RHEOLOGY OF CLAYS FROM THE CORUMBATAÍ FORMATION AND THEIR APPLICATION IN PORCELAIN TILE PRODUCTION

Prado,A.C.A.(1); Zanardo,A.(1); Menegazzo,A.P.M.(2); Moreno,M.M.T.(1); Roveri,C. D.(1); Coutinho Jr.,T.A.(1)

(1) IGCE - UNESP - Rio Claro, SP. Brazil
(2) CITEC/CCB - Santa Gertrudes, SP. Brazil
acap@rc.unesp.br

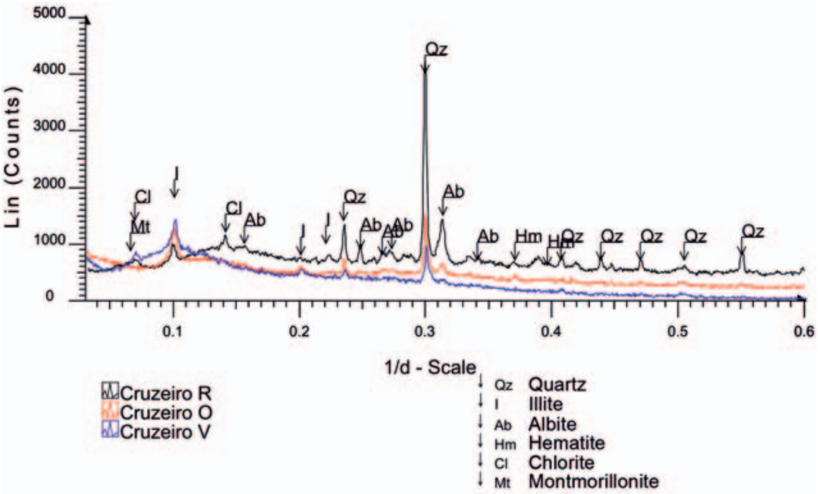
Clays of the Corumbataí Formation are used almost in their entirety for the manufacture of ceramic tiles with water absorption (WA) between 6 and 10%, prepared by dry milling. Among the ceramists of the Ceramic Pole of Santa Gertrudes the idea reigned that these clays did not deflocculate, due to the results of the first tests performed in the companies, probably because they used clays from the top of the Formation (highly altered material); however, in more recent studies, the less altered clays have deflocculated satisfactorily.

Three samples (**R**, **O** and **V**) originating from the Cruzeiro deposit of the city of Limeira (São Paulo - Brazil) were analysed, preparing deflocculation curves using sodium silicate and curves of the variation of viscosity and pH with preparation time. The bodies were constantly stirred with a mechanical stirrer in the first 6 hours of the test and their viscosities measured after 0.5, 1, 2, 3, 4, 5 and 6 hours. They were left to stand for 18h (24h from the start); viscosity was measured, followed by stirring for 2 min. and a new reading. This procedure was repeated for 48, 72, 96 and 120 hours.

The samples were also characterised by chemical analysis (table 1) and mineralogical analysis (graph 1). The bodies were prepared by the wet method for 30 minutes, with the most appropriate deflocculant percentage calculated theoretically. Later they were dried, re-granulated with a moisture content (Hu. Pr.) of 8%, pressed to a density (D. Pr.) of approximately 2.00g/cm^3 and fired at 1060, 1070, 1080, 1090 and 1100°C, in fast firing cycles (three minute hold at these temperatures) in an electric kiln. Loss on ignition (LOI), linear drying shrinkage (CLS) and total linear shrinkage (CLT), WA, bulk density (DA) and the modulus of rupture by bending (TRF) in the dry and fired samples were determined. These results are set out in table 2.

SAMPLE	LOI	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5
R	2,69	68,18	14,20	5,31	0,61	0,06	0,72	1,88	2,66	3,59	0,20
O	3,04	67,47	14,40	5,04	0,65	0,10	1,15	1,90	2,69	3,33	0,24
V	2,27	69,28	13,97	5,45	0,54	0,02	0,45	1,64	3,11	3,22	0,11

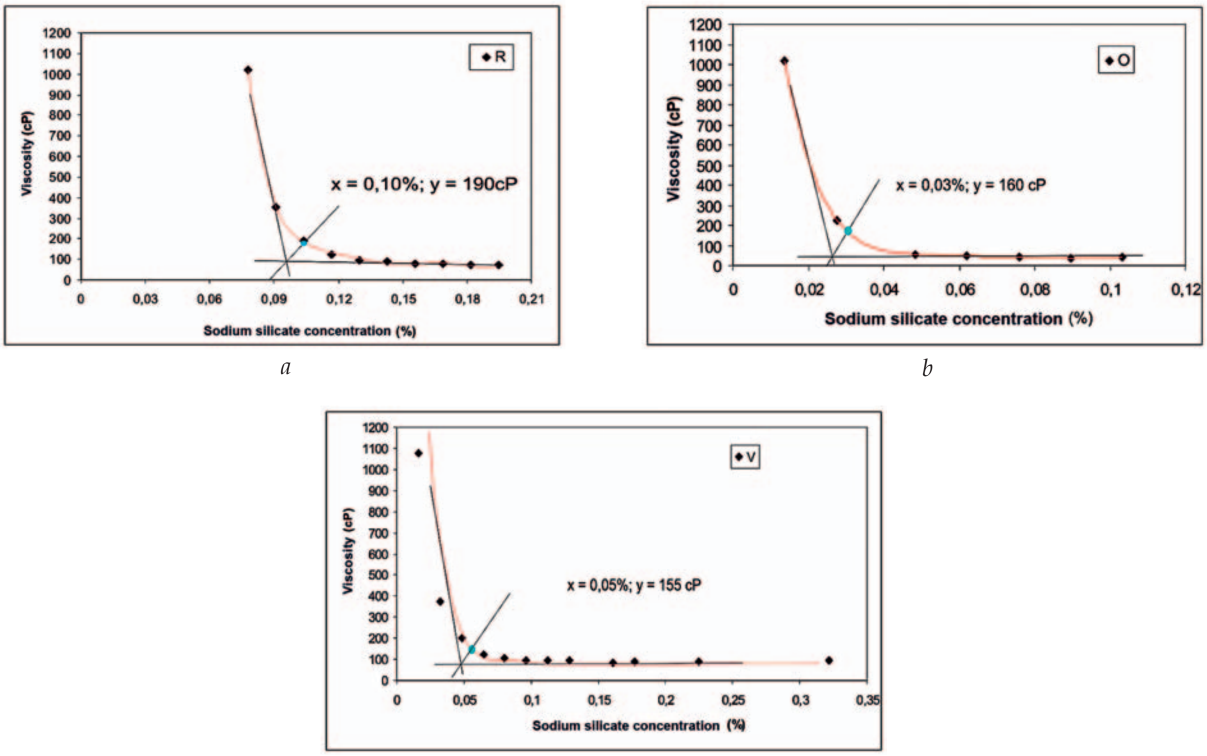
Table 1. Percentage of main chemical components.



Graph 1. X-ray diffraction of the samples.

All the samples contain quartz, illite, albite and hematite. **O** and **V** also have montmorillonite and, **O** and **R**, chlorite. The chlorite content in **O** is greater than in **R**. In sample **V** there is more Na_2O and SiO_2 than in **O** and **R**, which indicates that the amount of albite and quartz in **V** is greater. The amounts of organic carbon in **R**, **O** and **V** are, respectively, 840, 1340 and 790 ppm.

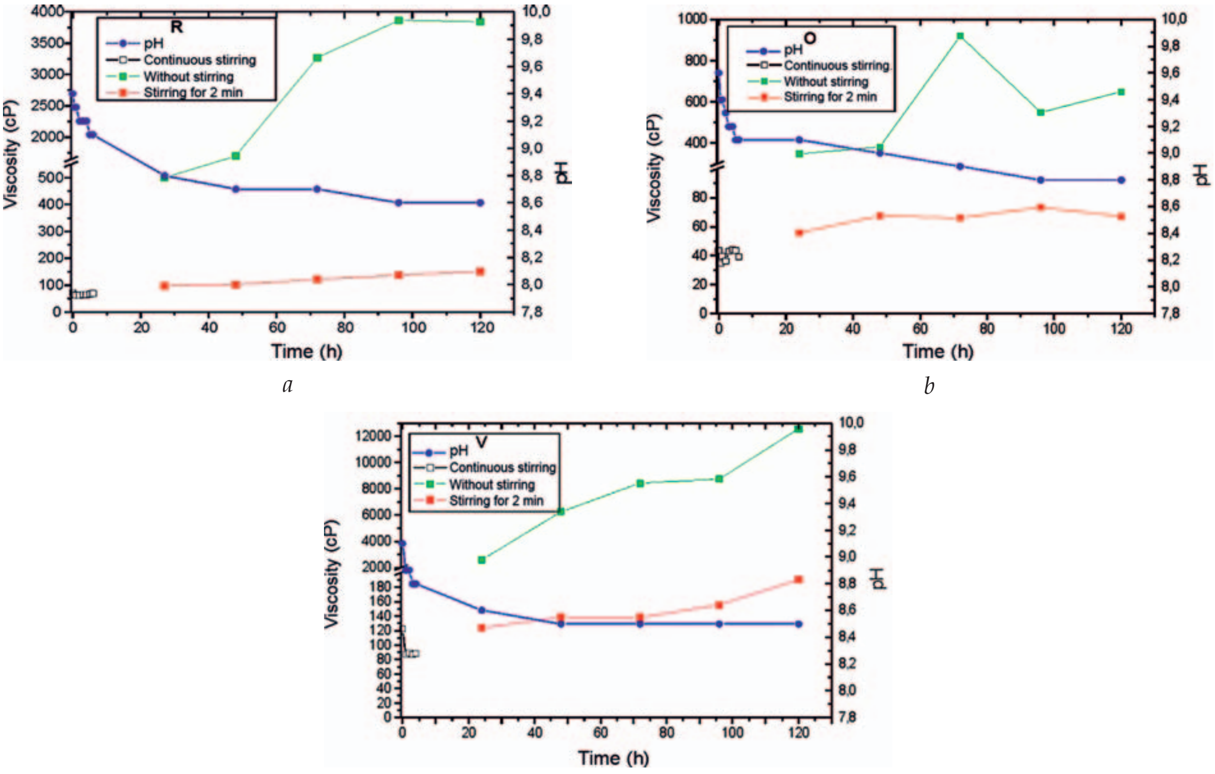
When 0.10, 0.03 and 005% sodium silicate were added in samples **R**, **O** and **V**, their viscosities were 190, 160 and 155cP, respectively (see graph 2). Sample **O** deflocculated more easily owing its greater amount of organic matter. And sample **V** needs an intermediate amount of deflocculant, because it contains less clay mineral (more albite and quartz). The montmorillonite, in contrast to expectations, can help in the deflocculation; it is very fine and the quantity is very small; it lines the side of the kaolinite plate, making it negative[2]; in this case the montmorillonite coats the illite.



a *b*

c

Graph 2. Deflocculation curves (% by weight with respect to the dry solid, x is the most appropriate deflocculant content: (a) ***R*** *(x = 0.10%); (b)* ***O*** *(x = 0.03%); (c)* ***V*** *(x = 0.05%).*



a *b*

c

Graph 3. Variation of viscosities and pH with time: (a) ***R****; (b)* ***O****; (c)* ***V****.*

As a function of time the viscosities of **O** and **R** are approximately equal and that of **V** diminishes a little (due to thixotropy) 6 hours after preparation. At rest, the viscosities are very high and increase with time. When the bodies are stirred for 2 min. the viscosities decrease, but not to the initial values. The viscosities of **O** and **V** are 1.5 times greater 120 hours after the beginning of the test and that of **R** is 2.1 times greater. Th pH diminishes with time. This increase in viscosity and reduction of pH is due to the break-up of simple particle aggregates, which reduces the amount of deflocculant per unit surface area of the clay[1].

	R		O		V			R		O		V	
	Med	D	Med	D	Med	D		Med	D	Med	D	Med	D
Tests of dry samples							**Tests of samples fired at 1080ºC**						
Hu. Pr. (%)	7,26	0,21	7,99	0,25	7,75	0,10	LOI (%)	2,73	0,04	2,79	0,05	2,21	0,07
D Pr. (g/cm³)	2,00	0,02	2,01	0,02	2,01	0,01	CLT (%)	8,97	0,54	8,72	0,26	9,51	0,07
CLS (%)	-0,04	0,05	-0,02	0,04	0,01	0,04	TRF(MPa)	59,50	2,87	54,36	4,26	60,78	5,81
TRF(MPa)	2,17	0,71	1,11	0,22	1,96	0,11	WA (%)	0,17	0,04	0,27	0,06	0,10	0,06
							DA (g/cm³)	2,41	0,01	2,36	0,01	2,43	0,01
Tests of samples fired at 1060ºC							**Tests of samples fired at 1090ºC**						
LOI (%)	2,84	0,08	2,80	0,05	1,94	0,06	LOI (%)	2,85	0,08	2,79	0,05	2,25	0,02
CLT (%)	8,41	0,26	8,54	0,59	8,55	0,80	CLT (%)	8,62	0,22	8,17	0,12	9,24	0,03
TRF(MPa)	49,93	6,32	45,26	6,55	56,21	6,85	TRF(MPa)	60,35	1,96	44,61	3,84	55,63	5,16
WA (%)	1,36	0,34	2,28	0,85	1,04	0,60	WA (%)	0,11	0,04	0,17	0,04	0,09	0,08
DA (g/cm³)	2,40	0,02	2,34	0,04	1,98	0,06	DA (g/cm³)	2,34	0,02	2,29	0,01	2,39	0,00
Tests of samples fired at 1070ºC							**Tests of samples fired at 1100ºC**						
LOI (%)	2,74	0,07	2,80	0,07	2,20	0,12	LOI (%)	2,77	0,03	2,90	0,03	2,35	0,07
CLT (%)	9,60	0,20	9,19	0,20	9,65	0,15	CLT (%)	7,58	0,52	6,86	0,91	8,46	0,19
TRF(MPa)	59,14	5,65	49,11	14,46	61,28	9,60	TRF(MPa)	50,91	1,63	42,06	2,90	55,72	5,78
WA (%)	0,31	0,09	0,36	0,16	0,24	0,07	WA (%)	0,15	0,07	0,22	0,02	0,20	0,03
DA (g/cm³)	2,44	0,01	2,39	0,01	2,44	0,00	DA (g/cm³)	2,28	0,01	2,21	0,03	2,36	0,03

Table 2. Physical characterisation of the samples with the mean (Med) values and standard deviation (D).

The WA of the samples is less than 0.5% when they are fired at temperatures at or above 1070°C. **R**, **O** and **V** display TRF above 35MPa if they are fired at or above 1060°C; the TRF of **V** is greater than that of **R**, which is greater than in **O**. The CLT and DA maximise at 1070°C. Thus, the samples exhibit the characteristics of porcelain when they are fired in an electric kiln at temperatures at or above 1070°C. **V** has more appropriate physical characteristics for this type of tile than **R** and **O**, possibly because of its greater albite content.

All the samples deflocculated very well. The sample that contains more organic matter, **O**, deflocculated better. The overfiring is clear at 1090 and 1100ºC. In these preparation conditions, the clays must be fired in this electric kiln at temperatures around 1070-1080°C, because below these, the WA is not below 0.5% and above these, the CLT and DA decrease considerably, which indicates that overfiring has occurred.

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