate for concrete, Materials Science Forum 958(2019), 111-115. https://doi.org/10.4028/www.scientific.net/MSF.958.111

[14] L. Fusade, H. Villes, C. Wood, C. Burns, The effect of wood ash on the properties and durability of lime mortar for repointing dump historic building, Construction and Building Materials 212(2019), 500-513. https://doi.org/10.1016/j.conbuildmat.2019.03.326

[15] M.N.L. Leroy, F.M.C. Dupont, R. Elle, Valorization of wood ashes as partial replacement of Portland cement: mechanical performance and durability, European Journal of Scientific Research 151(2019) 4, 468-478.

[16] ABNT, NBR 7181-84, Soil: Granulometric Analysis, Rio de Janeiro, Brazil, 1984.

[17] ABNT, NBR 6459-84, Soil: Determination of the Liquid Limit, Rio de Janeiro, Brazil, 1984.

[18] ABNT, NBR 7180-84, Soil: Determination of the Plastic Limit, Rio de Janeiro, Brazil, 1984.

[19] ASTM International, ASTM C 373-88, Standard Test Method for Water Absorption, Bulk Density, Apparent Porosity and Apparent Specific Gravity of Fired Whiteware Products, West

Conshohocken, ASTM International, 2006.

[20] A. Harabi, F. Zenikheri, B. Boudaira, F. Bouzeraba, A. Guechi, L. Foughali, A new and economic approach to fabricate resistant porous membrane supports using kaolin and $CaCO_3$, Journal of the European Ceramic Society 34(2014) 5, 1329-1340. https://doi.org/10.1016/j.jeurceramsoc.2013.11.007

[21] G.P. Souza, R. Sanchez, J.N.F. Holanda, Thermal and spectral properties of some anhydrous and hydrated rare earth hydrazinecarboxylates, Journal of Thermal Analysis and Calorimetry 73(2003), 293-305. https://doi.org/10.1023/A:1025114431307

[22] G.P. Souza, S.J.G. Sousa, L.A.H. Terrones, J.N.F. Holanda, Mineralogical analysis of Brazilian ceramic sedimentary clays used in red ceramic, Cerâmica 51(2005) 320, 381-386. https://doi.org/10.1590/S0366-69132005000400012

[23] F.A.C. Milheiro, M.N. Freire, A.G.P. Silva, J.N.F. Holanda, Densification behaviour of a red firing Brazilian kaolinitic clay, Ceramics International 31(2005) 5, 757-763. https://doi.org/10.1016/j.ceramint.2004.08.010

[24] M. Dondi, Technological characterization of clay materials: experimental methods and data interpretation, Cerâmica Industrial 11(2006) 3, 36-40.

Acknowledgements