Quantitative analysis of clay materials and thermal treated bricks

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Abstract. In this work we present a mineralogical analysis of natural clay deposits from Rio de Janeiro State, Brazil. The samples were sieved to prepare a homogeneous powder representative of the natural soil. This powder was extruded to form bricks and submitted to a firing process in a furnace with controlled heating and cooling rates. Brick samples were prepared with firing temperatures varying from 300°C to 1200°C. X-ray powder diffraction data allowed quantitative analysis by the Rietveld method using the refinement program GSAS. The Rietveld analysis showed that the ceramic high resistance after treatment at 1200°C is associated with the formation of mullite, cristobalite and hematite phases. In contrast to the analysis of the bulk material, Rietveld quantitative analysis for the clay, silt and sand fractions revealed quantifiable concentrations of kaolinite, illite, gibbsite, goethite, quartz, anorthoclase and muscovite. The effect of the thermal treatment in the clay structural properties was also analyzed by infra-red spectroscopy.

Introduction

A large quaternary sediment basin situated in the northern Rio de Janeiro State, Brazil, supplies raw material for the production of ceramic materials, mainly bricks and roof tiles, which is an important economical activity in this region. Several studies have been carried out in order to characterize the raw material from this sediment-hosted clay deposit. A quantitative mineralogical analysis for the natural soil (not separated) using the Rietveld method was previously reported [1], where the results indicate kaolinite as the main phase (about 86% in mass), followed by quartz and gibbsite. The environmental impact of the gas emitted during firing of these clay materials was also evaluated [2].

In the present work, we used the Rietveld method to perform a structural analysis of ceramic samples produced from natural soil fired at 1200°C. Furthermore, the Rietveld method was also used to analyze the raw material, which was separated into the three granulometric fractions: Clay, silt and sand. This procedure is suitable for the identification of minor crystalline phases, which could not be detected in the natural soil, hence allowing a better quantitative analysis.

Experimental

The material collected at the mining site was dried, grounded, and passed through a sequence of sieves yielding a homogeneous powder with particle size smaller than 74 μm. Only 5 % of the original mass was rejected in this procedure, indicating that samples were quite representative of the original raw material. This powder was separated according to its particle size in three granulometric fractions, named clay (the fraction with grain sizes below 2μm), silt (grain sizes between 2 and 60μm) and sand (above 60μm). The separation was performed following the Brazilian ABNT technical standards [3]. Brick samples of the raw material (not separated soil) were also prepared by mixing the powder with water and extruding at 36 MPa. The result was a rectangular bar with a 20 x10 mm cross-section, which was cut into bricks 100 mm long. After drying at room temperature in air for two weeks, the residual water was removed at 110°C for 24 h. The samples were then thermally treated at different temperatures: 300, 400, 500, 600, 700, 800, 850, 900, 950, 1000, 1050, 1100 and 1200°C, using a heating rate of 2°C/min, constant temperature for 3 h, and cooling rate of 1.5°C/min.
Powder diffraction data were collected at room temperature with a Seifert URD65 diffractometer, equipped with a diffracted beam monochromator. The experimental conditions for the non-treated samples were $6° \leq 2\theta \leq 60°$, $\Delta 2\theta = 0.02°$, counting time 5 s and CoKα radiation. For the determination of the crystalline volume fraction of the bricks treated at different temperatures, their diffraction patterns were collected with $3° \leq 2\theta \leq 75°$, $\Delta 2\theta = 0.03°$, counting time 3 s and CuKα radiation. Two different X-ray sources were used due to a necessary substitution of the X-ray tube in this period. Of course, direct comparison was done only for diffractograms obtained under the same experimental conditions.
The brick bending rupture tension was determined with a universal testing machine using the three-point loading test with a crosshead speed of 0.1 mm/min, following the ABNT standard procedure [4]. The bending strength BS was calculated using the relation $BS = 3PL/2bd^2$, where P is the maximum breaking load, L is the distance between the sample supports, b is the brick width and d is the brick thickness.

Results

X-ray diffraction patterns show a typical evolution as a function of the firing temperature (see, for instance, reference [2]). For the natural powder soil and for brick samples treated up to 400°C the diffractograms were very similar, suggesting a large fraction of kaolinite, and small quantities of illite, gibbsite, goethite and quartz. Between 400 and 500°C the kaolinite transforms to a non-crystalline phase, metakaolin, according to the reaction $Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O$ while the other crystalline phases remain unchanged up to 950°C. Treatments at 1000°C or higher cause the sample recrystallization, with the formation of mullite, cristoballite and hematite phases.

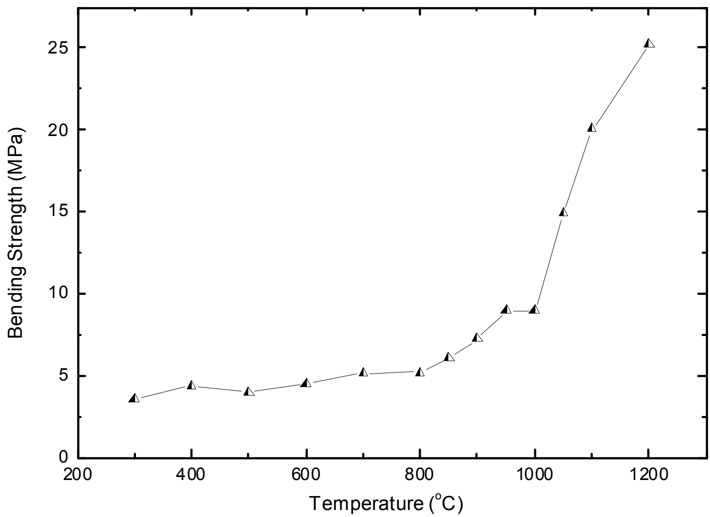

Figure 1. Bending Strength for bricks samples fired at different temperatures.

The bricks bending strength as a function of the firing temperature is shown in figure 1. The rupture tension presents a strong increase from 8.9 to 25.2 MPa in the temperature range from 1000°C to 1200°C. This behaviour suggests that the recrystallization occurs during a sintering process, leading to the improvement of the ceramic performance. The Rietveld Method was applied to study the mineralogical composition of the brick fired at 1200°C, which has the best ceramic properties. The refinement was performed using the program GSAS [5] with profile function 4 and without refining preferred orientation. Furthermore, the natural soil was separated in three granulometric fractions and, from this separation procedure, it was determined that the clay fraction correspond to 56.1% of the total soil mass, while the silt fraction corresponds to 40.1% and sand to 3.8%. The mineralogical composition of the clay fraction was also analyzed using GSAS. The asymmetric line broadening for the three main clay phases was refined through parameters Sxxx and ptec of profile function 4, which indicate anisotropic strain and crystallite size broadening respectively [5]. The sublattice anisotropic broadening (sfec) parameter, typically due to stacking faults, stayed invariable at its default value during the refinement. The parameter eta indicates a Lorentzian asymmetric broadening for kaolinite. The refinement results are presented in figure 2, and the corresponding crystalline phases and parameters are presented in tables 1 and 2. A comparison between the diffractograms in figure 2, and between the mineralogical compositions results in tables 1 and 2 shows the drastic changes that occur upon heating. Furthermore, the Rietveld results for the silt and sand fractions are resumed in table 3, and revealed the presence of some minor phases, as muscovite and anorthoclase, undetected in the complete soil powder. Differences in the compositions are due to the process of separation in fractions.

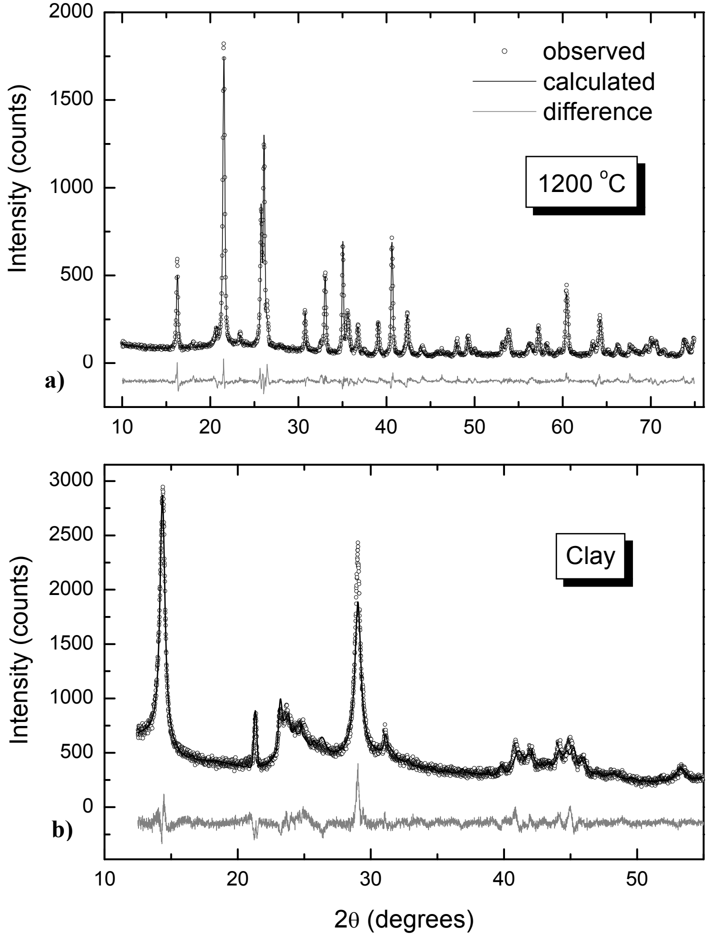

Figure 2. X-ray powder diffractogram and Rietveld calculated diffraction patterns for a) brick fired at 1200℃; b) soil clay fraction.

Table 1. Crystalline phases, lattice parameters and weight fractions for the brick fired at 1200 °C.
R_{wp} = 9.52% R_p = 7.15% R_{Bragg} = 6.65% χ^2 = 1.019

Phase	Mullite	Cristobalite_a	Cristobalite_b	Quartz	Hematite
Space group	P b a m	P 41 21 2	F d -3 m	P 32 2 1	R -3 c
a (Å)	7.5265(4)	5.48 (1)	7.1299(8)	4.933	5.027
b (Å)	7.6842(4)	5.48 (1)	7.1299(8)	4.933	5.027
c (Å)	2.8810(1)	6.23 (2)	7.1299(8)	5.430	13.822
α (deg.)	90.000	90.000	90.000	90.000	90.000
β (deg.)	90.000	90.000	90.000	90.000	90.000
γ (deg.)	90.000	90.000	90.000	120.000	120.000
Wt. Fraction	0.7640(9)	0.115(2)	0.071(2)	0.029(1)	0.021(1)

Table 2. Crystalline phases, lattice parameters and weight fractions for the clay fraction.
R_{wp} = 6.44% R_p = 5.12% R_{Bragg} = 2.98% χ^2 = 2.04

Phase	Kaolinite	Illite	Gibbsite	Quartz	Goethite
Space group	C1	C 1 2/c 1	P 1 21/n 1	P 32 2 1	P n m a
a (Å)	5.128(5)	5.137(3)	8.710(3)	4.921	9.957
b (Å)	8.797(3)	8.62(1)	5.031(1)	4.921	3.026
c (Å)	7.368(2)	20.4(1)	9.741(1)	5.390	4.594
α (deg.)	95.89(4)	90.000	90.000	90.000	90.000
β (deg.)	103.76(7)	94.8(3)	94.64(4)	90.000	90.000
γ (deg.)	90.4(1)	90.000	90.000	120.000	90.000
Wt. Fraction	0.3629(9)	0.434(3)	0.177(2)	0.0115(9)	0.014(5)

Table 3. Crystalline phases and weight fractions for the silt (R_{wp} = 12.61% R_p = 9.37% R_{Bragg} = 8.99% χ^2 = 6.140) and for the sand (R_{wp} = 11.64% R_p = 8.56% R_{Bragg} = 9.67% χ^2 = 4.961).

<table>
<tr><td rowspan="2">SILT</td><td>Phase</td><td>Quartz</td><td>Anorthoclase</td><td>Muscovite</td><td>Kaolinite</td><td>Gibbsite</td><td>Goethite</td></tr>
<tr><td>Weight Fraction</td><td>0.302(2)</td><td>0.180(2)</td><td>0.365(4)</td><td>0.114(2)</td><td>0.026(1)</td><td>0.012(1)</td></tr>
<tr><td rowspan="2">SAND</td><td>Phase</td><td colspan="2">Quartz</td><td colspan="2">Kaolinite</td><td colspan="2">Gibbsite</td></tr>
<tr><td>Weight Fraction</td><td colspan="2">0.34(2)</td><td colspan="2">0.559(6)</td><td colspan="2">0.105(5)</td></tr>
</table>

Concluding remarks

The composition of the clay fraction of natural soil, mainly illite, kaolinite and gibbsite, is clearly different from the composition of fractions silt and sand. The highest amount of kaolinite was found in the sand fraction, with about 2.13 wt% (absolute value). Quartz is mainly present in the fractions silt and sand. For the brick treated at 1200 ^{o}C, the refinement with GSAS profile function 4 indicate a well crystallized sample with no significant preferential orientation and a composition of mainly mullite and cristobalite, with about 76 % and 19 % respectively. This composition results from a recrystallization during the sintering process, which leads to the improvement of the ceramic performance with a strong increase of the rupture tension.

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