Drying of Mudstone from Corumbataí Formation Used in the Ceramic Center of Santa Gertrudes - Brazil.

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Abstract. The majority of the ceramic industries in the Ceramic Center of Santa Gertrudes have been using only raw materials from Corumbataí Formation to compose their base mass. The drying of different raw materials: hard, intermediate and soft; in the proportion required by basis mass, has been made in yards drying, to support the process of homogenization. Depending on the degree of weathering, these materials show different humidities, although the drying speed depends more on the mineralogy and rock texture than on the water content. Experiments have showed that the materials, which are more difficult to dry, take about 6 hours more than fast drying materials to reach 5% moisture. However, this time may decrease if these materials were wetted for 5 minutes. Air streams, forced by a fan, together with the intense sun did not promote good results and, the samples, with air streams and without sun, have not reached the required moisture content at all. Research to understand the loss of moisture in these materials is intended to improve the knowledge about the drying process. The results can be used to develop methods of drying, extraction and homogenization according to the production process of the Pole Ceramic Santa Gertrudes.

Introduction

The Ceramic Center of Santa Gertrudes is Americas largest manufacturer of surfacing ceramics a segment that encompasses flooring and wall tiles [1]. Its production reached 506 million square meters in 2011, corresponding to a turnover of 3 billion reais . This volume represents 86% of the production in São Paulo and 60% of Brazil's production. The overall consumption of clay adds up to about 8 million tons. [2].

Located in São Paulo State, this center encompasses, besides the town of Santa Gertrudes, the towns of Cordeirópolis, Iracemápolis, Ipeúna and Rio Claro (Fig. 1) and has 35 mines, 47 industries and 43 drying yards [2]. The great advantage of the region is the excellent quality of the raw material [3,4,5] which is extracted of Corumbataí Formation (Permian of Paraná Basin) [6]. However, growing pressure of environmental control agencies forces the industry to develop new drying methods in order to reduce dust emissions associated with transporting and drying natural clay [7].This implies the modification of the current drying methods keeping the low costs of the final product.So, this paper investigates the behavior of the raw material during the drying process to allow changes in current practice that may contribute to the reduction of dust from the drying yards. Of course, other aspects like economic, technical and environmental proceses need to be properly evaluated in further studies.

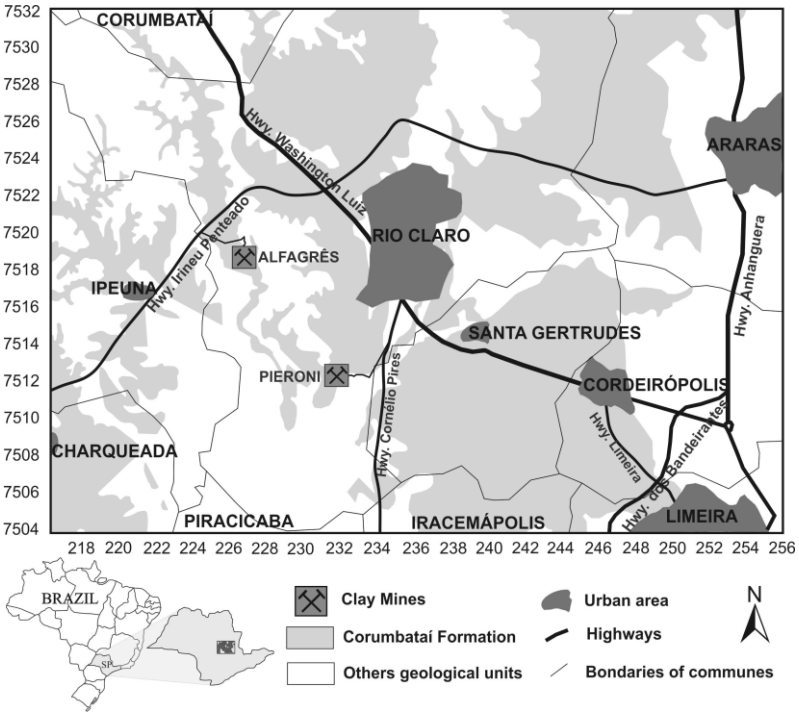

Figure 1. Schematic figure showing the location of the mines, the Corumbataí Formation and the cities belonging to the Ceramic Center of Santa Gertrudes-Brazil.

Materials and Methods

The dry-way method uses different types of raw materials (hard, intermediate and/or soft) to compose the ceramic mass used by industries in the Ceramic Center of Santa Gertrudes. In this study each of the three kinds of raw materials was used. The choice was made according to mineralogical composition; diagenesis and weathering of the ore from Corumbataí formation [8]. Samples D (hard), I (intermediate), M (soft), when compared to other materials of the same type of this region are the most difficult to dry and therefore good testing materials for possible new methods. Samples D and I are from Alfagrês Mine, the soft sample (M) is from Pieroni. Both mines are located near Rio Claro – SP (Fig. 1) and geologically are in the Corumbataí Formation. These raw materials were chemical analyzed by X-ray fluorescence spectroscopy (XRF) and ICP-MS. To investigate the crystalline phases and the minerals present in the samples, they were analyzed with a powder diffractometer (XRD) in an interval of 3 to 40 °C, using a Cu tube and a scanning rate of 2 °C/min. The mineralogical association, texture and structure of these rocks were verified by transmitted light microscopy. The samples were manually comminuted in fraction <3 cm, in order to simulate the size of the fragments in the drying yard. To understand the drying difficulty of these materials, 1kg of each material was exposed to sun light for 12 hours. The materials moisture and the air's temperature and humidity were checked every 2 hours. The moisture was checked using a balance of resistance at 110 ° C for 5 minutes for each sample. Therein, were placed 3.5 grams of samples smaller than 0.5 mm previously sprayed and sieved. The temperature and air humidity were measured by a thermo hygrograph. Since august 2012, this procedure was being done once a month in order to understand the temperature and humidity changes through the year and to verify its effect to the drying process. However, other types of tests were made like using a fan to provide air streams (during the sun light exposure and also in a closed room, with no sun light) and like wetting the materials for 5 minutes in flowing water to simulate a fast rain during the drying by sun.

Results and Discussion

According to the optical mineralogy sample D consists of claystones, reddish in color with illite predominantly and faintly laminated structure.The pelitic texture is orientated and generates aspects of undeveloped slate cleavage. It is consisting of tiny minerals with dimensions smaller than 5 µm involving phyllosilicates, and also quartz and feldspar typically smaller than 80 µm. The

presence of iron, such as oxides and hydroxides, gives the material a reddish color. Small amounts of other minerals such as muscovite, biotite, adularia and apatite can be found in this material. Due to the passage of fluids through the material, it can present white and green shades, containing higher porosity and therefore showing higher moisture. Further, facies in the hard material rich in quartz and with less phyllosilicates, provides greater strength to the rock.

Sample I is a clayey siltstone and its structure is weakly anisotropic marked by rhythmic intercalation with discontinuous lamination. The texture show dominantly pelitic levels rich in diagenetic phyllosilicates, detrital biotite, detrital muscovite and hematite. Less frequently, the rocks show psammitic levels with quartz predominantly. Rarely, this levels can reach 1 mm of thickness. Additionally, albite, siliceous fossil traces, zircon and tourmaline were found in this material.

Sample M is an illitic silty claystone with diffusely laminated structure, pelitic texture (marked by phyllosilicates) and small psammitic lenses with orientated texture consisting mainly of quartz. Overall, the sample has phyllosilicates with homogeneous aspect and dimensions of silt and clay. This rock has closed micropores, which occur in higher density in psammitic areas. The orientation is enhanced by breakage and fluid passage along the planes and microfractures, depositing iron hydroxide and possibly generated montmorillonite out of the diagenetic phyllosilicates.
The result of the chemical and mineralogical analysis of the raw materials used in the study, are in table 1 and figure 2 respectively.

The petrographic and chemical analysis correlated with the XRD patterns, obtained for the hard material (D) (Fig. 2a) shows, that it consists mainly of phyllosilicates with 10 Å (illite), fillossilicatos between 14 and 17 Å (smectite or montmorillonite group), quartz and albite.The diffractogram corresponding to the burned material shows the presence of small amounts of chlorite (± 5%), aspect that justifies the higher MgO content comparing to the other ones. (Table 1). The mineralogy approximately includes: illite and micas (40 %), montmorillonite and interstratified (30%), chlorite (less than 5%), hematite (5 %), albite (10%), potash feldspar (less than 5%) and quartz (10%).

The diffractograms obtained to intermediate sample (I) (Fig.2b) shows mineralogical composition similar to the hard material, with smaller peaks and more open to phyllosilicates between 14 and 17 Å, showing fewer peaks and lower crystallinity, which seems to be a result of the supergenic change. The fine and glycol diffractogram shows that the clayminerals are expandable (montmorillonite or smectite group) and the fraction diffractogram (burned) does not indicate the presence of chlorite. The content of illite and micas is more than 50% by volume, followed by quartz (about 25%), smectite group minerals and interstratified (about 15%), albite (less than 5%) and hematite (about 5%).

The XRD patterns corresponding to the soft material (M) (Fig.2c), as expected, are showing a higher weathering than the intermediate material. Peaks in 7 Å and between 14 and 17 Å disappear completely when the material is burned, suggesting low crystallinity with kaolinite composition relevant to the higher content of aluminum, iron and loss of alkalis.

In the diffractogram (glycol samples), the open peak corresponding between 14 and 17 Å, shows shift to the left indicating the presence of expansive materials (mineral groups of smectite and interstratified). This raw material is composed of illite and micas (about 40%), phyllosilicates group as smectite and interstratified (about 20%), kaolinite with low crystallinity (about 10%), quartz (about 20%), alkali feldspar (about 5%) and oxides and hydroxides of iron (about 5%).

Table 1. Chemical composition of raw ceramic materials .

Sample	SiO2 (%)	Al2O3 (%)	Fe2O3 (%)	CaO (%)	Na2O (%)	K2O (%)	MnO (%)	TiO2 (%)	MgO (%)	P2O5 (%)	LOI (%)
Hard (D)	65.47	13.96	5.07	0.90	1.36	3.41	0.06	0,58	2.42	0.17	6.4
Intermediate (I)	63.16	15.30	5.85	0.24	0.38	3.86	0.06	0.65	2.20	0.07	8.0
soft (M)	62.74	16.53	6.24	0.16	1.36	2.98	0.05	0.68	1,67	0.07	8.6

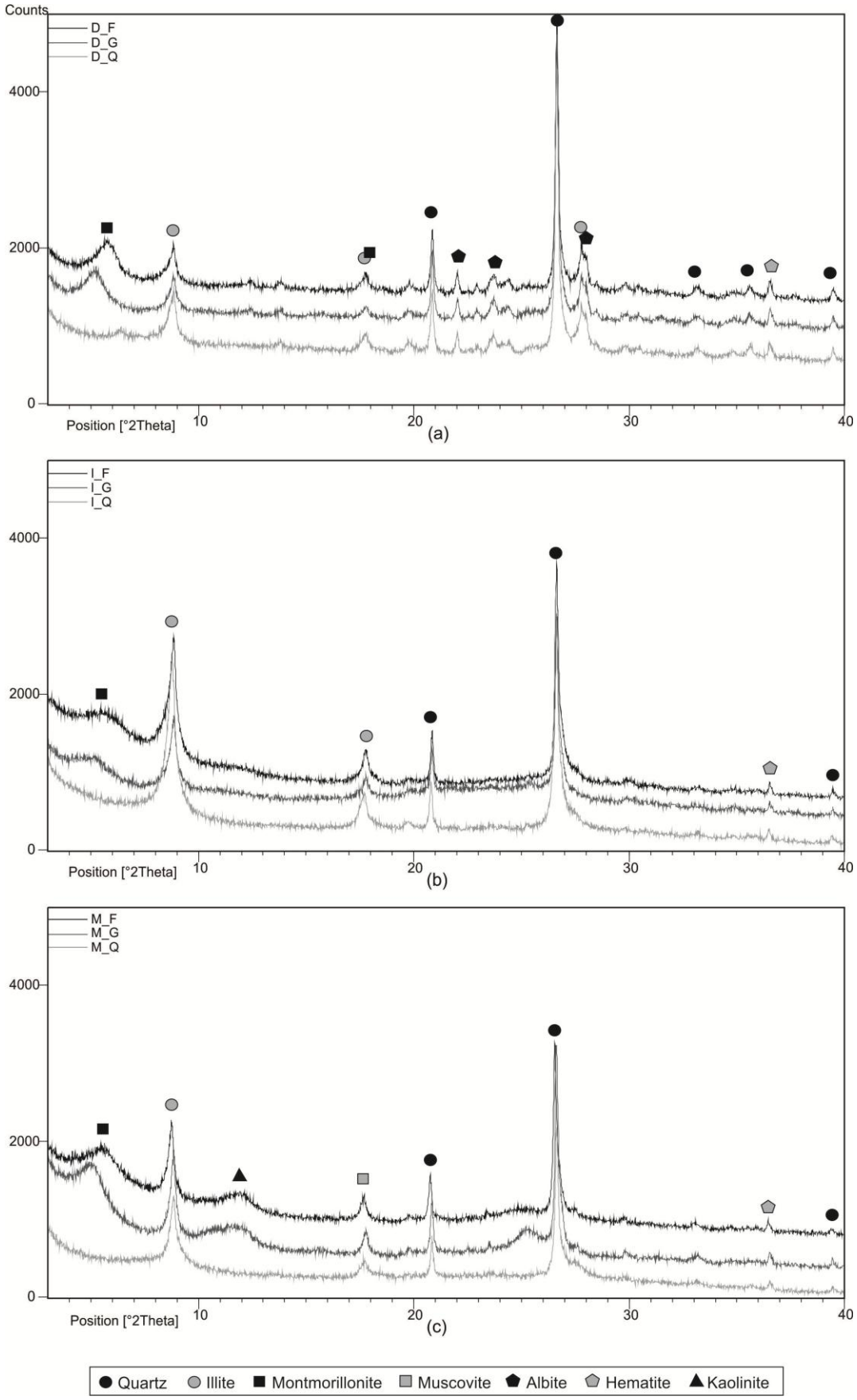

Figure 2. XRD of different samples a) Hard material: D; b) Intermediate material: I and c) soft material: M. F: thin; G: glycol and Q: burned at 550°C.

The results obtained in the sun-drying-tests during one day, once a month (Table 2) show the lowest and highest moisture value by each type of material. The hard material (D) dries quickly, reaching 5% of moisture in the sun from 10 am. The intermediate (I) and soft (M) materials require higher temperatures and a longer exposure time to achieve the desired moisture content of 5%. The table emphasizes the values when the lowest and highest moisture is less than or equal to 5%.

Table 2. The highest and lowest moisture values (%) measured in the samples (D,I and M) over the months.

Samples	D		I		M	
Drying	lowest	highest	lowest	highest	lowest	highest
6h	6,1	8,4	16	17,9	16,6	19
8h	5,6	7,1	14,3	17,2	11,1	16,9
10h	3,1	5	5,3	11,2	6,9	14,3
12h	2,4	4,2	3,9	8,2	3,7	6,9
14h	2,4	3,5	4	6	3,5	5,8
16h	3,1	4	3,8	4,4	3,6	5,0
18h	2,9	4,3	3,8	4,9	3,8	4,8
18h	2,4	4,7	9,2	16,5	9,8	17
24h	3,2	4,8	4,8	9,9	5,5	6,9
6h	3,2	5,3	5,5	8,6	5,1	7,3

Furthermore, the second value for 18h (highlighted) was measure on sample debris lying beneath the rest of the material. This values show, that for an efficiant drying process it is nescessary that all parts of the sample (including the small grained debris) are exposed to the sun. Otherwise there will be more than 5% of moisture remaining especially in the intermediate and soft samples.

The data obtained at midnight and six o‘clock in the morning, were made in order to check the moisture absorption during the night. The results show that this absorption can increase the materials moisture of 2%.

Using an air stream, created by a fan to support the drying process in combination with the intense sun, did not yield in good results. The reason is that the air stream removes the required heat from the sample and thereby minimally slows down the drying process. Samples dried only with an air stream and without sun, did not achieve the required moisture content, because it did not reach the moisture inside the larger fragments of the rocks.

For another test the samples were wetted for 5 minutes in flowing water and then, they were put in the midday sun in order to dry. They can achieve a total content of moisture of 5% in less than 4 hours. Wetting the samples before the drying process leads to another result: because of the significant loss of moisture in relatively short time, the samples are easier to dry because they are breaking into smaller fragments.

Measurements of moisture (%) performed consecutively, showed that the moisture never reaches 0 %. The values are stable around 1 %, even after the 5th measuement (Table 3). Also, for the raw materials in this study it could be verified that due to the conditions of the ambient humidity, it can acquire more than 5% of moisture during one day, inside the lab.

Table 3. Moisture values (%) measured in the samples (D,I and M) consecutively.

Samples	1°	2°	3°	4°	5°	1 day
D	1.1	0.8	1	0.9	1	5
I	1.1	1.4	1.1	1.4	1.2	6
M	1	1	1.4	1	1.1	6.2

Experiments showed, that the best drying performance is achieved in October and November, which are the month with the best combination of low humidity and high temperatures. This combination promotes a more efficient drying process, mainly between midday and 14 pm, verified in the overlap of the curves (Fig. 3).

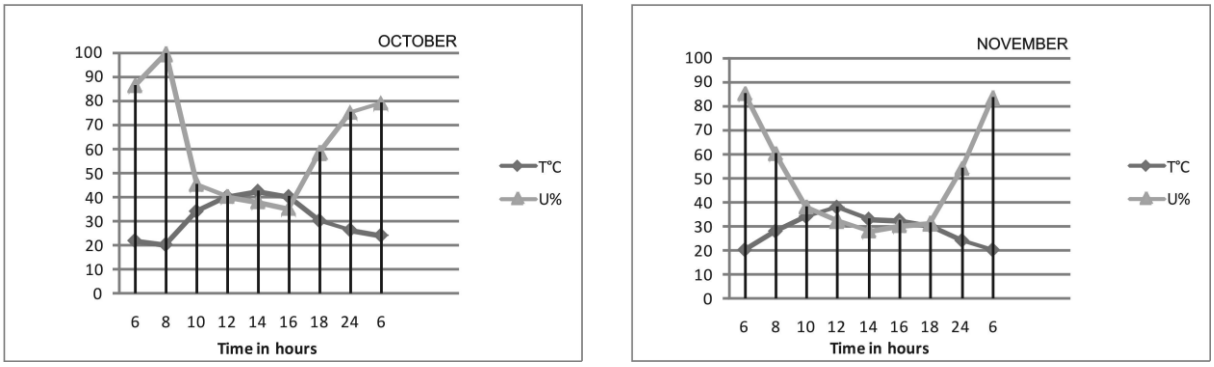

Figure 3. Humidity and temperature values obtained in October and November by a thermohygrograph.

Conclusion

According to the results of the drying experiments, drying the materials separately improves the drying performance, due to the easier drying material eventually impede the more difficult drying material to reach 5% of moisture while overlaying the rocks, which is still wet.

The hard ore D (almost unchanged) has about 7% of moisture, the intermediate ore I (with visible change) about 17% and the soft ore M (amended) near 18%.

The duration of the drying process is related to the amount of smectite (more amount of smectite is more difficult to dry) and the rock weathering degree (the higher the microporosity, the greater the difficulties of drying).

The industry activity in the Ceramic Center of Santa Gertrudes has shown that all type of materials are ready for grinding when the moisture content is around 5%. So, it is not necessary to dry to a value less than 5%, due to the fact that the materials will absorb moisture from the environment which will lead to a moisture content of around 5% again. Especially the materials more altered frequently reach more than 5% of moisture, when exposed to the environment during the night.

Finally, experiments showed that large contact surfaces (grainsize < 3 cm) of the materials with the sun, improve the drying process. Wetting of the material leads to an early breaking of the material and to a bigger microporosity, which also improves the drying process.

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