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# Effect of use residual sludge from water treatment plants as a partial substitute for clay for refractory bricks production

# Efecto del uso de lodo residual de las plantas de tratamiento de agua como un sustituto parcial de arcilla en la producción de ladrillos refractarios

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**Abstract**

The sludge generated from water treatment has been classified as a potential environmental pollutant. Because of its chemical composition similar to clay, was proposed to evaluate the effect of its incorporation as a partial substitute for traditional clay materials in the manufacture of aluminosilicate refractory bricks. The raw materials used were characterized by XRD and XRF; the prototypes designed were mixed, extruded, dried and firing at 1200 °C, evaluating their linear shrinkage, apparent density, porosity, water absorption and mechanical and pyroscopic resistance (melting cone softening point). The results show the addition of 10% of sludges from industrial water treatment plant, contributed to elevate the softening point the clay that obtaining a refractory brick capable to supporting a temperature up to 1430 °C.

**Keywords:** pyroscopic resistance; refractory bricks; residual sludge; water treatment plants.

**Resumen**

El lodo generado por el tratamiento de agua ha sido clasificado como un contaminante ambiental potencial. Debido a que su composición química es similar a la arcilla, se propuso evaluar el efecto de su incorporación como un sustituto parcial de los materiales arcillosos tradicionales en la elaboración de ladrillos refractarios de aluminosilicatos. Las materias primas utilizadas se caracterizaron por DRX y FRX; los prototipos diseñados se mezclaron, extruyeron, secaron y dispararon a 1200 ° C, evaluando su contracción lineal, densidad aparente, porosidad, absorción de agua y resistencia mecánica y piroscópica (punto de reblandecimiento por conos de fusión). Los resultados muestran que la adición de un 10% de lodos residuales del tratamiento de agua industrial contribuyó a elevar el punto de reblandecimiento de la arcilla obteniendo un ladrillo refractario capaz de soportar temperaturas de hasta 1430 °C.

**Palabras clave:** pyroscopic resistance; ladrillos refractarios; lodos residuales; planta de tratamiento de agua.

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## 1. Introduction

Natural water contains three types of contaminating solids: suspended solids, with a particle size greater than 100 μm, transported due to the action of dragging and the movement of water, their surface electric negative charge makes them repel, preventing their agglomeration, therefore they do not precipitate; dissolved solids (organic and inorganic matter), less than 100 μm in size, are invisible separately, they do not sediment and generally cause smell, taste, color and health problems, unless they are precipitated and removed by physical and chemical methods; and colloidal solids (fine silt, bacteria, color-causing particles, viruses) are between suspended and dissolved solids, being mostly non- sedimentable [1] [2] [3].

According to scientific literature, chemical coagulation is the most commonly used process in water treatment plants. In this process, chemical coagulants are used, generally iron or aluminum salts, which neutralize the charges of the colloidal particles forming aggregates of greater sedimentability, called flocs [4] [5].

The chemical coagulants, as the aluminum salts are added to water in proportions of 2-900 mg/L, and iron salts at 4-800 mg/L [6] [7]. Generally, the flocculation process of the destabilized suspension is assisted by slow agitation systems, to generate a scenario in which the particles come into contact and unite with each other [8].

The sludge generated from water treatment has been classified as a potential environmental pollutant, due to its high load of heavy metals, and its conventional disposal being the direct discharge into nearby water bodies or into landfills after their respective drying [9] [10] [11], generating four main drawbacks: their decomposition produces large quantities of pestilent gases, the pathogenic microorganisms in their composition are dangerous for human health, having a very likely relationship with the occurrence of diseases such as Alzheimer's and children mental retardation [12] [13] and their toxic compounds, especially heavy metals, are dangerous for plants and animals, in addition to promoting uncontrolled growth of aquatic plants by increasing presence of phosphates and nitrogen [14] [15].

While an adequate process generates costs for preliminary treatment (screening, crushing), primary thickening, stabilization of liquid mud (anaerobic digestion, aerobic digestion, addition of lime), secondary thickening, elutriation, drying, final treatment (composting, drying, addition of lines, incineration, wet oxidation, pyrolysis, disinfection), storage, transport and final destination (landfill, agriculture / horticulture, others), inadequate disposal only involves storage and transportation costs [16] [17].

The dry sludge incineration and their use in the production of construction materials and soil improvement are the most used methods for its adequate final disposal [18] whose costs, in European countries, China, Poland and Sweden are rising at rates of USD 72-210, USD 240-375, USD 240-360 and USD 125-280 per ton, respectively; while the costs for inadequate disposal in sanitary landfills and water sources are only $16-24 USD/t; this is why companies tend to adopt cheap disposal methods [19] [20].

There are previous investigations that address the search for new alternative sources for raw material, as residual sludges from industrial and potable water treatment, for production of various clay-based construction materials. These studies have the objective of analyzing the effects on physical and mechanical behavior, concluding that the results sometimes are not satisfactory for one or more properties, according with the type and amount of sludge has been used in the matrix and temperature.

The incorporation of 2% (w/w) sludge from the poultry slaughterhouse wastewater treatment system in the ceramic mass for the production of tiles did not significantly alter the properties of the material, being even possible to reduce the consumption of fuel in burning [21]; a similar results was showed by [22], who estimated that an energy saving of 15–47% could potentially be achieved during firing with 10–40% tannery sludge-amended bricks chrome-rich, also obtaining, an increase of the compressive strength and water absorption, of 170% and 190%, respectively.

Contrary to these results, [23] reported that increasing the paper sludge content in the clay mixture for structural bricks production decreases its mechanical strength, even though provides the material with improved properties regarding its thermal and acoustic insulation. This behavior in the mechanical resistance also was reported by [24], indicating that increasing content of sludge from the oil refining industry or sludge from the olive's pomace oil extraction industry resulted in a loss of brick compressive strength and thermal conductivity, due to decreasing bulk density and increasing water absorption, when the additions were exceeding 10% or 15%.

Other studies, as [25] evaluated the use of sewage sludge in the production of ceramic floor tiles, obtaining that was possible to produce tiles that abided by ISO standards for water absorption <10% with a maximum addition of 7% sludge, fired at 1150 °C; while additions of 5-10% sludge, fired at 1100 °C and 1150 °C, respectively, increased water absorption to more than 10%.

A review of some others researches on the use of sludge from wastewater treatment plants as raw material in the construction industry, shows its use for the manufacture of bricks made of clay [26] and as aggregate for concrete [27]. However, there are not many studies about the use of sludge from water treatment plants in the production of refractory materials, so there are still unknown effects to consider in terms of physical and mechanical behavior, due to is expected a highly content of $Al_2O_3$ in the residual sludge that it comes from the flocculants used in the decanting process.

About the physical and mineralogical composition of these wastes, some studies reported that the mineralogical composition indicates the majority presence of phases of quartz, illite, calcite and albite in similar proportions to clay chemical composition [28] [29], and the organic matter content of the dry sludge is approximately 25%, and the particle size distribution is between 75-300 µm [30]. Torres, Hernández & Paredes [31] report that 55.5% of sludge particles have diameters smaller than 25 µm and more silt (24%) than clays (16%) [10].

It can be predicted that due to its mineralogical composition and particle size, this material can be incorporated in the manufacture of ceramic bricks, since these must contain between 20-50% of particles larger than 20 µm [32], and because of their high content of organic matter its addition without previous treatment in the manufacture of a solid body will generate a significant loss by ignition, therefore it can be used effectively as a pore-forming agent [29].

In view of the problems generated by the disposal of residual sludge from water treatment and its potential use in the manufacture of construction materials derived from clay [33], it is proposed to evaluate the effect of the incorporation of this waste as a partial substitute for clay materials in the manufacture of refractory bricks in the metropolitan area of Cúcuta, Colombia.

## 2. Method

The materials used were: Kaolin JM325 supplied by Minerals and Services company, Clay Peracos (PE) supplied by a ceramic company in the metropolitan area of Cúcuta, Colombia; residual sludge from water treatment (LPTAI) for the production process of glazed tiles from a company in Cúcuta, Colombia, and residual sludge from drinking water treatment (LPTAP) was supplied by a drinking water treatment plant in one of the municipalities of the Cúcuta metropolitan area. Clay and sludge were ground to diameters less than 1 mm (ASTM D18 mesh) in a laboratory hammer mill brand Servitech model CT-058.

Quantitative analyzes of chemical composition of clay PE were performed using the QUANT-EXPRESS (Fundamental Parameters) method in the sodium (Na) to Uranium (U) range, on a BRUKER brand S8 wavelength dispersive X-ray Fluorescence 4K sequential spectrometer. TIGER of the Ray Laboratory at the Industrial University of Santander, under the following conditions: type of detector: Scintillation (heavy elements) and Flow (light elements), X-ray source: Rhodium (Rh) tube, high precision goniometer for theta and 2 theta angles.

The chemical composition of the sludges LPTAI and LPTAP was determined by the X-Ray Fluorescence (XRF) technique using a 4 KW dispersive wavelength X-Ray Fluorescence sequential spectrometer, calcining the sample at 950 ° C and analyzed in the WROX application by the method of Molten Pearl. Finally, chemical composition of JM325 Kaolin was supplied by the provider in the product data sheet.

For mineralogical composition, the selected specimens from the samples were ground and homogenized in an agate mortar and brought to a particle size of less than 38 µm (400 mesh). Subsequently, the selected specimens were mounted in polymethylmethacrylate (PMMA) sample holders using the frontal filling technique. The analysis was performed on a BRUKER model D8 ADVANCE powder diffractometer with DaVinci geometry from the X-ray Laboratory of the Industrial University of Santander, under the following conditions: voltage: 40 kV, current: 30mA, divergence slit: 0.6 mm, slits primary soller: 2.5°, sampling: 0.02035° 2theta, measuring range: 3.5-70° 2theta, radiation: CuKαI, filter: nickel, use of anti-air disperser: yes, detector: Linear Lynx Eye, sweep type: stepper, sampling time: 0.6 seconds.

Qualitative analyzes of the crystalline phases present in the selected specimens of the samples were performed by comparing the observed profile with the diffraction profiles reported in the PDF-2 database of the International Center for Diffraction Data (ICDD). And its quantification (see table 2) was performed by refining the observed profile by the Rietveld Method, adding to the selected specimens of the samples identified with PE, LPTAI and LPTAP codes a known quantity of an internal standard (Aluminum oxide, Corundum , α-phase).

Table 1. Chemical composition of raw materials

| Material | $SiO_2$ (%) | $Al_2O_3$ (%) | $TiO_2$ (%) | $Fe_2O_3$ (%) | CaO (%) | MgO (%) | $K_2O$ (%) | $Na_2O$ (%) | LOI* |
|---|---|---|---|---|---|---|---|---|---|
| PE | 67.08 | 24.29 | 0.88 | 5.21 | 0.43 | 0.52 | 1.14 | 0.45 | 5.82 |
| JM325 Kaolin | 59.5 | 33.0 | 2.0 | 1.8 | 0.1 | 0.5 | 1.0 | 0.2 | N/A |
| LPTAI | 65.72 | 11.49 | 0.35 | 1.90 | 5.90 | 1.16 | 2.14 | 2.22 | 4.26 |
| LPTAP | 54.42 | 14.90 | 0.57 | 3.14 | 1.36 | 0.55 | 1.60 | 0.86 | 24.03 |

Source: Authors.

Table 2. Mineralogical composition of raw materials

| Crystalline Phase | Name | Composition of Raw Material (%) | | |
|---|---|---|---|---|
| | | PE | LPTAI | LPTAP |
| $SiO_2$ | Quartz | 36.05 | 51.70 | 41.60 |
| $Al_2 (Si_2O_5) (OH)_4$ | Kaolinite | 29.30 | 11.14 | 29.70 |
| $NaAlSi_3O_8$ | Albite | - | 12.86 | 3.0 |
| $SiO_2$ | Low Cristobalite | 3.57 | - | - |
| $Fe_2O_3$ | Hematite | 1.36 | 1.50 | - |
| $CaMg (CO_3)_2$ | Dolomite | - | 1.10 | - |
| $K (Al Si_3 O_8)$ | Microline | - | 8.61 | - |
| $Ca (CO_3)$ | Calcite | - | 0.82 | - |
| $Al_2Si_2O_5(OH)_4$ | Nacrite | - | - | 16.2 |
| $K Al_2 Si_3 Al O_{10} (OH)_2$ | Muscovite | 29.72 | 12.30 | 7.70 |
| $Ti_{0.72}O_2$ | Anatase | - | - | 1.1 |
| $(NH_4)_2 SiF_6$ | Criptohalite | - | - | 0.8 |

Source: Authors.

According to the results obtained in previous investigations identified in the state of the art, where additions greater than 10% can suddenly alter the technical properties of the final product, six mixtures were formulated to produce low refractory silico-aluminous bricks, with Pyrometric Equivalent Cone (CPE) not lower than Orton Cone No. 15 (1430 °C) according to NTC 706 [34], likewise had a consideration that due to its chemical composition the mixtures were composed of not less than 25% and not more than 30% alumina oxide and greater than 90% between Alumina and Silica with minor impurities of $TiO_2$, $Fe_2O_3$, CaO, MgO, $K_2O$, $Na_2O$ [35]. The mixtures composition in the percentage weight/weight is shown in table 3.

For the preparation of mixtures for molding processes, its initial humidity was determined using an OHAUS MB45 thermobalance, and the Pfefferkorn plasticity index was determined with a Pfefferkorn plastic meter. According to the result obtained from the plasticity, mixtures were manually wetted with 28-34% w/w of water, where the extreme of this range corresponding to M1 and M2 with 33% and 34% w/w respectively; for mixtures M3, M4, M5 and M6 the wetting was 28%, 29%, 31% and 32% w/w, respectively. The wetted mixtures were kept for 12 hours to get good homogenization.

Table 3. Mixtures Composition

| Mixture | Composition (%w/w) | | | | | |
|---|---|---|---|---|---|---|
| | M1 | M2 | M3 | M4 | M5 | M6 |
| PE | 100 | 70 | 65 | 60 | 65 | 60 |
| Kaolin JM325 | | 30 | 30 | 30 | 30 | 30 |
| LPTAI | | | 5 | 10 | | |
| LPTAP | | | | | 5 | 10 |

Source: Authors.

Next the ceramic pastes obtained were extruded using in a vacuum laboratory extruder model *new wave* manufactured by the company Metal Souza Ltda., with a pressure of 35mmHg, and using a rectangular mold of 41x10 mm. The length of the piece was adjusted in 110 mm. The shaped specimens were subjected to natural drying for 24 hours in order to carry out a slow process of the water output in order to avoid the formation of tensions in the test pieces. Later they were dried at a temperature of 110 °C in stove drying electric resistance up to constant weight.

Finally, the specimens were firing in an electric muffle furnace with oxidizing atmosphere, with a firing curve of nine (9) hours and 40 minutes, where it was kept for one hour at a maximum temperature of 1200 °C, the figure 1 shows the firing curve used for the heat treatment applied to the material. The cooling stage was carried out by leaving the specimens inside the muffle until room temperature. The burning and cooling process, simulating a firing process of the region's traditional ceramic industry, where it would be expected to be able to manufacture refractory bricks in beehive kilns.

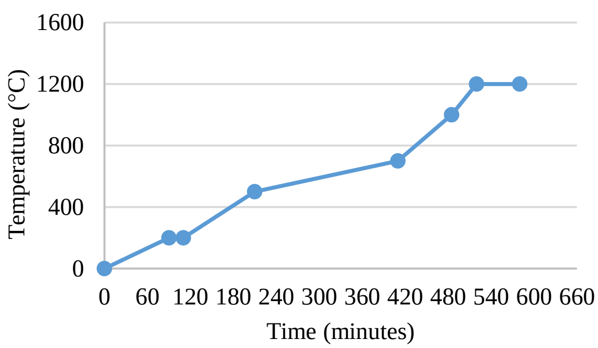

Figure 1. Firing curve.

The properties of apparent porosity, water absorption, apparent specific gravity and apparent density were determined according to Colombian Technical Standard NTC 674 [36]; likewise, the percentages of dry shrinkage, firing shrinkage, loss of dry, loss of ignition, mechanical bending strength and modulus of rupture were evaluated. The determination of the Pyrometric Equivalent Cone (CPE) was carried out under the NTC 706 [34].

The melting point or CPE indicates whether or not a material is suitable above a certain operating temperature. It is a piece molded with refractory materials in the shape of a truncated pyramid, with a triangular base, of standardized dimensions, which is identified with a characteristic number, equivalent to a certain temperature, in degrees Celsius (°C), when in a heating regime under recommended conditions, the end of the pyramid touches the supporting plate.

## 3. Results and discussions

### 3.1. Chemical and mineralogical composition

The chemical and mineralogical composition of the raw materials shown in table 2 and table 3, respectively, is analyzed as follows.

About chemical composition, it is important to highlight the concentration of alkaline and alkaline earth elements in the sludge used. In the case of alkalis, a higher concentration of sodium and potassium is evident in comparison with traditional clays, a fact that could favor the formation of a vitreous phase in mixtures containing these raw materials, bringing with it a decrease in porosity and an increase in the mechanical resistance of the brick. In the case of alkaline earths such as calcium and magnesium, their concentration is also higher in sludge and their presence could favor the formation of phases with higher thermal conductivity such as anortite and wollastonite, or stable phases at high temperatures such as periclase (MgO) [37, 38, 39].

The presence of $SiO_2$, $Al_2O_3$, $K_2O$, $CaO$, $Na_2O$ and $Fe_2O_3$ revealed in the XRF is accord with the phases obtained in the XRD.

The mineralogical composition of both sludge: LPTAI and LPTAP, indicate the majority presence of quartz (40-50%), with presence of kaolinite, moscovite and albite phases; which coincides with the mineralogical characterizations reported in the literature [25, 28, 29]. It is interesting to highlight the presence of the nacrite phase in the mineralogy result in table 2, this phase is associated with the mineral group of the phyllosilicates (serpentines), which has not been mentioned in previous works reported in the region.

PE is essentially composed of three minerals which, in total, account for more than 90% and which had a significant influence on the behavior of the properties evaluated: the quartz that favors water extraction during drying, degasification of impurities and reduction of dimensional contraction; kaolinite that provides the clay with much wider firing temperature ranges, higher temperatures and slower glassy phase formation, generating low porosities above 1200 °C, greater dimensional stability, low linear contraction, minimum water absorption and low thermal expansion; and hydrated mica (muscovite) that provides almost all of the potassium oxide that the clay possesses. The absence of fluxing minerals, such as feldspars, was favorable, as these decrease the softening temperature of the refractory [40].

This chemical and mineralogical composition is similar to clay, so it is considered as a potential additive in the manufacture of products derived from clay. However, the content of $Al_2O_3$ is not as high as it was considered according to the scientific bibliography; this could be due to the amount of flocculants used in the process of water treatment according to the conditions of raw water and the output requirements, which can change not only locally but also internationally.

### 3.2. Characterization of fired samples

The results of the physical and mechanical characterization of the developed specimens are shown in Table 4, and are analyzed as follows.

The drying shrinkage data in table 1 and figure 2 shows that each mixture has a very particular behavior. The higher values of M1 and M2 are associated with the greater presence of clay phases (kaolinite and muscovite) in these materials according to the XRD results in Table 2. Clays due to their morphological characteristics and structures can retain a greater amount of water, which brings greater humidity to perform extrusion forming. This water retained between the layers of the clay, when removed through heat, causes a greater contraction during the drying stage [41]. In the case of M3 to M6, the greater presence of degreasing mineralogical phases such as quartz, feldspars (see table 2) retain little amount of water, even under very fine grain sizes [41, 42]. This characteristic does not generate the effect seen on the clays. This effect is corroborated as more mud is added to the mixture, since the content of degreasers is increased and if it reduces the content of clay phases by decreasing the amount of mass of the PE.

In relation to loss of dry, the behavior of the table 4 and figure 2 shows a behavior that does not show significant differences in almost all the mixtures, with the exception of M1. This behavior of M1 could be due to the fact that it does not contain kaolin in its composition, in addition to this it is important to highlight that M1 is composed only of peracos clay which, as previously mentioned, is rich in clay phases. This fact can hinder the exit of the water from the molding in this material [41].

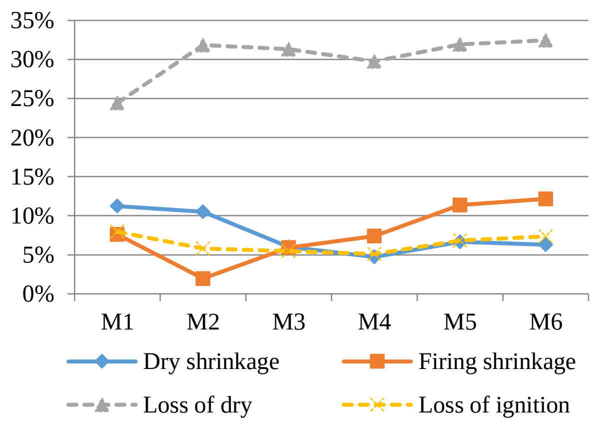


Figure 2. Drying and firing behavior

Table 1. Chemical composition of raw materials

| Properties / Mixture | M1 | M2 | M3 | M4 | M5 | M6 |
|---|---|---|---|---|---|---|
| **Dry shrinkage (%)** | 11.23 ±0.24 | 10.50 ±1.02 | 6.00 ±1.38 | 4.73 ±0.34 | 6.68 ±0.27 | 6.28 ±0.14 |
| **Loss of dry (%)** | 24.43 ±0.45 | 31.86 ±0.27 | 31.33 ±0.12 | 29.74 ±0.17 | 31.93 ±0.15 | 32.46 ±0.21 |
| **Firing shrinkage (%)** | 7.60 ±0.20 | 1.97 ±0.19 | 5.93 ±0.28 | 7.38 ±0.32 | 11.38 ±0.16 | 12.16 ±0.14 |
| **Loss of ignition (%)** | 7.96 ±0.04 | 5.80 ±0.05 | 5.47 ±0.05 | 5.10 ±0.03 | 6.84 ±0.06 | 7.37 ±0.03 |
| **Apparent porosity (%)** | 0.50 ±0.4 | 33.37 ±1.65 | 24.56 ±1.43 | 20.17 ±0.46 | 0.77 ±0.50 | 0.27 ±0.05 |
| **Apparent specific gravity** | 2.36 ±0.01 | 2.44 ±0.01 | 2.49 ±0.01 | 2.48 ±0.01 | 2.15 ±0.06 | 2.13 ±0.04 |
| **Apparent density ($g/cm^3$)** | 2.35 ±0.02 | 1.62 ±0.04 | 1.88 ±0.04 | 1.98 ±0.01 | 2.13 ±0.07 | 2.12 ±0.04 |
| **Water absorption (%)** | 0.21 ±0.17 | 20.59 ±1.55 | 13.09 ±1.07 | 10.17 ±0.30 | 0.37 ±0.24 | 0.13 ±0.02 |
| **Mechanical bending strength (N)** | 1942.85 ±141.72 | 1192.02 ±184.66 | 1251.60 ±88.62 | 1298.00 ±128.38 | 1410.88 ±291.74 | 1312.79 ±201.60 |
| **Modulus of rupture ($N/mm^2$)** | 49.29 ±3.81 | 23.70 ±4.19 | 25.28 ±1.63 | 26.83 ±2.44 | 33.14 ±6.88 | 31.33 ±4.78 |

Source: Authors.

This last proposition is supported by the results of loss of ignition in Table 1 and figure 2, where it is evident that it is this mixture that presents the highest values. These mass losses are related to the mass loss data presented in the chemical composition result by XRF and possibly correspond to the vast majority to the residual molding water and to the dehydroxylation of the clay [41, 43].

Loss of mass due to the presence of organic matter or decomposition is very unlikely since in previous characterizations by thermal analysis no event of mass loss of this class was evidenced [43]. In the same way, the results of mineralogical composition show the absence of carbonates in this raw material. In the case of M5 and M6, the value of said losses does seem to be influenced by the presence of organic matter, in accordance with the results of the chemical composition table, where it is evident that the drinking water sludge does have high losses of ignition.

The firing shrinkage data shows a very particular behavior, the shrinkage order can indicate as follows M1, M6, M5, M4, M3 and M2. The explanation for this result can be influenced by three factors. The first of these is the effect generated by the clay phases in the formation of the glassy phase and also by the effect caused by the dehydroxylation of this class of minerals. The second factor is related to the presence of fluxing elements and finally the effect caused by the addition of kaolin to the mixtures [44, 45].

In the first case, in the available literature it has been established that the presence of clay phases such as kaolinite and illite act favorably to achieve the vitreous state [41]. The material in this state, can flow and fill the pores and favor the sintering of the grains, leading to a decrease in probes due to the densification of the material [41]. In relation to the dehydroxylation of the clay phases, this effect is reflected in the volume of the probes due to the shrinking of the distance between the sheets of the mineral, due to the exit of the hydroxyl groups from the clay in the form of water vapor [41]. As M1 is the material with the highest clay phase content, a greater shrinkage is expected through this medium. Something similar happens with M5 and M6 that contain clayey phases, only this case highlights the nacrite phase.

In relation to fluxing oxides, the results in Table 1 support this proposition. In this case, M2 (mixture of pearls and kaolin) is the one that has less cooking contraction since, in its chemical composition, less content of elements that favor fusion such as sodium, potassium and iron [41]. On the contrary, the M3 to M6 mixtures have higher contractions since the muds LPTAI and LPATP that were used in the mixtures are rich in these fluxes even in higher concentration than the peracos clay (PE).

Finally there is the possible effect of adding kaolin; the addition of 30% kaolin seems to have an influence in the reduction of firing shrinkage, an assumption is that this kaolin within its mineralogical composition contains different mineralogical phases than kaolinite and that these are not very reactive in the temperature range used. For example, one could think of the presence of aluminum minerals (aluminum oxides) such as bauxite that only react above 1200 ° C with the glassy phase to form mullite [46]. This means that below this temperature the sintering of this class of minerals is very low, bringing with it less volume changes in the fired specimens.

The porosity and water absorption percentage (see table 4 and figure 3) results seem to be consistent with the analysis of the firing shrinkage results, an exception of M3 and M4. Although it was expected to have a porosity similar to that of the M5 and M6 mixes due to the greater amount of flux elements in LPTAI, this does not happen. Although it is clear that a greater addition of LPTAP contributes to decrease the porosity due to this fact. A possible explanation for this behavior would be the presence of calcium and magnesium (limestone) carbonates in the mud used in M3 and M4, the results of chemical and mineralogical composition support its existence. In the available literature, it has been indicated that the addition of limestone to ceramic pastes slows down the process of formation of the vitreous phase and contributes to the formation of porosity due to the release of carbon dioxide gas due to the decomposition of carbonates [41, 42].

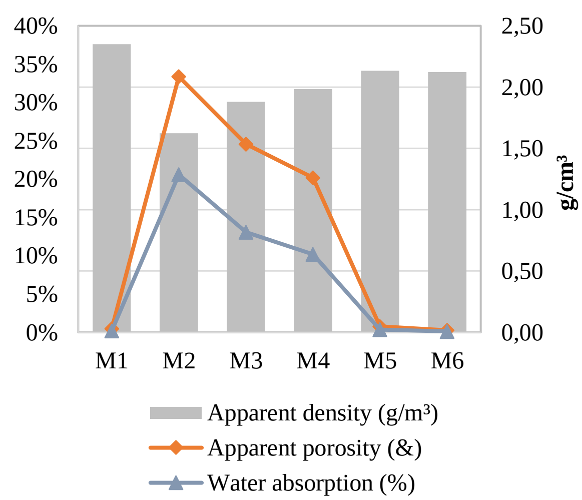


Figure 3. Porosity, density and water absorption.

Finally, there are the data associated with mechanical resistance, the results in table 4 and figure 4 in general maintain the inversely proportional relationship between porosity and breaking load. In other words if the porosity decreases, the mechanical resistance must be increased [47, 48]. Likewise, porosity is unfavorable for fracture resistance (or modulus of rupture) for two reasons: pores reduce the area of the section through which the load is applied and act as stress concentrators [49].

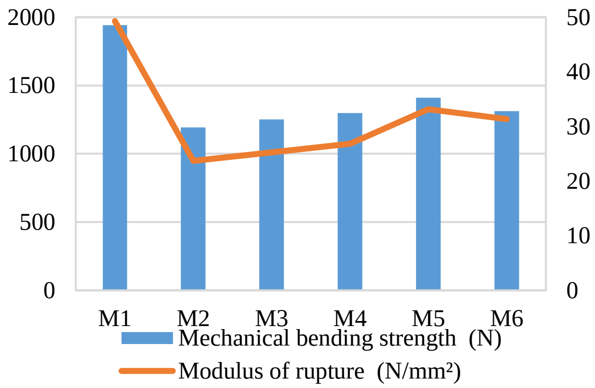


Figure 4. Mechanical resistance

The lower mechanical resistance values in the mixtures with the presence of LPTAI and LPTAP (M3 to M6) could be associated with the lower existence of a glassy phase to act as a cementitious agent and / or the lower existence of the mullite phase, which is recognized for promoting this property technological [41, 46, 50]. These previously mentioned phases are favored in the ceramic process by the presence of kaolinite and muscovite, which are lower in LPTAI and LPTAP compared to PE which is the only constituent of M1 [51, 52].

Mechanical resistance reported for M3-M6 mixtures is higher than M2, being this positive because it indicates that it is possible to use LPTAI, LPTAP in replacement of clay in the manufacture of refractory bricks, without compromising their -mechanical properties.

### 3.3. Pyrometric equivalent cone

M1, M2 and M4 were selected to perform the equivalent pyrometric cone analysis. M1 represents a traditional brick made with clay from the region with the highest alumina content, M2 is the traditional mixture of a refractory brick composed of 70% clay and 30% kaolin, M4 was the mixture of which is known that its chemical and mineralogical composition of its raw materials and allowed to highest porosity, which contributes to less heat transfer, better physical and mechanical properties, and at the same time allowing the use of major percentage of residual sludge from the treatment of industrial water in the manufacture of refractory bricks, representing a product with added value for the regional ceramic sector.

Due to the heterogeneity of their composition and structure, ceramic refractories do not exhibit a uniform melting point. Refractoriness is characterized by the optical determination of the equivalent of the pyrometric cone, that is: temperature at which the tip of a cone made with the sample material softens.

Figure 2 shows the equivalent cone of M1, M2 and M4 specifying the characteristics of the material processed and the temperature load it supports. In this case, M1 it started softening at a temperature of 1337 °C, while M2 and M4 endured practically immobile up to 1430 °C, equivalent to a No. 15 cone, observing a very slight curve in M2.

The observation in figure 5 for M4, where unlike M2, did not present a marked softening point at 1430 °C, indicates an increase in the pyroscopic resistance, which could be due to the higher CaO content of the LPTAI, which could generate phases stable crystals at high temperature as anortite and wollastonite [37, 38, 39]. As explained in the mineralogical characterization section, even when the concentration of $SiO_2$ and $Al_2O_3$ is decreased.

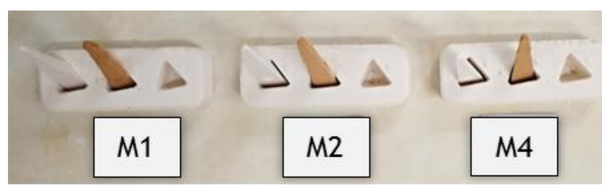


Figure 5. Pyrometric Equivalent Cone. Source: Authors

### 4. Conclusions

The properties of the designed refractory ceramic bodies change according to the mixtures and the percentage (%) of residues used. The high loss of mass in drying is due to the amount of residual water before conformation, which must necessarily be high (15-25% in weight). Although high contractions in firing at temperatures above 1180 °C are common, it should be noted that the greater the addition of LPTAI and LPTAP to replace clay, the contractions in firing are higher than those of M2.

The losses by calcination with very variable because it includes the water of constitution of the materials, the losses due to accessory minerals, the combustion of the carbonaceous matter of the clay and the organic matter of the sludge after the treatment of the water. The addition of LPTAI and LPTAP contributed to decrease the apparent porosity, water absorption and apparent specific gravity of the specimens, as well as increase in apparent density and flexural strength.

The results allow to conclude that the addition of LPTAI up to 10% in weight in mixtures from clayey materials, under working conditions, allows to obtain silica refractory bricks with low refractory aluminous according to the parameters of NTC 623, which can be used in the beehive furnaces of the ceramic industry of Norte de Santander.

## 5. Recommendations

It is recommended that a future research project calculate the environmental footprint of the production of bricks of this type of mixtures. The content of $Al_2O_3$ in the residual sludge from the treatment of drinking and industrial waters is highly probable that it comes from the flocculants used in the decanting process, and therefore it is these Aluminium Sulphates - $Al_2(SO_4)_3$, which during the calcination of ceramic bodies decomposes at 770 °C in reducing atmospheres producing $SO_3$ emissions into the atmosphere, which then with the ambient humidity and the steam from the combustion gases of the furnace would end up being emitted by the chimney as Sulphuric Acid - $H_2SO_4$ [53], which would contribute to air pollution around the production plant.

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