DRY MILLED CLAYS FROM THE CORUMBATAÍ FORMATION USED IN MANUFACTURING RED STONEWARE WITH VERY LOW WATER ABSORPTION

Prado, A.C.A. [(1)], Zanardo, A. [(2)], Moreno, M.M.T. [(2)]

[(1)] Pós-graduação em Geologia Regional - IGCE - UNESP - Rio Claro
(São Paulo – Brazil)
e-mail: acap@rc.unesp.br

[(2)] Department of Petrology and Metallogeny - IGCE - UNESP
- Rio Claro (São Paulo – Brazil)

The Ceramic District of Santa Gertrudes (São Paulo-Brazil) is the main ceramic tile manufacturing district of Brazil, in which most companies use dry milled clays from the Corumbataí Formation region for manufacturing BIIb type tiles (6% ≤ water absorption ≤ 10%). These clays have a Fe_2O_3 concentration of approximately 6%, which decreases firing temperature and contributes the red colour of the tiles. The commercial success of the District is due to the quality and low price of the tiles, the low price being based on the abundance of raw material and greater simplicity of the process. On the other hand, porcelain tile is the fastest growing type of ceramic tile world-wide, due to its high technical and aesthetic quality. The possibility of producing red stoneware with very low water absorption, using dry milled clays from the Corumbataí Formation as major raw material, enables companies to market a superior quality product without a high production cost.

Relatively fluxing Corumbataí Formation clays from two mines in the region (referenced clay A and B) were selected as the main raw materials. In this study, we also material with a fine particle size from a diabase mine, as well as basalt and a manganese mineral. The raw materials were dry milled separately. Mixtures were then prepared of clay A with diabase, adding 15, 25 and 35% diabase to the clay; clay B with diabase: A with basalt and B with basalt in these same proportions. Samples were further prepared by a double charge: clay A or B with a top layer of mixtures of manganese and the corresponding clay (the compositions in per cent by weight of raw material are detailed in Table 1).

Sample	Clay A	Clay B	Diabase	Basalt	Mn mineral
A	100%	-	-	-	-
B	-	100%	-	-	-
M1	85%	-	15%	-	-
M2	75%	-	25%	-	-
M3	65%	-	35%	-	-
M4	-	85%	15%	-	-
M5	-	75%	25%	-	-
M6	-	65%	35%	-	-
M7	85%	-	-	15%	-
M8	75%	-	-	25%	-
M9	65%	-	-	35%	-
M10	-	85%	-	15%	-
M11	-	75%	-	25%	-
M12	-	65%	-	35%-	
M13	100% of the base layer / 95% of the top layer	-	-	-	5% (top)
M14	100% (base) / 90% (top)	-	-	-	10% (top)
M15	100% (base) / 80% (top)	-	-	-	20% (top)
M16	-	100% (base) / 95% (top)	-	-	5% (top)
M17	-	100% (base) / 90% (top)	-	-	10% (top)
M18	-	100% (base) / 80% (top)	-	-	20% (top)

Table 1. Raw materials composition, in per cent by weight.

The raw materials were analysed chemically and mineralogically. The minerals illite, kaolinite, quartz, feldspar, hematite and an irregular interstratified montmorillonite-vermiculite were found in the clays, of which B exhibited a smaller amount of clay mineral, but more crystalline materials and a larger amount of feldspar and quartz than clay A (see Figure 1). The diabase and basalt contained augite, pigeonite, magnetite, montmorillonite and calcium feldspars, and the manganese mineral mainly contained pyrolusite, muscovite and quartz.

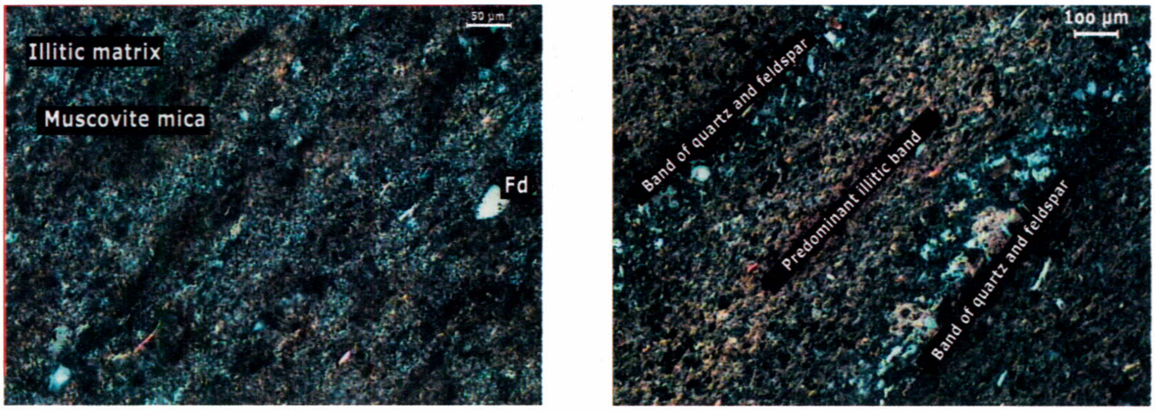

Figure 1. Micrograph of (a) clay A; (b) clay B. (Fd = feldspar)

The test specimens were formed by uniaxial pressing, measuring 2x7 cm, dried in an oven at 110°C for 24 hours and fired at three temperatures: 1030°C, 1050°C and 1070°C in fast firing cycles of 38 minutes with 3 minutes at peak temperature. In order to classify the resulting product, physical tests were run on 5 test specimens for each temperature and composition. The tests were: linear drying shrinkage (LS) and total shrinkage (TLS), water absorption (WA), bulk density (DA), dry and fired flexural modulus of rupture (TRF), and breaking load (CR). The WA, CR and TRF tests were based on the methods of the Brazilian Association of Technical Standards ABNT - NBR 13818/1997 and the results obtained were compared with the requirements of this Standard for BIa class products. The M3 sample fired at 1070°C was also characterized chemically and its deep abrasion resistance was determined. The samples were polished to visualize the final appearance of the surface.

The objective, which was to make products with very low water absorption, based on clays from the Corumbataí Formation, was achieved in some of these mixtures at certain firing temperatures, generating products with low water absorption (average $\leq$ 0.5%), high mechanical strength (average $\geq$ 35MPa), great chemical stability and a pleasant aesthetic effect, without impairing dimensional stability (A/1030°C; B/1030°C; M1/1050°C; M1/1070°C; M4/1050°C; M4/1070°C; M5/1050°C; M5/1070°C; M6/1050°C; M6/1070°C; M16/1030°C; M17/1030°C; M18/1030°C).

During the performance of this research, small differences were found between presumably similar levels of the Corumbataí Formation. This difference affected composition behaviour ranging from grindability (where clay B obtained the best particle size distribution) to the reactions that occurred in firing, which were reflected in the superior physical characteristics of B in relation to clay A, because of the greater amount of feldspar in clay B. The most appropriate firing temperature to produce tiles with porcelain tile characteristics is 1030°C; above this value overfiring occurs.

The addition of diabase increases the most appropriate firing temperature (1050°C or 1070°C) and has the ability to contribute greater stability to the physical characteristics of the samples with the variation in firing temperature. The samples formed by clays and basalt, with up to 25% of this material, displayed similar physical characteristics to BIa type products, and required firing the tiles at 1050°C or 1070°C. The manganese addition gave rise to many problems of dimensional instability, with the deformation of most of the samples; this was probably due to the formation of low viscosity liquid phase at relatively low temperatures.

The polished surface appearance of the pure clay test specimens, mixtures of clays with diabase, clays with basalt and clays with manganese, can be observed in Figures 2, 3, 4 and 5, respectively. The test specimens consisting of pure clays (A and B) display a red brown colour and the additives did not produce the total darkening of the piece. The mixtures consisting of clays and diabase or basalt displayed a microgranite type of appearance with black and brown spots, which was aesthetically very agreeable, while the test specimens modified with manganese mineral exhibited deformation at 1050°C and 1070°C

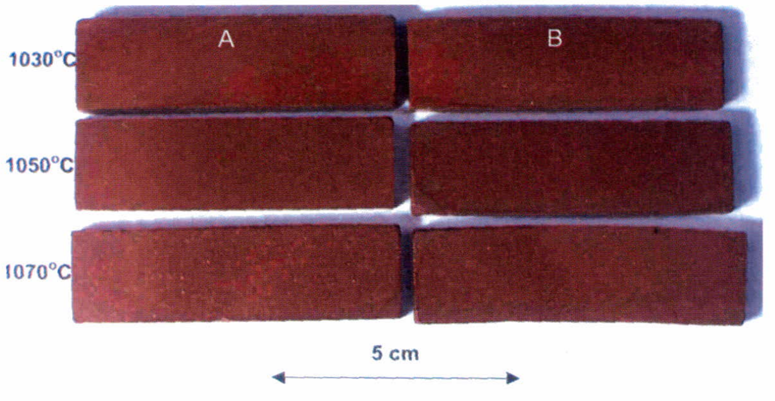

Figure 2. Photos of test specimens A and B.

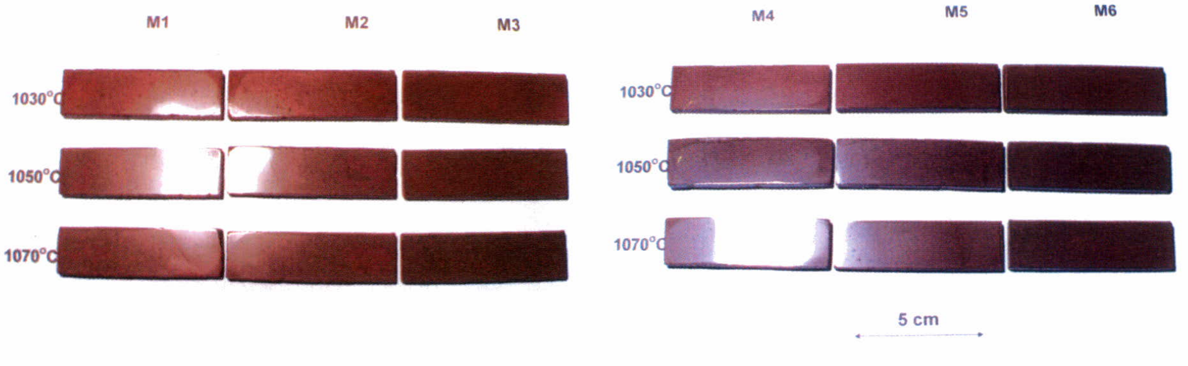

Figure 3. Test specimens made up of: (a) clay A with diabase; (b) clay B with diabase.

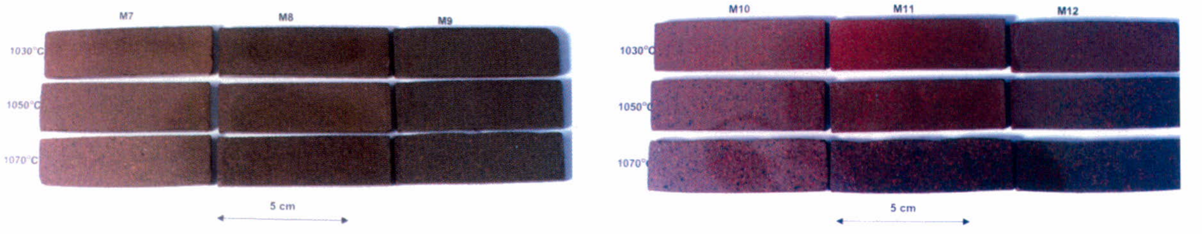

Figure 4. Test specimens made up of: (a) clay A with basalt; (b) clay B with basalt.

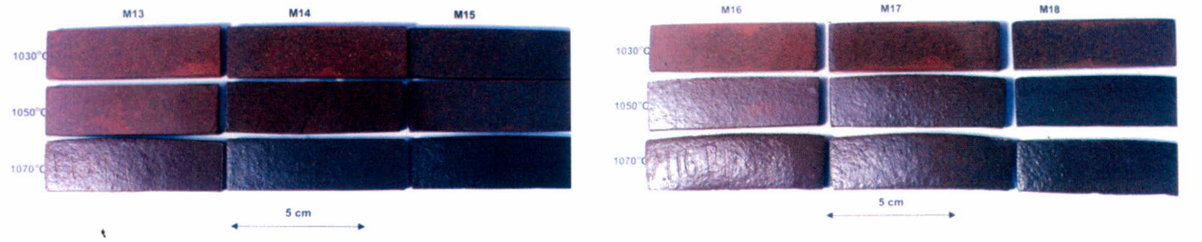

Figure 5. Test specimens made up of: (a) clay A and manganese; (b) clay B and manganese.