Technological characterization of Colombian clay during the stages of the production process

R A García-León1,2, W Quintero-Quintero1, and E Espinel-Blanco1
1 Universidad Francisco de Paula Santander, Seccional Ocaña, Colombia
2 Instituto Politécnico Nacional, Ciudad de México, México

E-mail: ragarcial@ufpso.edu.co

Abstract. Clays are of great importance at the industrial level because they can be used to make masonry products such as blocks, roof tiles, bricks, and tiles, among others. Currently, many companies in the ceramic sector get a lot of waste due to the lack of technical analysis of the raw material to forecast the behavior of the ceramic mixtures and to improve the quality of the final product. In this paper, the physical and chemical characterization of the clay used in one of the companies dedicated to the manufacture of masonry products for construction in Ocaña, Norte de Santander, Colombia was conducted. The development of the investigation was achieved by means of the execution of physical and chemical tests to the sample of selected clay from different points of the production process with which the granulometry, index of plasticity and the mineralogical composition were determined. The results obtained show that the clays currently used by the company are at a low level for masonry products for construction. This is why the addition of other clays is considered, with which an optimum mixture is achieved with which can meet the requirements of the current regulations in force. It is essential to technologically characterize the clays to optimize the mix and thus avoid defective products. It will obviously improve the company's environmental and economic resources.

1. Introduction

Currently, Colombia is not a great power in industrial manufacturing of clay-based products, even though there is a great abundance of excellent raw material in the soil. The ceramic sector in the Norte de Santander, Colombia, area is widely used, being recognized not only nationally, but also internationally. In spite of this, in the ceramic factories in the region, there is a wide ignorance of the characteristics and behavior of the raw materials used in the manufacture of clay products [1]. Clays are generally used in the manufacture of products for construction, with an equivalent to 90%, the remaining 10% have other uses such as rubbers, paints, molding sands, agriculture, paper, among other products. According to its capacity of production and technological development, brick kilns have been classified into chirecales, small, medium, and large brick kilns.

On the other hand, there is a great variety of natural deposits, but despite this, the department whose export of materials made of clay does not exceed 5.7% of total exports at the regional level, representing approximately 13.7 million dollars for the department's economy as of July 2013. Understanding that these figures in relation to construction materials are only reflected for the municipality of San José de Cúcuta and its metropolitan area, as it is the only municipality that owns small and medium-sized enterprises in terms of the manufacture of clay materials [2]. The process of clay transformation is mainly composed of three phases: preparation of the ceramic paste, molding of
the piece and cooking. The preparation process is the first phase. Here the composition and plasticity are modified adding other clays from the region in order to obtain a homogeneous ceramic paste. In the second phase of molding the desired shape must be considered if it will take pressure of extrusion. Once the molded piece has been obtained, the drying is done, being this the last phase, where the rate of water evaporation is controlled in order to avoid defects in the piece. Subsequently, the piece is sintered, that is, subjected to the cooking process in order to decrease porosity, increase density and mechanical strength [3-6]. The physical, chemical, and mineralogical characteristics of clays vary widely, even between the layers of the same clay deposit. Therefore, in any ceramic industry, the control of the quality of the products begins with the characterization and control of the quality of their clays.

It is important to identify the process and the variables that intervene in each of its stages of the production process [4], as well as the characterization of the raw material (clay) by different methods such as: Physical, chemical and mechanical tests, in order to know the behavior in the different stages of production and how to validate the final product with quality conditions based on the current regulations in force such as NTC 4017 and 4205 that govern the masonry products for construction [5-7]. Other studies analyzed a sample of red clay and determined its chemical composition and crystalline phases; In addition to the granulometry distribution and thermal analysis, the density and limits of Atterberg were also determined; where they subsequently evaluated the samples thermally at 1050 °C, in addition to chemical analyzes such as X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis [8-12].

Considering the above, this article shows a study through physical and chemical analysis (technological characterization) of the clays used by a company dedicated to the manufacture of masonry products for construction. There the raw material is analyzed in each of the stages of the process to validate their cooking behavior by means of physical analysis with hydrometric tests and in this way, validate the results with chemical and mineralogical analysis with the help of the chemical analyzes.

2. Materials and method
The clay samples were collected directly from the mines of the company by direct observation. Likewise, the results of the analyzes that were obtained from the samples were determined the variables studied for the approach and implementation of the experimental studies, making laboratory analysis to identify the variables and thus design the optimal mix in manufacturing of blocks H-10 [7,13]. Regarding the above, samples were selected M1 (Extraction), M2 (Disintegrator), M3 (Laminator I), M4 (Laminator II), M5 (Humidification) and M6 (Mixed) [14]. Figure 1 presents a detailed description of the different stages of clay processing:

From the petrographic point of view, clays are classified according to their mineralogy (rich in kaolinite), chemism (high content of alumina), geological origin (sedimentary type), physical properties (plasticity, humidity, resistance, etc.), industrial use (refractory sector, construction, etc.), among other parameters. Based on mineralogy, which is one of the main ways to classify them, clays are contained clay minerals and non-clay minerals, which are those that provide the plasticity and the drying and cooking properties of the final products made because of this raw material. The clay minerals correspond to the phyllosilicates, the aluminum, iron, and magnesium silicates hydrated with layered structures including the palygorskite and the sepiolites [6].

It is for the foregoing, that one of the most important characteristics to be evaluated in clays is the chemical and mineralogical composition since it directly influences the properties of the obtained ceramics. For example, clays with a high content of kaolinite will allow obtaining ceramic products with refractory character, clear coloring, and good mechanical resistance. High contents of illite and montmorillonite confer high plasticity to ceramic pastes, which translates into an easy conforming of the pieces, but also in a large contraction of the same during drying and sintering, can lead to the formation of cracks [15]; in such cases, degreasing material (sand) must be added to adjust the plasticity of the paste. Therefore, plasticity is another important parameter to control this, being
understood as the property that clays have of forming a plastic mass with water. One of the simplest methods to determine such property is that of the Atterberg limits [16], which include the liquid limit (% humidity that a soil has when it is on the boundary between the liquid state and the plastic state), limit plastic (which corresponds to the lowest humidity at which a soil can be molded) and plasticity index, which is the difference of the two previous limits and indicates the range of workability of the clay.

Figure 1. Description of the stages of the process.

The granulometric distribution is another variable of great importance since it will depend on the degree of the packaging of the particles and, therefore, the physic mechanical properties of ceramics (porosity, water absorption, resistance to bending, etc.). On the other hand, the granulometric distribution allows to predict the plastic or degreasing character of the clay, taking into account that the clayey material has small particle sizes, of the order of a few microns, while the degreasing or sandy fraction has a particle size much older.

The characterization of the clays must also include their thermal analysis, such as thermogravimetry (TG) and differential thermal analysis (DTA). The great importance of these analyses is that they can predict various thermal phenomena that occur during the firing of clays, such as crystallization of phases, solid-state reactions, dehydration, fusion, oxidation, etc [12, 16, 17].

3. Results and discussions

The technological characterization of raw materials is of vital importance to predict their behavior in the production process and in this way to obtain quality products required by customers and current standards. It is in this way that the granulometry of the selected samples was obtained as well as the chemical characterization by X-ray fluorescence and X-ray diffraction. In addition, sieving particle size is fundamental to define particle size distribution, soil gradation and to predict problems that may arise in the future [7]. This analysis is complemented with the hydrometry and granulometry, which allows knowing the percentage of fine material present in a soil sample, data that cannot be determined by means of sieve granulometry and that is indispensable to predict its behavior. When tabulating the data, the clay percentage of the soil sample is determined, that is, the particles with a diameter smaller than 0.002 mm.
Next, the percentages of sands, silts and clays are defined in detail, joining of the sifted and hydrometric analyzes in a single diagram, considering that particles with values up to 100 millimeters correspond to gravels, among 100 and 0.08 millimeters correspond to sand, between 0.08 and 0.005 millimeters correspond to silt and particles with a diameter between 0.005 and 0 millimeters correspond to clay. From which the following results present in Figure 2 were obtained.

![Figure 2](image)

**Figure 2.** Classification of the soil from the sieving and hydrometric graphs.

Taking into account the previous Figure 2, the percentages of sands, silts, and clays were calculated in the following Table 1, which are of great importance for the characterization of raw materials based on ceramics:

| Sample | % SANDS | % LIMES | % CLAY |
|--------|---------|---------|--------|
| M1     | 36.0    | 32.0    | 32.0   |
| M2     | 36.6    | 31.6    | 31.8   |
| M3     | 36.0    | 26.0    | 38.0   |
| M4     | 37.0    | 17.0    | 46.0   |
| M5     | 37.5    | 25.8    | 36.7   |
| M6     | 37.0    | 32.0    | 31.0   |

To estimate the plasticity index of the soil, it is necessary to determine the liquid limit and the plastic limit of the samples and the plasticity index will be the difference between these two values. In case of being decimal, it approaches the nearest integer. In case of being zero (0) or less, the soil sample is assumed as "no plastic". Next, Figure 3 shows the graphic representation of the plasticity index (LP) and liquid limit (LL), taking into account the Atterberg indexes. This diagram is used to determine the percentage of water that must be applied to the ceramic paste for its conformation.

It was determined from the previous Figure 3(a) that the samples vary in a low percentage in the different stages of production, being in the zones of the CL, OL and ML diagram; being mostly inorganic clays of low to medium plasticity, clays with gravel, sandy clays, silty clays "CL", with traces of organic silts and silty organic clays of low plasticity or inorganic silts and very fine sands, clean silts, fine sands, silty or clayey, or clayey silt with slight "ML" plasticity. On the other hand, in Figure 3(b), it was possible to identify that most of the samples are clays difficult to extrude. It occurs because the large percentage of sand they have.
Figure 3. (a) Plasticity in the Casagrande diagram. (b) Prediction diagram of the extrusion and/or molding through the Atterberg limits.

With the X-Ray Fluorescence analysis, the chemical composition of the sample was determined qualitatively and quantitatively [18,19]. The importance of the knowledge of the chemical composition and clay materials lies in principle as a complementary method in the identification of clay minerals. The results of this analysis are in the following Table 2.

| Name           | Element   | Composition % |
|----------------|-----------|---------------|
| Oxido de aluminio | Al₂O₃      | 20.67         |
| Oxido de calcio   | CaO       | 1.94          |
| Oxido de hierro   | Fe₂O₃      | 6.56          |
| Oxido de potasio  | K₂O       | 2.89          |
| Oxido de magnesio | MgO       | 1.52          |
| Oxido de sodio    | Na₂O      | 0.62          |
| Oxido de silicio  | SiO₂      | 54.74         |
| Trióxido de azufre| SO₃       | 0.07          |
| Carbonato de calcio | CaCO₃   | 7.89          |
| Perdidas por ignición | LOI     | 4.01          |

The above describes that the clay has the following characteristics for each chemical element:

- Silica (SiO₂) of 54.743% for the two mixtures respectively. It causes a rapid drying process, in cooking a decrease in the contraction. There was Alumina in high percentages for the two mixtures. Taking into account that chemical characteristics recommended for construction are 50% to 60%.
- Alumina (Al₂O₃) of 20.670% for the two mixtures respectively, conferring resistance to high temperatures and a reduction of breaks in cooking. Taking into account that recommended chemical characteristics for construction is 20% to 30%.
- Montmorillonite clays because their chemical composition is: SiO₂: 48% - 56%, Al₂O₃: 11% - 22%, MgO: 0.3% - 0.8%.
- Iron oxide (Fe₂O₃) of 6.567% for the two mixtures respectively are normal because they are less than 10%. This oxide will give it a red color after burning. Due to its percentage, the black heart effect may not appear.
- The low content of alkaline oxides (sodium and potassium) and alkaline earth oxides (magnesium and calcium) makes it possible for the clay to generate the vitreous phase at relatively high temperatures (higher than 900 °C), giving it properties of semi-hardness.

The presence of high content of potassium oxide (K₂O) of 2.89%, above the other alkaline and alkaline earth oxides, classifies it as an illitic material, the other elements are in low proportions that
do not affect the structure of the Final product. Table 2 shows the chemical analysis of X-ray fluorescence made to the raw material used for the mixture of the paste. Taking into account the bibliography, the clays suitable for the manufacture of ceramic bricks should contain SiO$_2$ between 64.1-83.1%, Al$_2$O$_3$ between 21.6%-27.1% and Fe$_2$O$_3$ between 3.0-6.1% according to Środon [20]. For the results obtained, these values are between 54.73%-56.52% SiO$_2$, Al$_2$O$_3$ between 20.56%-20.67% and Fe$_2$O$_3$ between 6.56-6.61%, so the values are very similar. On the other hand, the content of potassium oxide (K$_2$O) in the sample reaches a value of 2.89%, a fact that suggests the existence of micaceous in relatively high proportions, although the existence of other minerals in layers cannot be ruled out.

In order to corroborate the information of the data obtained, the X-ray diffraction analysis was carried out, which allows the identification of both clayey and non-clayey crystalline phases. Because all crystalline solids have a characteristic diffractogram, their interpretation is qualitative as well as quantitative [21]. For the most part, clay mixtures have a composition, for example, 50% kaolinite + 30% quartz + 20% potassium feldspar.

In the following Figure 4 shows the diffractogram of minerals with clay-sized particles. Oriented, glicolated and calcinated patterns. *Expansive clay: montmorillonite, nontronite or beidellite.

![Figure 4. Result of the X-ray diffraction analysis.](image)

In general, the name of the clays used in construction is ceramic clays or common clays. They are composed of two or more clay minerals, generally illite, kaolinite, and smectite, with significant amounts of other minerals that are not phyllosilicates (carbonates, quartz, etc.) and are generally used for the manufacture of building materials and aggregates.

The samples present a diverse composition, of which certain tendencies are appreciated. Some clays find their main field of application in the absorbent sector because they can retain water or other molecules in the interlaminar space (smectite) or structural channels (sepiolites and palygorskite). The hydration and dehydration of the interlaminar space are characteristic properties of smectites, and their importance is crucial in the different industrial uses. Therefore, the smectites in the form of montmorillonite are considered to absorb a large amount of water between their interlaminar spaces, which are their main characteristic. As for the clay minerals, it is observed that most of the samples are constituted by the illite in an important proportion (it is generally the second most important mineral after quartz).

The analyzes obtained by X-ray diffraction for one of the selected samples show that the mineralogical composition consisted of smectite (38.1%-40.9%), montmorillonite (1.5%-2.6%), muscovite (18.4%-19-4%) and kaolinite (16.1%-21.4%). These results, together with the experimental analyzes, allow us to conclude that the company uses natural sediments that can be considered as good to medium quality plastic clays to prepare its masonry products for construction. The content of Fe$_2$O$_3$ iron oxide seems to indicate the presence of iron oxides and the low content of alkaline oxides such as sodium and potassium that give the clay the possibility of generating the glass phase at relatively high temperatures, allowing for the diffract gram.
4. Conclusions
The samples had a similar behavior observing their curves in the hydrometric and sieving charts, but individualizing the tests that behaved more regularly was sample 1, with 36% of Sand and 32% of Clay. However, the composition of these clays does not depart much from the optimum range, in addition, said composition can be easily reached with the mixture of such clays.

The results of the granulometry tests indicate that most of the company samples have an average index of 45% of fine sand taking into account the graph for this purpose; a result of great importance for the manufacture of ceramic pastes, because it allows to classify the samples as materials of low compaction, low plasticity, which should not be used individually for production because they will have low resistance in dry and cooked, as well as high water absorption. Also, the sand is necessary for the extrusion, because it helps to reduce the drying time and prevents the formation of cracks in the pieces. Obviously, the problem in the block manufacturing process is in the size of the sand particles, which are up to 2.0 millimeters, so the crushing and rolling process is not effective getting bad spray, which makes that the final product has characteristics of high water absorption that weakens the resistance to compression as evidenced in the technological tests.

The chemical characterization by XRF and XRD is of great importance because it was possible to identify the elements present in their percentage by weight, as well as the crystalline phases that can be obtained during the cooking process, which is the most critical variable during the process of transformation of clay.

In general, the evaluated samples have high sand contents, greater than 25%. Low contents of sand are considered those less than 10%, medium contents between 10% and 25% and highs above 25%. The ideal percentages of sand for the production of extruded ceramic products range between 16% and a maximum of 35%. Considering the above, the mixtures do not need the extra addition of sand to be able to extrude properly.

References
[1] Gelves J and Sánchez J 2009 Comportamiento de las arcillas del área metropolitana de Cúcuta sometidas a proceso de moldeo por extrusión Respuestas 14(2) 32
[2] Diaz L and Torrecillas R 2002 Arcillas cerámicas: Una revisión de sus distintos tipos, significados y aplicaciones Bol. la Soc. Esp. Ceram. y Vitr. 41(5) 459
[3] Martínez A and Aguilar T 2012 Impacto socioeconómico de la Minería en Colombia Sect. Minería a Gran Escala 1(1) 50
[4] Muñoz R, Muñoz J, Mancilla P and Rodríguez J 2007 Caracterización fisicoquímica de arcillas del municipio de Guapi- costa pacífica caucana Colombiana Química 31(1) 537
[5] García-León R and Flórez Solano E 2016 Determinación de la ventana del proceso productivo en la fabricación de bloques H-10 en Ocaña Norte de Santander y la región Ingenio UFPSO 9(1) 35
[6] García-León R, Bolívar R and Flórez E 2016 Validación de las propiedades físico-mecánicas de Bloques H-10 fabricados en Ocaña Norte de Santander y la región Ingenio UFPSO 10(1) 17
[7] García-León R and Bolívar R 2017 Caracterización Hidrométrica de las Arcillas Utilizadas en la Fabricación de Productos Cerámicos en Ocaña, Norte de Santander Inge CUC 13(1) 53
[8] Zuluaga D 2016 Caracterización térmica, química y mineralógica de un tipo de arcilla roja propia de la región andina Colombiana, empleada para la producción de ladrillos para construcción Rev. Colomb. Mater. 9(1) 53
[9] Peralta N and Barrera M 2013 Análisis estructural por DRX de una arcilla natural Colombiana modificada por pilarización Rev. Investig. - Univ. del Quindío 24(1) 100
[10] García-León R, Flórez-Solano E and Acevedo-Peñaloza C 2018 Clay surface characteristics using atomic force microscopy Rev. Fac. Ing. Univ. Antioquia 87(2) 9
[11] García-León R, Flórez-Solano E and Medina-Cárdenas Y 2018 Caracterización física de las arcillas utilizadas en la fabricación de productos de mampostería para la construcción en Ocaña Norte de Santander Espacios 39(53) 1
[12] Amado J, Villafrades P and Tuta E 2011 Caracterización de arcillas y preparación de pastas cerámicas para la fabricación de tejas y ladrillos en la región de Barichara, Santander DYNA 78(167) 50
[13] García-León R, Acosta M and Flórez E 2015 Análisis del comportamiento de los frentes de disco de los vehículos a partir de la aceleración del proceso de corrosión Tecnura 19(45) 53
[14] García-León R, Flórez-Solano E and Rodriguez-Castilla M 2019 Application of the procedure of the ISO 50001:2011 standard for energy planning in a company ceramic sector *DYNA* 86(209) 113
[15] Vieira C, Sánchez R and Monteiro S 2008 Characteristics of clays and properties of building ceramics in the state of Rio de Janeiro, Brazil *Constr. Build. Mater.* 22(5) 781
[16] García-León R, Flórez-Solano E and Acevedo-Peñaloza C 2018 Caracterización Térmica de mezclas de arcillas utilizadas en la fabricación de productos de mampostería para la construcción *Rev. Colomb. Tecnol. Av.* 31(1) 22
[17] Díaz E 2018 *Diagnóstico del cumplimiento de la calidad de los bloques H-10 fabricados por la ladrillera hora limitada en Ocaña Norte de Santander* (Ocaña: Universidad Francisco de Paula Santander)
[18] Roquet M 2012 Métodos analíticos en geoquímica (DRX-FRX) y Pegmatitas (Argentina: Universidad Nacional de San Luis)
[19] Duitama L, Espitia C, Mojica J, Quintero J and Romero F 2004 Composición mineralógica y química de las arcillas empleadas para cerámica roja en las zonas de Medellín *Rev. Acad. Colomb. Cienc.* 34(109) 555
[20] Środron J 2006 Identification and quantitative analysis of clay minerals Dev. *Clay Sci.* 1(C) 765
[21] Rozo Rincón S, Sánchez Molina J and Gelves Díaz J 2014 Evaluación de minerales alumino silicatos de Norte de Santander para fabricar piezas cerámicas de gran formato *Fac. Ing.* 24(38) 53