Characteristics and physical-mechanical properties of fired kaolinitic materials
(Características e propriedades físico-mecânicas de materiais cauliníticos queimados)

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Abstract

This work presents the results of a study on the suitability of the clayey materials from Campos-RJ (Brazil) region for application in structural ceramic. The clayey materials, i.e. red clays available in this region, were selected so that their characteristics regarding chemical composition, rational analysis, X-ray diffraction, particle size analysis, thermal behavior, plasticity and as dried and fired properties could be studied. The results revealed that the studied samples are typically kaolinite based materials. In addition, it was found that almost all properties of these materials are led to the manufacture of structural ceramic. Mechanical strength test data resulted in Weibull distributions.
Keywords: Characterization, kaolinitic materials, properties.

Resumo

Este trabalho mostra os resultados de um estudo sobre a adequação dos materiais argilosos da região de Campos-RJ (Brasil) para aplicação em cerâmica estrutural. Os materiais argilosos, isto é, argilas vermelhas disponíveis nesta região foram selecionadas tal que suas características com respeito a composição química, análise racional, difração de raios X, análise de tamanho de partículas, comportamento térmico, plasticidade e as propriedades de secagem e queima pudessem ser estudadas. Os resultados revelaram que as amostras estudadas são tipicamente materiais à base de caulinita. Além do mais, foi determinado que quase todas as propriedades destes materiais são direcionadas para fabricação de cerâmica estrutural. Os dados de resistência mecânica resultaram em distribuição de Weibull.
***Palavras-chave**: Caracterização, materiais cauliníticos, propriedades.*

INTRODUCTION

There are important sedimentary environment originated clayey materials deposits in South-Eastern Brazil (Campos-RJ). The local ceramic industry, which assembles about 110 plants, is mainly based on the manufacturing of structural ceramic products, such as filled and hollow floor bricks, roofing tiles and facing bricks. Only three plants effectively produce roofing tiles, and only one produces rustic floor tiles. The net annual mean production of Campos-RJ ceramic industry is around 2000000 tons. Thus, these clayey materials deposits are of high interest from a technical-economical point of view.

The local plants have empirically exploited these clayey materials deposits. Nevertheless, there is little information on the characteristics and properties of these materials [1-3]. As a consequence, the final products generally present minor quality. However, it is known fact that in developed countries [4, 5], thorough physical-chemical-mechanical understanding of clayey materials is considered the most essential step before processing them into any tailor-made product. Thus, it is very important to perform an extensive characterization of these materials in order of generate more knowledgment, which can contribute for obtaining of enhanced properties.

The main aim of this work is to study individually five clayey materials samples used by Campos-RJ region plants. Emphasis is given to the chemical-mineralogical-physical characteristics, and their physical-mechanical properties, with special reference to the suitability of these materials for manufacturing of clay based structural ceramic. A wide range of techniques was employed, including X-ray diffraction (XRD), thermogravimetry (TG), differential thermal analysis (DTA), atomic emission spectrophotometry (AES), dilatometry and three point bending testing.

MATERIALS AND METHODS

Five clayey materials samples were collected from deposits located in South-Eastern Brazil (Campos-RJ). These deposits are representative and widely used by ceramic plants for the production of clay based structural ceramics.

Chemical analysis of the clayey powders was determined by atomic emission spectrophotometry with inductively coupled plasma (ICP-AES instrument, ARL-3410). Mineralogical analysis was done by DRX (URD-65 Diffractometer, Seifert) with Cu-k_α radiation on non-oriented clay specimens.

TGA/DTG/DTA were carried out on the as-received samples (SDT-2960 Simultaneous TGA-DTA, TA Instruments) under air atmosphere from room temperature up to 1150 ºC at a heating rate of 10 ºC/min. Dilatometric analyses of rectangular samples (35.7 x 7 x 7 mm^3) were taken within the 5 ºC-1000 ºC range using a heating rate of 5 ºC/min under air atmosphere (RB-115 Dilatometer, BP Engineering).

Particle size analysis of the samples was determined by the combination of sieving and sedimentation procedures according to NBR 7181-84. Atterberg limits were determined according to the NBR 6459-84 and NBR 7180-84 standardized procedures.

Clayey masses (- 20 mesh) after drying at 110 ºC for 24 h were humidified to 7.0% (moisture mass / dry mass) and kept enclosed in a disecator for 24 h.

Rectangular ceramic bodies (115 x 25.4 x 10 mm^3) were obtained by uniaxial pressing at 2400 N/mm^2. After pressing, the green ceramic bodies were dried (24 h at 110 ºC) and slowly fired in a muffle type electric furnace (24 h cold to cold; maximum temperatures of 850 ºC, 950 ºC and 1050 ºC). The choice for these applied firing temperatures is related to the fact that plants in Campos-RJ region burn their products close to that range of temperature, depending on the employed energy source. The following properties as-fired have been determined: linear shrinkage, water absorption and apparent density. In addition, the flexural strength (σ) was determined by three-point bending test (model 1125, Instron) at a loading rate of 0.5 mm/min according to

$$\sigma = 3 PL / 2bd^2 \qquad (A)$$

where P is the load at rupture, L is the distance between supports, b is the specimen width, and d its thickness.

The fracture strength data after firing for each sample was treated by means of Weibull Statistics [6, 7], which is based on the extreme value theory. The sampling size used was N=30. The fracture probability (F) was determined according to the method of accumulated distribution of symmetric samples, using a probability estimator F = (i-0.5)/N, where i is the ith specimen and N is the total number of specimens.

RESULTS AND DISCUSSION

Chemical composition of the studied materials is shown in Table I. In this table the percentages of SiO_2, Al_2O_3 and loss on ignition are comparatively reported to reference kaolinite ($Al_2O_3.2SiO_2.2H_2O$). Among the chief elements, SiO_2 varies from 40.24 to 46.88, Al_2O_3 from 26.92 to 34.29 and Fe_2O_3 as Fe^{3+} [8] from 9.91 to 16.22. With respect to the less frequent components, their variation is smaller: TiO_2 (1.13-1.34), MgO (0.62-0.94) and K_2O+Na_2O (1.32-1.82). The content of Fe_2O_3 is high, which characterizes the studied clayey materials as red clays. Alkaline fluxes contents (K_2O + Na_2O) are low. MgO and CaO contents indicate that these clayey materials are non-carbonatic. The losses on ignition correspond to the reference kaolinite value (Table I).

X-ray diffractograms of the studied materials are shown in Fig. 1. The materials are mainly constituted by clay minerals, quartz and gibbsite. The clay minerals are a mixture of kaolinite and illite/mica with predominance of kaolinite. It was also identified potassium feldspar and goethite. Rational mineralogical composition analysis [9] showed that they contained: kaolinite (63.3% - 81.8%), mica moscuvite (7.7% - 12.0%), silica (4.7% - 17.5%), and gibbsite (4.8% - 7.2%). Because of their composition, throughout this paper the studied clayey materials are referred to as kaolinitic materials.

DTA curves of all samples are shown in Fig. 2. It can be seen that the investigated polymineralic kaolinitic materials exhibited three characteristic endothermic peaks within the 60.0 ºC-63.7 ºC, 267.8 ºC-275.8 ºC and 499.3 ºC-503.2 ºC temperature ranges. These events are associated to removal of adsorbed physically water, removal of gibbsite crystallization water, and dehydroxylation of the silicate lattice leading to the formation of metakaolinite, respectively. An exothermic peak within the 949.5 ºC - 959.0 ºC range observed for all samples was due probably to the formation of new crystalline phases such as a Si-containing γ-Al_2O_3 with spinel structure or a 2:1 mullite [10,11]. In addition, the endothermic events are accompanied by mass loss as shown in the TG/DTG curves (Fig. 3).

Dilatometric curves (Fig. 4) indicated that the materials exhibited

Table I - Normalized chemical compositions (wt%) of the kaolinitic materials.
[Tabela I - Composições químicas normalizadas dos materiais cauliníticos (% em peso).]

Sample	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	MgO	CaO	K_2O	Na_2O	LOI
CAM1	46.88	26.92	9.91	1.20	0.04	0.94	0.23	1.53	0.29	12.05
CAM2	40.24	34.29	8.21	1.34	0.02	0.62	0.12	0.97	0.35	13.83
CAM3	41.54	26.49	16.22	1.13	0.06	0.64	0.15	1.21	0.32	12.25
CAM4	42.09	30.90	10.92	1.28	0.03	0.74	0.13	1.04	0.32	12.55
CAM5	42.73	32.40	8.61	1.32	0.03	0.77	0.11	1.24	0.28	12.50
Kaolinite	46.55	39.50								13.95

LOI = Loss on ignition

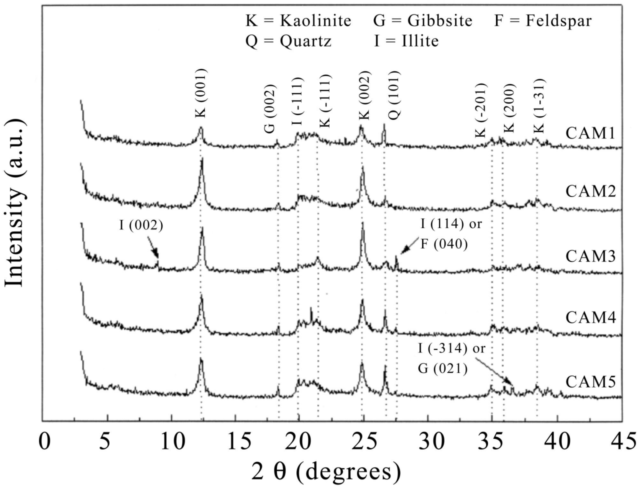

Figure 1: X-ray diffraction patterns for powders of kaolinitic materials.
[Figura 1: Difratogramas de raios X para os materiais cauliníticos.]

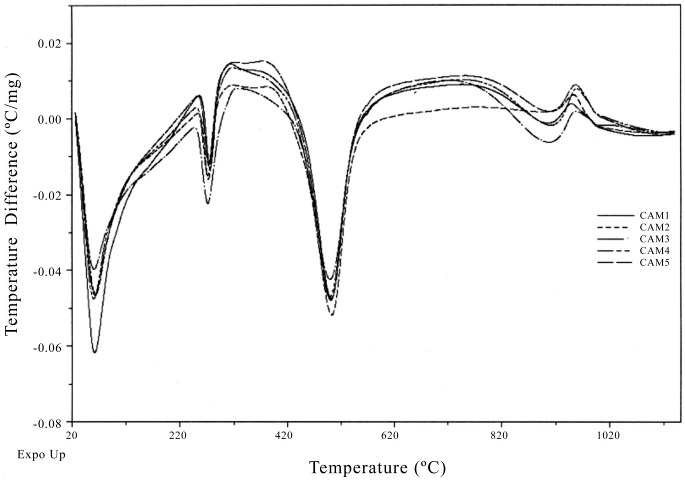

Figure 2: DTA curves for the kaolinitic materials.
[Figura 2: Curvas de DTA para as amostras de materiais cauliníticos.]

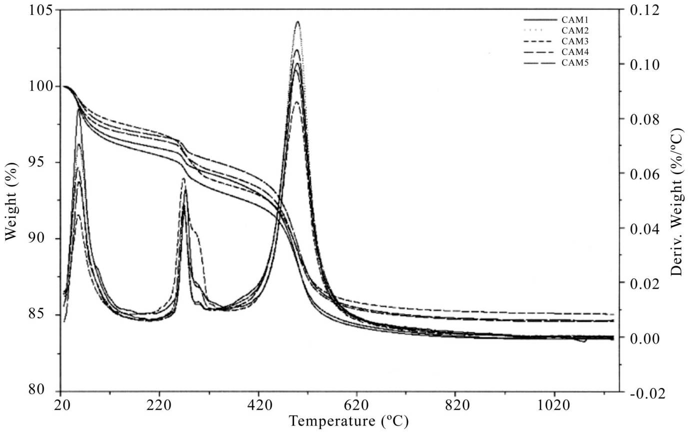

Figure 3: TG-DTG curves for the kaolinitic materials.
[Figura 3: Curvas TG-DTG para as amostras de materiais cauliníticos.]

a typical behavior of kaolinitic clays [12]. As it can be noticed, the dilatometric curves shown are apparently quite similar among themselves. The slight differences between them should be mainly attributed to dissimilar proportions of the major clay mineral (kaolinite). In general, it can be observed a expansion up to 500 ºC followed by three shrinkages at 500 ºC-650 ºC, 650 ºC-950 ºC and above 950 ºC. The first shrinkage may be due to metakaolinite formation with concomitant loss of water. The second shrinkage is less harsh, and can be attributed to particles sintering. The third shrinkage seems to be due the recrystallization of new ceramic phases and vitrification.

Particle size distribution data are shown in Table II. The results revealed that all samples consisted of a finely ground material in the range of 2-200 µm. The clay fraction varies from 42% to 70%, followed by silt from 25% to 43% and sand from 5.0% to 18.0%. When plotted in the Winckler's diagram [13] as shown in Fig. 5, the granulometric data from the samples CAM1 and CAM3 showed consistence as adequate raw-material for obtaining high quality ceramic products. The other samples are placed out of the characteristic fields for ceramics products. Therefore, it is essential that manufacturers assign mixtures from distinct materials types, in order to obtain clay based products with desired properties.

Plastic properties of the kaolinitic materials are presented in Table III. The plastic limit (water of plasticity) varies from 25 % to 30%, liquid limit from 65% to 70%, and the plasticity index from 35% to 44%. In terms of soils mechanical these materials may be classified as belonging to the group of high plasticity inorganic clays [14]. In the dried state (Table IV), the specimens

Table II - Particle size distribution of the kaolinitic materials.
[Tabela II - Distribuição de tamanho de partículas para os materiais cauliníticos.]

Samples	% sand (µm)			% silt (µm)			% clay	% fraction		Density
	fine	medium	gross	fine	medium	gross	(<2 µm)	(2-20 µm)	(>20 µm)	(g/cm³)
CAM1	12.0	3.0	-	20	16	7	42	36	22.0	2.65
CAM2	5.0	-	-	12	8	5	70	20	10.0	2.54
CAM3	17.0	1.0	-	16	16	6	44	32	24.0	2.57
CAM4	6.0	1.0	-	18	13	6	56	31	13.0	2.65
CAM5	6.5	0.5	-	14	16	7	56	30	14.0	2.55

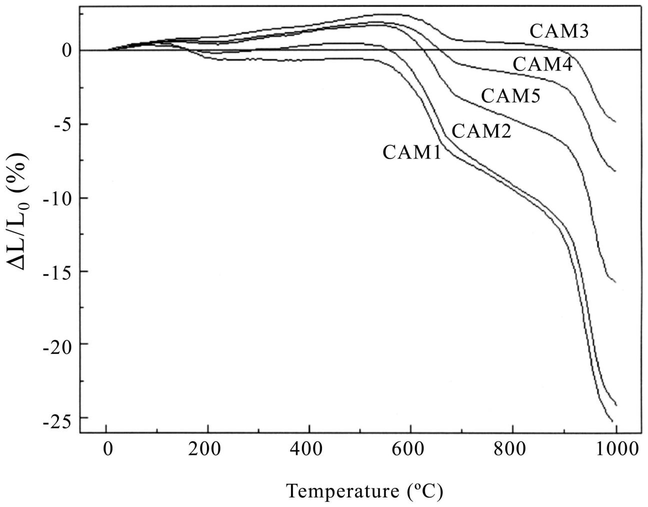

Figure 4: Dilatometric curves for kaolinitic materials powder compacts.
[Figura 4: Curvas dilatométricas para os materiais cauliníticos.]

Table III - Atterberg's consistency limits for the kaolinitic materials.
[Tabela III - Limites de consistência de Atterberg para os materiais cauliníticos.]

Samples	Plastic Limit PL (%)	Liquid Limit LL (%)	Plasticity Index PI (%)
CAM1	30	65	35
CAM2	29	68	39
CAM3	27	70	43
CAM4	29	69	40
CAM5	25	69	44

Table IV - Technological properties in the dried state at 110 ºC.
[Tabela IV - Propriedades tecnológicas no estado seco em 110 ºC.]

Samples	Lineal Shrinkage (%)	Bending Strenght (MPa)
CAM1	0.12	3.1
CAM2	0.18	2.3
CAM3	0.05	2.0
CAM4	0.07	2.9
CAM5	0.12	3.0

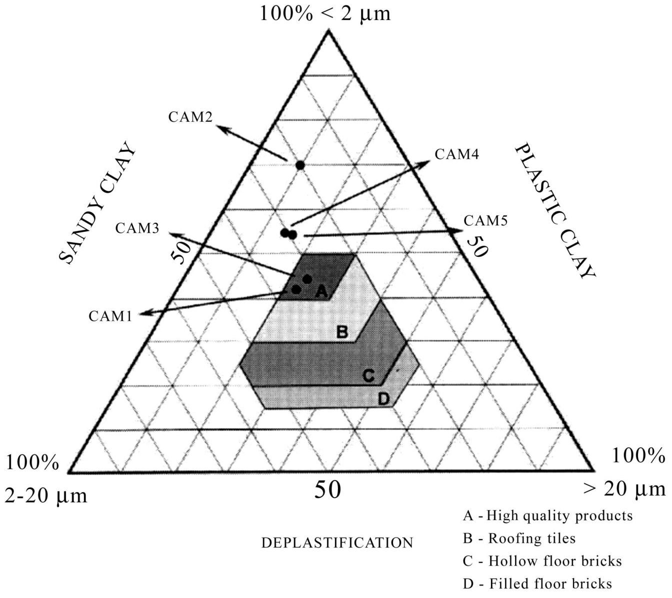

Figure 5: Granulometric classification for the kaolinitic materials samples according to Wincklercs diagram.
[Figura 5: Classificação granulométrica para as amostras de materiais cauliníticos de acordo com o diagrama de Winckler.]

showed relatively high strength (2.0 MPa-3.1 MPa), but low lineal shrinkage.

The obtained results demonstrate that the properties are altered for higher firing temperatures (Table V). The materials showed low firing shrinkage at 850 ºC (1.58%-2.39%), whilst at 1,050 ºC a higher range of values is presented (5.58%-7.83%). It is shown that the water absorption (open porosity) presented a significant variation (22.16%-29.67%), while the apparent density presented only a small variation (1.52 g/cm^3-1.66 g/cm^3) at the temperature of 850 ºC. In this case the sintering was dominated by particle-to-particle contact mainly of metakaolinite platelets. Moreover, the ceramic bodies in this temperature tend to have a more open structure due the transformation from kaolinite to metakaolinite. Between 950 ºC and 1050 ºC relevant variations occur. This behaviour is related to the beginning of glassy phase formation, with likely predominance of viscous flow sintering on the material densification. In addition, the crystallization of high-temperature ceramic phases from metakaolinite contributes for a higher densification at this range of temperatures. The values of flexural strength becomes higher with the firing temperature, mainly above 950 ºC. The correlation between mean flexural strength and water absorption of the fired materials is well established.

The specified values of water absorption (wa) and mechanical resistance (σ) for Brazilian clay based products [15] are: dense bricks (wa < 25% and $\sigma \geq 2.0$ MPa), ceramic blocks (wa < 25% and $\sigma \geq 5.5$ MPa) and roofing tiles (wa < 20% and $\sigma \geq 6.5$ MPa). These results show that dense brick and ceramic block specifications were achieved up to 950 ºC, while roofing tile specifications are attained only at 1050 ºC for all materials. These property data support the need to make up kaolinitic materials mixtures in order to manufacture ceramic products, principally roofing tile, according to Brazilian standard specifications.

Weibull approach was used to analyze the flexural strength data for fired kaolinite based materials. Typical weibull plots (ln.ln (1/(1-F)) versus lnσ) representative of flexural strength data were used to signify the Weibull modulus (shape parameter) and characteristic strength (at which the probability of failure is 63.2 %), whose results are summarized in Table VI. Weibull modulus(m) and characteristic strength (σ_o) are strongly dependent upon the firing temperature. The value of m is a criterion for the variability of ceramic materials quality. It is desirable that σ_0 is as high as possible. The shape

Table V - Technological properties of fired bodies obtained with Campos-RJ kaolinitic materials for three firing temperatures.
[Tabela V - Análise de Weibull de dados de resistência à flexão de materiais cauliníticos de Campos-RJ em função da temperatura de queima.]

Samples	850 ºC				950 ºC				1050 ºC			
	LS	WA	σ_R	BD	LS	WA	σ_R	BD	LS	WA	σ_R	BD
CAM1	1.58	23.56	7.81	1.62	2.91	22.68	10.36	1.68	5.58	16.57	15.87	1.86
	[0.37]	[0.65]	[0.73]	[0.01]	[0.20]	[0.87]	[1.34]	[0.03]	[1.54]	[2.35]	[3.12]	[0.09]
CAM2	2.39	26.75	5.99	1.53	4.41	23.65	8.27	1.65	6.74	18.54	11.83	1.80
	[0.47]	[0.61]	[0.52]	[0.02]	[0.14]	[0.86]	[1.15]	[0.02]	[1.73]	[4.33]	[2.05]	[0.11]
CAM3	2.28	29.67	5.58	1.52	3.20	26.81	8.30	1.62	7.83	16.62	14.64	1.89
	[0.47]	[1.44]	[1.82]	[0.03]	[0.23]	[0.78]	[0.83]	[0.02]	[1.30]	[2.85]	[1.99]	[0.07]
CAM4	1.97	25.61	5.44	1.66	3.59	23.53	10.91	1.66	6.07	14.02	12.75	1.90
	[0.06]	[1.48]	[0.49]	[0.08]	[0.22]	[0.66]	[1.35]	[0.02]	[0.68]	[1.78]	[1.68]	[0.06]
CAM5	1.96	22.169	7.32	1.63	2.37	22.68	10.76	1.71	6.46	12.69	14.96	1.90
	[0.30]	[1.12]	[1.97]	[0.02]	[0.09]	[0.87]	[0.95]	[0.02]	[1.10]	[1.78]	[4.44]	[0.08]

LS = linear shrinkage (%); WA = water absorption (%); σ_R = bending strength (MPa); BD = bulk density (g/cm^3); [ ] is standard deviation.

Table VI - Weibull analysis of bending strength data from Campos-RJ kaolinitic materials related to firing temperature.
[Tabela VI - Propriedades tecnológicas de corpos queimados obtidos com materiais cauliníticos de Campos-RJ em função da temperatura de queima.]

Samples	850 ºC			950 ºC			1050 ºC		
	m	σ_0	R	m	σ_0	R	m	σ_0	R
CAM1	12.7	7.81	0.976671	9.7	10.54	0.940865	5.8	16.49	0.914811
CAM2	13.9	5.98	0.930459	8.8	8.40	0.965568	6.8	12.18	0.919074
CAM3	3.4	6.11	0.992673	12.1	8.32	0.941864	8.9	15.17	0.978365
CAM4	12.6	5.44	0.947296	9.8	11.01	0.970276	9.0	12.94	0.980013
CAM5	4.0	7.79	0.912967	13.8	10.74	0.957207	3.6	16.05	0.886238

m = Weibull modulus; σ_0 = characteristic strength (MPa); R = correlation coeficient.

parameter m of Weibull distributed data, applied to ceramic materials, varies in practice between $3 < m < 15$ [16].

The fired kaolinitic materials presented Weibull modulus values in the range of 3.4-13.9. These values are relatively high for clay based products. The obtained variability for the data in this work can be mainly attributed to variation in materials compositions and firing temperatures. The higher the firing temperature, the more dispersed are mechanical strength data, except for samples CAM3 and CAM5. Specifically for these samples, the Weibull moduli increased up to 950 ºC and decreased at 1050 ºC. Moreover, the highest values of Weibull modulus found in the present work for CAM1, CAM2 and CAM4 (at 850 ºC) and CAM3 and CAM 5 (at 950 ºC) can be attributed to better homogeneity of these samples. Their strength, however, is less than those fired at 1050 ºC. It can also be noticed that the fired samples characteristic strength increased with firing temperature due to a more pronounced sintering process. The characteristic strength varies over 5.44 MPa-16.49 MPa. It is also observed that, in general, the calculated correlation coefficients presented values of R→1, which indicates that the experimental flexural strength data fit are well adjusted to Weibull distribution. The parameters of that distribution, as shown in Table V, result from testing of specimens under given conditions. These parameters can will differ if whole finish ceramic units out of a full-scale production flow are tested according to the relevant standard testing procedure.

CONCLUSIONS

As a general rule, all studied materials are suitable for structural ceramic products. Notwithstanding, ceramic bodies made up as a result of clayey materials mixtures are essential for obtaining better properties. Moreover, clay mixtures allow higher lifetimes for quarries exploited by the ceramic plants.

From a mineralogical point of view, the outstanding phase present in these materials is kaolinite, with gibbsite, illite/mica and quartz as main impurities. The samples are basically consisted of a finely grained material in the range of 2 μm-200 μm. Also, the mentioned kaolinitic materials can be classified as highly plastic inorganic soils. These materials presented low firing shrinkage at 850 ºC. The variation of Water absorption is significant, and apparent density display only a small variation for ceramic bodies fired at 850 ºC and 950 ºC. At 1050 ºC relevant variation occur probably due to vitrification. The results showed that specifications for dense bricks and ceramic blocks have been achieved at 950 ºC, regarding mechanical strength and porosity, whereas roofing tiles can only be obtained at 1050 ºC.

Flexural strength data for the studied clayey ceramic bodies are distributed according to a Weibull distribution (correlation coefficient $R \rightarrow 1$). The obtained Weibull moduli are in the range of 3.4-13.9 for the given testing conditions. In general, higher resistance data scattering occurs with increase of the firing temperature. The latter may be expected due to the degree of vitrification resulting in a less porous ceramic body.

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