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To cite this article: A O Florez *et al* 2018 *J. Phys.: Conf. Ser.* **1126** 012036

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Technological characterization of Guayabo group clays from Cúcuta-El Zulia sector for use in ceramic industry

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Abstract. The present study characterized the clays found in the *Guayabo* group in the metropolitan area of Cúcuta. Material samples were taken at 2km south of Cúcuta – El Zulia road, right on the border between the two municipalities. The objective was to evaluate the chemical, mineralogical composition and behavior of the raw material for the elaboration of ceramic tiles. Techniques such as X-ray diffraction and X-ray fluorescence were used. Physic-ceramic parameters were determined, such as the percentage of shrinkage per shot, water absorption and resistance to bending. The results showed a majority composition of quartz (above 57%), which is consistent with a high silica content (higher than 68%). Firing parameters revealed low contractions, a medium degree of water absorption, and a lower resistance value compared with the standard, therefore it is recommended to mix this clay with materials that improve the resistance value in order to comply with product quality standards.

1. Introduction

The attributes of the ceramic pieces depend mainly on their shaping processes and the raw materials used [1], the former have tended to normalize due to the imitation of efficiency standards among the companies of the guild, adding to each manufacturing point particular elements according to the environment in which it develops, while the latter tend to be agents with their own characteristics that differ from the others due to a complex and unique geological evolution during their forming process [2]. Therefore, in the execution of any project, it is necessary to carry out a detailed study of the raw materials used, to know their chemical composition, structure and technological qualities, since this way their behavior is known in relation to manufacture operations [3].

Ceramic paste is usually a tight mixture of three types of compounds: plastic materials that give it malleability, not plastics materials that mitigate the deformation in the finished product, and fluxes that accelerate the formation of the vitreous phase thus decreasing the firing interval, which represents an energy saving [4]. The main raw material of the industry is clay since it can provide all the properties described above, although regularly, it is lacking in non-plastic or flux components, being necessary to mix it with other materials such as sands or feldspars, respectively, and to compensate the insufficiencies.

The metropolitan area of Cúcuta is characterized by the production of high quality ceramic articles [5] that are sold in international markets despite not having significant technological advances [6]. The socio-economic impact of this industrial group on the community is of great importance, a reflection of



this is its high participation in the indices of generation of wealth [7]. One of the causes of this situation is associated with the raw materials used, which exhibit interesting technological properties, especially their clays, which allow them to be competitive; the region has large reserves of this last material, thanks to the deposits found in the geological group called *Guayabo*. This geological group outcrops in some sectors, as in the border area between the municipalities of Cúcuta and El Zulia [8], where deposits appear on slopes on both sides of the intermunicipal road that connects the two locations. The present investigation carried out a chemical, mineralogical and technological characterization of the clays found in that sector, located within a mining title belonging to one of the leading companies, in the country, in the production of enamelled supports for floors, interested in evaluating their behavior for the elaboration of this type of products.

2. Materials and methods

In the area, eight exploratory trenches were excavated, in which samples of clay were collected at 2 meters depth (15 to 10kg each), obtaining a fresh material without any alterations by atmospheric agents. Subsequently the material sampled was crushed, quartered and properly mixed to provide 8 statistically valid representative samples, one for each excavation (T1, T2, T3, T4, T5, T6, T7 and T8), in which 0.5kg of the sample was removed for chemical and mineralogical analysis, and additional 3.0kg to determine technological properties.

2.1. Analysis methods

Granulometric distribution of the representative samples was determined with Stokes' law, using the hydrometer technique, which identified the texture of the material considering that the falling speed of a particle within a fluid is influenced by its diameter and specific gravity as well as the viscosity and density of the receptor liquid [9]. The tests were performed by mixing 50g of each sample, a size smaller than 75 μ m, with water and sodium hexametaphosphate, sedimentation was measured with a hydrometer reference 152H.

Of the 500g for the mineralogical and chemical analyses, 250g were selected, continuing the cracking until reaching 100g. Finally, the material was pulverized to grain sizes below 150 μ m for X-ray diffraction (XRD) analysis. Results were obtained by means of an X-ray diffractometer ARL Thermo Fisher model 9900 Work Station with cobalt radiation. The sample was measured in a Bragg-Brentano optical configuration with a high-speed solid-state detector for data acquisition.

The quantification and normalization to 100% of the mineral phases it was determined with Rietveld technique, which provides a qualitative and quantitative identification of the changes and imperfections in the structure, since it compares the wave spectra that the samples emit considering structural and micro structural aspects with respect to a theoretical mineral pattern [10]. The chemical composition of the samples was determined with the X-ray fluorescence (FRX) using the same XRD equipment. The sample was measured on a calibration curve of general oxides. Pearling procedure was used for preparation, melting the material with a Lithium Metratetaborate flux for 20 minutes at 1100°C.

The physical ceramic tests were developed initially with the preparation of the slip, the mixture was dried at 105°C for 24 hours to get the paste. 560 g of paste is crushed to obtain particle sizes below 425 μ m. Subsequently, rectangular samples are prepared by pressing technique and cooked under the following temperature ranges: 1080°C, 1100°C, 1120°C, 1140°C, 1160°C and 1180°C, similar to those used in industry.

Length and weight (characteristics in cooking) were measured in each sample. With variations in volume compared to the dimensions dry, the shrinkage percentage was determined in cooked (% FS) for the indicated temperatures to above. The cooked pieces were immersed in water at boiling temperature for 2 hours. The percentage of water absorption (% WA), was determined by the difference in weight before immersion and after immersion according to the norm NTC 4321-3 [11]. With the NTC 4321-4 standard, the values of flexural strength in the study samples were determined [12].

3. Results and discussions

3.1. Particle size distribution

In general, all the samples revealed dominant clayey size with values higher than 57%, followed by silt ranging from 31.2 to 24.4% and sands between 16.1 and 7.7%, as shown in Figure 1, values that agree with other studies developed in the region [13]. This is favorable for the industry, because fine fractions $<2\mu\text{m}$ are of great applicability in the production of ceramic supports, being necessary to grind and sieve those materials with grain $>50\mu\text{m}$ [14]. However, a small dispersion was observed among the samples, for example, trench 4 had the highest concentration of clay size (64.8%) and a slight fraction of sand (10.8%), as opposed to trench 3, where its sand percentage is higher (16.1%) to the others and the clayey fraction (57.9%) is the lowest.

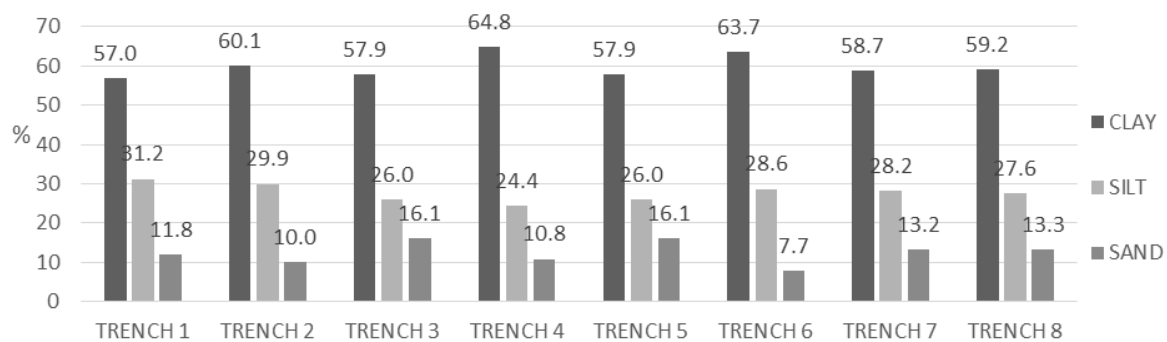


Figure 1. Composition of clays by grain size.

3.2. Mineralogical composition

The results of the XRD are recorded in Table 1. Quartz is the mineral that most contributed to the compositional total with an average value of 60%. However, there were variations, for example, T8 was the highest concentration of ore with 62.8%, contrary to T7 with 57.6%. After quartz, kaolinite is the compound with the greatest presence, highlighting samples T4 with 24% and T3 with 20%. The percentages of kaolinite for the other trenches are in intermediate ranges at T3 and T4. According to the study, the clays analyzed contain concentrations of kaolinite greater than 20%, it is possible to infer that they can withstand high temperatures in cooking processes [15].

Table 1. Mineralogical composition of the study samples.

Sample	Quartz (%)	Hematite (%)	Kaolinite (%)	Muscovite (%)	Anatase (%)
T1	59.2	3.0	22.1	15.0	0.7
T2	59.9	2.3	22.7	14.4	0.7
T3	61.7	2.1	20.0	15.7	0.6
T4	58.6	2.5	24.0	14.2	0.7
T5	59.1	2.9	20.6	16.7	0.7
T6	58.7	2.7	22.2	15.5	0.8
T7	57.6	1.8	23.0	16.8	0.7
T8	62.8	1.0	21.1	14.4	0.7

Continuing with the analysis, the Muscovite, which gives the material flux characteristics, was the third predominant compound. According to the XRD results, the T7 clay is the richest in Muscovite with 16.8%, while the T4 trench is the poorest with 14.2%; in the remaining trenches the Muscovite concentration ranged around 15.5%. Hematite was the fourth mineral in contribution in the samples analyzed. It maintained an average value of 2.1%, although in the representative T1 it reached a maximum of 3.0% and in the trench 8 a minimum of 1.0%; according to the reference [16] values lower than 5% are not considered as impurities in non-refractory clays.

Finally, anatase was the compound with the lowest participation in mineralogical results. Its maximum value was determined in trench 6 with 0.8%. In trench 3 the value was set at 0.6%. For the other trenches the percentage of the anatase compound was 0.7%.

3.3. Chemical composition

Table 2 shows the values of the chemical composition for the study samples. Silicon dioxide is the representative element with an average value of 70%. Some maximum values are evident, especially in trench T3 (71.64%), and minimum values in T4 (68.79%). These results agree with the XRD analysis where the quartz, the crystalline phase of SiO₂, was the dominant mineral with 60%. The percentage compositional difference between quartz and silica may be due to the different crystalline phases in the silicates, so its content may be higher than that of quartz [15]. The above indicates low deformability in the products manufactured because SiO₂ contributes to reduce the strong contractions that occur in the piece after cooking. Alumina (Al₂O₃) is the second most predominant compound, has melting properties that allow to lower the melting temperature of the paste, and has an average value of 15.8%, with a high peak in trench 4 of 17.31% and a low of 15.08% in trench 3. It can be seen that the contents of alumina and silica were inversely proportional between trenches 4 and 3, which recorded the highest / lowest values.

Iron oxide Fe₂O₃ is the third compound that contributes to the composition of clays, its value is between 6% (in T5) and 3.75% (in T8), being located in an applicable margin for the ceramic industry. Fe₂O₃ is a flux oxide that contributes reddish coloration to manufactures due to Fe⁺³ cations [17]. K₂O is one of the fluxing alkaline oxides, its maximum value reaches 1.98% in trench 5 and a minimum value of 1.69% in trench 2. In the other representative samples, the values reach an average of 1.83%. This percentage tends to adjust to the results of the Muscovite in the study by XRD because it contributes almost all of K₂O in the clays. It is estimated that the content of potassium oxide in these micas is 6.7% [2]. CaO and MgO (0.49-0.61%) provide oxygen to the tetrahedral silica chain (Si-O₄) weakening the structure, increasing the coefficient of expansion, and increasing the rate of expansion / contraction of the material [18].

Table 2. Chemical composition of clays (%).

Compound	Representative (%)							
	T1	T2	T3	T4	T5	T6	T7	T8
Al ₂ O ₃	15.43	15.98	15.08	17.31	16.09	15.98	16.59	15.55
CaO	0.17	0.20	0.22	0.20	0.22	0.18	0.19	0.23
Fe ₂ O ₃	5.65	4.58	4.84	4.81	6.00	4.71	4.71	3.75
SiO ₂	70.16	70.77	71.64	68.79	68.98	70.55	69.38	71.23
K ₂ O	1.81	1.69	1.88	1.72	1.98	1.78	1.96	1.83
MgO	0.32	0.35	0.35	0.36	0.38	0.32	0.40	0.38
P ₂ O ₅	0.12	0.12	0.15	0.11	0.14	0.10	0.10	0.10
Na ₂ O	0.11	0.10	0.10	0.10	0.08	0.08	0.09	0.12
TiO ₂	0.86	0.86	0.77	0.89	0.82	0.86	0.81	0.85
Cr ₂ O ₃	0.04	0.04	0.05	0.04	0.05	0.04	0.05	0.04
ZnO	0.04	0.04	0.03	0.04	0.04	0.04	0.04	0.04
ZrO ₂	0.055	0.04	0.04	0.04	0.04	0.04	0.04	0.05
LOI	5.13	5.20	4.79	5.54	5.17	5.34	5.57	5.79

3.4. Technological properties

In Colombia, the standard NTC 919 [19] establishes the quality standard for a ceramic support by the amount of water absorbed. The study samples were subjected to a burning process at temperatures of 1140°C, simulating the industrial process of ceramic tile production in companies in the region. The results, Figure 2, show that all clay samples are in the medium absorption group called BIIB. The values are estimated to be greater than 6% and less than or equal to 10% and remain constant until temperatures close to 1180°C. Upon reaching the temperature of 1180°C, the ceramic samples indicate an absorption

percentage of around 8%, except for specimens T3 and T4 with values of 9.3% and 6.1, respectively. At temperatures of 1080°C the ceramic samples increase the percentage of water absorption to 10%, classifying themselves as a high absorption group.

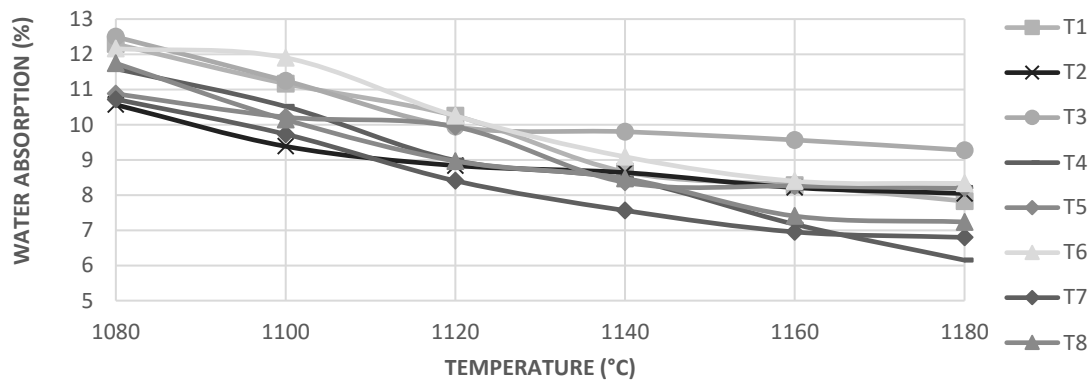


Figure 2. Absorption of water in test pieces analyzed.

The percentage of water absorption is related to the porosity of the pieces. According to the results, the percentage of porosity of the samples decreased significantly after 1100°C. This can be explained by the degree of inclination of slopes in terms of the increase of the liquid phase on the surface of the samples, reducing the number of pores and their distance [17]. Finally, at temperatures above 1140°C, water absorption exhibits smoother and constant slopes with the exception of T4, possibly due to a higher content of fine particles in its composition.

In general, the firing contractions revealed smooth curves as seen in Figure 3. This type of behavior is beneficial in the shaping of ceramic products because large longitudinal variations in a short temperature range result in irreversible deformations in the final product. The situation can be attributed to non-uniform burning environments in which parts of the piece that are subject to higher cooking temperature will contract more than the rest, causing the mismatch and lack of fullness in the finished product [20].

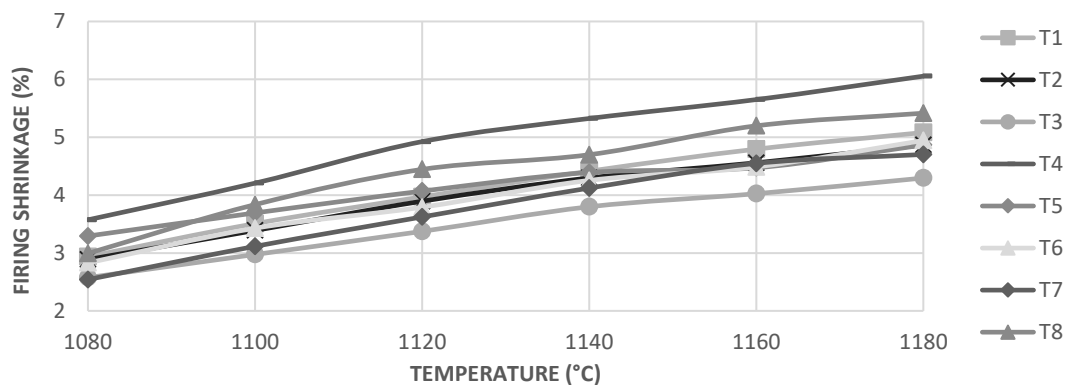


Figure 3. Firing shrinkage of the specimens studied.

According to Figure 3, a shrinkage percentage of 4.4% was found at a temperature of 1140°C (local burning temperature), slightly higher than the standard of the pulp used for the manufacture of ceramic tiles [21]. A maximum percentage of 5.3% is evidenced for the T4 samples due, very possibly, to the granulometric composition higher than 63 μ m with respect to the other samples analyzed. This distribution in the grain size confers less amount of degreaser affecting its inertia in the burning process. For the T3 samples rich in silica, the contraction percentages were determined in 3.9%, showing the lowest values of the whole system studied. There are no strong changes in the contraction curves in the

temperature range between 1120°C and 1140°C due to a reduction in the porosity of the ceramic samples [22].

Figure 4 shows the results of the flexural strength. An improvement in function of the increase in the cooking temperature is evidenced, due to the decrease of the open porosity and the increase of the contraction [20]. However, taking into account that all samples belong to the medium absorption group according to industrial burning conditions, only trench 8 exceeded 18N/mm². The other trenches showed values below the requirement of the modulus of flexural breakage specified by the NTC 919 norm in the Colombian case. A minimum value of 5.36N/mm² is highlighted in the T6 samples due, quite possibly, to the low concentrations of carbonates, calcium silicates, alumina and MgO that prevented the formation of a hard structure in the cooking process [17].

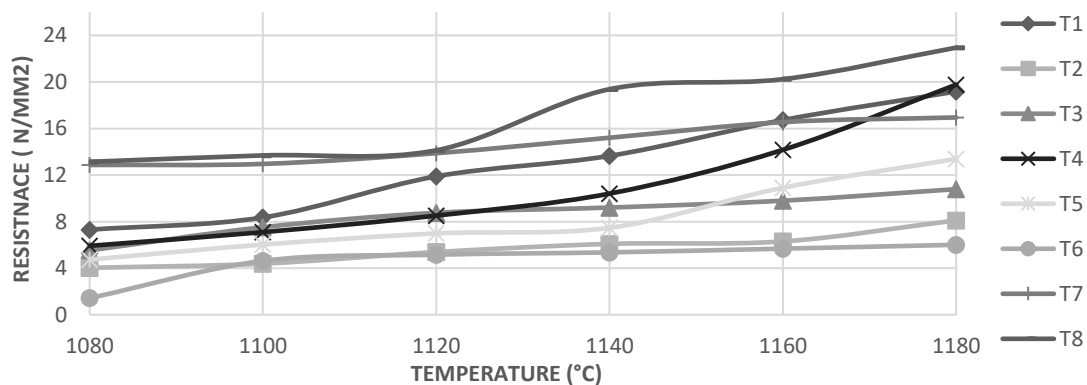


Figure 4. Flexural strength of the samples.

4. Conclusions

The granulometric analysis of the clay deposits, with grain sizes below 2µm, reveal suitable conditions for their use in the ceramic sector. This characteristic facilitates the physic-chemical reactions between the elements of the ceramic paste and an energy saving in the grinding and screening processes. The material from the trench one needs greater control grain size because only 50% with the optimum granulometry meets for use in industrial ceramic processes.

The results of the mineralogical composition by XRD and chemical composition by FRX were consistent. The study showed high levels of quartz in the samples analyzed, which shows the abundant amount of silica, especially in the T3 trench material (71.64% SiO₂). It is expected that tiles manufactured from this clay show low shrinkage values.

The weak internal structure of the ceramic pieces, probably due to the low concentration of carbonates and MgO, can lower the quality standards of the products to be developed specifically in the capacity to withstand stresses. Only one of the eight samples studied showed values of flexural strength greater than 18N/mm². This is the minimum value that manufactured parts should achieve with respect to their percentage of water absorption. Due to this characteristic, it is recommended to mix, in suitable proportions, with other clayey materials for the manufacture and commercialization of ceramic products, only in this way the exploitation of clays becomes viable and competitive.

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