ELSEVIER

Ceramics International 31 (2005) 353–358

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Discussion

Effect of oily waste addition to clay ceramic

S.N. Monteiro, C.M.F. Vieira*

Advanced Materials Laboratory-LAMAV, State University of the North Fluminense-UENF,
Av. Alberto Lamego 2000, Campos dos Goytacazes, RJ 28015-602, Brazil

Received 2 March 2004
Available online 2 September 2004

Abstract

Oily wastes are being generated in increasing amounts in the northern region of the State of Rio de Janeiro, Brazil, due to offshore petroleum extraction. More than 100 active clay ceramic industries in the region could provide a solution for the destination of such wastes by adding them to final products, mainly bricks. Thus, the effect of an oily waste obtained from a petroleum separation process on the properties of clay ceramics was investigated. The results showed that the addition of 5–10 wt.% of such oily waste produces an increase in mechanical strength, while the apparent density, linear shrinkage and water absorption remained practically unchanged. These results are not in agreement with the conclusions of a recent paper in which the incorrect interpretation of experimental data appears to be the main reason for the presented contradictions concerning the effects of oily waste additions on the properties of clay ceramics.

Keywords: A. Firing; B. Porosity; D. Clays; D. Traditional ceramics; Oily waste

1. Introduction

The production of petroleum is increasing rapidly in Brazil. Today over 1.6 million barrels are extracted daily and large amounts of related oily wastes of all kinds, from extraction to distribution, are expected to be generated in coming years. In a recent paper, Souza and Holanda [1] studied the densification behavior of clay ceramics to which one of these petroleum wastes had been added. The waste studied was an oily sludge originally produced on offshore rigs and brought to the city of Macaé, in the north of the State of Rio de Janeiro, to be encapsulated with bentonite and disposed of in landfills. Seeking a better environmental solution for such waste disposal, the authors studied the addition of this material to local clay, in amounts of up to 20% (all percentages in this work are wt.%). These authors concluded that the main effect of the waste addition was the inclusion of barite ($BaSO_4$) and quartz particles in the ceramic matrix. Moreover, they stated that the mechanical strength was severely reduced and suggested an upper limit of 5% of waste for clay-based industrial products. Even though no criticism is made regarding Souza and Holanda's [1] experimental results, except perhaps for the absence of a $BaSO_4$ quantitative analysis, serious doubts may be raised concerning their interpretation and conclusions. Investigations such as that cited above [1] are crucial in terms of establishing the potential for economic and environmental solutions. However, the scientific and technological aspects of any solution must be very carefully analyzed to provide the best practical orientation for optimum waste disposal. The present work will present results on an oily sludge addition and intends to show that the main conclusions in Ref. [1] are probably incorrect and even misleading in significant aspects of practical interest.

Investigations on the addition of oily wastes to clay ceramics have been carried out for over 10 years. Okongwu [2] was among the first to report on the subject by investigating up to 8% additions of spent lubricating oil on the properties of clay bricks fired at 950 °C. Practically no change was observed in the water absorption and the density. By contrast, the compressive strength of the bricks produced showed an improvement at around 1–2% oil, followed by a noticeable decrease. Tena et al. [3] studied the addition of

---

doi of original article: 10.1016/S0272-8842(03)00070-1.

* Corresponding author. Tel.: +55 22 27261533; fax: +55 22 27261533.
E-mail address: vieira@uenf.br (C.M.F. Vieira).

0272-8842/$30.00 © 2004 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2004.05.002

oily wastes from exhausted mineral oils in ceramic pieces for civil construction. They concluded that fired products can be obtained with the same or even slightly better technological characteristics, for waste addition percentages not greater than 5%.

Other publications [4–7] were restricted to specific local interest and, consequently, had limited potential for international discussion. Nevertheless relevant results were obtained for different types of oily wastes, which did not necessarily contain $BaSO_4$ or quartz particles. From these results it is worth mentioning the fact that, at least for a few percent of added oily waste, an increase in the mechanical strength may occur.

In more recent years, international publications [8–11], other than those presented by Souza and Holanda [1,12–14], have provided additional information on the subject. In particular, the increase in strength associated with a few percent of added oily waste has indeed been confirmed and an explanation of the role of hydrocarbon content on the microstructure was proposed [9,10].

Since there is an apparent contradiction between most conclusions drawn from the addition of oily waste to clay ceramics [2–11] and those of Souza and Holanda [1], the present work will analyze this question with supplementary results.

2. Experimental procedure

The oily waste used in the present work was a crude sludge (CS) obtained directly from the petroleum/residues separation process that is carried out on offshore rigs in Brazil. This oily waste is of the same type used as precursor for the bentonite encapsulated waste in reference [1].

The chemical composition of the CS waste, obtained by X-ray fluorescence (XRF) in a Philips PW 2400 equipment is given in Table 1. Before the XRF analysis, samples were dried at 110 °C for 24 h to determine the water content, and then calcinated at 920 °C for 1 h. The quantity of organic matter, which corresponds to hydrocarbons in the oily waste, was estimated by the weight difference between the original material and the remaining inorganic ashes. The chemical composition of another oily waste, produced by a bentonite encapsulating (BE) treatment, similar to the one investigated by Souza and Holanda [1], is also presented in Table 1. The potential advantage of investigating the addition of the CS waste to clay ceramic is basically the possibility of saving the cost of the bentonite encapsulation treatment demanded by the BE waste. This saving could then be passed on by the CS producer to compensate a ceramic industry for adding oily waste into its ceramic product.

Table 1
Chemical composition of the oily wastes (wt.%)

	SiO_2	Al_2O_3	Fe_2O_3	SO_3	BaO	CaO	TiO_2	K_2O	Na_2O	MgO
CS	13.7	2.52	6.69	11.1	9.97	4.46	0.18	0.95	2.30	0.42
BE	40.0	6.56	7.33	11.5	10.11	5.55	0.35	1.54	1.10	0.71
	Cr_2O_3	CuO	ZnO	SrO	MnO_2	Cl	NiO	H_2O	Hydrocarbons	
CS	0.27	0.23	0.18	0.65	0.07	0.42	0.05	12.7	33.1	
BE	0.14	0.20	0.16	1.04	0.10	<0.01	<0.01	4.3	9.3	

Table 2
Chemical composition of the clay body (wt.%)

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	LoI
50.2	25.5	8.9	1.3	2.0	0.5	0.4	1.1	10.2

The clay into which the oily waste was added was actually a mixture of three different kinds commonly used by the ceramic industries in Campos dos Goytacazes, in the north of the State of Rio de Janeiro [15]. This clay mixture was obtained from a local industry and its chemical composition is given in Table 2.

The oily waste was added at levels of 5, 10, 20 and 30%. Both, the waste-free and waste-containing clay bodies were extruded to produce 100 mm long rectangular (30 mm × 11 mm) specimens. All specimens were initially dried at room temperature for 3 days and then at 110 °C in a stove for 24 h. Firing of the specimens was performed in an electrical laboratory furnace at 750 and 950 °C. These two temperatures correspond to the limits defining the interval commonly used in Campos dos Goytacazes for firing bricks. The fired specimens were tested to determine the apparent density, linear shrinkage and water absorption by standard methods [16]. The mechanical strength was measured by the three points flexural rupture test using an Instron universal testing apparatus.

3. Results and discussion

The values obtained for the properties measured, with corresponding standard deviations, are shown in Table 3.

Fig. 1 shows that the measured apparent density mean values increase from 750 to 950 °C for each given percentage of waste addition. This indicates an effective densification with temperature, which is commonly found in clay ceramics [17]. Within the statistical error limits, no change is observed for any of the investigated temperatures. The same general behavior appears to hold for the apparent density versus waste percentage in reference [1]. However, the authors refer to it as a complex variation of density, very similar to the one they observed for the water absorption. It will be discussed later that, within the error limits, no significant variation exists up 10% addition in the water absorption results in Ref. [1].

Fig. 2 shows that the level of linear shrinkage increases from 750 to 950 °C. At each of these temperatures, within the error limits, no change occurs with waste addition except for a small decrease at 30%. By contrast, Souza and Holanda [1] stated that a decrease in shrinkage could be noted as the petroleum waste is added. According to their data, however,

Table 3
Properties determined for the experimental compositions of added oily waste ceramics

Percentage of oily waste	Apparent density (g/cm^3)		Linear shrinkage (%)		Water absorption (%)		Rupture strength (MPa)	
	750 °C	950 °C	750 °C	950 °C	750 °C	950 °C	750 °C	950 °C
0	1.47 ± 0.21	1.58 ± 0.20	6.7 ± 0.4	9.5 ± 0.7	25.2 ± 3.3	24.5 ± 2.8	6.2 ± 0.6	10.4 ± 0.8
5	1.48 ± 0.15	1.62 ± 0.17	6.7 ± 0.3	9.9 ± 0.8	25.1 ± 2.9	23.6 ± 3.0	6.9 ± 0.5	12.1 ± 0.9
10	1.50 ± 0.19	1.66 ± 0.14	6.7 ± 0.3	10.1 ± 0.5	25.1 ± 3.5	23.2 ± 2.6	6.3 ± 0.5	10.9 ± 0.7
20	1.46 ± 0.23	1.60 ± 0.19	6.7 ± 0.4	10.5 ± 1.1	26.6 ± 3.8	24.4 ± 2.8	4.2 ± 0.4	7.2 ± 0.7
30	1.50 ± 0.22	1.64 ± 0.17	5.6 ± 0.2	8.0 ± 0.7	25.6 ± 4.1	24.7 ± 2.4	3.4 ± 0.3	6.8 ± 0.5

this clearly does not hold for 750, 800, 850 and 950 °C. Therefore the argument that non-plastic components of the waste ($BaSO_4$ and quartz) are playing a major role does not seem to apply to their results below 1000 °C. It certainly does not apply to the results in the present work at 750 and 950 °C.

Actually, Souza and Holanda [1] did not show a detailed quantitative analysis of their oily waste, which could support the proposed participation of $BaSO_4$. The general composition of the oily sludge they presented was that provided by PETROBRAS [7] and not that corresponding to the actual BE waste used [1]. The detailed compositions obtained in the present work, Table 1, show that, in both wastes (CS and BE), barium compounds (probably $BaSO_4$ and BaO) as well as SiO_2 are present in significant amounts. However, the role they play in the waste containing ceramics, Fig. 2, cannot be associated with changes in the linear shrinkage on firing, at least below 1000 °C.

Fig. 3 shows that the mean values of water absorption decrease from 750 to 950 °C. This suggests, together with the results in Fig. 1, a more efficient densification: a tendency that is normally observed in ceramics with increasing temperature [18]. At each temperature investigated, within the error limits, no change occurs in the values of water absorption with waste addition, which implies unchanged porosity. Once again, a contradictory opinion was given by Souza and Holanda [1]. They stated that the water absorption decreased with waste addition up to 1000 °C, which would correspond to a decrease in porosity. A detailed analysis of their data, however, indicates that, within the error limits, no change occurs at any temperature, up to a 10% addition. The only exception was the result for 900 °C. Consequently, the explanation that the temperature had an intricate effect does not appear to be a valid one. Even above a 10% addition, changes in water absorption are relatively modest at all temperatures [1] to merit elaborate explanations.

Another serious misinterpretation of Souza and Holanda's [1] was the indication that waste-containing bodies present values of water absorption above 750 °C, which are below 25%, a standard requirement for bricks in Brazil [19]. Their experimental data, however, clearly show that only above 950 °C is this requirement fulfilled. Since 950 °C is the maximum temperature used in Campos dos Goytacazes for brick fabrication, not even the waste-free clay used by Souza and Holanda [1] could be practically applied for this purpose. In addition, according to the Brazilian norms [20] the maximum water absorption level accepted for roofing tiles is 18% and not the 20% mentioned by Souza and Holanda [1]. In this case, only the mixtures fired at 1150 °C in that study would be in accordance with the norm. This temperature, however, is considered excessively high for roofing tile fabrication in Campos dos Goytacazes. The refractory bricks currently used in the local industrial furnaces would not resist temperatures above 1100 °C.

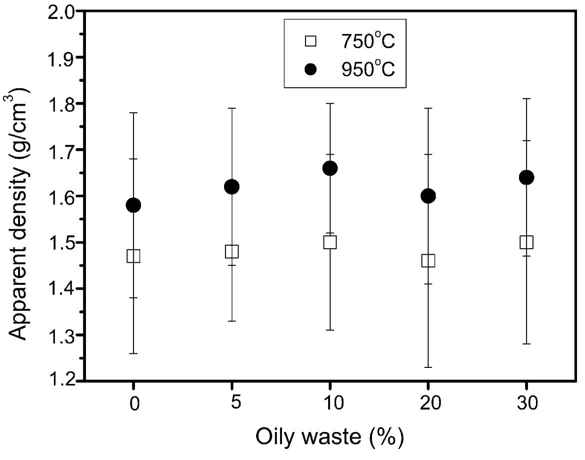

Fig. 1. Apparent density mean values for the experimental compositions fired at 750 and 950 °C.

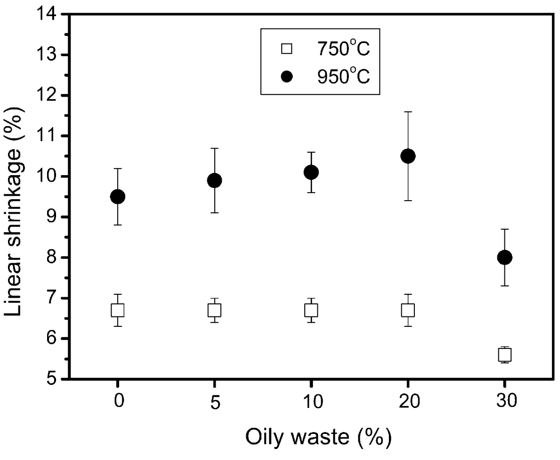

Fig. 2. Linear shrinkage values the experimental compositions fired at 750 and 950 °C.

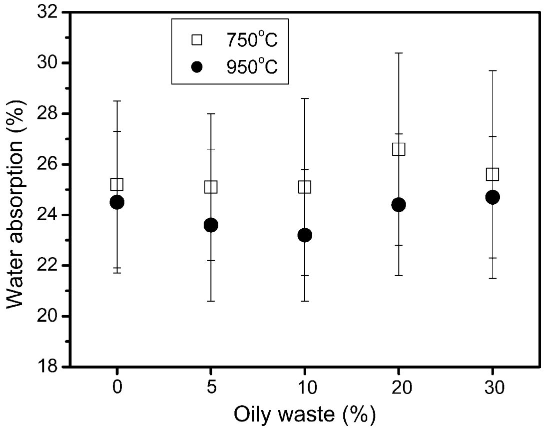

Fig. 3. Water absorption values for the experimental compositions fired at 750 and 950 °C.

Fig. 4 shows that the level of rupture strength increases from 750 to 950 °C for each given percentage of waste addition. This can also be attributed to an increase in densification [18]. At both temperatures investigated, the mean values of the rupture strength initially exhibit an increase up to 5–10% of waste addition and then a decrease. As mentioned, this initial increase in strength with oily waste addition has already been reported in the literature [2,4,5,9]. A possible explanation attributed the effect to the participation of the oil in the waste. It was suggested [9] that the oily films formed between particles act as lubricant during the clay body forming, extrusion or pressing, permitting a more efficient packing. This would favor an increase in mechanical strength after firing. Greater percentage of waste, above 10% in the present work, however, could generate oil pockets in addition to films. These pockets result in pores after firing and contribute to a decrease in strength [9]. A different situation was presented by Souza and Holanda [1]. They stated that, for all temperatures, the compressive strength decreased with waste addition. Furthermore, they suggested that $BaSO_4$ and quartz might be responsible for the impaired mechanical strength of the fired ceramic. A correlation between the values of compressive strength and water absorption was also suggested [1].

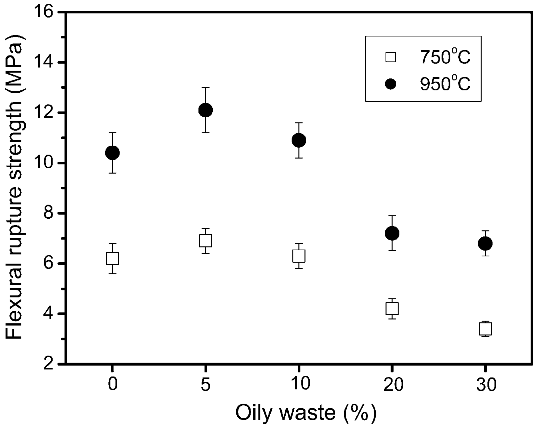

Fig. 4. Rupture strength values for the experimental compositions fired at 750 and 950 °C.

A close analysis of the Souza and Holanda [1] data with regard to the strength versus waste percent relationship reveals that, within the error limits, no change actually occurs at 750 and 950 °C, for any addition. Moreover, the results at 900, 1100 and 1150 °C do not appear to depict a consistent decrease with waste addition up to 10%. In other words, their results fail to show any relevant effect caused by the waste addition on the mechanical strength of clay ceramics. In fact the bentonite encapsulating treatment of the waste used in Ref. [1] renders it relatively inert in terms of the oil content [15]. As shown in Table 1, the oil or hydrocarbon content of the BE waste is relatively small. Consequently one should not expect an improvement in strength if a BE waste is added to a clay ceramic. Conversely, no significant deleterious effect should be expected either, except at higher addition percentages. In this case, a probable explanation is that the combustion of any remaining oil could form additional pores that contribute to a reduction in strength [9].

Another possibility for a mechanism provoking a decrease in strength may be attributed to $BaSO_4$ particles. Souza and Holanda [1] suggested that a small amount of these particles could act as nucleation sites for cracks. Table 2 shows that $BaSO_4$ exists in both wastes (CS and BE) in amounts of the order of 10%. In the present work, the $BaSO_4$ could thus have a participation greater than 1% only in ceramics with 20% or more of waste addition. This may, consequently, contribute to impair the strength at higher waste percentage as shown in Fig. 4. By contrast, however, the $BaSO_4$ could not be responsible for any reduction in strength above 1000 °C, under which conditions Ref. [1] reports a clear decrease for more than 10% of waste addition. The reason is, that at temperatures from 975 to 1300 °C, the $BaSO_4$ in fact decomposes and acts as a flux [21]. This tends to reduce porosity and could not contribute to the proposed crack formation, which could lead to a reduction in strength.

Quartz could also contribute in reducing the strength due to its volumetric variation at 573 °C forming macrocracks [22]. According to Table 2, the amount of SiO_2 in the CS waste, 13.7% is less than that in the clay, 50.2%. Consequently, one should not expect any additional effect due to quartz. This would not be the case in Ref. [1]. The amount of SiO_2, 40%, in type BE waste is comparable to that in the clay. Since the waste has a larger particle size in the sand fraction [1], this may perhaps contribute to some reduction in strength but only for a limited number of conditions, those 900 °C and above 1000 °C (for more than 10% waste), for which this reduction does clearly occur.

As previously discussed, Souza and Holanda [1] suggested a correlation between the water absorption and the strength. Indeed this correlation appears to exist for their results indicating that, at least up to 10% waste addition, no change in either water absorption or strength is taking place as a function of the level of waste addition. Consequently, the suggestion that the mechanical strength is severely reduced [1] is not only an overstatement but also an unjustified interpretation of experimental data. Furthermore, the associated conclusion that the presence of $BaSO_4$ and quartz particles is detrimental to densification is misleading, regarding the actual role played by the oily waste addition to clay ceramics. The present work confirms what already exists in the literature [2–9], that small additions of oily wastes do indeed tend to improve the ceramic strength with no major effects on other properties such as density, linear shrinkage and water absorption.

As a general comment, it should be said that the hydrocarbon content of an oily waste may be beneficial to the mechanical strength of a clay ceramic for small additions. If the hydrocarbon content is too small or has been encapsulated inside the waste, no change should be expected in the ceramic properties except for the effect of other components in the waste. In principle, the incorporation of an oily waste into the ceramic body is advantageous to the industry for the following reasons [4–9]:

- Increase in industrial productivity due to a better plasticity of the body in association with an increase in the forming speed.
- Saving in electrical power related to the operational equipment for mixing and forming.
- Reduction in maintenance costs due to less wear of the equipment.
- Saving in fuel consumption due to both, less water being required to process the body and additional combustion provided by the hydrocarbon content in the waste.

To these advantages, one may add the improvement in the mechanical strength of the ceramic product, at least for small percentage of waste. For instance, the crude sludge oily waste investigated in the present work could be used up to 10%. At higher waste percentages, porosity caused by oil pockets or larger particles, such as sand in the case of Ref. [1] or $BaSO_4$, in the present work, may impair the strength.

4. Conclusions

The addition of a crude sludge oily waste, containing 33.1% of hydrocarbons, into clay ceramics at 750 and 950 °C did not alter the density and water absorption up to the maximum of 30% addition investigated. The linear shrinkage remained unchanged for levels of waste addition bellow 30%. Above this level a significant reduction occurred. The flexural strength increased up to 5–10% addition and then decreased at higher waste percentages. These findings are in good agreement with most investigations carried out so far [2–9] for different types of oily wastes.

The mechanism proposed for the initial increase in strength was based on a more efficient packing of the ceramic body particles, before firing, due to the lubricant action of oily films. For greater waste percentages, oily pockets, in addition to films, form pores after firing and may contribute to a decrease in strength.

These results contradict the conclusions of a recent study [1] using the same type of oily waste, but which had, however, been encapsulated and thus contained much less hydrocarbons. A detailed analysis revealed no basic effect due to the encapsulation of waste in spite of the authors assertion that $BaSO_4$ and quartz particles could cause a severe reduction in mechanical strength. The present work has shown that this assertion and other statements were incorrect interpretations of the presented experimental data. The importance of this comparative analysis is to avoid potentially misleading information on the real advantages of adding oily wastes to commercial clay ceramics.

Acknowledgements

The authors acknowledge the support to this investigation provided by the following Brazilian agencies: CNPq (proc. 1500444/03-6), CAPES, FAPERJ and FENORTE.

References

[1] G.P. Souza, J.N.F. Holanda, Densification behaviour of petroleum waste bearing clay-based ceramic bodies, Ceram. Int. 30 (1) (2004) 99–104.

[2] D.A. Okongwu, Effects of additives on the burnt properties of clay brick, Am. Ceram. Soc. Bull. 67 (8) (1988) 1409–1411.

[3] A. Fernandez Tena, P. Ramos, J. Bueno, M. Prieto, Study on the influence of using oily residues (mineral oils) as an additive in the fabrication of ceramic pieces for construction (in Spanish), Bol. Soc. Esp. Ceram. Vidrio 30 (4) (1991) 257–260.

[4] S.P. Amaral, G.H. Dominguez, Application of oily residues in the fabrication of ceramic materials (in Portuguese), in: Proceedings of the 4th Brazilian Congress on Petroleum, Rio de Janeiro, 1991, pp. 1–3.

[5] R.R. Zucchini, N. Ortiz, S. Saka, R. Zandonadi, Improvement on the properties of structural ceramics using industrial oily residues (in Portuguese), in: Proceedings of the 37th Brazilian Congress on Ceramics, São Paulo, 1993, pp. 424–431.

[6] A.J.B. Barreto, Use of industrial residues in the production of ceramic bricks: technical, economical and environmental aspects (in Portuguese), Final Report to the Environmental Science Post-Graduation Course at the Gama Filho University, Rio de Janeiro, 1995, pp. 1–23.

[7] E.A. Carvallho, E.M.S. Oliveira, S.N. Monteiro, Use of oily waste in fired clay bricks, in: Proceedings of the 53rd Congress of the Brazilian Society for Metallurgy and Materials, Belo Horizonte, 1998, pp. 1–12.

[8] M. Dondi, M. Marsigli, D. Fabbri, Recycling of industrial and urban wastes in brick production—A review, Tile & Brick Int. 13 (3) (1997) 218–223, (part 1), 302–308 (part 2).

[9] S.N. Monteiro, E.A. Carvallho, E.M.S. Oliveira, N.L. Mendes, Use of oily waste in structural ceramics—an environmental solution, in: Proceedings of the Global Symposium on Recycling, Waste, Treatment and Clean Technology, San Sebastian, 1999, pp. 745–755.

[10] S.N. Monteiro, E.A. Carvallho, E.M.S. Oliveira, R.S. Santos, Structural changes related to the addition of oily wastes in red clay ceramics, Acta Microsc. 8A (1999) 73–74.

[11] F.A.N. Silva, S.N. Monteiro, Microstructure of ceramics incorporated with inert oily waste, Acta Microsc. 9A (2000) 247–248.

[12] R.S. Santos, G.P. Souza, J.N.F. Holanda, Characterization of waste of petroleum industry containing clayey masses and its application in structural ceramics, Cerâmica 48 (307) (2002) 115–120.

[13] G.P. Souza, J.N.F. Holanda, Sintering behavior of petroleum waste containing clayey masses, Cerâmica 49 (310) (2003) 128–132.

[14] G.P. Souza, R.S. Santos, J.N.F. Holanda, Recycling of a petroleum waste in ceramic bodies, Mater. Sci. Forum 418 (2003) 743–747.

[15] S.N. Monteiro, C.M.F. Vieira, Characterization of clays from Campos dos Goytacazes, North Rio de Janeiro State, Tile & Brick Int. 18 (3) (2002) 152–157.

[16] American Society for Testing and Materials, Water absorption, bulk density, apparent porosity and apparent specific gravity for fired whiteware products, ASTM, 1972, pp. C372–373.

[17] E. Fancincani, Tecnología Cerámica—los Ladrillos, Faenza Editrice Ibérica S.L., Barcelona, 1993.

[18] W.D. Kingery, H.K. Bowen, D.R. Uhlmann, Introduction to Ceramics, 2nd ed., John Wiley & Sons Inc., New York, 1976.

[19] ABNT (Associação Brasileira de Normas Técnicas), Bloco cerâmico para alvenaria, NBR 7171, Rio de Janeiro, 1992, pp. 1–8.

[20] ABNT (Associação Brasileira de Normas Técnicas), Telha cerâmica tipo romana, NBR 13582, Rio de Janeiro, 1996, pp. 1–7.

[21] G.P. Emiliani, F. Corbara, Tecnologia Cerâmica – Le Materie prime, Gruppo Editoriale Faenza Editrice S.p.A. Faenza, 1999, pp. 91–118.

[22] V. Kilikoglou, G. Vekinis, Y. Maniatis, Toughening of ceramic earthenwares by quartz inclusions: an ancient art revisited, Acta Metall. Mater. 43 (8) (1995) 2959–2965.