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Densification behaviour of petroleum waste bearing clay-based ceramic bodies

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Abstract

Processing of petroleum waste bearing clay-based ceramic bodies for application in structural ceramic products is described. Oily wastes are produced from oil rigs during the liquid/solid impurities separation step. The waste was added in gradual proportions to a kaolinitic clay from zero up to 20 wt.%, in order to study its effect on the densification behaviour of the fired samples (linear shrinkage, water absorption and apparent density). Ultimate compressive strength has been also assessed. The samples were unidirectional dry pressed in a cylindrical steel die and fired at temperatures ranging from 750 to 1100 °C. XRD and SEM were used to identify the present phases and degree of densification. The results revealed that the petroleum waste added was responsible for the inclusion of barite and quartz particles to the clay powder. The densification behavior was found to be influenced by the petroleum waste added. Significant morphological changes and phase transformations occurred during sintering.

1. Introduction

Special attention has been recently devoted to the process of waste minimization, pollution prevention and self-sustainable development as applied to the materials field [1–3].

The petroleum industry produces a great amount of waste materials in its four principal areas [4]: (i) extraction of crude oil from the ground, (ii) conveyance to refineries and product distribution centers, (iii) refining into finished products, and (iv) marketing or selling. Those wastes are basically made up of complex mixtures of hydrocarbons in the form of oil, water and solids in different proportions according to each area. Thus, the use of different waste minimization technologies for final disposal is necessary.

Campos-RJ county (Brazil) has the largest Brazilian oil basin, which is responsible for more than 80% of the national oil production. However, during the processes of exploration and extraction of oil and gas from beneath the ocean floor, great amount of an oily sludge is produced. This waste in particular is sealed in tanks and brought to land to be mixed with an encapsulating agent, hydrophilic bentonite. Yet less harmful, the resulting material cannot be simply disposed in landfills or just pilled up. Potential adverse impacts of improper disposal of petroleum wastes include: (i) pollution of the marine environment, (ii) surface soil and water degradation, and (iii) groundwater contamination. As a consequence, efforts have been made to find a permanent solution for the management of the referred waste, without causing major risks to the environment. The development of new technologies for petroleum waste recycling, which are consistent with the current needs is of high economic and environmental interest. In previous works [5,6], it has been shown that petroleum waste–clay mixtures have potential application in clay-based products. However, the densification behaviour during the firing step, which is a complex process, is not still thoroughly understood.

The main aim of the work reported in this paper is to investigate the densification behaviour of ceramic bodies containing petroleum waste. Emphasis is given to the powder characteristics, their effects on the physical-

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mechanical properties of the end product, and the microstructural evolution of the pressed specimens during densification.

2. Experimental procedure

A series of waste-clay powder mixtures with waste additions up to 20 wt.% have been prepared (Table 1). The kaolinitic clay powder utilized is chemically constituted by SiO_2 (42.75 wt.%), Al_2O_3 (32.60 wt.%), Fe_2O_3 (8.71 wt.%), TiO_2 (1.32 wt.%), MnO (0.03 wt.%), MgO (0.77 wt.%), CaO (0.11 wt.%), K_2O (1.24 wt.%), Na_2O (0.32 wt.%) and an ignition loss of 12.05 wt.%. The oil sludge waste composition[6] in average consists of solid material (62.0 wt.%) such as clay minerals, silt, sand and barite ($BaSO_4$), water (21.0 wt.%), oil (16.0 wt.%), others (1.0 wt.%).

The waste-clay mixtures prepared were characterized by X-ray diffraction (URD-65 Diffractometer, Seifert), using monochromatic Cu-K_α radiation over non-oriented specimens. Scanning speed was set to 1.5° (2θ)/min. The phases were identified from peak positions and intensities using reference data from the JCPDS handbook [7]. Particles size analysis of the samples was determined by procedures according to NBR 7181-84. Plastic properties were determined according to the NBR 6459-84 and NBR 7180-84 standardized procedures.

Specimens were prepared by uniaxial pressing technique in a 10 mm diameter steel die at 25 MPa. The resulting 10 × 10 mm cylindrical pellets were dried at 110 °C for 24 h. The firing step was carried out at soaking temperatures varying from 750 to 1150 °C for 1h. The heating rate until 600 °C was 2 °C/min, followed by a 1 h hold at 600 °C, and 10 °C/min until maximum temperature.

The densification behaviour was described in terms of linear shrinkage, water absorption and apparent density. Linear shrinkage values upon drying and firing were evaluated from the variation of the length of the cylindrical pellets. Water absorption values were determined from the weight differences between the as-fired and water saturated samples (immersed in boiling water for 2 h). The apparent density values were determined by the Archimedes method of immersion in water.

Table 1
Mix compositions of the prepared batches (wt.%)

Raw materials	No.				
	M1	M2	M3	M4	M5
Clay	100	95	90	85	80
Waste	0	5	10	15	20

Diametrical compressing strength [8–10] have been also determined. An universal testing machine (model 5582, Instron) was used and both contact plates were covered with latex sheet. Crossbar speed was hold at 0.5 mm/min for all tests. A PC displayed real time load versus displacement. The ultimate compressive load just prior to collapsing of the pellets was recorded. All as-fired specimens dimensions were measured and used to determine individual ultimate compressive strengths.

The phase identification of the fired ceramic specimens was performed by X-ray diffractometry. The sintered microstructure was observed by scanning electron microscopy (DSM 962, Zeiss). Secondary electrons (SE), back-scattered electrons (BS) and EDS were used to identify the constituent phases.

3. Results and discussion

The XRD patterns of the waste-clay mixed powders are shown in Fig. 1. The waste-free sample (0 wt.%) presents peaks, which are characteristics of the kaolinite as the principal clay mineral. Moreover, small amounts of illite/mica, quartz, gibbsite and goethite were detected by the XRD analysis. It can be clearly observed from Fig. 1 that barite or barium sulfate is incorporated to the clayey powder with waste additions. Barite is a universal component of suspended matter in the oceans and have a biogenic origin [11]. However, the barite observed is probably related to the drilling fluid employed in the process of exploring and extracting oil and gas from beneath the ocean floor. This material is used because its high density makes it suitable for controlling hydrostatic pressure [12].

Particles size distribution data are shown in Table 2. The clay fraction varies from 47.0 to 57.0 wt.%, followed by silt from 36.4 to 39.1 wt.%, sand from 6.6 to 13.9 wt.%. It was also observed that the clay fraction content is reduced with increasing waste additions. In

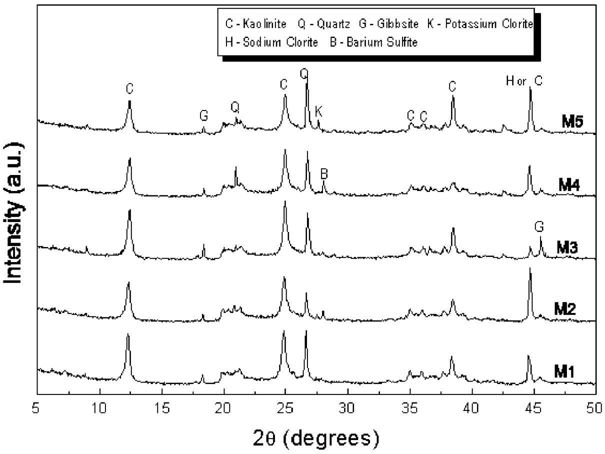


Fig. 1. X-ray diffraction patters for the prepared batches.

contrast to the clay fraction, the sand content is increased. This result is probably related to the addition of particles such as barite. Besides barite particles, the waste presents appreciable amounts of quartz [6]. These materials are non-plastic and influence the overall plasticity of the mixes, as shown in Table 3. The plasticity index was reduced from 44 to 29%. Nonetheless, all the waste-clay system powders presented an adequate consistency state to the manufacture of clay-based products [13].

Densification was monitored by measuring three physical parameters: linear shrinkage, water absorption and apparent density. Fig. 2 shows the linear shrinkage of the specimens as a function of waste percent for all range of firing temperatures. It can be noticed a

Table 2
Particle size distribution of prepared batches (wt.%)

Batches	Clay (<2 μm)	Silt ($2 \leqslant x < 60$ μm)	Sand ($60 \leqslant x < 600$ μm)
M1	57	36.4	6.6
M2	56	37.2	6.8
M3	54	38.5	7.5
M4	50	38.5	11.5
M5	47	39.1	13.9

Table 3
Atterbergs consistency limits for prepared batches

Batches	Plastic limit (%)	Liquid limit (%)	Plasticity index (%)
M1	69	25	44
M2	64	28	36
M3	62	27	35
M4	56	26	30
M5	53	24	29

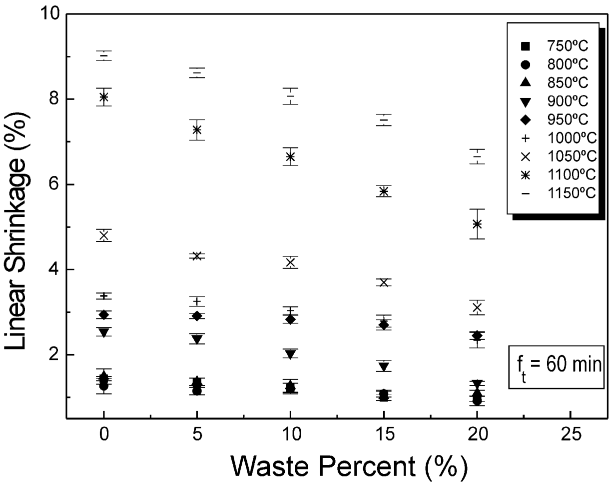


Fig. 2. Linear shrinkage as a function of waste content and firing temperature.

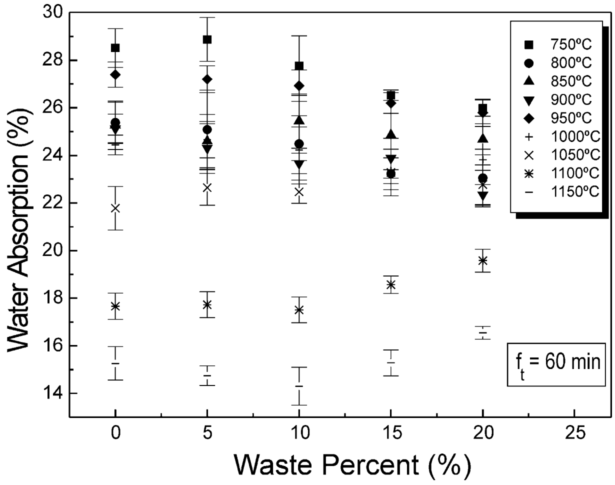


Fig. 3. Water absorption as a function of waste content and firing temperature.

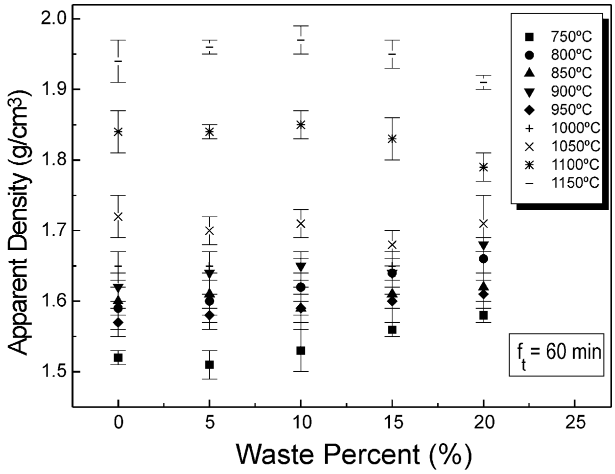


Fig. 4. Apparent density as a function of waste content and firing temperature.

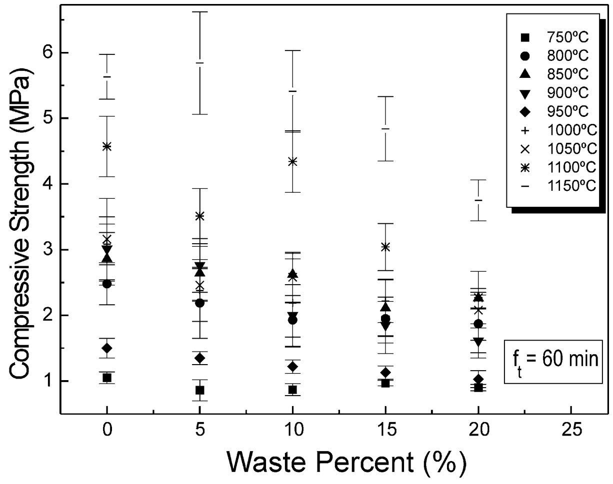
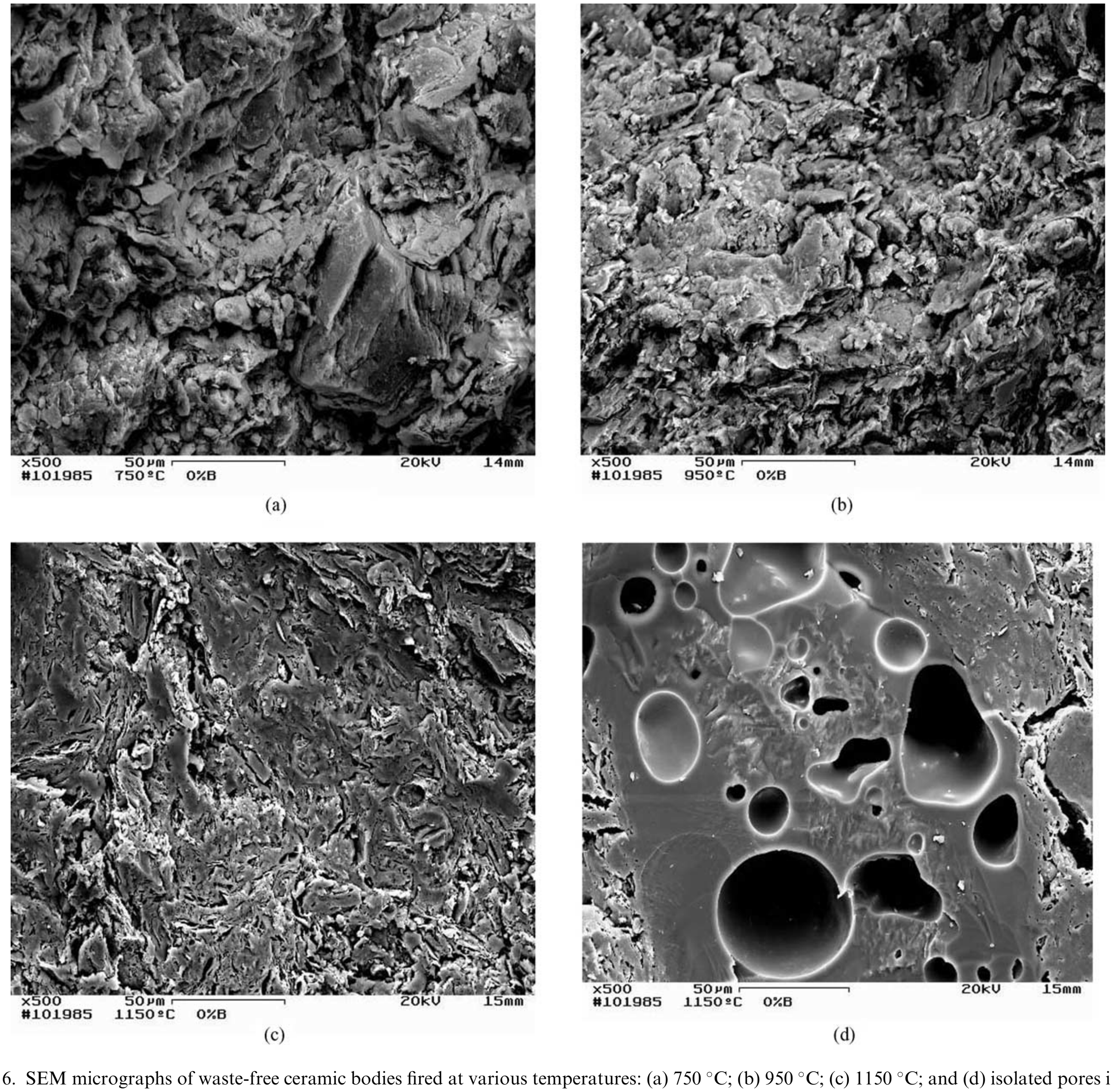


Fig. 5. Compressive strength as a function of waste content and firing temperature.

decrease in shrinkage as the petroleum waste is added. This effect is more noticeable at higher temperatures. Accordingly, the more the waste is added, the less shrinkage is undergone by the ceramic bodies, which means that non-plastic components of the waste (barite and quartz) are playing a major role. These materials do not suffer the same physical-chemical reactions as the clay minerals. In fact, this is a positive result regarding to the decrease in dimensional change by the ceramic body on firing. As a result, an overall decrease of shrinkage, followed by a better dimensional control of the finished ceramic products can be expected by the manufacturer. Moreover, the obtained shrinkage values (0.92–9.02%) for the waste containing bodies are within the limits for industrial production. The role of the temperature was to raise the linear shrinkage of the bodies, essentially above 1000 °C, probably due to glassy phase formation onset.

Fig. 3 shows the water absorption variation with the waste percent and firing temperature. The water absorption decreased with waste addition, until 1000 °C. At 1050 °C this parameter did not reveal any significant variation, raising above 1100 °C and 1150 °C. Therefore, the waste addition decreased the porosity of the ceramic bodies up to 1000, and had its effect inverted above this temperature, raising the porosity. An explanation for this behaviour can be related to the glassy phase formation above 1000 °C leading to a finer and



(a) (b)

(c) (d)

Fig. 6. SEM micrographs of waste-free ceramic bodies fired at various temperatures: (a) 750 °C; (b) 950 °C; (c) 1150 °C; and (d) isolated pores in the vitrified matrix.

more densified microstructure. This microstructure is more susceptible to crack formation and waste bearing particle unattachment, leading to porosity. Thus, the temperature had a intricate effect on the water absorption of the ceramic bodies, although its major role was to diminish this parameter, and consequently the porosity of the fired bodies mainly above 1000 °C. Water absorption is a parameter, which according to Brazilian standard specifications [14], defines the class to which any clay-based products suit. Thus, the water absorption parameter appears to be of crucial importance to this densification study. The specified values of water absorption (wa) are: facing bricks and ceramic blocks ($w_a < 25\%$), and roofing tiles ($w_a < 20\%$). As shown in Fig. 3 the waste containing bodies present values of water absorption below 25% to temperatures above 750 °C, indicating their conformity to facing bricks and ceramic blocks. Roofing tile specification is attained only above 1050 °C for all batches. The fired density of the pellets is shown as a function of waste percent and firing temperature in Fig. 4. The complex variation of density is very similar to that observed for the water absorption.

The ultimate compressive strength of the fired bodies as a function of waste percent and firing temperature is shown in Fig. 5. It can be observed that, for all temperatures, the compressive strength decreased with the waste addition. Until 950 °C, this decreasing was minor, being noticeable between 950 and 1050 °C, and even more expressive above 1050 °C. It is possible that the waste components such as barite and quartz may be responsible for the impaired mechanical strength of the fired ceramic bodies. The effect of the temperature was to increase the compressive strength by means of densification, although imposing slight compressive strength variations with the waste addition, as previously discussed. Moreover, the results suggest a correlation between the values of compressive strength and water absorption of the fired bodies.

In order to enlighten the ceramic bodies behaviour on firing, the as-tested surface morphology of waste-free ceramic bodies fired at 750, 950 and 1150 °C are presented in Fig. 6(a)–(d), respectively. At 750 °C (Fig. 6a), the morphology is coarse with loose particles and large pores. A finer morphology is found at 950 °C (Fig. 6b), showing well bound aggregates rather than detached particles. It seems also that a glassy phase starts to emerge. At 1150 °C (Fig. 6c) the morphology is definitely compact, revealing a welded texture embedded in the glassy phase. In fact, at this temperature a dense and well-developed structure (Fig. 6d) is formed. Pores become isolated and nearly spherical, which is characteristic of the viscous flow sintering mechanism [15]. Some pores can also be related to the entrapped gas originated during the fabrication process of the pellets. Fig. 7 shows the fractured surface of waste added ceramic pellet (sample M5) fired at 950 °C. As can be observed, waste-containing pellets had a microstructure similar to that of waste-free pellets (Fig. 6b), except for the presence of barite particles. These particles are the brighter particles in the SEM micrograph by using back-

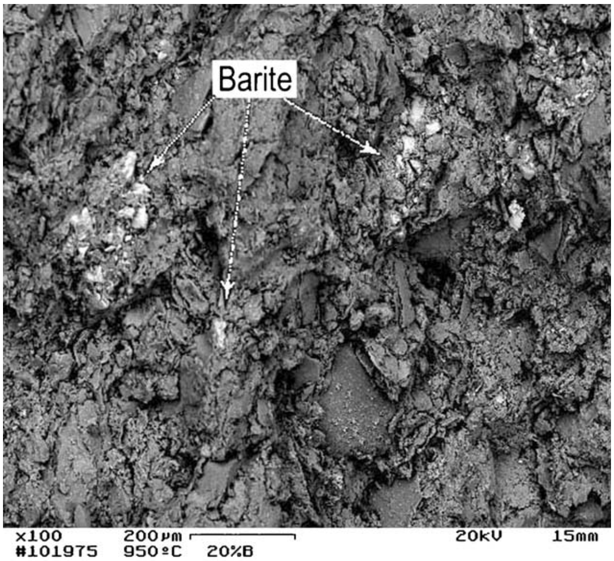


Fig. 7. SEM/BSE micrograph of waste containing pellet (Batch M5) fired at 950 °C.

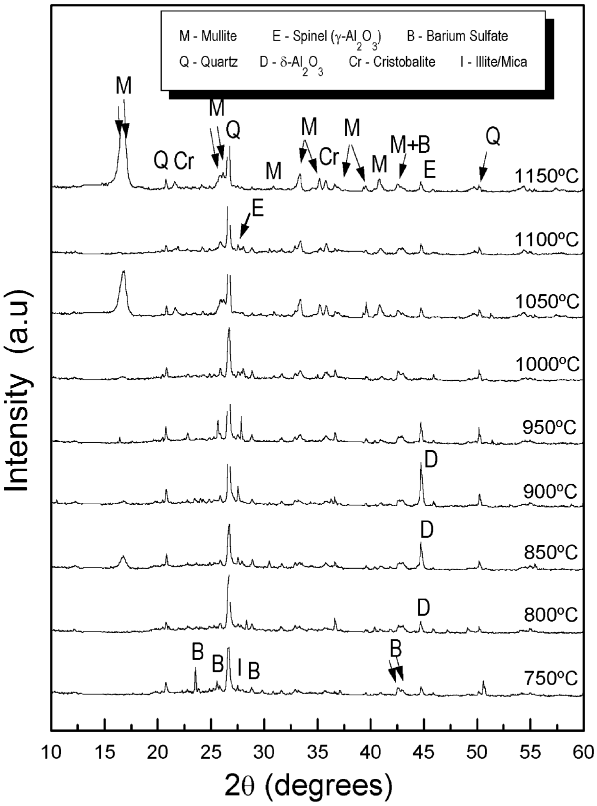


Fig. 8. X-ray diffraction patterns for the batch M5 fired at various temperatures.

scattered electrons. Thus, the presence of non-plastic mineral impurities provided by the waste may be more deleterious to the fired ceramic bodies when the morphology depicts a finer texture, once at lower firing temperatures the coarser texture renders itself the material a limited strength.

Besides the glassy phase formation, the microstructural evolution of the ceramic bodies on firing exhibits phase transformations. XRD patterns of the 20 wt.% waste added powder specimens heat treated at various temperatures are shown in Fig. 8. From previous XRD patterns (Fig. 1), the 20 wt.% waste added powder pellets underwent a series of phase transformations as the temperature was raised from room temperature to 1150 °C. At 750 °C only quartz, barite and illite/mica peaks appear, the former and the later being present at all firing temperatures. At this temperature, kaolinite has already been transformed into amorphous phase matakaolinite [16–19]. In addition, the sintering is dominated by particle-to-particle contact mainly of metakaolinite platelets, which makes a more open porous structure in the fired pellet. At 950 °C, 2:1 primary mullite and γ-Al_2O_3 spinel small peaks can be observed, and illite/mica begins to disappear. However, there are still questions regarding the formation of those phases [20,21]. Vitrification (formation of glassy phase) should probably be in progress at this temperature. From 1050 to 1150 °C cristoballite crystallizes and mullite and γ-Al_2O_3 spinel peaks remain.

4. Conclusions

From the results presented above the following conclusions can be drawn. It has been established that the petroleum waste added influenced the characteristic properties of the clay. The main effect concerning the addition of petroleum waste was the inclusion of barite and quartz particles in the clay matrix.

The densification was also influenced by the petroleum waste. The presence of barite and quartz particles in some extent is detrimental to densification, mainly over 5 wt.%, as observed by water absorption tests. Although the specifications for facing bricks, ceramic blocks and roofing tiles have been achieved at some temperatures, it was observed that the mechanical strength was severely reduced. Thus, this study suggests that the limit for petroleum waste addition should be 5 wt.% for the manufacturing of clay-based products.

Important morphological changes and phase transformations during the sintering process of the ceramic bodies were observed. Kaolinite dehydroxylation, formation of primary mullite, γ-Al_2O_3 spinel and cristoballite have been observed. Glassy phase formation had an important role in the densification of the ceramic bodies.

Acknowledgements

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