CHARACTERISATION AND POTENTIAL USE OF AN ANALCIME-BEARING CLAY FROM THE CORUMBATAÍ FORMATION – PARANÁ BASIN (BRAZIL)

Maria Margarita Torres Moreno, Antenor Zanardo, Rogers R. da Rocha

DPM – IGCE – Universidade Estadual Paulista Julio de Mesquita Filho
mmoreno@rc.unesp.br

The industries of the main Brazilian Pole of ceramic floor and wall tile manufacture by dry processing extract the raw material from the Corumbataí Formation, a stratigraphic unit of the Paraná Basin (Figure 1), whose predominant lithology involves silitites and silts of varying colours together with fine arenites and carbonate beds. Among the various compositional variations found in this formation is analcime zeolite, with a basic chemical composition $NaAlSi_2O_6H_2O$ of hydrothermal origin[1] formed during diagenesis from solutions rich in silica at temperatures between 80 and 95ºC, and which remains stable above 100ºC. When temperature rises a slow transformation of albite ($NaAlSi_3O_8$)[2] takes place. This is found in different concentrations, generally associated with carbonates (calcite or dolomite, or both), and mainly quartz and clayey minerals. This group of components forms a natural balanced mass of potential use in the manufacture of porous tiles, whose bodies are normally prepared by wet processing. The manufacture of porous ceramic tiles requires high additions of carbonate in order to form stable phases to avoid moisture expansion, requiring a differentiated firing curve. The calcium and magnesium content diminishes the shrinkage due to the formation of calcium and magnesium silicate at low temperatures. Control of the large carbonate grains in the body is also important to avoid other defects such as pinholes. The manufacture of porous tiles by dry processing also has the disadvantage of needing to control the iron content, in order not to interfere with the degree of sintering of the fired pieces. The raw material for this study was extracted from a clay deposit located in the district of Araras (figure 1), containing approximately 18% dolomite, 18% analcime and feldspar, and 2% iron in the form of oxides or hydroxides.

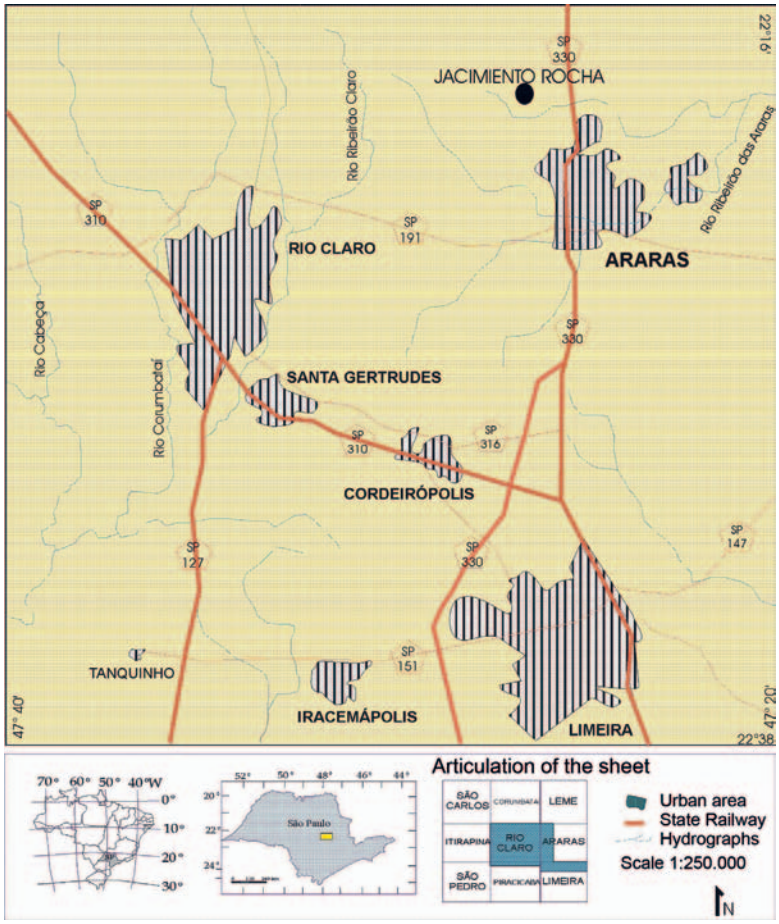

Figure 1. Map of the location of the clay deposit[3].

Chemical and mineralogical characterisation was done by X-ray fluorescence and X-ray diffraction, respectively. In order to study the ceramic properties, the mineralogical composition in different grain size ranges was analysed; test pieces measuring 7x2cm were also prepared, varying the pressing density and firing temperature (in a laboratory kiln with a programmable temperature). The measured parameters were: water absorption (WA), linear firing shrinkage (CLC), bending strength (RF) and bulk density (DA).

Figure 2. Crystalline minerals identified by X-ray diffraction: (a) total sample - the analcime zeolite peaks stand out; (b) sample fired at 1060ºC; (c) silt in natural form, fired at 500ºC and glycolate.

The chemical composition of the clay, determined by X-ray fluorescence, is shown in table 1; the high values of calcium, magnesium and loss on ignition (LOI) are due to the existence of dolomite (~18%), and those of sodium to the analcime and

albite (~18%). Figure 2 shows three X-ray diffractograms, first of the total sample (A) in which the analcime peaks stand out; the second diffractogram (B) corresponds to the pieces after firing at 1060ºC, showing that the excess crystalline material corresponds to quartz and feldspar (analcime and dolomite have disappeared); and the third diffractogram shows the fraction smaller than 2μm (separation made of the sample ground in a hammer mill), revealing poor crystallisation, reduced quantities of clay minerals of 10 Å in the silt, and irregular stratifications that point to transition between clay minerals. The diffractograms of other ranges of larger grain size show that the illite with the best crystallisation is in the largest-size fractions. In relation to the analcime zeolite, this appears well defined in all the fractions indicating that there is no prevailing concentration in a specific particle size fraction. The material displays a high concentration of fine grains (table 2), around 89% between silt and loam.

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI*
58,51	0,34	10,13	2,82	0,07	4,37	6,54	2,54	1,65	0,12	12,95

**Loss on ignition at 1000°C of the dry sample*

Table 1. Chemical composition of the clay

GRANULATION (Φ - μm)	Φ>250	250>Φ>180	180>Φ>125	125>Φ>53	2<Φ<53	Φ <2μm
%	0,11	0,46	0,83	9,95	52,63	36,02

Table 2. Grain size distribution (Φ) of a sample ground in hammer mill

The results of the ceramic tests with pressing bulk density at 1,9g.cm^{-3} are shown in table 3, which shows that at 1100ºC the firing shrinkage is very high, while at lower temperatures bending strength is small. In order to improve the properties, the pressing density was increased to 1.99 g.cm^{-3}, firing at 4 temperatures (table 4), obtaining the best results for the peak temperature of 1060ºC, pressing bulk density of 2.0 g.cm^{-3}, moisture 8%, and holding the peak temperature for two minutes.

Tmax°C	WA(%)	RLQ(%)	Dq(g/cm^3)	TRF(Kgf/cm^2)
1030	24±1	0,30±0,06	1,59±0,01	99±4
1050	24±1	0,51±0,02	1,60±0,01	97±12
1060	23±1	0,87±0,02	1,61±0,01	108±13
1070	21±1	1,87±0,01	1,63±0,01	140±3
1080	20±1	2,0±0,1	1,65±0,01	146±7
1100	14±2	4,9±0,6	1,80±0,03	220±8

Table 3. Physical properties of the test specimens (7x2cm) pressed with 8% moisture and density of 1,88±0,04 g.cm^{-3} (resulting in 0.24±0,02% drying shrinkage and 1,75±0,02 dry bulk density of the test specimens) fired holding the peak temperature for 2 minutes.

Tmax°C(min)	WA(%)	RLQ(%)	Dq(g/cm³)	TRF(Kgf/cm²)
1050 (2)	19±1	0,8±0,2	1,69±0,01	69±
1060 (2)	18±1	1,6±0,3	1,73±0,04	184±8
1070 (2)	17±2	2,0±0,3	1,7±0,1	195±18
1090 (2)	13±1	3,8±0,4	1,83±0,03	242±8

Table 4. Physical properties of the test specimens (7x2cm) pressed with 8% moisture and density of 1,99±0,02 g.cm^{-3}, (with 0,29±0.06% drying shrinkage and 1,87±0,03 dry bulk density), holding the maximum temperature for 2 minutes.

The preliminary results of the studies performed in the laboratory, using raw material containing analcime-feldspar-carbonate with low iron contents and fine granulation, show that this type of clay has qualities for producing pressed porous products of good quality, with the advantage of being a balanced natural body. Other parameters will have to be studied in accordance with the observed variations in the raw material in the Corumbataí Formation.

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