INCORPORATION OF GLASS POLISHING SLUDGE WASTE INTO CLAY BRICKS

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Abstract
The kaolinitic clays from Campos dos Goytacazes, state of Rio de Janeiro, Brazil, are known by their refractory behavior with elevated porosity after the firing stage. In the present work, the incorporation of up to 40 wt.% of a sludge waste from the polishing stage of soda-lime glass into a typical kaolinitic clay body from Campos dos Goytacazes was evaluated. The raw materials were characterized by XRD, XRF, particle size distribution and DTA/TGA techniques. Specimens were uniaxially pressed at 20 MPa and fired at 900 and 1000°C. The technological properties were evaluated in terms of water absorption, linear shrinkage and flexural rupture strength. The microstructure of the ceramics was evaluated by SEM. The results indicated that the waste incorporation improved both the ceramic water absorption and the mechanical strength. Finally, this work indicated that clay brick production is a viable and technically advantageous alternative for recycling this type of waste, also bringing real benefits to the quality of ceramics.

Keywords*: traditional ceramics; clayey body; residue; sustainable production.*

1. Introduction

In past decades, the reuse and recycling of industrial wastes has become a matter of worldwide concern [1]. For the industries, the final destination of a residue has to comply with ever stiffer legislation, while for the environment, both pollution and climate changes are imposing restrict levels of tolerance [2]. A typical case is that of residues generated during the large-scale fabrication of common soda-lime flat glass [3]. In particular, the sludge from the final polishing stage, after cutting the glass plate, contains a large amount of silica (SiO_2) as a non-degradable pollutant, which may cause health problems, such as silicosis, a lung disease caused by inhaling tiny bits of silica [4]. The direct recycling of this sludge in the glass industry is usually not convenient due to re-smelting cost and impurities pick-up. A viable solution might be the incorporation of this sludge into conventional clay ceramic for construction materials [5]. Indeed, at temperatures above 800°C, the common soda-lime glass in contact with clay forms low viscosity phase that could infiltrate in the sintered ceramic structure and close the pores [6]. The reduction in porosity contributes to improve the technological properties by reducing the water absorption and increasing the mechanical strength [7].

The municipal area of Campos dos Goytacazes, northern region of the state of Rio de Janeiro, Brazil, is an important industrial pole for fabrication of inexpensive conventional ceramic products for civil construction, mainly bricks and tiles [8]. More than one hundred industries take the advantage of large and easy-to-mine alluvium clay deposits [9]. However, the predominant kaolinitic type of clays found in Campos dos Goytacazes display not only a high plasticity but also a refractory behavior. These characteristics make it difficult for both the forming and the sintering stages during the clay ceramic fabrication [10]. As a consequence, the usual practice of extrusion and relatively low firing temperatures, below 800°C, for non-structural masonry brick fabricated in Campos dos Goytacazes result in ceramic products with properties difficult to attend the specifications. Until recent years the commercialization was not much affected whether the bricks comply or not with specifications. Today local governmental housing programs are demanding building materials controlled within the Brazilian standards.

A possible and effective way to improve the technological specifications of the clay ceramics fabricated in Campos dos Goytacazes is by simultaneously increasing the firing temperature and adding a fluxing raw material. Therefore, the objective of this work was to improve the technological properties of a local clay ceramic incorporated with glass polishing sludge.

2. Materials and methods

The basic raw materials used to compose the specimens in this work were a glass polishing sludge (GPS) and a typical kaolinitic clay from Campos dos Goytacazes. The GPS was obtained from the Brazilian industry named Viminas located in the city of Serra, State of Espírito Santo, Brazil. This sludge, containing up to 40% water, corresponds to the material retained in the press-filter, which received the glass particle contaminated water used in the polishing stage after the initial glass cutting operation. Figure 1 illustrates the aspect of the GPS retained in the press-filter and all the productive-chain of this by-product.

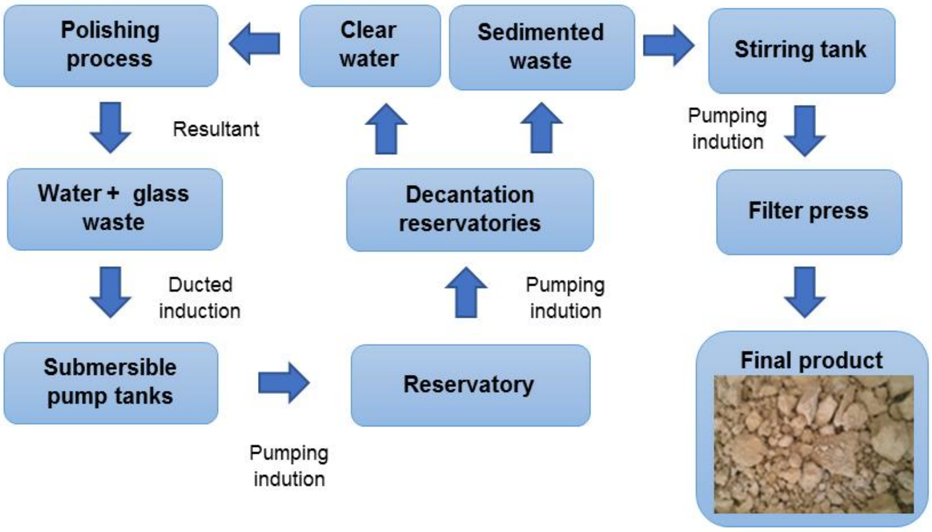

Fig. 1 Waste generation process

The clay was obtained from the typical ceramic industry located in Campos dos Goytacazes. Similar clays were investigated in recent works [11-18], in which their physical and chemical characteristics were presented. In short, the main clay mineral is kaolinite. Additionally, quartz, goethite and gibbsite are also constituents of the clay [8-10]. The plasticity limit is above 30%, which indicates to be very plastic as well as refractory clay. In general, this type of kaolinitic clay requires high temperature firing and fluxing agents to produce ceramics within the specification for building materials [10]. The chemical composition of the GPS was obtained by X-ray fluorescence (XRF) in a model DRX 7000 Shimadzu spectrometer.

Both the GPS and the clay were first dried in open air and harrowed before sieved to 35 mesh. Formulations of 0, 5, 10, 20, 30 and 40 wt% of GPS with clay were homogenized in a ball mill for 20 min and the moisten with 8 wt% of water to facilitate the forming operation. Parallelepiped 115 x 25 x 10 mm specimens were uniaxially pressed at room temperature (RT) under 20 MPA followed by drying at 110°C in a stove for 24 hours. These specimens were separated by lots corresponding to the amount of GPS incorporation, including the plain (0 wt%) clay used as reference. All specimens were fired in a type muffle electrical laboratory furnace at 900°C. The heating rate was 2°C/min with a dwell time of 180 min followed by cooling inside the switched off furnace. The technological properties of water absorption, linear shrinkage and three points bending tests performed in a model 5582 Instron machine, were carried out according to the corresponding ASTM norms [19,20].

3. Results and discussion

3.1. Chemical composition

Table 1 presents the chemical composition, obtained by XRF, of the glass polishing sludge (GPS) and given in terms of oxide percentage, although the elements may exist as different compounds. It is important to notice that most of the GPS is composed of SiO_2 with significant participations of Na_2O and CaO, as expected for soda-lime glass chemical composition [3].

It also should be noted the moderate amount of Fe_2O_3, which may contribute to the reddish color of the GPS incorporated fired ceramic. In addition, the presence of K_2O, which is a chemical compound with fluxing agent properties, might also contribute to form liquid phases, being responsible to porosity closing and to improving the technological properties.

In relation to the traditional clayey body, the silica (SiO2) is usually found in the form of free silica (quartz) or may be present in the formation of clay minerals. The aluminum oxide (Al2O3), which is the second most abundant element in the composition of this clayey body, is found as part of the chemical structure of some aluminosilicate minerals such as kaolinite and micaceous minerals, as well as may be present forming gibbsite.

Tab. 1 Chemical composition in terms of oxide (%) of the glass polishing sludge

	SiO_2	Na_2O	CaO	MgO	Al_2O_3	Fe_2O_3	K_2O	SO_3	TiO_2	NiO	ZrO_2	Cr_2O_3	P_2O_5	LoI
GPS	**67.88**	13.57	8.44	2.44	2.31	1.25	0.30	0.25	0.17	0.11	0.10	0.09	0.05	2.80
Clayey body	**49.45**	0.34	0.29	0.39	31.31	1.44	3.26	-	1.88	-	-	-	-	14.75

LoI = Loss on Ignition

3.2. Particle size distribution

Figure 2 represents the particle size distribution curve of the glass polishing sludge. It is noted that this waste has a fine particle size distribution of more than 96% of particles smaller than 100 µm (0.1 mm). The d50, which corresponds to the average grain size and through which fifty percent of the particles pass is 10 µm (0.01 mm). This result is extremely important from the point of view of ceramic processing since finer sizes indicates greater reactivity of the material, facilitating its action as a fluxing agent, as well as minimizing eventual defects such as stress concentrators.

It is observed that the clayey body presents a percentage of clay fraction of 53.1%, this means a high percentage of clay minerals which have equivalent spherical diameter less than 0.002 mm, that is, it acts as a plastic material. The sand fraction, which consists about the particles with grain size above 0.02 mm, act as plasticity reducer and presented a percentage of 27.7%. It is important to emphasize that the contents of plastics and non-plastics materials are directly related to plasticity, being able to influence the technological factors such as shaping parameters, drying shrinkage, and other properties such as mechanical resistance.

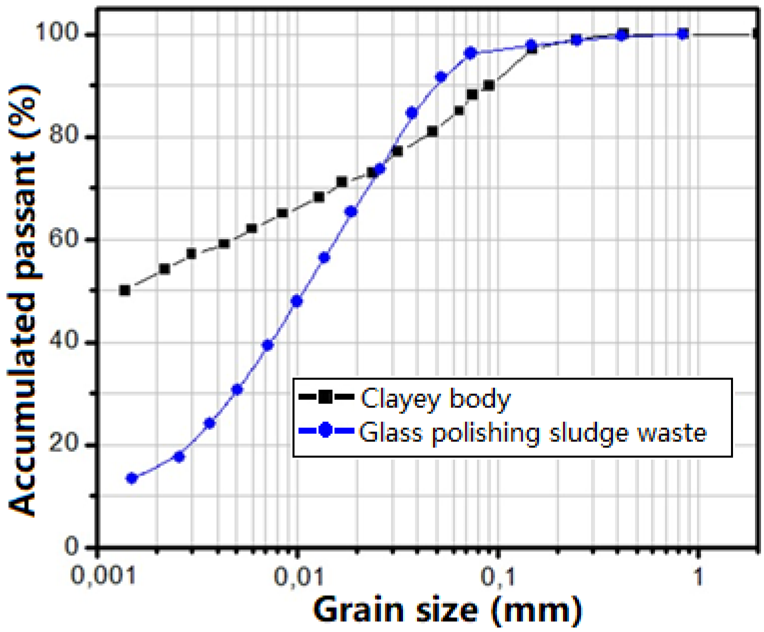

Fig. 2 Particle size distribution of the glass polishing sludge.

3.3. Morphological analysis (SEM) of glass polishing sludge

Figure 3 shows two micrographs of the glass polishing waste. Irregular particles of relatively same sizes are noted. In Figure 4, the micrograph of the area corresponding to the EDS (energy dispersive X-ray spectrometry) mapping is observed. It was verified the predominance of Si, which is related to the glass chemical constitution. In this analysis two smaller peaks related to the sodium and calcium elements were also identified, corroborating with the results of the chemical analysis (FRX). The gold peak is associated with the metallization of the material.

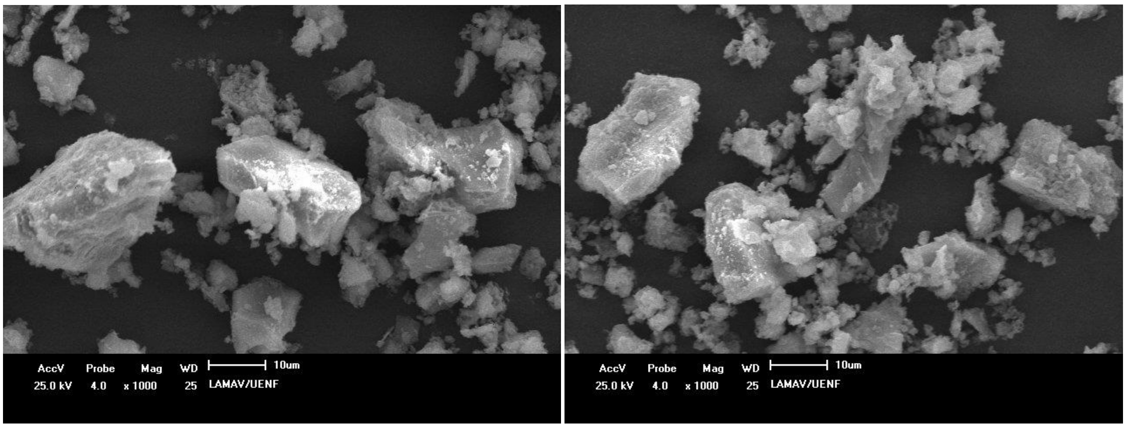

Fig. 3 Glass polishing sludge SEM.

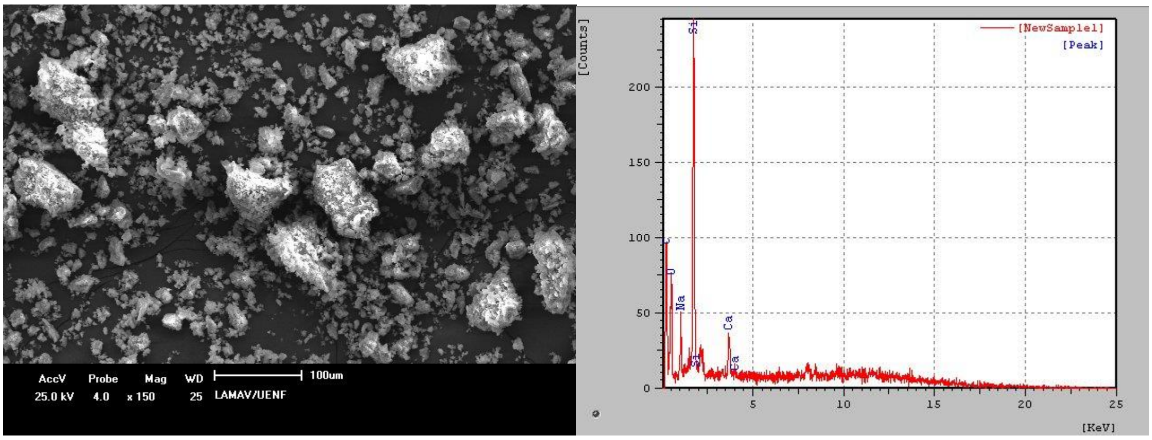

Fig. 4 Glass polishing sludge SEM with EDS.

3.4. Optical dilatometry

In Figure 5 are represented the results of optical dilatometry analysis (hot stage microscopy) of the glass polishing waste. It is possible to observe, according to the sequence of images, the glass transition (Tg) and softening (Ts) temperatures at 690 and 810 ° C, respectively; where Tg indicates the temperature that a non-crystalline material transforms from a super-cooled liquid into a rigid glass and Ts the maximum temperature that the product can be handled without causing significant dimensional changes [21].

It is also observed that the GPS has a working range, corresponding to the operating limits of a glass, from 810 to 1078 °C. These data are compatible with those reported in the literature for soda-lime glass types, which ranges from 700 to 1000 °C [21]. The melting temperature (Tm) means that the glass is fluid enough to be considered liquid, in which case the Tm is 1115 °C.

In this sense, the results showed that for the firing temperatures evaluated in this paper (850, 900, 950, 1000 and 1050 ºC), the glass waste can contribute to reduce the porosity of the specimens through the formation of viscous flow. Thus, this by-product has the potential to improve the sintering and consolidation of the ceramic products, being able to increase the mechanical resistance and also decrease the water absorption.

Furthermore, it can be stated that 810 ºC (glass softening temperature) is a temperature compatible with the industrial production of traditional ceramics, which firing temperature varies between 600 and 850 °C in the most ceramic-industries from Campos dos Goytacazes [22].

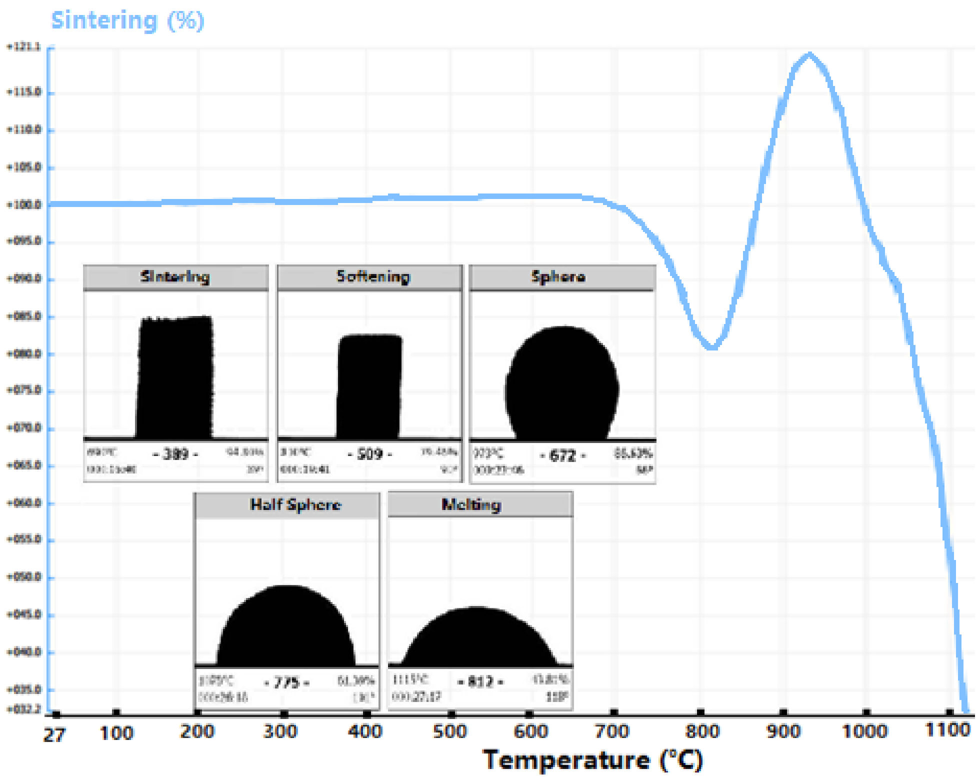

Fig. 5 Optical dilatometry of glass polishing sludge

3.5. Plasticity

Figure 6 shows the location of the formulations, which is identified by the corresponding number of the amount of glass waste incorporated, in a graph elaborated from Atterberg limits which indicates regions of optimal and acceptable extrusion [23]. The plasticity limit (PL) indicates the minimum amount of water that the clay or clayey body must contain to be shaped. The liquidity limit (LL) corresponds to the maximum amount of water that the clay or clayey body can contain to still be moldable. The plasticity index (PI) represents the difference between the LL and LP, indicating the plastic consistency range.

The water added into the clayey body acts basically by two ways. Firstly, the added water acts in the filling of the particle's pores, being called interstitial water. The second one is located between the particles, which facilitates the product's shaping. This type of water is called lubricating water, and its elimination in the drying stage is responsible for the shrinkage of the products.

It is interesting to note that the addition of up to 10% of GPS was able to move the plasticity of the clayey body to the optimum extrusion region. In addition, up to 20% of glass waste can be added, since even with this amount of waste the plasticity still remains in the region of acceptable extrusion. On the other hand, the waste incorporation above 20% is no longer advisable since the formulations with this amount of waste is located outside the acceptable extrusion area.

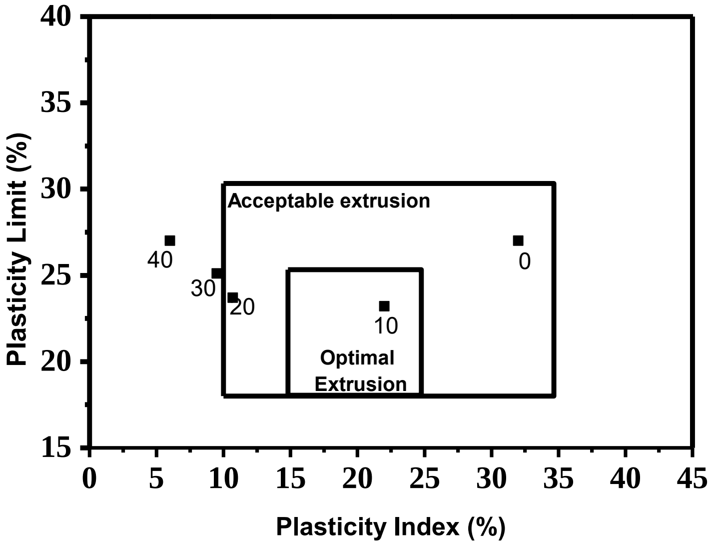

Fig. 6 Extrusion prognosis of the formulations identified by the corresponding number of the quantity of waste incorporated.

3.6. Technological properties

Figure 7 shows the water absorption of fired ceramics at two temperatures (900 °C and 1000 °C) as a function of the percentage of incorporated GPS. It is noted that the temperature increasing leads to a reduction of water absorption for all formulations, and for the formulations that contains glass polishing sludge the reduction of water absorption was more pronounced.

It is also possible to observe that incorporating up to 20 wt.% of GPS there is a tendency to reduce the water absorption property, and with this amount of waste incorporated and fired at 1000 °C this reduction was of 60%. This behavior is attributed to the viscosity reduction of the GPS with the temperature increasing, thus, favoring the porosity filling of the specimens. Even though the water absorption of the formulations containing 30 and 40 wt.% of GPS were higher comparing to the formulation containing 20 wt.% of GPS, even so, in relation to the standard formulation, the water absorption value of all formulations was lower. Possibly the excess of glass waste is causing the appearance of cracks in the ceramics due to the different coefficient of thermal expansion in comparison to the clay matrix.

Finally, all the ceramics formulations evaluated for the both firing temperatures (900 and 1000 °C) meet the technical standards that specify a maximum water absorption for roofing tiles and bricks of 20 and 22%, respectively [24,25].

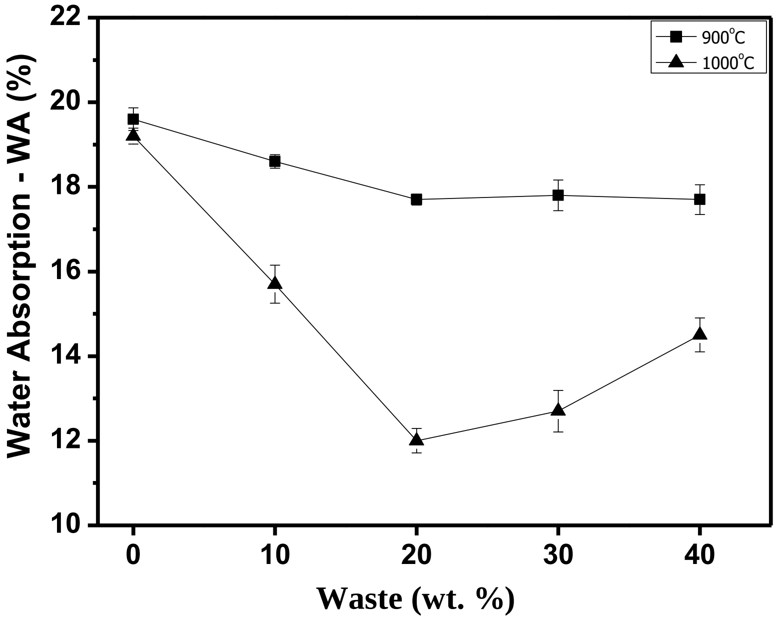

Fig. 7 Water absorption of the fired specimens as function of GPS incorporation.

Figure 8 shows the linear shrinkage of the fired specimens. It is noted that both increasing the firing temperature and increasing the content of the incorporated waste lead to a significant linear shrinkage increasing of the specimens. The shrinkage of the ceramic products caused by the firing stage is a consequence, besides the dehydroxylation of the clay minerals and some hydroxides (goethite and gibbsite), of the sintering mechanisms responsible for consolidating the final product. When adding GPS to the clayey body, the increase of the viscous flow provided by eutectics reaction contributes to the sintering process which facilitates the liquid phase flow through the porosity of the ceramic. One way to measure the sintering degree of silicates ceramics is by measuring the linear firing shrinkage, that is, by keeping other variables constant, the higher the sintering degree the greater the shrinkage of the ceramic products. Thus, by analyzing the results, it can be affirmed that the glass waste contributed to increase the sintering degree of the specimens.

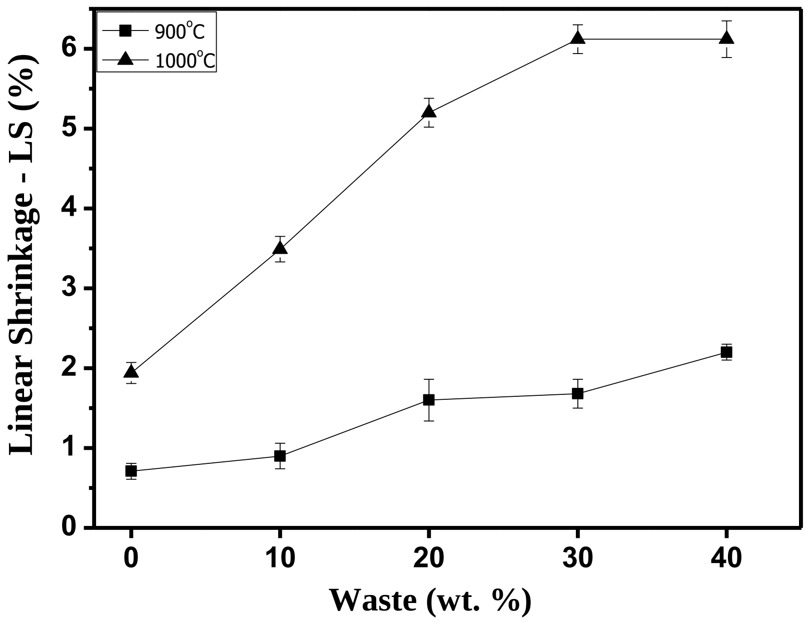

Fig. 8 Firing linear shrinkage of the fired specimens as function of GPS incorporation

Figure 9 shows the results of flexural rupture strength by three-points bending test (FRS) as function of the amount of incorporated GPS in clay ceramics fired at both temperatures (900 and 1,000 °C). In relation to the products fired at 900 °C, the incorporation of the glass sludge waste up to 30 wt% continuously increases the mechanical strength, with a tendency to decrease afterwards. The maximum value for FRS at 900 °C is observed at 30 wt.% of GPS incorporated. Thus, by incorporating amounts of glass waste greater than 30 wt.%, a reduction of FRS is observed. This can be explained by the difference in the thermal expansion coefficient between the waste and the ceramic matrix, which are capable of generating stresses that the sintered material at this temperature is not able to withstand.

In relation to sintered specimens at 1000 °C, no reversal point of the curve was observed with the incorporation of up to 40 wt.% of waste. Thus, the maximum mechanical resistance among all experimental plots investigated was obtained at the temperature of 1000 °C with the formulation containing 40 wt.% of GPS, under these conditions, the increase provided in this property was 82% over the standard clayey body.

This promising result can be attributed to the viscosity reducing and also to the higher liquid phase formation through eutectics reaction provided by GPS incorporation, which reduces the porosity and consequently improves the mechanical properties [7].

As a final remark, it is relevant to emphasize the fact that any industrial waste generated in large scale such as the GPS is a problem to the environment. By recycling the waste into another productive sector, it helps to reduce the pollution impact. Therefore, the GPS possibility of improving the properties of a material such as the clay ceramic for civil construction, which is also produced in large amounts, constitute not only a technical advantage but also economic and environmental benefits to our society [5]. These factors are associated with the modern concept of a sustainable development that, in addition to the aforementioned advantages, also saves the clay as an important natural resource.

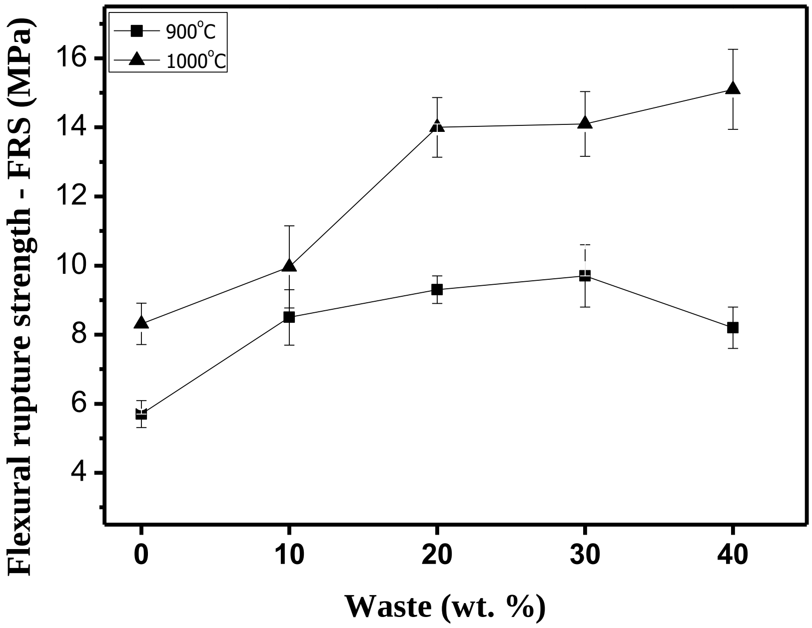

Fig. 9 Flexural rupture strength of the fired specimens as function of GPS incorporation

3.7. Microstructural analyses

Figures 10 and 11 present the microstructural analysis by optical microscopy of the ceramics containing 0, 20 and 40% of glass waste (a, b and c, respectively) fired at 900 and 1000 ºC, respectively. The quartz grains, identified by means of black circles, are naturally present in clays and although it brings benefits to ceramics through the adequacy of plasticity it is also generally responsible for some decrease of the mechanical resistance [26].

It can be seen in Figure 11 that the glass begins to appear in a viscous state and that the ceramic surface has a smoothed microstructure compared to the lowest temperature (900 °C).

In Figure 10, it is possible to note the presence of glass waste (evidenced by the black arrows), which did not reach their softening temperature and remained inert in the matrix. Thus, with increasing the amount of waste in the clayey body these particles became more evident.

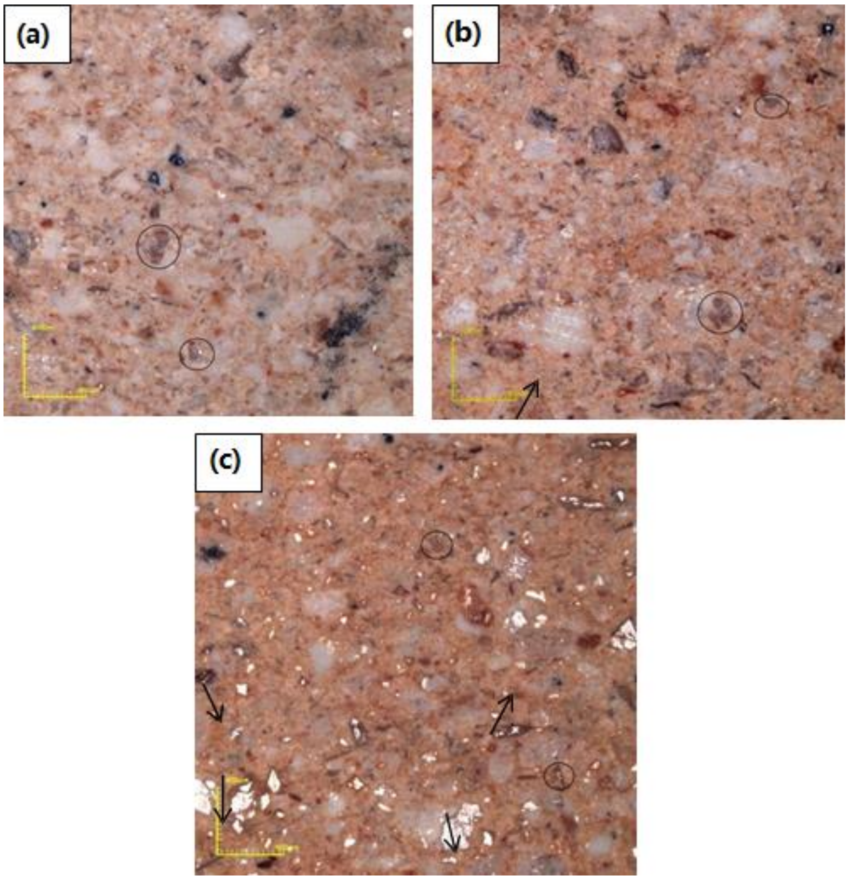

Fig. 10 Optical microscopy of the formulations containing 0, 20 and 40% of GPS fired at 900ºC.

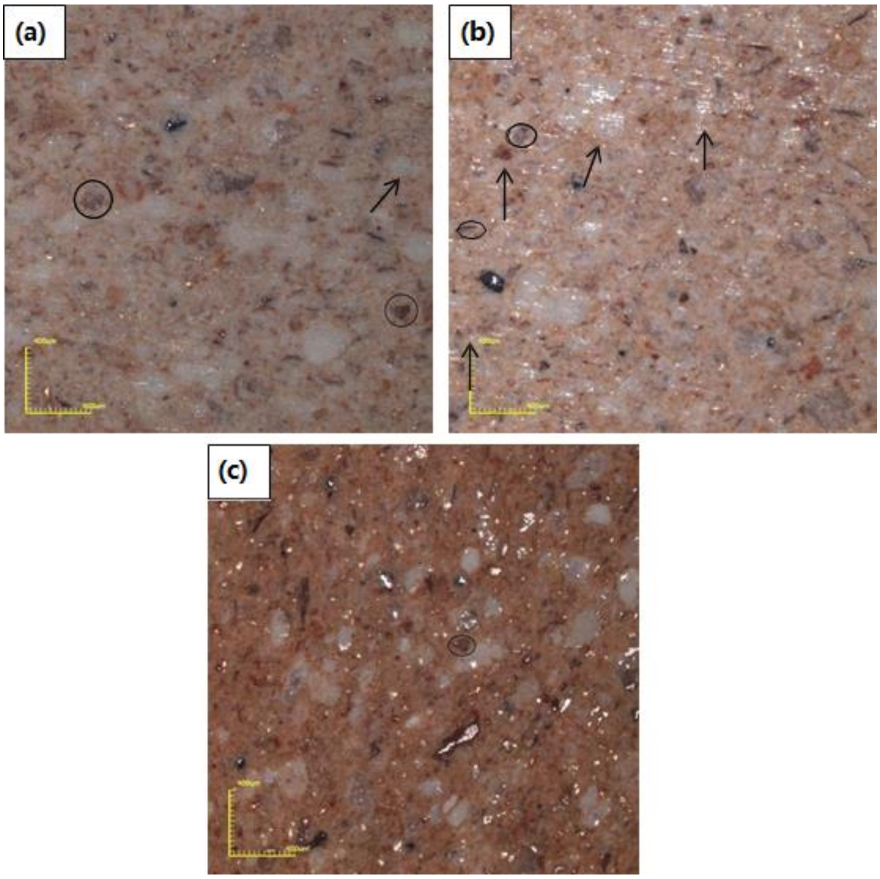

Fig. 11 Optical microscopy of the formulations containing 0, 20 and 40% of GPS fired at 1000ºC.

3.8. Scanning electron microscopy (SEM)

Figure 12 shows the micrographs obtained by scanning electron microscopy for the samples containing 0, 20 and 40% of waste (a, b and c, respectively) fired at 1000 ºC. It can be observed that with the increasing of waste amount the structure is significantly denser. The glass waste was able to achieve the smoothing stage at this temperature and penetrate the ceramic matrix, being able to favor the formation of liquid phase which promotes the sintering. In addition, it can also be observed that the residue presents bubbles associated with the softening of the glass residue.

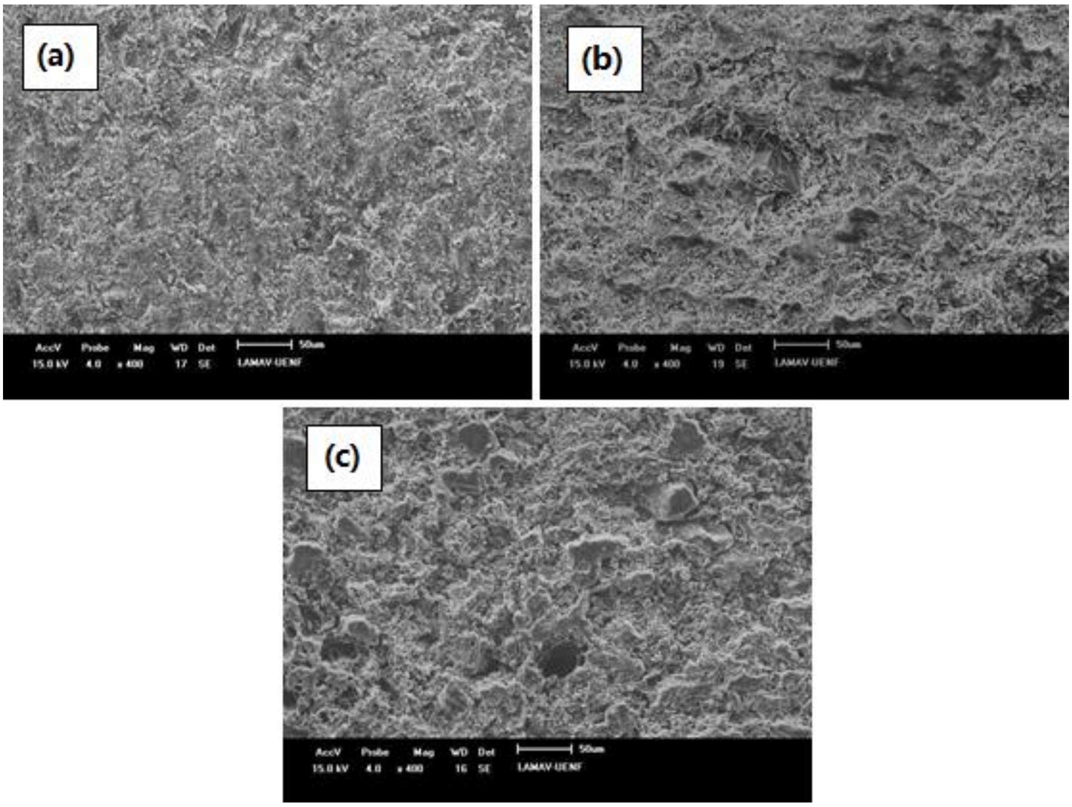

Fig. 12 Scanning electron microscopy of the formulations containing 0, 20 and 40%of GPS fired at 1000 °C.

4. Conclusions

The purpose of this study was to evaluate the effect of the incorporation of up to 40 wt% of a waste (by-product) generated in the form of sludge from the lapidation stage of glassmaking into a clayey body to produce traditional ceramics, so it can be concluded that:

- This waste has typical chemical composition of soda-lime glass, consisting predominantly of silica (SiO_2), followed by oxides of sodium (Na_2O) and calcium (CaO). In addition, it presents characteristics of liquid phase forming materials, both due to the fine granulometry and the presence of alkali oxides, being able to reduce the firing temperature of the ceramics;
- The most pronounced liquid phase formation with the incorporation of glass waste occurs at 850 °C, which is the temperature compatible with the industrial processing of traditional ceramics;
- The glass polishing sludge waste also acts as a non-plastic material, being able to considerably reduce the plasticity of the clayey body. In this way, it is recommended to use this by-product in admixture with a clay or some clayey body with high plasticity;
- From the laboratory tests, it can be seen that the formulation that presents the best results are the samples containing 20 wt.% of glass waste and fired at 1000 °C. This is due to the lower water absorption and higher mechanical strength compared to the standard clayey body (without glass waste addition). Under these conditions, the water absorption of the products was reduced by 60%, and in relation to the flexural rupture tension, an increase of 68.5% was obtained;
- Finally, the results indicated that the incorporation of glass waste had a positive effect on the sintering mechanisms which reflects to the technological properties improvement. In addition, this practice is an alternative that can minimize the environmental problems provided by the final disposal of the glass polishing sludge, can reduce the clay extraction which is a natural non-renewable resource, and also can avoid the soils degradation due to the clay mining process.

5. Acknowledgements

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