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-economic 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 knowledge, 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-kα 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 mm³) were taken within the 5 °C-1000 °C range using a heating rate of 5 °C/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 diseccator for 24 h.

Rectangular ceramic bodies (115 x 25.4 x 10 mm³) were obtained by uniaxial pressing at 2400 N/mm². 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 temperature of 1150 ºC). After firing, the products were slowly cooled in the furnace (35.7 x 7 x 7 mm³) within the 5 °C-1000 °C range observed for all samples was due probably to the dehydroxylation of the silicate lattice leading to the formation of new crystalline phases such as a Si-containing 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 crystalline phases such as a Si-containing γ-Al2O3 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 three characteristic endothermic peaks within the 60.0 °C-63.7 °C, 267.8 °C-275.8 °C and 499.3 °C-503.2 °C 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 °C - 959.0 °C range observed for all samples was due probably to the formation of new crystalline phases such as a Si-containing γ-Al2O3 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).

Table I - Normalized chemical compositions (wt%) of the kaolinitic materials.

| Sample | SiO₂ | Al₂O₃ | Fe₂O₃ | TiO₂ | MnO | MgO | CaO | K₂O | Na₂O | 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

RESULTS AND DISCUSSION

Chemical composition of the studied materials is shown in Table I. In this table the percentages of SiO₂, Al₂O₃ and loss on ignition are comparatively reported to reference kaolinite (Al₂O₃,2SiO₂,2H₂O). Among the chief elements, SiO₂ varies from 40.24 to 46.88, Al₂O₃ from 26.92 to 34.29 and Fe₂O₃ as Fe³⁺ [8] from 9.91 to 16.22. With respect to the less frequent components, their variation is smaller: TiO₂ (1.13-1.34), MgO (0.62-0.94) and K₂O+Na₂O (1.32-1.82). The content of Fe₂O₃ is high, which characterizes the studied clayey materials as red clays. Alkaline fluxes contents (K₂O + Na₂O) 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 moscovite (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 °C-63.7 °C, 267.8 °C-275.8 °C and 499.3 °C-503.2 °C 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 meta kaolinite, respectively. An exothermic peak within the 949.5 °C - 959.0 °C range observed for all samples was due probably to the formation of new crystalline phases such as a Si-containing γ-Al₂O₃ 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
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 an 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 III - Atterberg’s consistency limits for the kaolinitic materials.

| 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.

| Samples | Lineal Shrinkage (%) | Bending Strength (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                    |

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/cm³-1.66 g/cm³) 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 to 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 σ ≥ 2.0 MPa), ceramic blocks (wa < 25% and σ ≥ 5.5 MPa) and roofing tiles (wa < 20% and σ ≥ 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 (σo) 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 σo is as high as possible. The shape
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 $R \rightarrow 1$, 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

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**Table V - Technological properties of fired bodies obtained with Campos-RJ kaolinitic materials for three firing temperatures.**

| Samples | 850 ºC | 950 ºC | 1050 ºC |
|---------|--------|--------|---------|
|         | LS     | WA     | $\sigma_n$ | BD | LS | WA | $\sigma_n$ | BD | LS | WA | $\sigma_n$ | 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] |

$LS = linear\ shrinkage\; (%)$; $WA = water\ absorption\; (%)$; $\sigma_n = bending\ strength\ (MPa)$; $BD = bulk\ density\ (g/cm^3)$; $\{\}$ is standard deviation.

**Table VI - Weibull analysis of bending strength data from Campos-RJ kaolinitic materials related to firing temperature.**

| Samples | 850 ºC | 950 ºC | 1050 ºC |
|---------|--------|--------|---------|
|         | $m$   | $\sigma_n$ | $R$ | $m$   | $\sigma_n$ | $R$ | $m$   | $\sigma_n$ | $R$ |
| 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 |

$m = Weibull\ modulus; \; \sigma_n = characteristic\ strength\ (MPa); \; R = correlation\ coefficient.$
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 °C. The variation of Water absorption is significant, and apparent density display only a small variation for ceramic bodies fired at 850 °C and 950 °C. At 1050 °C relevant variation occur probably due to vitrification. The results showed that specifications for dense bricks and ceramic blocks have been achieved at 950 °C, regarding mechanical strength and porosity, whereas roofing tiles can only be obtained at 1050 °C.

Flexural strength data for the studied clayey ceramic bodies are distributed according to a Weibull distribution (correlation coefficient R→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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