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Obtainment of porcelain floor tiles added with petroleum oily sludge

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Abstract

This study focuses on the processing of vitrified floor tiles incorporated with a petroleum oily sludge. Floor tile formulations containing up to 5 wt% of the petroleum oily sludge in replacement of kaolin were prepared. The tile formulations were granulated by the dry process, pressed, and fired at temperatures between 1200 and 1250 °C using a fast-firing cycle. The specimens were characterized before and after firing. XRD was used to identify the crystalline phases present during sintering and SEM was used to show how the structure changes during densification. Three parameters were used to describe densification: linear shrinkage, water absorption, and flexural strength. The results showed that the petroleum oily sludge could be used as an alternative raw material in the floor tile formulations. The densification behavior of the floor tile pieces is influenced by the petroleum oily sludge addition and firing temperature. The vitrified floor tiles produced reached the technical characteristics of porcelain floor tiles, depending on petroleum oily sludge content and firing temperature.

Keywords: A. Firing; B. Porosity; E. Structural applications; Oily sludge

1. Introduction

Every year the petroleum industry generates large amounts of by-products (oily sludges) worldwide [1–3]. These oily sludges are basically complex mixtures of hydrocarbons (oil), water, inorganic materials, and traces of heavy metals [3,4]. For this reason, the oily sludges are considered to be hazardous waste materials. The management of these oily sludges has been over the years a major concern of the petroleum industry and environmentalists. In Brazil, the oily sludges have been mainly disposed in pounds, dykes, and landfarms (biodegradation). More recently, these oily sludges have been disposed in sanitary landfills after treatment with bentonite clay [5,6]. However, these options are usually expensive and environmentally unsustainable. In addition, Brazil is now increasing the regulatory pressures on these management options, thus the development of new management methods for this waste material is very important.

The oily sludge treated with bentonite clay is characterized as a petroleum waste material composed of clay minerals, quartz, barite, calcium sulpfate, calcite, and hydrocarbons [6]. Thus, it has some potential to be used as ceramic raw material. In fact, several works have shown promising results on the reuse of petroleum oily sludge in the production of clay bricks [7–12]. However, insufficient attention was devoted to the use of petroleum oily sludge in vitrified floor tiles [13]. Floor tiles are vitrified ceramic products of low porosity with excellent physical and mechanical properties. These materials are produced via powder technology: raw materials preparation (dry or wet grinding), dry uniaxial pressing, drying, and single-fast-firing cycles [14–16].

Brazil is currently the second worldwide producer of ceramic tiles, ahead of India, Italy and Spain, and behind China [17]. In 2009, Brazilian ceramic tile production totaled 715 million square meters, which corresponds to about 8.4% of the world production. This production can grow still more due to the high internal demand and opportunities for exportation. In fact, the domestic market is the second largest tile consumer in the world with 645 million square meters (7.6% of the world consumer). The need to increase

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production to meet the increasing demand has triggered academic and technological researches focused primarily on the development of new deposits of raw materials. In this context two important aspects should be considered: (i) the tile industry faces scarcity of good quality raw materials; and (ii) the tile formulations are strongly affected by locally available raw materials. Thus, the reuse of waste materials into tile formulations seems to be one of the best alternatives to reduce the extraction of virgin raw materials, preserving limited natural resources.

This paper discusses, in detail, the preparation of vitrified floor tiles using petroleum oily sludge. The densification behavior of the tile formulations containing petroleum oily sludge was investigated. Emphasis is given to the formulation characteristics, their effects on the technological properties of the end product, and the microstructural evolution of the fired specimens.

2. Experimental procedure

Different floor tile compositions were formulated (Table 1) using mixtures of kaolin, Na-feldspar, quartz, and petroleum oily sludge. The oily sludge was added up to 5 wt% in gradual replacement of kaolin. A standard composition (40 wt% kaolin, 47.5 wt% Na-feldspar, and 12.5 wt% quartz), referred to as MC0 formulation, was used as ref. [18]. Commercial kaolin, Na-feldspar, and quartz were used. The petroleum oily sludge was collected in the Brazilian oil company. Table 2 gives the chemical compositions of the raw materials and the prepared formulations.

Table 1
Ceramic floor tile formulations (wt%).

Raw materials	Formulations			
	MC0	MC1	MC2	MC3
Kaolin	40.00	38.75	37.50	35.00
Oily sludge	0.00	1.25	2.50	5.00
Na-feldspar	47.50	47.50	47.50	47.50
Quartz	12.50	12.50	12.50	12.50

The raw materials were dry-ground and mixed using a laboratory mill, and then passed through a 325 mesh (45 μm ASTM) screen. The tile compositions prepared by the dry process were mixed, homogenized and granulated using a high intensity mixer (Eirich, type R02) with moisture content of 14% (moisture mass/dry mass). After reducing the moisture content to 7%, the granulated powder is sent to the sieve to eliminate agglomerates coarser than 2 mm.

Mineralogical analysis of the tile formulations was done by X-ray diffraction (URD-65 Diffractometer, Seifert), using copper radiation (Cu-Kα = 1.54056 Å). Scanning speed was set to 1.5°(2θ)/min. JCPDS-ICDD cards were used to identify the crystalline phases. Thermogravimetric analysis (TGA and DrTGA) of the tile powder sample was performed within the 25–1200 °C temperature range under air atmosphere with a heating rate of 10 °C/min. The size distribution of the granulated powders was determined by procedures according to the NBR 7181 standard. The plasticity was determined by the Atterberg method according to the NBR 6459 and NBR 7180 standardized procedures. The real density was determined by the picnometry method according to the NBR 6508 standard. The morphology and the surface topography of the granules were observed by scanning electron microscopy (SEM). The Hausner index and screening residue have been also determined.

The powders were uniaxially pressed in a 11.5 cm × 2.5 cm rectangular die at 50 MPa, and dried at 110 °C. The samples were fast-fired in a laboratory kiln at temperatures varying from 1200 to 1250 °C. The whole firing cycle lasts less than 60 min.

The densification behavior of the tile formulations was described by the linear shrinkage, water absorption, and flexural strength. Linear shrinkage values upon drying and firing were evaluated from the variation of the length of

Table 2
Chemical compositions of the raw materials and tested formulations (wt%).

Compounds	Raw materials				Formulations			
	Kaolin	Sludge	Na-feldspar	Quartz	MC0	MC1	MC2	MC3
SiO_2	49.07	41.73	69.55	98.97	65.06	64.97	64.88	64.69
Al_2O_3	33.74	10.93	18.82	0.41	22.49	22.21	21.92	21.35
Fe_2O_3	0.22	7.63	0.14	0.01	0.16	0.25	0.34	0.53
TiO_2	0.01	0.52	0.02	0.02	0.01	0.02	0.03	0.04
Na_2O	0.52	0.44	9.63	0.13	4.80	4.80	4.80	4.79
K_2O	1.97	0.95	1.47	0.18	1.50	1.49	1.48	1.45
CaO	0.30	7.76	0.17	0.01	0.20	0.30	0.39	0.58
MgO	0.06	5.87	0.09	0.01	0.07	0.14	0.21	0.36
MnO	–	0.02	–	–	–	–	–	–
P_2O_5	–	0.09	–	–	–	–	–	–
BaO	–	5.03	–	–	0.00	0.06	0.13	0.25
SrO	–	0.29	–	–	0.00	0.00	0.01	0.01
LoI^+	14.01	18.74	0.32	0.26	5.79	5.85	5.91	6.03

LoI^+—loss on ignition.

the rectangular specimens. Water absorption values were determined from weight differences between the as-fired and water saturated samples (immersed in boiling water for 2 h). The flexural strength was determined by three-point bending test (model 5588, Instron) at a loading rate of 0.5 mm/min according to the ASTM C674 standard.

The sintered microstructure of fractured surfaces was observed by scanning electron microscopy (DSM 962, Zeiss), where the accelerating voltage was kept constant at 15 kV. Electrical charging was avoided by gold coating the specimens. The mineralogical characterization of the fired specimens was performed at room temperature by X-ray diffraction using cobalt radiation (Co-Kα = 1.78897 Å).

3. Results and discussion

The XRD patterns of the green floor tile formulations are shown in Fig. 1. The main crystalline phases identified were kaolinite ($Al_2O_3.2SiO_2.2H_2O$; JCPDS-ICDD card: 14-0164), albite ($NaSi_3AlO_8$; JCPDS-ICDD card: 20-0572), quartz (SiO_2; JCPDS-ICDD card: 46-1045), barite ($BaSO_4$; JCPDS-ICDD card: 02–1199), montmorillonite ($Na_{0.3}(AlMg)_2Si_4O_{10}OH_2.6H_2O$; JCPDS-ICDD card: 12–0219), hematite (Fe_2O_3; JCPDS-ICDD card: 33–0664), and calcium sulfate ($CaSO_4.2H_2O$; JCPDS-ICDD card: 01–0385). The addition of petroleum oily sludge to the basic tile formulation caused only minor differences in the intensity of the diffraction peaks. The mineral phases identified by XRD are consistent with the chemical compositions of the tile formulations (Table 2).

The grain-size distribution of the granulated powders produced by the dry process is shown in Fig. 2. As can be observed, the replacement of kaolin with petroleum oily sludge alters the grain size distribution of the ceramic formulations. The largest fraction of the granulated powder MC0 is in the grain-size range of 250–850 μm, while in the granulated powders with petroleum oily sludge additions (MC1, MC2, and MC3) the largest fraction is < 150 μm. This behavior can be related with the finer particle sizes of the formulations containing petroleum oily sludge after grinding. Nevertheless all granulated powders have granule size distribution that provides good reactivity during firing. Fig. 3 shows a SEM micrograph of granules of the formulation MC2. The irregular shape is typical of granules produced by mechanical agglomeration of finely dry-ground particles. These observations hold for all the prepared tile powders.

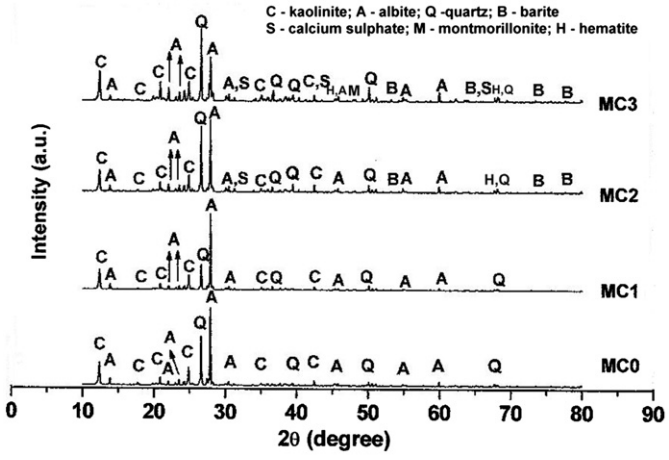

Fig. 1. X-ray diffraction patterns of the green tile formulations.

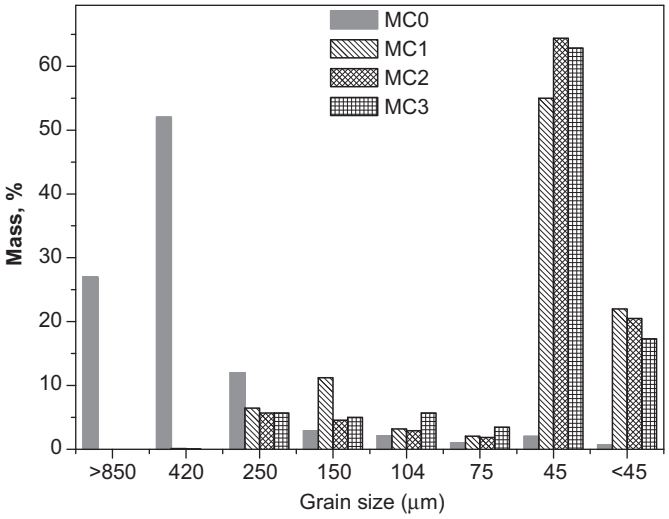

Fig. 2. Grain-size distribution of the tile powders granulated by the dry process.

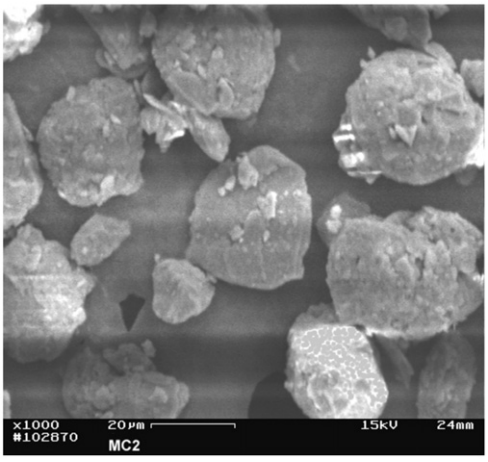

Fig. 3. Morphology of the granulated powder.

Table 3 gives the physical characteristics of the tile formulations. The real particle density of the tile formulations reflects their mineralogical compositions. It was found that the replacement of kaolin with up to 5 wt% of petroleum oily sludge had negligible effect on the real particle density. The plastic index (PI) was determined by PI = UPL − LPL, in which UPL is the upper plastic limit and LPL is the lower plastic limit. It can be seen that the PI value tends to lightly decrease (14.0%–12.9%) with the petroleum oily sludge addition. However, the values of plasticity obtained for all tile formulations are within the adequate range for floor tile production [19]. Concerning

Table 3
Physical characteristics of the floor tile formulations.

Formulation	ρ (g/cm^3)	PI (%)	HI	R (%)
MC0	2.60	14.00	1.03	4.15
MC1	2.61	12.90	1.04	3.87
MC2	2.61	13.60	1.04	3.69
MC3	2.62	13.00	1.04	3.47

ρ—real density; PI—plastic index; HI—Hausner index; R—screening residue.

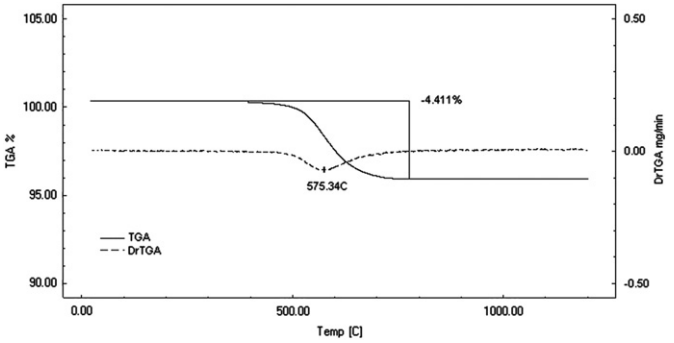

Fig. 4. TGA/DrTGA curves of the MC2 formulation.

to the Hausner index, the tile formulations also presented only small changes (1.03–1.04) when the kaolin was partially substituted with petroleum oily sludge. The values of Hausner index around unity indicate that the granulated powders prepared with the dry process shows good fluidity. This characteristic is important to the automatic die filling during the compaction step. It was also observed that all tile formulations presented screening residue (< 63 μm) adequate to obtain good reactivity during fast-firing cycle.

The thermogravimetric curves (TGA and DrTGA) for the MC2 formulation (with 2.5 wt% oily sludge) are shown in Fig. 4. At 575.34 °C, there is an endothermic event with mass loss, which can be mainly related to the dehydroxylation of clay minerals. The volatization of oil (hydrocarbons) of the petroleum oily sludge also contributes to the loss of mass during heating. The mass loss of the samples during heating are in 4.41–4.63% range. These values are consistent with the values of ignition loss (Table 2).

The properties of the floor tile pieces in the dried state at 110 °C have been determined. There is no significant difference in the drying density (1.89–1.91 g/cm^3) of the tile pieces. This is important to make comparisons of fired properties and densification between the different formulations. The tile pieces had low value of linear shrinkage (0.03–0.07%). This is recommended by the ceramic tile industry. The flexural strength of the dry pressed samples is between 3.25 and 3.86 MPa. According to the literature [20], values above 2 MPa are recommended (Table 4).

Fig. 5 shows the XRD patterns of MC0 specimens after firing between 1200 and 1250 °C. The results indicate the

Table 4
Physical properties of the tile pieces in the dried state at 110 °C.

Properties	Formulations			
	MC0	MC1	MC2	MC3
Linear shrinkage, %	0.07	0.05	0.03	0.06
Bulk density, g/cm^3	1.89	1.89	1.89	1.91
Flexural strength, MPa	3.25	3.32	3.42	3.86

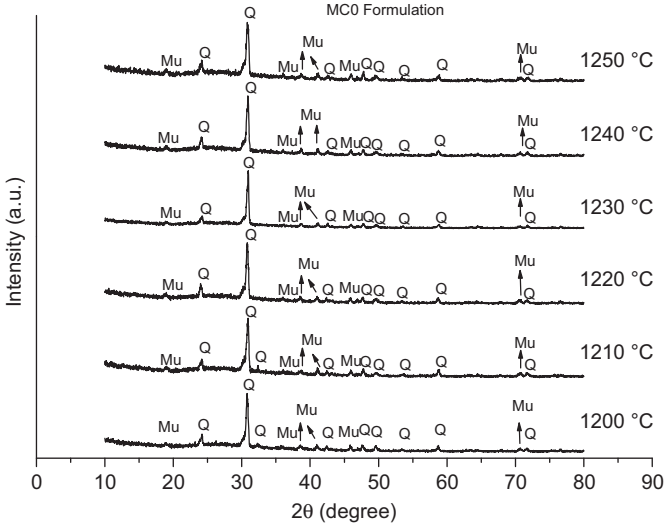

Fig. 5. X-ray diffraction patterns of the MC0 formulation fired at various temperatures: Q—quartz; and Mu—mullite.

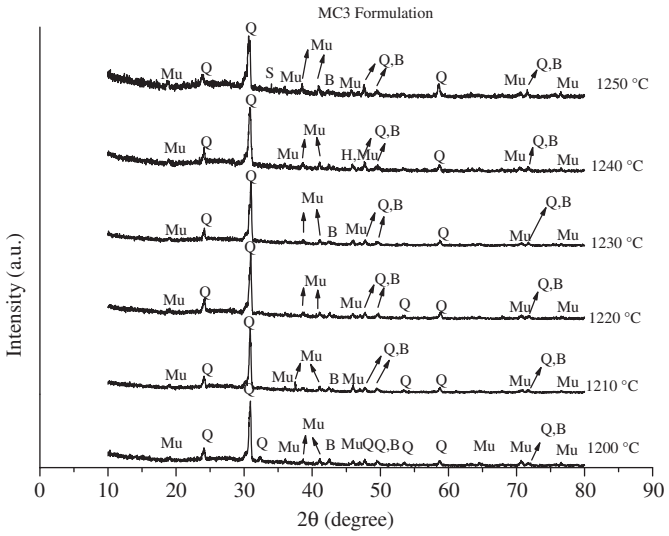

Fig. 6. X-ray diffraction patterns of the MC3 formulation fired at various temperatures: Q—quartz; Mu—mullite; B—barite; S—calcium sulphate; and H—hematite.

presence of mullite ($3Al_2O_3 \cdot 2SiO_2$) and quartz (SiO_2) for all firing temperatures. Only small differences in the peak intensities are present. Quartz found in the fired samples is residual from the original raw materials. Mullite forms during the firing process. At -980 °C, mullite is developed

from the metakaolinite by topotactical reaction [21,22]. Additionally, an amorphous band in the $2\theta = 10^{\circ}$ and 35° ranges can be observed. This is due to the formation of a viscous liquid phase at the ternary eutectic temperature, which is then cooled to glass. XRD patterns of specimens containing petroleum oily sludge (MC3 formulation) are shown in Fig. 6. In addition to mullite and quartz, characteristic peaks of barite ($BaSO_4$; JCPDS-ICDD card: 02-1199), hematite (Fe_2O_3; JCPDS-ICDD card: 33-0664), and anhydrite calcium sulphate ($CaSO_4$; JCPDS-ICDD card: 03-0368) were identified. Thus, the partial replacement of kaolin with solid petroleum oily sludge influenced the phase evolution of the vitrified floor tiles. Despite this, as shown in Fig. 7, the formulations are all within the quartz–albite–mullite triangle of compactibility (i.e., SiO_2–$NaAlSi_3O_8$–$3Al_2O_32SiO_2$) and the mullite primary phase field .

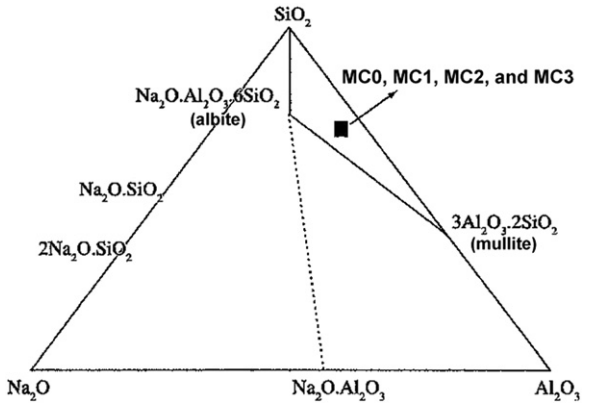

Fig. 7. Floor tile formulations plotted in the ternary phase diagram of SiO_2–Al_2O_3–Na_2O system.

SEM micrographs of the fractured surfaces of MC3 samples fired at various temperatures are shown in Fig. 8 a–d. They show the typical microstructural evolution of the MC3 formulation (with 5 wt% oily sludge) as firing temperature increases. Between 1200 and 1230 °C (Fig. 8a–c), the specimens exhibits an advanced sintering stage. In this temperature range the sintered microstructure is characterized by few nearly spherical isolated pores and signs of high vitrification. At 1240 °C (Fig. 8d), however, the structure is highly porous. In this case, the swelling of pores within the structure occurred. Larger and more irregular pores can be observed.

The densification behavior of the tile pieces is described by the gresification diagram (Fig. 9a–d). This diagram shows the effects of the petroleum oily sludge addition and firing temperature on the densification of floor tile bodies. The gresification diagram of the MCO formulation, as shown in Fig. 9a, indicates that the water absorption decreases and the linear shrinkage increases continuously with the firing temperature. This is related to the formation of an abundant liquid phase that infiltrates the open pores of the structure and causes densification via liquid phase sintering. The predominant sintering mechanism is viscous flow [23]. The tile pieces exhibited linear shrinkage values between 6.7% and 8.2%, which are in accordance with the limits recommended for floor tile production. In addition, the floor tile pieces reach only 0.08% of water absorption at 1240 °C and 1250 °C. It can also be noticed that the densification behavior (Fig. 9a–d) depends substantially on the petroleum oily sludge content. In general, higher petroleum oily sludge content tends to retard densification during firing. This behavior can be caused by two combined

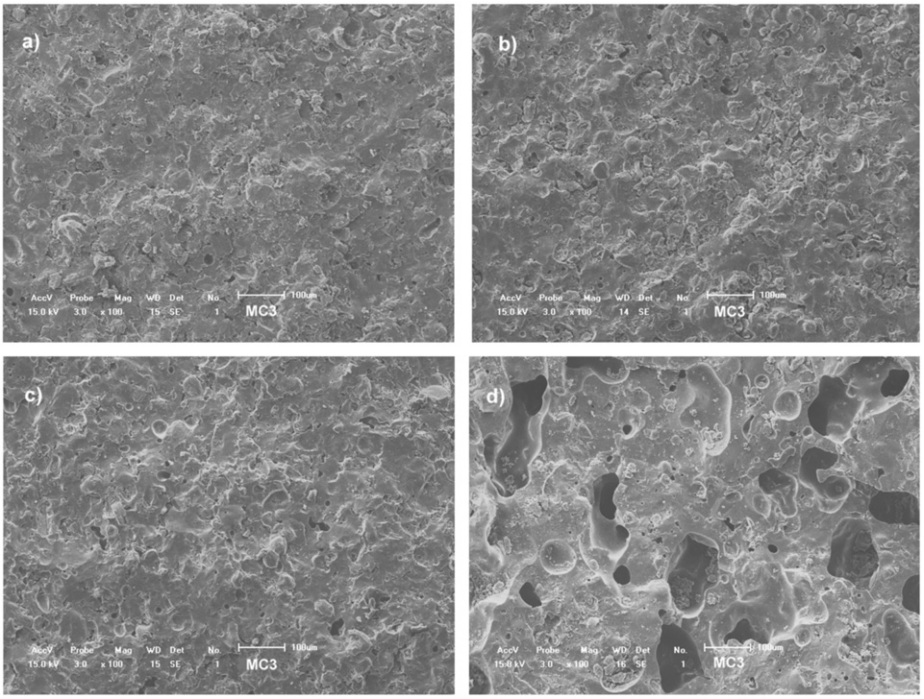

Fig. 8. SEM micrographs of fired specimens (MC3 formulation): (a) 1200 °C; (b) 1220 °C; (c) 1230 °C; and (d) 1240 °C.

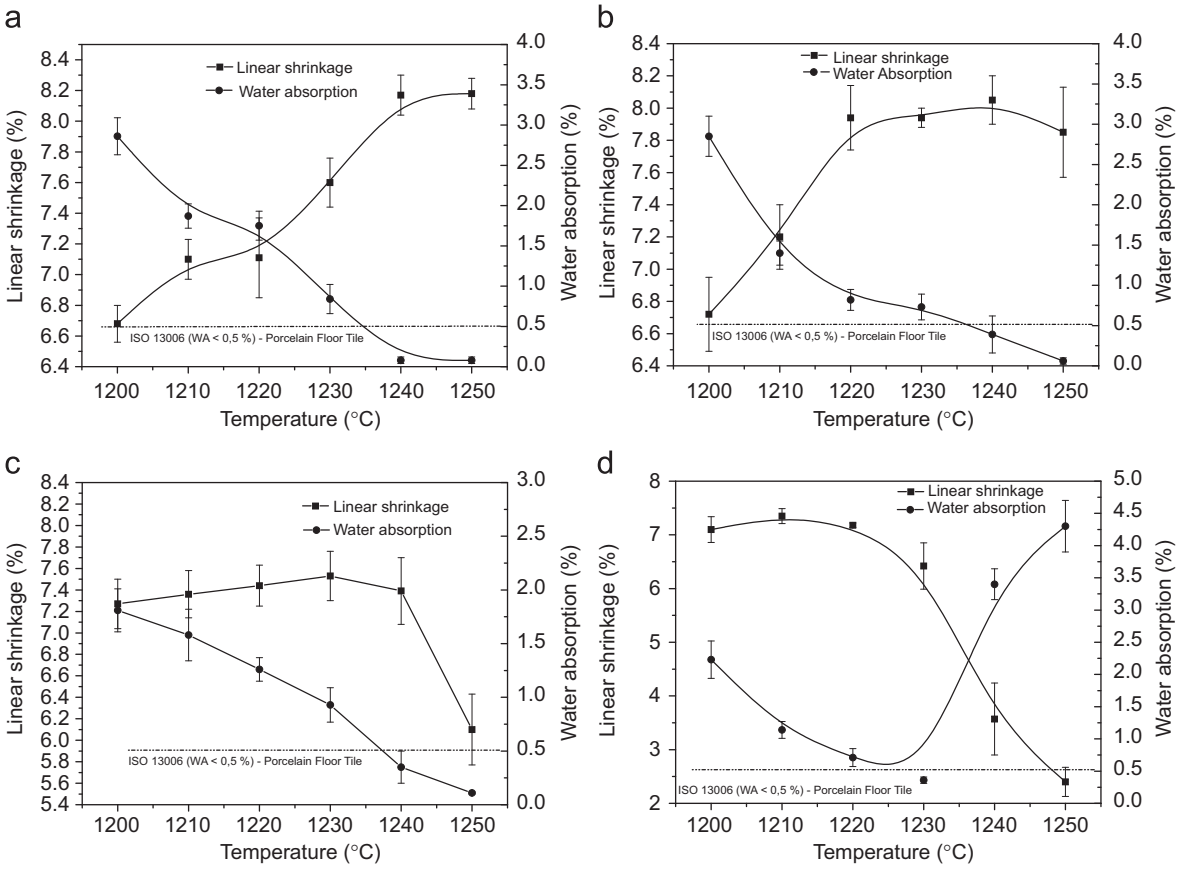

Fig. 9. Gresification diagram of the fired tile pieces: (a) MC0; (b) MC1; (c) MC2; and (d) MC3.

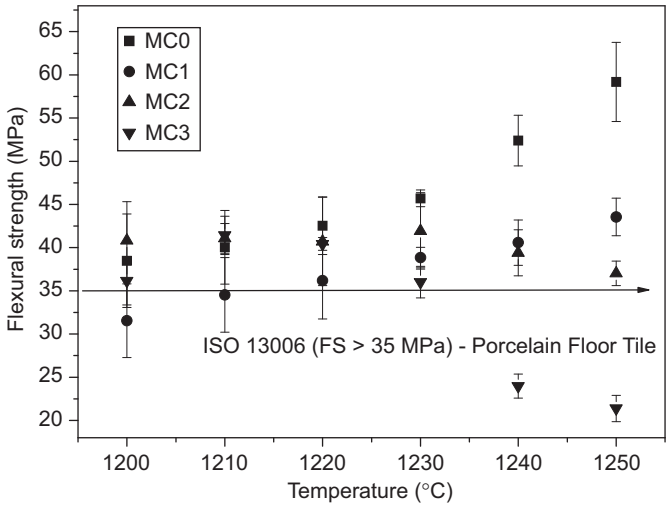

Fig. 10. Flexural strength as a function of petroleum oily sludge content and firing temperature.

effects: (i) the incorporation of higher concentration of non-plastic mineral particles into the tile formulation; and (ii) volatization of hydrocarbons (oil) of the petroleum oily sludge that generates pores, resulting in structure expansion. This effect limits the addition of petroleum oily sludge in replacement of kaolin.

The flexural strength of the fired tile pieces is shown in Fig. 10. The mechanical behavior is quite correlated with the microstructure and other studied properties. The floor tile pieces exhibited flexural strength values within the 21.4–59.2 MPa range. The flexural strength of the MC0 and MC1 formulations increases continuously with the increasing firing temperature. This is essentially due to the higher amount of glassy phase formed during firing, which decreases the open porosity of the tile pieces. On the other hand, the flexural strength of the MC1 formulation was lower than that of the MC0 formulation (reference formulation). This result is likely related to the higher porosity of the tile pieces containing petroleum oily sludge. For the MC2 formulation, the flexural strength presented only slight variation within the dispersion limits up to 1240 °C, and then tends to decrease at 1250 °C. For the MC3 formulation, the flexural strength presented only slight variation within the dispersion limits up to 1230 °C. Above 1230 °C, however, a significant decrease in the values of flexural strength was observed. This effect is likely to be a result of gas trapped (gas bubbles) in the glassy phase during firing, resulting in closed porosity and structure expansion [16]. This behavior agrees with the observation of the structures (Fig. 8d).

Water absorption and flexural strength are properties which, according to the International Standard ISO 13006

Table 5
Classification of the floor tiles containing petroleum oily sludge.

Formulation	1200 °C	1210 °C	1220 °C	1230 °C	1240 °C	1250 °C
MC0	BIb	BIb	BIb	BIb	BIa	BIa
MC1	BIb	BIb	BIb	BIb	BIa	BIa
MC2	BIb	BIb	BIb	BIb	BIa	BIa
MC3	BIb	BIb	BIb	BIa	BIIa	BIIa

[24], define the class to which any tile products belong. As can be seen in Figs. 9 and 10, the partial replacement of kaolin with petroleum oily sludge produced floor tiles with excellent technical properties. More specifically, porcelain floor tile (ISO standard 13006 Group—BIa) could be produced with the formulations MC0, MC1, and MC2 fired between 1240 °C and 1250 °C and formulation MC3 fired at 1230 °C. This is very important because the petroleum oily sludge can be used as an alternative low cost raw material in floor tile compositions. This petroleum oily sludge reuse would prevent the negative environmental impact associated with final disposal of this pollutant waste (Table 5).

4. Conclusions

The following conclusions may be drawn from the experimental results and their discussion.

It has been established that the partial replacement of kaolin with petroleum oily sludge, in the range up to 5 wt%, allows the production of vitrified floor tile with good technical properties. The main effect concerning the addition of petroleum oily sludge was the change of mineralogical composition (quartz, barite, calcium sulfate, and hydrocarbons) in the tile formulations.

It was found that the addition of petroleum oily sludge tends to retard the densification process mainly over 2.5 wt% oily sludge, as observed by the linear shrinkage, water absorption, and flexural strength tests. Important morphological changes and phase composition during the firing process of the floor tile formulations were observed. The floor tile pieces also presented, for all formulations, good dimensional stability with linear shrinkage values between 6.7% and 8.2% for a wide firing temperature range.

The specified requirements for porcelain floor tile (ISO standard 13006—Group BIa) were obtained for the following tested formulations: (i) MC_0, MC_1, and MC_2 for 1240 °C and 1250 °C; (ii) and MC3 for 1230 °C.

Acknowledgments

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