PONENCIA 127 – C1 GEOLOGICAL AND TECHNOLOGICAL EVALUATION ON BALL AND PLASTIC CLAY IN BRAZIL

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ABSTRACT

Ball and plastic clays is a clayey material constituted by kaolinite, illitic mica, or sericite, fine quartz and other minerals, with small amounts of organic matter, that play an important role in the worldwide ceramic industry providing strength, plasticity, light cream to white fired color and others special characteristics for sanitary-ware, floor and wall tile, tableware, electric insulator, refractories, glaze and frits. In addition, plastic clays have other nonceramic usages such as coating or filler in rubber, adhesives, sealants and fiberglass.

The major users of plastic clay are the sanitary-ware, wall and floor tile producers. Only for the tile industry the estimated consumption is over 10 million tons of plastic clays yearly, and demand is going up for the coming years, mainly for porcelain stone production.

Brazilian ceramic tile industry produces around 600 million square meters of floor and wall tiles by year, including 33 million of porcelain stone and around 130 million of other white body tiles. It requires a domestic supplying of around 1 million tons of plastic clay per year. In spite of the small amount of porcelainstone tile produced in Brazil, its production is growing rapidly (18% in the period of 2004-2005). This fact will demand more plastic clay each year as well as feldspar and other raw material and processed minerals.

This paper deals with an evaluation of Brazilian plastic clays to supply present and future market. The study involved several deposits in the country and around 40 samples were selected for detailed investigation on mineralogy, chemical composition, ions exchange capacity, carbon content, particle size distribution and ceramic properties.

After shows these characteristics and properties of individual samples and deposits this paper discusses its relationship with geological setting and evaluates the potential for ball and plastic clay in Brazil.

INTRODUCTION

From literature, including technical papers, mining agency directories (DNPM 2007), commercial magazines and previous works from the authors (*e.g.* Motta et al. 1993, 2004 and 2007) where selected 83 plastic clay and ceramic kaolin occurrences for preliminary evaluation. Then, it was analyzed available data concerning to reserves, clay quality (low iron content, high alumina content and plasticity), geologic classification and logistics (location, distance from ceramic plants, infrastructure for transportation). Then, 35 occurrences were selected to further studies including mineralogical, chemical, physical determination as well as ceramic properties, which are presented in this paper.

STUDY METHODS

The following method was used to develop the present study:

Data collecting and preliminary analysis for occurrences selection

Data collecting and evaluation on supplying and consumption of plastic clays; sourcing for main deposits and occurrences, and its for characteristics.

Field works: geology of deposits and sampling

Field works (geologic profile description and sampling) were carried out in clay pits, deposits under evaluation and as well in new occurrences.

Laboratory studies.

Samples from clay pit, outcrops and wells were prepared for several determinations and experiments, as follow:

granulometry: particle size distribution of clays was done by sieving and laser method; **chemical analyses :** in all samples were determined major oxides content by X ray spectrometry; pH; organic carbon content; and cation exchange capability;

mineralogical studies: samples were characterized by binocular and optical microscopy, X ray diffratometry and thermal analyses.

ceramic experiments: it was evaluate dry and fired properties of clays (110 °C, 1.200 °C and 1.250 °C), such as water absorption, strength, shrinkage, firing colour and density.

RESULTS AND DISCUSSION

Main deposits and geological features

The clay cycle presented by Millot (1964) shows that the main generation of kaolinite - the most important clay mineral present in the plastic clay - are placed in the humid and hot areas of the earth surface by weathering of aluminum silicate rocks. Once kaolinite are formed on the surface it remain *in situ* for a while and then it is transported (mainly by water) and it is deposited as a detritus in fluvial, lacustrine and coastal environment.

Based on this point of view, the Brazilian deposits of plastic clay were classified in two main types, named as **alterite** (*in situ* weathered clayey material) and **sedimentary** deposits. The first type is generally less plastic than the sedimentary one, because sedimentary deposits have its plasticity enhanced by the transportation and sedimentation. The Figure 1 shows the plastic/non plastic and fluxing/refractory relationship between both types.



Figure 1 – Chart for plastic characteristics of clays and other raw material

In this study it was selected 83 plastic clay deposits, from which 37 were further detailed, as shown in the Table 1 and Figure 2.

State	Municipality	Occurrence Number	Geologic Type	Estimated Reserve
PI	Oeiras	10-A	Alt S	M
	Jaicós	10-B	Alt S	
	Colônia do Piauí	10-C	Alt S	
CE	Martinópole	10-D	Alt mS	М
PE	Ipojuca	11	Qa	S-M
BA	Itanagra	13	Alt S	М
	Camacã	14-A	Alt mS	М
	Canavieiras	14-B	Qa	S
	Santa Luzia	14-C	Alt mS	S-M
	Poços de Caldas	16	Qa	S-M
	Lavras	16-A	Qa	М
	Guarda Mor	17	Qa	L
SP	São Simão	18	Qa	S
	Mogi-Mirim	20	Qa	S
	Tambaú	Qa	Qa	S
	Porto Ferreira	24	Alt S	M-L
	Aguaí	25	Qa	S-M
	Pedreira	28-B	Alt p	S
	Sarapuí	29	Qa	S
	Piedade	30	Qa	S
	Pariquera-Açu	31	Тра	S-M
	Apiaí	32	Qa	S
	Capão Bonito	33	Qa	S-M
	Suzano	36	Qa	S-M
	Lagoinha	38	Qa	S
	Tremembé	39	Qa	S
PR	Tijucas do Sul	40	Qa	M-L
	Castro	41	Alt S	M-L
	Campo Largo	42	Qa	S-M
	São Mateus do Sul	43	Qa	М
SC	Campo Alegre	44	Alt β	M-L*
RS	Mariana Pimentel	47	Alt S	М
	Encruzilhada	49	Alt Y	M-L
	Leão	50	Und-Clay	S-M
	Butiá	50B	Und-Clay	S-M
ТО	Tocantins 1	51A	Alt S	M-L
ТО	Tocantins 2	51B	Alt S	M-L

Tabela 1 – Relationship of main plastic clay occurrences in Brazi

Key:

Key: Geologic type: Qa= sedimentary type quaternary fluvial; Tpa= sedimentary type Tertiary lacustrine; Alt= alterite type (S= sedimentary; mS= metassedimentary; Y= granitic rock; β= basaltic rock Reserves: S= small (smaller than 500.000 t); M= medium size (500t to 2 mi t); M-L= medium to large (2mi to 10 mi t)



Figure 2 – Main clay occurrences in Brazil

Physical Characteristics - Particles Size Distribution (PSD)

The PSD of studied samples is partially pointed out in the Figure 3. As observed, the samples show low content of particles lesser than 2 μ (< 40%) or even lesser than 4 μ (< 60%). Among sedimentary deposits, those with low content of coarse material are few, and are related to select layer in the small deposits (e.g. samples 43, 16 and 18 – Fig. 3) or related to a larger Quaternary environment, such as sample 31-A, which is related to an Upper Tertiary basin, which is, unfortunately, contaminated with iron minerals. The Figure 4 shows the PSD of São Simão clay, one of most known Brazilian ball clay, shows the granulometric curve with silt contamination, a common fact in most Brazilian clay deposits. Related to alterites, the sedimentary ones show has more content of fine particles then other clays, as show in the samples 10-C and 10-A (clays from Pimenteiras fm.- Devonian from

Parnaiba basin).



Figure 3 – Particle size distribution according to sedimentary and alterite clay type



Figure 4 - Particle size distribution of Brazilian São Simão ball clay

Among the non-sedimenatry alterites, one sample (14-C) from pelitic metassediments show best values. Most of the material containing fine material show unimodal PSD unimodal, while few samples with bimodal PSD distribution.

In general, Brazilian clays are coarser than the classical European clays as shown for selected sample in the Figure 5. This fact reveals that Brazilian deposits are more contaminated by silt and sand, due to the small size of deposits. This contamination varies among deposits and even in the same deposits and need control in the producing operations to give homogeneity to the commercial types.



Figure 5 - Granulometric characteristics of Brazilian and European plastic clays

Chemical Characteristics

The chemical composition for aluminum and siliceous oxides in the clays are pointed out in the Figure 6, and for potash, iron and titanium oxides in the Figure 7. For the first two oxides, the content of Al_2O_3 (in weight) varies between 12 and 38% for all sample, and between 20 and 30% for most samples. For silica, the content varies from 40 to 80%, but usually between 50 and 70%. The samples with highest silica are more contaminated with silt and sand (coarse material observed by PSD in the previous section). The Fe_2O_3 content is lower than 2% for most samples, and can reach around 1% for several samples, but occasionally can reaches higher values. K_2O content is normally low (under 1.5% for most samples, but occasionally higher in alterite clays) (Figure 8). The K_2O content is related to the presence of the minerals illite and feldspar.

Other two measured parameter were organic carbon and cation exchange capability (CTC). The first one is present in low values (less than 0.6%), unless for one sample of black clay (Figure 8). In relation to CTC, most of sample show low value, between 1 and 10 Meq/100g, compatible with kaolinite in literature, with an exceptional high value related probably to halloysite mineral (sample 49).



Figure 6 - Alumina and silica distribution in the samples according to deposit types



Figure 7 - Iron, potash and titanium oxides distribution in the samples according to deposit types



Figure 8 - Organic carbon content

Mineralogy

Kaolinite is the major clay mineral observed in the studied plastic clays, which can be along with other clay and non clay minerals. Kaolinite particles show hexagonal form, with well defined boundaries (mainly in alterites), and sometimes shows hexagonal form, with round pattern, mainly for sedimentary clays. The size varies from less than 1 µm up to 10 µm.

Illite is as minor clay mineral in most samples, but occasionally can occur as significant quantity, mainly in alterite clays. Smectite is generally absent in sedimentary clay and can occur as secondary mineral in alterites, but in small amount. In deep weathered profile gibbsite is usually present, while in lesser weathered material illite is present instead.

Quartz is the main non clay mineral in clay and can be the major constituent in silty/sandy clays. Feldspar occurs together quartz, and occasionally Ti minerals and other heavy minerals in minor amounts, mainly in sedimentary clays. Other different non clay minerals can also occur, depending on the mother rock type. For instance, in weathered granites and correlative rocks such as pegmatite, it's common tourmaline and mica in significant amounts. In the weathering environment, mineralogy assembly of clay deposit tends to be more variable.

Ceramic properties

The firing colors are white, cream and bege, for most samples in oxidizing conditions. The dry strength of the studied plastic clays is shown in the Figure 9. Best values (higher than 2 MPa) are presented by

sedimentary clay, reflecting its best plasticity properties, due to organic matter content, disordering in the structure of kaolinite and water adsorption. When fired (1200°C and 1250°C), about half of the samples reach good sintering values, and the other part of the samples behavior as refractory raw materials. Samples from alterite environment show better fusibility than sedimentary ones (Figure 10).



Figure 9 – Dry strength for clay samples according deposit types



Figure 10 - Fired strength for clay samples according deposit types

CONCLUSIONS

This study pointed out several deposits of plastic clay with good qualification for white ceramic, such as porcelain stone tiles. Furthermore, it was observed two different geological environments for clay generation, one in the classic quaternary detritic sedimentary sites, usually related to small basin of depressed areas (mainly fluvial); and other non-detritic material (alterite), formed by weathering of previous rock (mainly sedimentary). For the first one, most of deposit presented here is small in size but some new occurrence pointed out show medium size and potential for more reserves, but need further evaluation. In spite of the potential for major and good quality Tertiary ball clay deposits is indicate only for Northern Hemisphere, according some authors (e.g. Deens & Vicent 1997) the Brazilian terrane it's still open for evatuation on the upper Tertiary and Quaternary sediments, such as lacustrine environment in some specific geological and geographic areas of Brazil.

On the other hand, alterite clays is an alternative for sedimentary plastic clay, once it present enough qualities for ceramic uses, such as porcelain stone tiles, eventually with additional extra plastic clay as additive.

As conclusion, as observed in this study, in both environments it would be possible find clays with plasticity, white or light color, with good firing characteristics for porcelain stone tiles, and some for for other whiteware ceramics.

AKNOWLEDGMENTS

Authors would like to express thanks to FAPESP agency (Proc. 03/13762-4) for the financial support to this research, and to IPT and Unesp for facilities and technical support.

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