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THERMAL AND STRUCTURAL CHARACTERIZATION OF BRAZILIAN SOUTH-EASTERN KAOLINITIC CLAYS

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Abstract

This study focuses on the thermal and structural characteristics of some Brazilian kaolinitic clays. X-ray diffraction analysis have shown that the clay samples consist mainly of kaolinite, and quartz and gibbsite as principal impurities. On heating three endothermic transformations were identified as water loss from TG-MS data within the 60–64, 268–276 and 499–503°C ranges, followed by an exothermic transformation with maximum within the 950–959°C range. The endothermic valleys can be mainly interpreted as the release of free moisture, dehydration of gibbsite and dehydroxylation of kaolinite, respectively. The exothermic peak is associated with crystallization of new phases from metakaolinite. The quantification of kaolinite (59.6–74.2%) and gibbsite (5.9–10.2%) was taken by the thermogravimetric measurements. In addition, it was also demonstrated from the thermal curves that the character of the clays from South-Eastern Brazil (Campos-RJ) is predominantly kaolinic.

Keywords: kaolinitic clays, thermal analysis, X-ray diffraction

Introduction

In South-Eastern Brazil (Campos-RJ), there are quatenary clay deposits containing areas of about 800 km^2 mainly localized on the right riverside of the Paraíba do Sul river. These deposits hold kaolinitic clays, which are used as raw materials in the hollow floor bricks, roofing tiles and facing bricks factories [1].

Kaolinite is a two layer 1:1 silicate, $Al_2O_3\cdot 2SiO_2\cdot 2H_2O$, and is the principal specimen of its group [2]. It is structurally formed by one layer of silica tetrahedral (SiO_4), and one layer of octahedral gibbsite ($Al_2O_3\cdot 3H_2O$), neither bearing cations nor H_2O molecules between the structural layers. Kaolinite is a dioctahedral layer silicate, and the X-ray diffraction reveals that the spacing between the structural layers is of 7 Å. Its space group is P1 triclinic, and a kaolinite crystal has about 40–50 structural layers. The adjacent structural layers are held together by hydrogen bonds,

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Table 1 Normalized chemical compositions (mass%) of Campos-RJ clays

Samples	SiO_2	Al_2O_5	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

which act between the OH groups of the gibbsite layer of one unit and the oxygen atoms of the silica layer of adjacent units. The kaolinite crystals are pseudo-hexagonal platelets with size between 0.5 and 1.0 μm.

In the manufacturing process of bricks and roofing tiles the firing step is critical. On firing, clay-bearing materials undergo various physical-chemical transformations accompanied by thermal reactions and mass transfer processes of different origins in the characteristic temperature ranges [3–5]. The clays from Campos-RJ (Brazil) have been characterized restrictedly from the point of view of its thermal diffusivity properties [6], without relation to the endothermic and exothermic effects and mass loss. The lack of more knowledge on the characteristics and properties of these clays has led the local ceramic factories to exploit empirically the clay deposits. Consequently, the quality of the fired ceramic products is often poor, in particular water absorption (open porosity) and mechanical strength are not sufficient. In addition, these clays are also being submitted to testing in ceramic tiles. Brazil is currently the fourth worldwide producer and exporter of ceramic floor and wall tiles.

The study reported in the present paper shows the structural characterization by X-ray diffraction to determine the clay minerals and the attachment minerals as impurities, and the thermal behavior changes taking place during the firing of five representative natural clay samples from South-Eastern Brazil (Campos-RJ).

Experimental

Materials

Five clay samples were collected from three deposits localized in South-Eastern Brazil (Campos-RJ). These clay deposits are representatives and widely used by the ceramic factories. The samples were denoted CAM1 and CAM2 (deposit 1), CAM3 (deposit 2) and CAM4 and CAM5 (deposit 3), respectively. The samples CAM1 and CAM2 are related to two distinct layers of the deposit 1, whereas CAM4 and CAM5 are related to the deposit 3. The chemical compositions of the samples were determined by standard chemical analysis techniques for clays, given in Table 1. The particle size data of the samples summarized in Table 2 were determined by the combination of sieving and sedimentation procedure according to NBR 7181-84 [7].

Table 2 Granulometric data of the clay samples

Samples	Clay/%	Fraction/%	
	<2 μm	2–20 μm	>20 μm
CAM1	42	36	22
CAM2	70	20	10
CAM3	44	32	24
CAM4	56	31	13
CAM5	56	30	14

Methods

X-ray diffraction analyses were performed with a Seifert URD-65 diffractometer, using monochromatic CuK_α radiation at 40 kV and 40 mA over non-oriented clay specimens. Scanning speed was $1.5°(2\theta)\ min^{-1}$. The phases were identified from peak position and intensity using reference data from the JCPDS handbook [8].

TG/DTG/DTA were carried out with a TA Instruments SDT-2960 simultaneous TG-DTA on the as-received (untreated) samples. A simultaneous TG-MS (mass spectrometer Balzers 300) was used for identification of evolved water vapors [9]. The measuring parameters are summarized in Table 3. Gibbsite and kaolinite amounts were determined by thermogravimetric measurements.

Table 3 Measuring parameters of the STA and TG-MS data

Parameter	Conditions
Range temperature	Ambient to 1150°C
Reference sample (Al_2O_3)	Aluminum oxide (Al_2O_3)
Sample pans	Pt
Balance sensitivity	0.1 μg
ΔT sensitivity (DTA)	0.001°C
Purge gas rate ‘air’	10 and 100 mL min^{-1} (TG-MS)
Temperature calibration	Points three, Ag, Ir and Zn standards
Heating rate	10°C min^{-1}
Sample mass/mg	
CAM1	30.81
CAM2	30.25
CAM3	30.60
CAM4	29.87
CAM5	30.79
Mass spectrometry (ThermoStar^{TM})	
Mass range	1–200 amu
Gas connection	Quartz capillary
Capillary temperature	180°C

Dilatometric analysis of the clay samples were carried out on unfired test pieces (35.7×7×7 mm) with a BP Engineering RB-115 dilatometer within the 5–1000°C range using a heating rate of 5°C min^{-1} under air atmosphere.

Results and discussion

Structural characterization

The X-ray diffractograms of the clay samples from Campos-RJ region are shown in Fig. 1, followed by the summarized data as presented in Table 4. In this table the calculated interplanar spacings and relative intensities of the five samples are shown. The clay samples present peaks which are characteristics of clay minerals, quartz and gibbsite. Clay minerals are better identified by basal (001) reflections. From the diffraction data, kaolinite was identified mainly by its *d*-spacing within the range 7.15–7.20 (basal spacing), 3.57–3.59, 2.49–2.52 and 2.33–2.35 Å. Peaks within 9.96–9.99, 4.44–4.46 and 2.56–2.57 Å are characteristic of the illite/mica group.

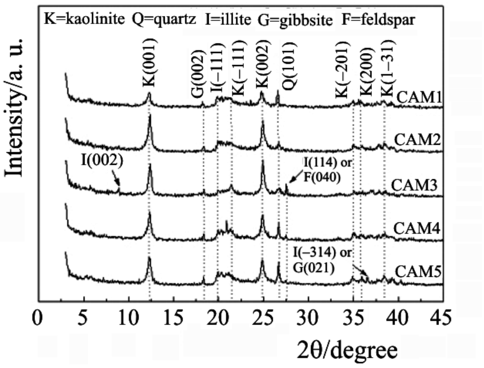

Fig. 1 X-ray diffractograms of clays samples from South-Eastern Brazil

However, previous work on Campos-RJ region clays [10] by X-ray diffraction analysis indicated that these clays have typically kaolinitic behavior. Quartz was identified by its 3.34–3.35 and 4.23–4.27 Å spacings. Gibbsite was mainly identified by the 4.83–4.86 Å spacing, which correspond to (002) plane, as well as by other weaker diffraction lines. Goethite has been identified by its 4.15–4.21 Å spacing, which correspond to (110) plane. There are also traces of potassium feldspar identified by its weaker diffraction lines. Moreover, a peak was identified for all samples around 1.49 Å, which probably corresponds to the diffraction of the (060) plane present in dioctahedral clay minerals, such as kaolinite.

Thermal characterization

The analysis of the thermal behavior of clayey materials with polymineral composition is usually a difficult task [11, 12]. It is a known fact that characteristic peaks (indicating exothermic reactions) or valleys (indicating endothermic reactions) of important events may be overlapped by others. DTA curves of all five clay samples are shown in Fig. 2. The endothermic and exothermic reactions, as well as the mass losses are summarized in Table 5. As can be observed from these results, the samples have behaved very similarly, independently of the clay deposit. In addition, these re-

Table 4 XRD data of the as received specimens of kaolinitic clay samples

CAM1		CAM2		CAM3		CAM4		CAM5	
d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
–	–	9.96	8	9.99	13	–	–	–	–
7.21	94	7.16	100	7.15	91	7.18	100	7.18	100
4.86	24	4.84	16	4.83	14	4.84	17	4.84	17
4.46	66	4.44	32	4.44	17	4.44	37	4.45	46
4.36	66	4.36	30	4.35	17	4.37	37	4.37	46
4.26	65	4.23	28	4.23	20	4.25	49	4.27	43
4.20	67	4.16	28	4.15	34	4.17	43	4.21	44
3.59	100	3.57	87	3.57	100	3.57	91	3.57	91
3.35	86	3.34	25	3.34	25	3.34	50	3.34	63
–	–	–	–	3.23	24	3.24	16	3.24	16
2.57	43	2.56	20	2.56	15	2.56	28	2.57	28
2.52	40	2.49	18	2.52	11	2.50	23	2.50	25
2.38	36	2.38	22	–	–	2.37	21	2.37	21
2.35	48	2.34	26	2.33	15	2.35	24	2.34	33
2.30	30	2.30	14	2.28	9	2.30	16	2.29	26
2.24	18	2.24	8	2.23	9	–	–	2.24	14
1.99	23	1.99	10	1.99	10	1.99	12	1.99	12
1.90	14	1.90	7	–	–	–	–	–	–
1.82	12	–	–	–	–	1.82	10	–	–
1.69	22	1.69	13	–	–	–	–	–	–
1.67	28	1.67	14	1.67	11	1.67	16	1.66	19
1.49	37	1.49	17	1.49	11	1.49	19	1.49	22

Table 5 TG/DTG and DTA results of kaolinitic clays

Samples	Mass loss TG/%	DTG max % °C^{-1}	DTA/°C					
			Endothermic			Exothermic		
			Onset	Max	Outset	Onset	Max	Outset
CAM1	4.3	56	25	61	183	897	950	1004
	2.6	272	251	276	340			
	9.2	499	340	502	743			
CAM2	3.8	57	25	64	181	899	953	1004
	2.1	273	249	273	342			
	10.4	501	342	503	744			
CAM3	2.8	56	25	61	181	905	959	1004
	3.5	268	253	272	342			
	8.3	498	342	499	744			
CAM4	3.3	55	25	60	181	911	959	1004
	2.4	271	251	268	342			
	9.4	497	341	499	744			
CAM5	3.0	58	25	62	179	958	958	1004
	2.0	270	253	273	342			
	10.0	499	341	501	741			

sults are also very similar to the thermal behavior of kaolinitic clays [2]. This is consistent with the results of X-ray diffraction. The explanation for this is related to the fact that, for clayey materials containing more than one type of clay mineral, their reactions are mainly those of the individual components and reactions between the components are relatively minor [13]. Thus, it seems to predominate the kaolinitic character of the studied clay samples.

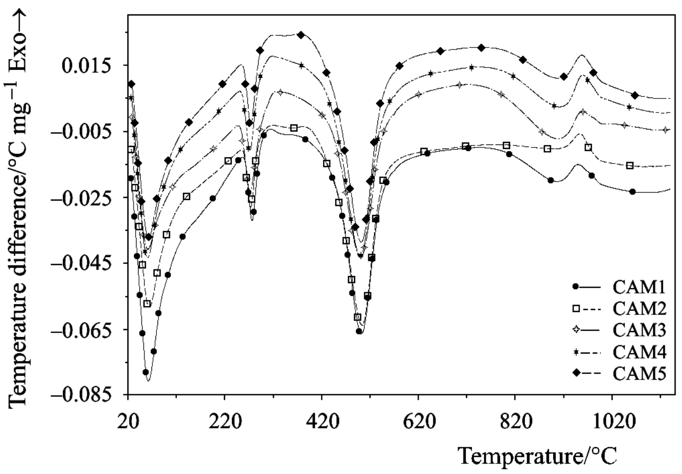

Fig. 2 Compiled DTA curves of clays samples from South-Eastern Brazil

It can be seen from the DTA curves that the investigated polymineralic clays exhibit three characteristic endothermic valleys within the 60–64, 268–276 and 499–503°C temperature ranges, respectively.

The first endothermic valley observed within the 60–64°C range is due the removal of physically adsorbed water typical of clayey materials such as kaolinite particles. The simultaneous analysis of clay samples series, using higher purge air rate of 100 mL min^{-1}, gave TG/MS curves with the same profile to all clay samples. Figure 3 shows the measurement of the sample CAM1, where the total ion current (TIC) of evolved water vapor (*m*/*z* 18) proves that the first mass loss (60–64°C), associated to the endothermic transformation, was the consequence of water desorption at a relative low temperature.

The second endothermic valley within the 268–276°C range may be related to the removal of gibbsite crystallization water, i.e. dehydration of aluminum hydroxide transforming to a transition alumina phase. There are a variety of transition aluminas [14]. These transitional aluminas are metastable phases, as well as have been thoroughly studied, since they are the basis of the Bayer aluminum process, and are widely used as catalyst [15]. Hence, the gibbsite dehydration process can be given by

$$Al_2O_3{\cdot}3H_2O\text{ (gibbsite) }\xrightarrow{268-276^{\circ}\mathrm{C}}\text{ transition alumina}$$

The third endothermic valley within the 499–503°C range is higher than the others, as correspond to mass loss associated to thermogravimetric curve, and is due

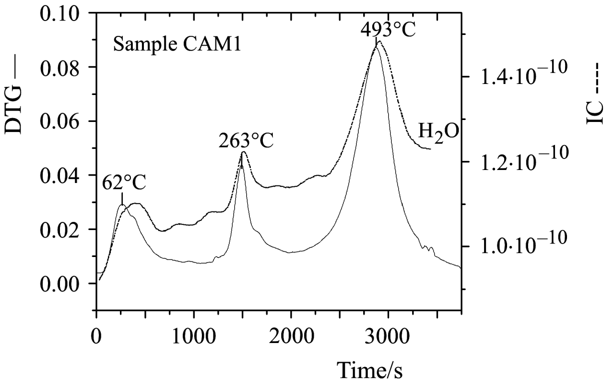

Fig. 3 Simultaneous TG-MS curves of the CAM1 sample

mostly to the formation of metakaolinite. The endothermic valley related to α–β quartz inversion should have been probably overlapped. In this case the removal of chemically bound water (dehydroxylation of the silicate lattice) occurred. This loss of structural H_2O does not modify the morphological aspect of the kaolinite pseudo-hexagonal platelets. However, this new phase is amorphous. The phase transformation from kaolinite to metakaolinite is given by

$$2SiO_2{\cdot}Al_2O_3{\cdot}2H_2O\text{(kaolinite)} \xrightarrow{499-503^\circ C} 2SiO_2{\cdot}Al_2O_3\ \text{(metakaolinite)}+2H_2O$$

An exothermic peak within the 950–959°C range observed for all samples was due to further disruption of the lattice, and probably related to the formation of new crystalline phases such as a Si-containing γ-Al_2O_3 or a spinel structure from metakaolinite [16]. Vitrification should be in progress at this point. However, it is still under debate whether a spinel or a Si-containing γ-Al_2O_3 is formed in this temperature range. In addition, it has been reported in the literature [17, 18] that 2:1 mullite, in certain extent, begins to form from metakaolinite in this temperature range. The physical-mechanical properties of clay-bearing products are strongly dependent of these crystallized phases from kaolinite. These phase transformations can be given by

$$2(2SiO_2{\cdot}Al_2O_3)\ \text{(metakaolinite)} \xrightarrow{950-959^\circ C} 2Al_2O_3{\cdot}3SiO_2\ \text{(spinel)}+$$
$$+SiO_2\ \text{(amorphous)}$$

or

$$2SiO_2{\cdot}Al_2O_3\ \text{(metakaolinite)} \xrightarrow{950-959^\circ C} Al_2O_3\ (\gamma\text{-alumina})+2SiO_2\ \text{(amorphous)}$$

The endothermic events are accompanied by an intense process of mass transfer in the samples as shown in the TG/DTG curves (Fig. 4) and summarized in Table 5.

From the TG results (Table 5), the samples presented a total mass loss during the heating within the 4.47–4.98 mg (14.2–16.3%) range. It should be noted that the samples showed only slight differences in total mass loss. This mass loss can be accompanied in three steps. In the first step, there is a loss between 2.8–4.3% due to the release of free moisture, which is the mechanical water usually added during manufacturing of structural clay products. The amount of free moisture released is dependent on the clay minerals content. In the second step, a small mass loss occurred between 2.0–3.5% due mostly to the decomposition of gibbsite, releasing H_2O molecules from its structure. In the third step, a higher mass of 8.3–10.4% is observed due mostly to the removal of chemical water bonded to the clay matrix. The more is the amount of clay minerals, the greater the mass loss is observed.

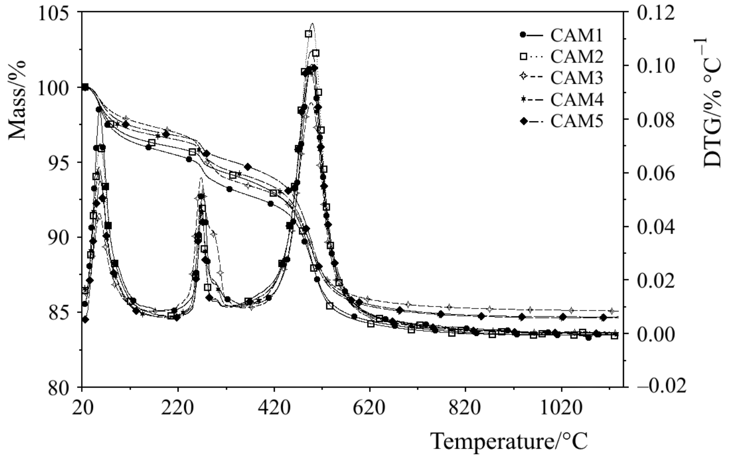

Fig. 4 Compiled TG-DTG curves of clays samples from South-Eastern Brazil

The clay fraction and gibbsite amounts can be estimated from the TG measurements, if the mass loss within the temperature range of 268–276°C is considered to be due to the dehydration of gibbsite, whereas that within the 499–503°C range is due to the dehydroxylation of clay components [19, 20]. The clay minerals of the studied samples are a mixture of kaolinite and illite/mica with great predominance of kaolinite. However, for calculation effect it was only considered kaolinite. The kaolinite and gibbsite amounts are given in Table 6. High relative amounts of kaolinites (66.3–74.2%) and gibbsite (5.9–10.2%) were observed. These results confirm the predominance of the kaolinite clay mineral in the studied samples, and are consistent with X-ray diffraction results. Furthermore, it is likely that Al_2O_3 (Table 1) does not occur in its free form in all samples, being bonded to the clay minerals and gibbsite structures.

The results of mass loss from the TG curves are also in accordance with the chemical composition data (Table 1). There is a close relation between the loss on ignition (12.05–13.83%) and total mass loss (14.6–16.3%), since the release of free moisture is taken into account in the TG measurements. The explanation for this is supported by the fact that the loss on ignition is always determined in clay samples dried at 110°C [2]. In contrast, the TG curves were obtained from the ambient temperature around 25°C. In addition, these values of mass loss are also close to the reference kaolinite value of 13.95%.

Table 6 Amounts of kaolinite and gibbsite in mass%

Samples	Kaolinite	Gibbsite
CAM1	66.3	7.7
CAM2	74.2	6.1
CAM3	59.6	10.2
CAM4	67.5	7.0
CAM5	71.6	5.9

The thermal expansion–shrinkage curves (Fig. 5) of the studied clays show very clearly in which areas there is drying and heating sensitivity. In general, the clays samples underwent expansion–shrinkage behavior (dilatometer curve) also very similar to kaolinitic clays [21]. As it can be observed, these curves are apparently quite similar among themselves. Their slight differences should be mainly attributed to dissimilar proportions of the major clay mineral (kaolinite), quartz and gibbsite.

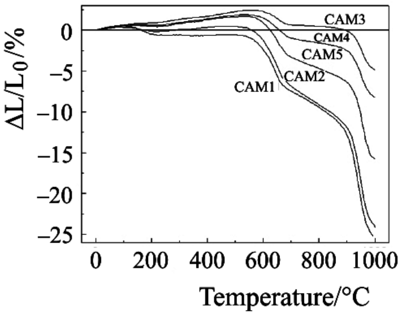

Fig. 5 Compiled dilatometric curves of clays samples from South-Eastern Brazil

In general, an expansion increases until a peak up to 500°C followed by three regions of active shrinkage at 500–650, 700–850 and 900–1000°C, respectively. The CAM1 and CAM2 samples (deposit 1), however, showed an additional shrinkage between 100–200°C on the dilatometer curve. This can be related to the free moisture content of the samples, which influenced the initial segment of these curves. The particles come closer together even at such temperatures when adsorbed water has not yet evaporated completely. The sharp increase at about 573°C is due to α–β quartz inversion. The first shrinkage within the 500–650°C range may be due to metakaolinite formation, along with a great loss of chemically bound water. The second shrinkage within the 700–850°C range is less harsh, being the onset of the sintering characterized by rapid growth of the interparticle neck. Between 900–1000°C a sharp shrinkage occurs caused by high-temperature ceramic phases recrystallization, and mostly the onset of vitrification leading to considerable shrinkage of the pieces.

Finally, the thermal behavior of studied clay samples as compared to other Brazilian clays [2] shows small but important differences. Endothermic processes involving mass loss from release of free moisture and dehydroxylation of the silicate lattice are in advance. In general, these processes occur in the Brazilian clays around 80–100 and above 520°C, respectively. The gibbsite occurrence in representative amounts is also very scarce. However, these observed differences could be related to the soil type from South-Eastern Brazil (Campos-RJ) essentially formed by recent quatenary sediments.

Conclusions

From the results presented above the following conclusions can be drawn.

X-ray diffraction analysis indicated that the natural clay samples representative of the ceramic industries from South-Eastern Brazil (Campos-RJ) used in this work are formed mainly by kaolinite, gibbsite and quartz, with predominance of kaolinite. This occurred regardless of the clay deposit.

In general, the fired clay samples behaved very similarly as shown in the TG/DTG/DTA curves. These samples underwent dehydroxylation around 499–503°C and subsequent recrystallisation within the temperature range of 950–959°C. This behavior is typical of kaolinitic clays. MS measurements proved that the mass losses associated with the endothermic transformations are mainly related to the formation of water vapor. TG measurements indicated high amounts of kaolinite, which corroborate XRD results. In addition, the thermal expansion–shrinkage curves also suggested that the character of the studied clay samples is predominantly kaolinic.

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