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Production and Characterisation of Ceramic Foams from Industrial Solid Waste

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This work has as objective to produce and to characterize ceramic foams from glass bottles, sludge from sewage treatment station and graphite (0 - 10 wt%) as a foaming agent. Different compositions were formulated and prepared to obtain materials with controlled porosity for applications where thermal insulation is the main requirement. The raw materials of the prepared compositions were mixed and uniaxially pressed at 40 MPa. Subsequently, the prepared samples were dried and fired at different temperatures (800 - 950 ºC) for 30 minutes, respectively. The raw materials and obtained ceramic foams were characterized in terms of their chemical, morphological, thermal and mechanical properties. The results showed that it is possible to produce ceramic foams for thermal insulation with optimized compositions containing 90 vol% glass and 10 vol% sludge with addition of 10 wt% graphite. The ceramic foams showed porosities between 40 and 70 %, thermal conductivity from 0.101 to 0.175 W/mK and compressive strength between 6.4 and 12.5 MPa.

1. Introduction

The use of ceramic foams is feasible in applications involving temperatures lower than 500 °C, for example in thermal insulation systems used in building construction such as panels, blocks rooftops, fireplaces, grills, and other systems (Scheffler and Colombo, 2005). In addition, ceramic foams have mechanical strength, chemical and thermal stabilities higher than the commonly employed polymeric foams (Bernardo et al., 2007). Among the materials used for the manufacture of ceramic foams it may cite alumina, mullite, silicon carbide, zirconia, hydroxyapatite and some composites (Zhu et al., 2002). Furthermore, it is possible to obtain porous ceramics from vitreous materials which can even be glass from recycling.

The volume of glass disposed in Brazil corresponds to 50 % of the amount produced, which, in general, represents thousands of tons of glass residues daily rejected and accumulated as waste (Assis, 2006). Each kilogram of recycled glass substitutes 6.6 kg of silica sand and the remelting of 1 t of glass consumes on average 70 % less energy than that required for glass manufacture from the usual raw materials. According to data from Brazilian Technical Association of Automatic Glass Industries, moreover, glasses produced from recycled materials reduce the amount of pollutant emissions in the air at about 20 % and in the water at approximately 50 % (ABIVIDROS, 2014).

The industries of ceramic tiles also generate significant amounts of wastes in the various process steps that not always have an adequate destination. However, higher amounts of wastes are generated in the sectors of glazes and dyes and ceramic body preparation as well as in the glazing/decorating line. In fact, in a plant of a company that produces approximately 300,000 m^2/month, 192 m^3 of liquid effluents are generated being that 117 m^3 of this volume is originated in the sectors of ceramic body preparation and glazes and dyes and 75 m^3 come from the glazing line and other sectors (Nandi et al., 2012). This entire liquid effluent, after the filter-pressing process generates large quantities of solid waste (~ 30 t/month). It is estimated that for each 100,000 m^2 of ceramic tiles produced, 10 t of ceramic sludge are generated. The ceramic sludge is mainly composed of silica, alumina and some heavy metals and for this reason it is classified as hazardous according to

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Brazilian Association of Technical Standards ABNT-NBR 10.004 and Waste Catalogue and Hazardous Waste List, EPA, 1996. Thus, the recycling of this waste may play an important role in the raw-material saving and declines in the environmental pollution caused by these industries (Pereira et al., 2006). This can be achieved by replacing one or more raw materials of the original composition by ceramic sludge respecting the technological characteristics of the process and the product properties (Casagrande et al., 2008). Thus, the use of waste is a great opportunity to elongate the life cycles of elements in anthroposphere, reducing the need for extraction from the environment (Galembeck, 2013).
In this context, this article presents results of a research work aimed to the production of ceramic foams from discarded glass bottles, waste (sludge) from a sewage treatment station (STS) generated in a ceramic tile industry and graphite, for applications where thermal and acoustic insulations are the main technical requirements.

2. Materials and methods

In this work glass bottles (VG) and a waste from a sewage treatment station (STS) generated in a ceramic tile industry and graphite (G) as pore forming agent (a residue from electrodes of electric melting furnaces for steel) were used as raw materials.
Chemical compositions of transparent glass bottles (VGT), green glass bottles (VGV), brown glass bottles (VGM) and sludge from a STS were obtained by X-ray Fluorescence (Philips model PW 2400) as shown in Table 1. The STS sludge used in this work (particle size, D_{50} = 10 μm) was provided by a ceramic tile company in southern state of Santa Catarina (SC)/Brazil.

Table 1: Chemical composition of the glasses and STS sludge used as raw materials

Materials/Oxides (wt%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	Na_2O	P_2O_5	TiO_2	ZnO
VGM	67.1	1.96	0.83	9.52	0.30	0.65	19.6	0.01	0.03	-
VGT	71.2	2.17	0.10	9.65	0.02	-	16.8	0.02	0.04	-
VGV	68.3	2.06	0.41	8.94	0.47	1.85	17.9	0.01	0.06	-
STS	58.4	16.2	0.54	8.06	2.92	2.32	1.42	-	0.13	5.11

The glass bottles (VG) exhibit sodium-calcium composition and the main differences are related to the chromophore oxides, particularly iron oxide, which, as expected, increases as the colour of the glass changes from clear to green and brown. The glasses and the STS sludge which is mainly composed of silica, alumina and some heavy metals are classified as hazardous according to ABNT-NBR 10.004 and Waste Catalogue and Hazardous Waste List, EPA, 1996. Detailed information on the preparation and characterization (including its inertness) of the STS sludge can be obtained from Nandi et al. (2012).
The glass bottles, mixed in the same proportions, were milled on a crusher (SERVITECH, CT-058), and the resulting powder was milled for 90 min in a fast mill (SERVITECH, CT-242) by using a porcelain jar containing alumina balls to yield particle size (D_{50}) of 3.5 μm (using a laser scattering particle size analyser, Malvern, ZEN-3600). The graphite was ground into a crusher (SERVITECH, CT-058) so that a powder with particle sizes lower than 106 μm was obtained.
The STS sludge was dried (110 °C/24 h) and deagglomerated in a fast mill (SERVITECH, CT-242) by using a porcelain jar containing alumina balls for 10 min. Subsequently, compositions containing glass bottles (70 - 95 vol%), STS sludge (5 - 30 vol%) and graphite (6 to 12 wt%) with respect each volume composition were prepared. The prepared compositions were humidified with 5 % water and homogenized in a fast mill (SERVITECH, CT-242) with a porcelain jar containing alumina balls for 10 min and, in a later step, uniaxially pressed in a steel die using a hydraulic press (ST Bovenau P10) at 40 MPa. The obtained disc samples (30 x 10 mm) were dried in a laboratory dryer (SP LABOR®) at 110 °C/2 h.
The thermal behaviour during firing of the raw materials and the prepared compositions were studied by means of an optical dilatometer (Expert System Solution Misura ODHT) at 10 °C/min (oxidizing atmosphere). Based on the dilatometric analysis the compacted compositions were fired at different temperatures (800 - 950 °C) and holding times (15 - 120 min) and subjected to different measurements and analyses.
The apparent density (ρ_{geo}) was calculated from the dimensions and mass of the samples. The true density (ρ_t) was determined by gas (He) pycnometry (Multi-Pycnometer, MVP-4DC). The void fraction (porosity (ε))

was determined by considering the relation between the densities, that is, [1- (ρ_{geo}/ρ_t)]. The microstructure of pores could be seen from images of surface fractures, obtained in a scanning electron microscope, SEM (JEOL, JSM-6390LV). The compressive strength of the ceramic foams was determined by averaging five cylindrical samples, with nominal diameters of 30 mm, using a universal testing machine (EMIC DL 2000), with loading speed of 1 mm/min. The thermal conductivity of the obtained materials was determined in a TCi Thermal Conductivity C-THERM TECHNOLOGIES on disk-shaped samples of 30 mm diameter and 10 mm thick.

3. Results and discussion

Figures 1 and 2 show curves of linear shrinkage of prepared compositions, i.e., VG (70 - 95 vol%) + STS (30 - 5 vol%) + 10 wt% graphite (Figure 1) and compositions containing 90 vol% VG and 10 vol% STS with 6 to 12 wt% graphite (G), with respect each volume composition (Figure 2).

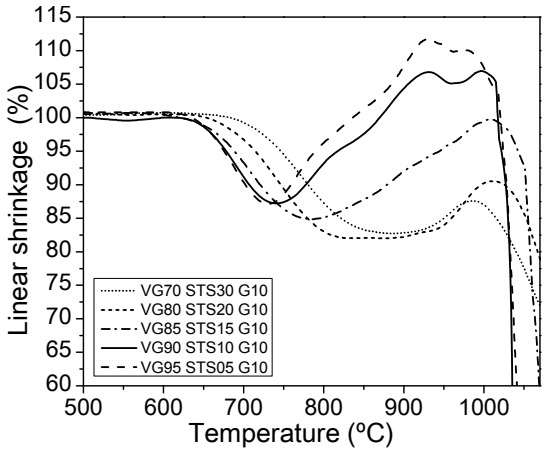

Figure 1: Linear shrinkage curves. VG (70 - 95 vol%) + STS (30 - 5 vol%) with addition of 10 wt% graphite (G)

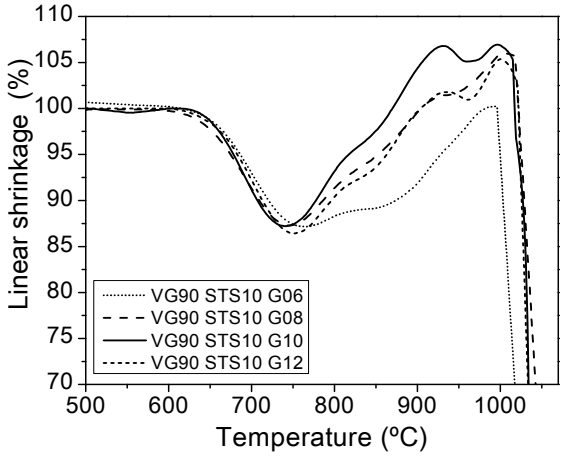

Figure 2: Linear shrinkage curves. 90 vol% VG and 10 vol% STS with addition of 6 to 12 wt% graphite (G)

In general (Figure 1), it can be seen that as higher is the STS sludge volume fraction higher is the densification temperature of the studied compositions. It occurs due to the refractoriness of the STS sludge. Such characteristic causes no expansion of the compositions containing 20 and 30 vol% STS sludge.
In compositions containing 5, 10 and 15 % STS sludge expansion occurred in the temperature range between 750 and 950 °C which corresponds to the temperature range of decomposition of the graphite. It can be seen that compositions containing 5 and 10 % STS sludge have similar expansion. Thus, the composition containing 90 % VG and 10 % STS sludge was selected. The amount of 10 wt% graphite was set because lower or higher graphite amounts were not sufficient to cause expansion in the prepared samples as shown in

Figure 2. It can be observed by the analysis of Figure 2 that the shrinkage (densification) of the selected composition takes place between 600 and 775 °C. Between 725 and 950 °C can be observed the expansion generated by the decomposition of graphite and from 950 °C the characteristic expansion of the glass bottle. It is observed that the expansion is growing for additions of graphite between 6 and 10 %. For larger additions of graphite (12 %) the expansion decreases. This behaviour is probably related to an increase in the volume of gas which results in increased internal pressure and thus the rupture of the walls of the pores allowing a portion of the generated gases to escape. In this way, the composition with 90 % VG, 10 % STS sludge and 10 % graphite was chosen since it has the optimal condition in terms of the relative amounts of raw materials. Figure 3 shows curves relating the porosity as a function of firing temperature and holding times for composition with 90 % VG, 10 % STS and 10 % graphite (G). As can be seen, the porosity increases (~40 - 70 %) as the firing temperature increases from 800 to 900°C (temperature of maximum porosity), independently of the holding time in a given temperature. At 950 °C the porosity remains almost constant. The maximum porosity at 900 °C, according to Figure 2, since at this temperature, among the selected firing temperature, the mixture containing 90 % VG, 10 % STS and 10 % graphite has a larger expansion. In fact, the SEM images in Figure 4 show the as before mentioned aspects. It can be observed from the analysis of Figure 4, a homogeneous distribution of pores. Furthermore, there is an increase in the size and number of pores as the temperature increases up to 900 °C, which is consistent with the porosity data shown in Figure 3. At 950 °C (Figure 4 (d)) there is a small decrease in pore size due to the high firing temperature which favours the increase of the internal pressure and the breaking of the pores, leading to a reduction of the size of them. However, no significant changes in the porosity occur.

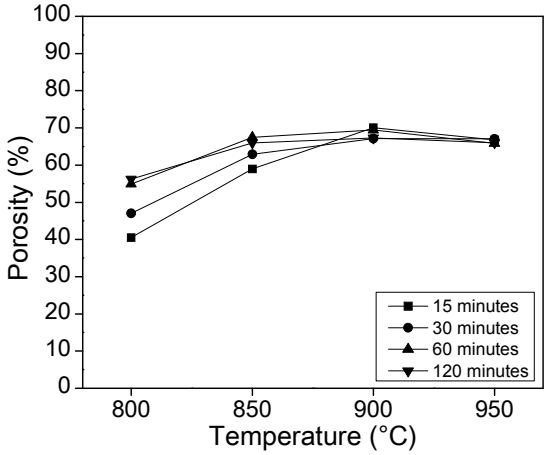

Figure 3: Porosity curves as a function of firing temperature and holding time for composition containing 90 vol% VG and 10 vol% STS sludge with addition of 10 wt% graphite

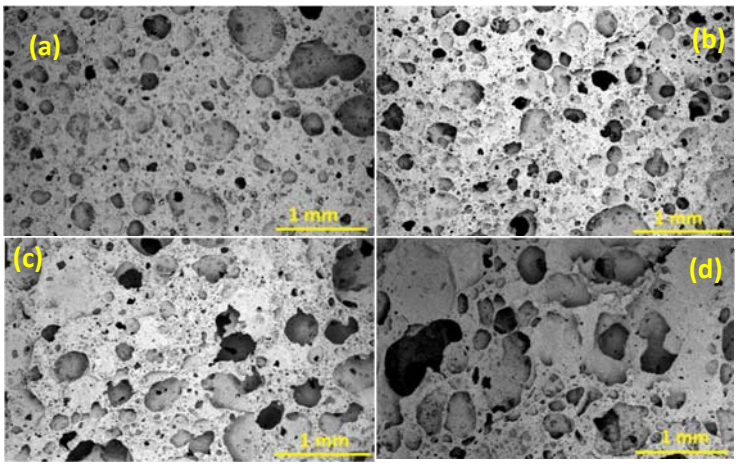

Figure 4: SEM images of fracture surfaces of samples fired at: (a) 800 °C, (b) 850 °C, (c) 900 °C and (d) 950 °C for 30 min

Figures 5 and 6 show curves of thermal conductivity and mechanical strength, respectively as a function of the firing temperature for 30 min for samples of composition containing 90 % VG, 10 % STS and 10 % graphite. It is observed in general (Figure 5) that the values of thermal conductivity decreases (0.175 to 0.101 W/mK) with increasing porosity. Furthermore, the thermal conductivity values are low with small variation among the compositions. The low thermal conductivity values are characteristic of ceramic foams for thermal insulations (Scheffler, 2005).

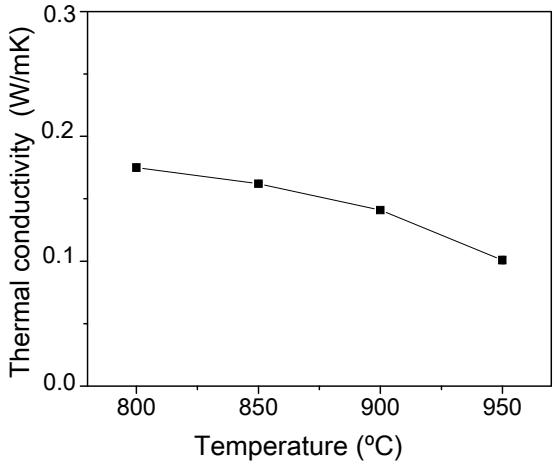

Figure 5: Curve of thermal conductivity as a function of the firing temperature for 30 min for samples of composition containing 90 vol% VG and 10 vol% STS with 10 wt% graphite

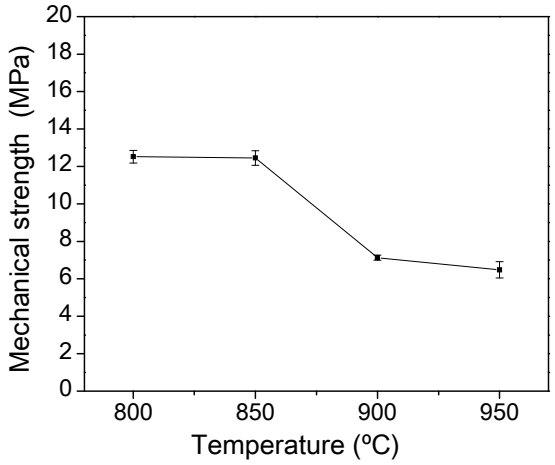

Figure 6: Curve of mechanical strength as a function of the firing temperature for 30 min for samples of composition containing 90 vol% VG and 10 vol% STS with 10 wt% graphite

The compressive strength decreases with increasing firing temperature, with values between 6.4 and 12.5 MPa. This result is related to the change of the porosity, i.e. as the porosity of the samples decreases the compressive strength increases. The mechanical strength values achieved are typical of ceramic foams.

4. Conclusions

The obtained results showed that it was possible to produce thermal insulators from an optimized composition containing 90 vol% VG and 10 vol% STS sludge with 10 wt% graphite, fired at temperatures between 800 and 950 °C for 30 minutes with porosity between 40 and 70 %, thermal conductivity between 0.175 and 0.101 W/mK and having mechanical strength between 6.4 and 12.5 MPa. The obtained materials are therefore potential candidates for applications requiring adequate combination of thermal conductivity, porosity and mechanical strength.

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