# DEVELOPMENT OF PORCELAIN STONEWARE TILE USING COLOMBIAN CLAYS SUBJECTED TO A WHITENING PROCESS

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## 1. ABSTRACT

The aim of this study was the development of porcelain stoneware tile bodies using Colombian clays that have the same technical characteristics present internationally in this type of products at the moment. For this purpose various raw materials were studied, including kaolinitic clays, feldspars and pozzolans, that come from the central area of the country, specifically from the regions of Cundimarca and Boyacá. As some of these raw materials have iron oxide percentages higher than 1%, they were subjected to both physical and chemical beneficiation processes with the purpose of reducing the amount of this colouring oxide. The pile leaching method with oxalic acid yielded the best results, with a reduction in the iron oxide content by 60% by weight. In this study natural pozzolan from the region of Boyacá was also used, which showed greater fusibility and reactivity compared to a nationally available feldspar. The addition of fluxes such as nepheline syenite and recycled glass were also studied. Porcelain stoneware tile body compositions were developed using these raw materials, obtaining water absorption values lower than 0.5%, in a range of temperatures from 1180 ºC to 1200 ºC.

## 2. INTRODUCTION

During the last few years, porcelain stoneware tile has been considered the fastest growing product type in the international market for ceramic floor and wall tiles, mainly due to its high technical characteristics and its constant aesthetic evolution. In Colombia, the porcelain stoneware tile market is focused mainly on importing this product, as shown by the import figures that went from 866,359 $m^2$ in 2000 to 19,942,525 $m^2$ in 2013, involving an approximate average annual growth of 31.81%.Despite the huge sales potential that Colombia has in this product, it is not produced in the country in great quantities, mainly as a result of the lack or limited presence of nationally sourced raw materials with the technical characteristics required for its development.

Among the technical characteristics needed by raw materials for developing porcelain stoneware tile, two stand out: the first is the high level of whiteness that these raw materials must possess, due mainly to the fact that the market is focused on light-coloured products. The second technical characteristic is the high level of sintering that they must achieve, due to the need to obtain low levels of porosity in the finished product.

On a national and international level there are not many raw materials that exhibit these exact characteristics, so thatdifferent investigations have been carried out [1-6], the purpose of which is the study and characterization of locally-sourced raw materials, with which formulations for porcelain stoneware tile bodies were developed, obtaining compositions that reach a high vitrification and a low porosity. In many cases these raw materials have high iron oxide contents, so that they are subjected to treatments and conditioning, using various physical and chemical techniques [7-13] with the aim of reducing the amount of this colouring oxide. The results of the experiments show a large improvement in the colour of the final product, obtainingceramic materials with notable whiteness. In terms of the need to reach a high degree of sintering, various studies have been carried out [14-17] in which different waste materials were included in compositions for porcelain stoneware tile bodies, such as: blast kiln slag, metallurgical slag, waste glass and ceramic industry waste, among others. The results obtained show that the introduction of these materials in the formulation of bodies can bring additional fusibility to feldspar and also lower the sintering temperature.

In this manner, considering the growing introduction of porcelain stoneware tile flooring and cladding into the market and in view of such strong competition in terms of prices along with new companies starting up in the sector, Colombian ceramic companies must lead the market towards innovation and differentiation. Therefore the general proposal of this study has been the development of porcelain stoneware tile with nationally-produced clays, attempting to maintain the required technical properties of currently marketed products, such as low water absorption, high mechanical strength and, at the same time, improvement in the level of whiteness. For this reason, various raw materials available in the ceramic industry were considered, which were subjected to a beneficiation process in order to use them in ceramic bodies for light-coloured porcelain stoneware tile, in addition to the incorporation of fluxing materials.

## 3. MATERIALS AND METHODS

The raw materials used belong to various geological units of the departments of Cundinamarca and Boyacá (Colombia). Some of these clays are currently used in the manufacture of red-body ceramic tiles. Within these raw materials, there are two kaolinitic clays,referenced AO and AT; a pozzolan of natural origin, referenced PZ; and a feldspar, FD, as well as two fluxes: nepheline syenite,referenced NF and recycled glass referenced VR. The raw materials with iron oxide contents greater than 1% were subjected to three beneficiation treatments, with the aim of reducing the percentage of this colouring oxide and to enable them to be used in the formulation of light-coloured porcelain stoneware tile bodies. The three treatments carried out were: sieving, sedimentation and leaching. The sieving treatment was carried out wet, using two sieves of 100µm and 150µm.For this treatment, slips were prepared using each of the raw materials with solids and water contents of 50% - 50% and 0.58% deflocculant, using a mechanical laboratory stirrer for 30 minutes. The free sedimentation technique was carried out in samples of 500ml, with a sedimentation time of 120 minutes. For the separation of the suspended solids fraction, a siphon system was used. For the leaching method, a pile leaching process was simulated, using 5kg of each of the raw materials mentioned above, with which four treatment piles were formed, one for each raw material, sprinkling with a solution of 0.4m oxalic acid over 60 days. This length of time was chosen as it is used for the maturation of mined clays. During the first week the piles were not moved; after this time the material was moved mechanically to allow ventilation and homogenisation.

Once the processing treatments had finished, the raw materials that produced the best results in terms of a significant reduction in iron were selected. They were used to develop formulations of porcelain stoneware tile bodies with the idea that at each stage of the ceramic process they would comply with the technical characteristics required for a porcelain stoneware tile body. Each formulation was ground in a planetary mill with solids and water contents of 60% and 40% respectively and 0.7% deflocculant, until a reject lower than 1% by weight was achieved on a 63 micron sieve. The slips obtained from each composition were dried and later ground. They were later moistened to 7% on a dry base and uniaxially pressed at 350kg/cm$^2$ for 3s, for this using a Nannetti press, model SS/EA with a rectangular die of 30 x 80mm.These shaped pieces were dried again in an oven at 110 ºC, then later fired in a gradient kiln with six chambers, Nannetti brand, model GR-98, using each chamber at a different temperature. For this, six temperatures were used: 1100, 1120, 1140, 1160, 1180 and 1200 ºC. This same procedure was carried out for the characterization of each of the raw materials.

The instrumental characterization techniques used for both the raw materials and the compositions were: Chemical analysis through X-ray fluorescence, using a BRUKER model S4 Explorer X-ray fluorescence spectrometer. Mineralogical analysis was performed by X-ray diffraction, using an X-ray diffractometer (XRD), D4 Endeavor Bruker-AXS with a variable range of 2-theta degrees, in steps of 0.05º/3s, by the random powder sample distribution method. The colorimetric parameters were measured using a KONICA MINOLTAmodel CM_3600d spectrophotometer, withD65 illuminant and Standard 10° observer. The chromatic coordinates used were those corresponding to the CIE L*a*b* system.

# 4. RESULTS AND DISCUSSION

## 4.1. RAW MATERIALS CHARACTERIZATION

### 4.1.1 CHEMICAL AND MINERALOGICAL ANALYSIS

Table 1 shows the chemical composition of each of the raw materials in percentage form and Table 2 shows their mineralogical composition. Based on these results, it can be observed that clay AT and feldspar FD have high $SiO_2$ contents, related to high quartz contents; this lowers their reactivity with temperature. Clay AO has illite as part of its mineralogy, which gives it more plastic and reactive behaviour with temperature. It can also be noted that clay AT and pozzolan PZ have iron oxide percentages greater than 1%, as a result of which they were subjected to beneficiation processes to reduce this value. The fluxing materials such as pozzolan and feldspar possess a very similar proportion of alkaline oxides ($Na_2O$ and $K_2O$), the same as their mineralogical composition. Nepheline syenite and recycled glass possess an increased proportion of $Na_2O$, especially the glass, and according to their chemical analysis they also have low $Al_2O_3$ contents, which indicates a greater fluxing capacity.

| RAW MATERIAL % by weight | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | $K_2O$ | $Na_2O$ | MgO | CaO | $P_2O_5$ | $SO_3$ | MnO | *LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| AO | 62.61 | 23.32 | 0.49 | 0.90 | 3.04 | 0.12 | 1.58 | 0.03 | 0.02 | 0.00 | 0.00 | 7.89 |
| AT | 76.59 | 13.48 | 1.52 | 0.75 | 0.81 | 0.11 | 0.37 | 0.13 | 0.13 | 0.00 | 0.00 | 6.11 |
| FD | 76.10 | 14.29 | 0.10 | 0.05 | 4.75 | 3.73 | 0.01 | 0.54 | 0.00 | 0.00 | 0.00 | 0.43 |
| PZ | 67.30 | 17.11 | 2.93 | 0.35 | 4.76 | 3.94 | 0.18 | 0.24 | 0.06 | 0.33 | 0.00 | 2.80 |
| NF | 55.94 | 24.54 | 0.24 | 0.20 | 9.14 | 7.94 | 0.19 | 1.14 | 0.03 | 0.00 | 0.00 | 0.64 |
| VR | 70.70 | 1.30 | 0.10 | 0.05 | 0.30 | 13.80 | 3.60 | 9.60 | 0.01 | 0.20 | 0.00 | 0.34 |

**LOI: loss on ignition expressed in % by weight*

***Table 1***

*Chemical analysis by X-ray fluorescence of the raw materials*

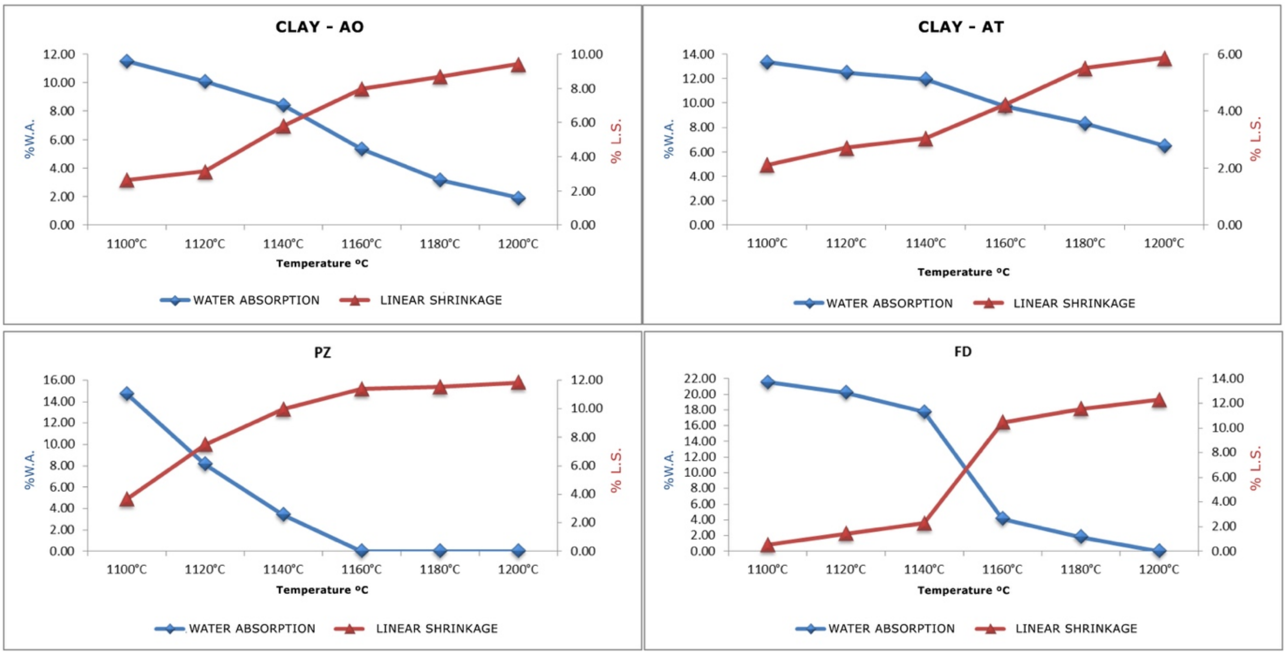
| RAW MATERIAL | MINERALOGICAL COMPOSITION |
|---|---|
| AO | Quartz, Kaolinite, Illite. |
| AT | Quartz, Kaolinite. |
| PZ | Quartz, Kaolinite, Albite, Microcline |
| FD | Quartz, Kaolinite, Albite, Orthoclase |

***Table 2***

*Mineralogical analysis of the raw materials*

### 4.1.2. VITRIFICATION DIAGRAMS

Vitrification diagrams are curves based on the temperature that links water absorption to the linear shrinkage of ceramic materials, in which the maximum shrinkage coincides with the minimum water absorption at the optimum firing temperature. Figures 1-4 show the vitrification diagrams of each of the raw materials, it can be observed that clay AO presents the lowest water absorption, below 2%, at 1200 ºC, compared to clay AT, which shows a more refractory behaviour. Regarding the fluxes pozzolan and feldspar, it can be observed that pozzolan presents a more reactive behaviour, which makes it more sensitive to temperature changes, obtaining water absorption values below 0.5% from 1160 ºC compared to feldspar, which acts as a non-plastic material between 1100 ºC and 1140 ºC. At 1160 ºC it presents a sudden change in its properties as it reaches its sintering point at that temperature. Above this temperature it presents a fluxing behaviour, obtaining a water absorption value lower than 0.5% at 1200 ºC.




***Figures 1 - 4*** *Vitrification diagrams of all raw materials*

## 4.2. PROCESSED RAW MATERIALS CHARACTERIZATION

As seen in the results of the chemical analysis (Table 1), clay AT and pozzolan PZ have iron oxide contents greater than 1%, a value typical of raw materials used in the formulation of porcelain stoneware tile. Therefore both raw materials were subjected to three beneficiation treatments (sieving at 100 and 150 µm, free sedimentation and pile leaching), with the purpose of reducing the percentage of this colouring oxide and to enable them to be used in the formulation of light-coloured porcelain stoneware tile bodies. After the beneficiation treatments, these raw materials were chemically characterizedby X-ray fluorescence and by colorimetry.

### 4.2.1. CHEMICAL ANALYSIS

As can be observed in the results of Table 3, the processing treatment of pile leaching using oxalic acid was the treatment that yielded the best results, achieving the greatest reduction in iron oxide ($Fe_2O_3$) in both raw materials. Clay AT obtained a reduction of 30.26% as its percentage went from 1.52% to 1.06%. In the pozzolan PZ a reduction of 64.16% was observed, as it went from 2.93% to 1.05%.With regard to the physical treatment of sieving, it can be observed that the 150 μm sieve with clay AT achieved a greater reduction in $Fe_2O_3$, reducing it by 8.42% compared to the 2.63% achieved with the 100 μm sieve. Regarding the pozzolan PZ it had a reduction of 32.42% with the 150 μm sieve and 25.94% with the 100 μm sieve. In the free sedimentation method a reduction was observed in the percentage of $SiO_2$, an increase in the percentage of $Al_2O_3$ and a reduction of 13.82 of $Fe_2O_3$ for clay AT and 26.96% for pozzolan PZ.

| RAW MATERIAL % by weight | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | $K_2O$ | $Na_2O$ | MgO | CaO | $P_2O_5$ | $SO_3$ | MnO | *LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| AT Original | 74.59 | 15.48 | 1.52 | 0.75 | 0.81 | 0.11 | 0.37 | 0.13 | 0.13 | 0.00 | 0.00 | 6.11 |
| 100 μm sieve | 73.95 | 16.02 | 1.48 | 0.74 | 0.85 | 0.12 | 0.39 | 0.14 | 0.13 | 0.00 | 0.00 | 6.18 |
| Free sedimentation | 73.31 | 16.16 | 1.31 | 0.65 | 0.68 | 0.85 | 0.38 | 0.27 | 0.16 | 0.00 | 0.00 | 6.23 |
| 150 μm sieve | 73.98 | 15.02 | 1.24 | 0.75 | 0.85 | 0.11 | 0.35 | 0.14 | 0.10 | 0.00 | 0.00 | 7.46 |
| 0.4M Oxalic acid | 74.62 | 14.83 | 1.06 | 0.76 | 0.85 | 0.13 | 0.34 | 0.12 | 0.09 | 0.00 | 0.00 | 7.20 |
| | | | | | | | | | | | | |
| PZ Original | 67.30 | 17.11 | 2.93 | 0.35 | 4.76 | 3.94 | 0.18 | 0.24 | 0.06 | 0.33 | 0.00 | 2.80 |
| 100 μm sieve | 67.95 | 17.31 | 2.17 | 0.17 | 4.80 | 4.46 | 0.00 | 0.25 | 0.06 | 0.07 | 0.03 | 2.73 |
| Free sedimentation | 65.09 | 20.33 | 2.14 | 0.24 | 3.28 | 4.69 | 0.07 | 0.16 | 0.05 | 0.02 | 0.11 | 3.82 |
| 150 μm sieve | 68.94 | 17.21 | 1.98 | 0.33 | 4.33 | 4.04 | 0.14 | 0.12 | 0.05 | 0.07 | 0.00 | 2.79 |
| 0.4M Oxalic acid | 69.00 | 16.83 | 1.05 | 0.30 | 4.91 | 4.78 | 0.11 | 0.13 | 0.03 | 0.06 | 0.01 | 2.79 |

**LOI: loss on ignition expressed in % by weight*

***Table 3***

*Chemical analysis of the processed raw materials treated with each of the beneficiation treatments*

### 4.2.1 COLORIMETRY

Colorimetric characterization was carried out with the chemically-treated raw materials, because it was the treatment that yielded the best results in terms of a significant reduction in iron. For this, the raw materials were subjected to the same ceramic process and firing cycle used in the previous raw materials characterization. Table 4 shows the results of the chromatic coordinates of the original raw materials as well as those treated chemically, after being fired at a temperature of 1180 ºC. It can be clearly observed that all of the treated raw materials presented a significant improvement in their level of whiteness, obtaining a greater L* coordinate compared to that of the original raw material.

| RAW MATERIAL | T (ºC) | L* | a* | b* |
|---|---|---|---|---|
| AT - ORIGINAL | 1180 | 80.94 | 4.08 | 21.43 |
| AT - TREATED | | 85.22 | 0.92 | 15.07 |
| | | | | |
| | | | | |
| PZ - ORIGINAL | | 36.60 | 5.69 | 7.33 |
| PZ - TREATED | | 45.76 | 10.21 | 15.91 |

*Table 4*
*Colorimetric coordinates of the treated and untreated raw materials*

### 4.3. DEVELOPMENT OF THE COMPOSITIONS

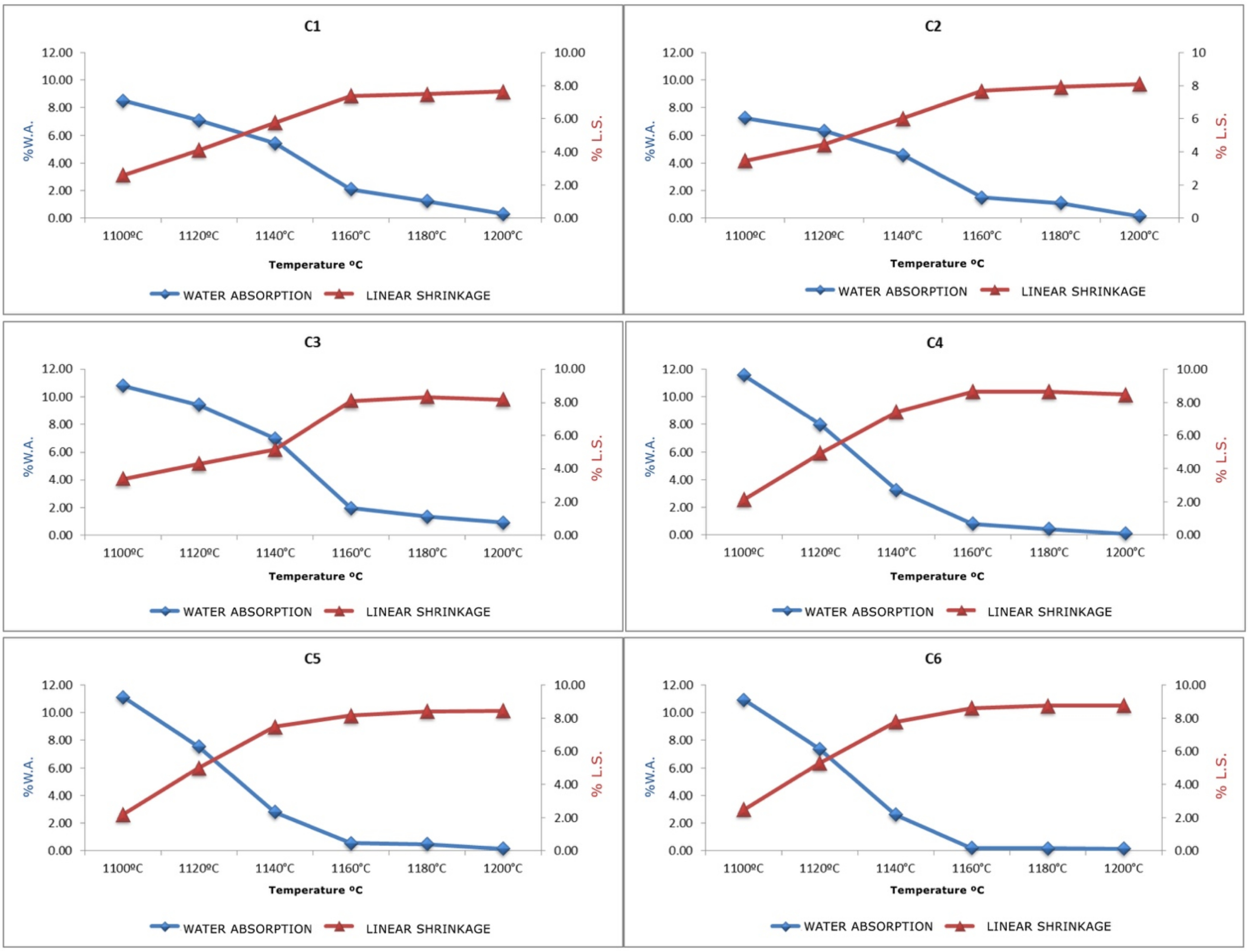
To develop the compositions for light-coloured porcelain stoneware tile bodies, each of the raw materials characterized above was used, including those chemically treated with oxalic acid as this method reduced the iron oxide content to 1%.These compositions are shown below in Table 5.

| RAW MATERIAL % by weight | C1 | C2 | C3 | C4 | C5 | C6 |
|---|---|---|---|---|---|---|
| AO | 20 | 20 | 20 | 20 | 10 | 10 |
| AT | 30 | 30 | 30 | 30 | 50 | 50 |
| PZ | 30 | 30 | | 50 | 35 | 35 |
| FD | 20 | 20 | 50 | | | |
| NF | | | | | 5 | |
| VR | | | | | | 5 |

***Table 5***
*Porcelain stoneware tilebody compositions*

To identify the effect of the processing treatments, composition C1 was developed into which both treated raw materials were introduced. Composition C2 was the same as C1 but with the untreated clays, with the purpose of observing the difference between the two. Alternatively, compositions were also formulated using other fluxes that replaced feldspar, seeking a greater reactivity at lower temperatures. The body compositions were ceramically characterizedsuch that the water absorption value and linear shrinkage of the fired test pieces were calculated. In this manner, figures 5 to 10 represent the variation of these properties based on the maximum firing temperature.

### 4.3.1 VITRIFICATION DIAGRAMS




***Figures 5-10:****Vitrification diagrams of the proposed compositions*

As seen in the vitrification diagrams (figures 5 - 10) of compositions C1 and C2, there are no significant differences in relation to their behaviour; therefore it can be concluded that the treatment given to raw materials clay AT and pozzolan PZ in order to whiten them did not affect their ceramic properties. These compositions did not achieve water absorption values lower than 0.5% up to a temperature of 1200 ºC and according to the linear shrinkage values at this same temperature they had not yet reached the maximum of this value.

In the vitrification diagrams (figures 5 - 10) of composition C3 that only had 50% feldspar and C4 which only had 50% pozzolan, a behaviour can be observed that was very similar to that analysed in the vitrification diagrams of each of these raw materials, in which the use of only pozzolan presented a more reactive behaviour than feldspar, obtaining water absorption values below 0.5% from 1160 ºC on, and also showing a great dimensional stability. The composition with just feldspar at 1160 ºC presented a sudden change in its properties as it began its sintering process and obtained the lowest water absorption value at 1200 ºC.

The use of fluxes Nepheline Syenite NF and Recycled Glass VR proved to be quite efficient when used as an additive to the porcelain stoneware tile compositions, as they reduced the firing temperature range, as can be observed in the vitrification diagrams (figures 5 - 10) of compositions C5 and C6, in which from 1160 ºC on, water absorption values below 0.5% were obtained, along with good dimensional stability from this temperature on. From this it can be concluded that the use of these fluxes reduces the firing temperature by around 40 ºC compared to composition C1.During firing, these fluxes accelerate the densification process, achieving low open porosity and lower water absorption, although it has the disadvantage of increasing linear shrinkage.

### 4.3.2 COLORIMETRY

The colorimetric analysis of the 6 developed compositions at their optimum firing temperatures, based on their vitrification diagrams, is indicated in table 6.In this analysis, there is a significant difference between composition C1, which is formulated with treated raw materials and composition C2 which has the same raw materials and the same percentages, but is formulated with the original clays, without any type of treatment. The L* coordinate of composition C1 was 10.74 points above that of composition C2.Therefore the beneficiation treatment applied was efficient for the development of a light-coloured porcelain stoneware tile.

Composition C3 had the highest L* coordinate out of all of the compositions and this is due mainly to the use of feldspar at 50%, which is white with quite a low percentage of iron oxide (0.10%). This composition can be compared to composition C4 which is formulated with 50% pozzolan where the L* coordinate is lower. It can also be observed that the use of nepheline syenite NS and recycled glass VR reduces the L* coordinate value. This may be consistent with the amount of glassy phase formed during the firing phase, as the higher the temperature achieved, the higher canthe amount of chromophore elements dissolved in this glassy phase be, which causes greater colouration.

| FORMULATIONS | CHROMATIC COORDINATES | | |
|---|---|---|---|
| | L* | a* | b* |
| C1 | 71.08 | 1.72 | 14.95 |
| C2 | 60.34 | 3.17 | 12.93 |
| C3 | 74.24 | 2.24 | 13.42 |
| C4 | 65.80 | 3.25 | 18.82 |
| C5 | 65.13 | 4.06 | 20.11 |
| C6 | 65.65 | 6.08 | 22.66 |

***Table 6***
*Chromatic coordinates of each of the compositions*

## 5. CONCLUSIONS

1) The whiteness levels of clay AT and pozzolan PZ were improved, through both physical and chemical beneficiation treatments. The best results were obtained with the chemical treatment of pile leaching with oxalic acid.
2) Various compositions of porcelain stoneware tile bodies were developed with raw materials available in Colombia.
3) The porcelain stoneware tile compositions developed with the treated raw materials had a higher level of whiteness, without altering the vitrification diagrams.
4) Potassium feldspar, available nationally, was completely replaced by other fluxes such as a natural pozzolan, nepheline syenite and recycled glass, generating a reduction in the firing temperature interval, and lowering the firing temperature by 40 ºC.
5) In this study pozzolan can be considered a new flux for the manufacture of porcelain stoneware tile, standing out for its greater ease of attainment of usable deposits.
6) With the porcelain stoneware tile compositions developed, it was possible to maintain the same technical characteristics currently possessed by this type of products.

## 6. REFERENCES

[1] Sánchez Muñoz, L., Nebot Díaz, I., Carda, J. B., Tuduri, F., *et al.,* "Obtención de soportes cerámicos de baja porosidad a partir de materias primas nacionales". *Cerámica Información*27 (272) 48–54.

[2] Marciano, J., Coelho, J., et al., "Materias primas para pastas de gres porcelánico en Brasil". In Memorias del IX Congreso mundial de la calidad del azulejo y del pavimento cerámico, QUALICER. Cámara Oficial de Comercio, Industria y Navegación, Pos 71 – 73.

[3] Sousa, M., Freitas, J., et al., "Fabricación de gres porcelánico con materias primas seleccionadas del noroeste de Brasil". In memory of the IX World Congress on Ceramic Tile Quality, QUALICER. Cámara Oficial de Comercio, Industria y Navegación, Pos 239 – 243.

[4] Abadira, M., Sallamb, E., et al., "Preparation of porcelain tiles from Egyptian raw materials". Ceramics International., **28,** 303-310.

[5] Ríos, C. "Uso de materias primas colombianas para el desarrollo de baldosas cerámicas con alto grado de gresificación". Universidad Nacional de Colombia, headquarters in Medellín.

[6] Faten Hammami-Ben Zaie, Riadh Abidi, Najet Slim-Shimi, Alireza K. Somarin."Potentiality of clay raw materials from Gram area (Northern Tunisia) in the ceramic industry". Applied Clay Science 112–113, 1–9

[7] Barrachina, E., Calvet, I., Fraga, D., Carda, J. B:"Ceramic porcelain stoneware production with Spanish clays purified by means of the removal of iron compounds and organic matter using physical methods". Applied Clay Science 143, 258–264

[8] Pérez Ayala, G., Vargas Rodríguez, Y., Córdoba Tuta, E. "Beneficio de una arcilla caolinítica de la región de Barichara (Santander) para la fabricación de refractarios". Escuela de Ingeniería Metalúrgica y Ciencia de Materiales, Universidad Industrial de Santander.

[9] Muñoz García, A. "Blanqueo de caolines de la Unión Antioquia usando métodos hidroelectrometalúrgicos". Universidad Nacional de Colombia, headquarters in Medellín.

[10] González, J.A., Ruiz, M del C. "Bleaching of kaolins and clays by chlorination of iron andtitanium" Applied Clay Science 33, 219–229

[11] Olvera Venegas, P. N., Hernández Cruz, L.E., Lapidus, G. T. "Estudio De La Remoción De Hierro De Una Arcilla Caolinítica Por Medio De Lixiviación Reductiva".Universidad Autónoma del Estado de Hidalgo, Área Académica de Ciencias de la Tierra y Materiales.

[12] P. Orosco, D. Lavarra, E. Perino, M. del C. Ruiz y J. González."Desferrificación De Arcillas De Uso En La Industria De Refractarios" Instituto de Investigaciones en Tecnología Química (INTEQUI-CONICET.Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis. Carbo San Luis S. A.

[13] Llop, J., Notari, M.D.,Barrachina, E., Nebot, I., Núñez, I.,Carda, J.B."Tratamientos en arcillas con vistas a mejorar sus coordenadas cromáticas para el proceso de fabricación de gres porcelánico". Bol. Soc. Esp. Ceram.V. 49, 6, 413-422.

[14] Guzmán, A., Torres, J., Cedeño, M., Delvasto, S., Amigó, V., Sánchez, E. "Fabricación de gres porcelánico empleando ceniza de tamo de arroz en sustitución del feldespato" Grupo de Investigación de Materiales Compuestos, GMC.Escuela de Ingeniería de Materiales, Universidad del Valle, Cali, Colombia

[15] Quaranta, N., Caligaris, M., López, H., Unsen, M. Y Lalla, N. "Inclusión de residuos industriales en la producción de materiales cerámicos". Grupo de estudios ambientales – Facultad Regional San Nicolás – Universidad Tecnológica Nacional, Colón 332, San Nicolás-Argentina.

[16] Lázaro, C., Ramón Trilles, V., Gómez, F., Allepuz.S., Fraga, D y Carda J.B."Incorporación de residuos derivados de la fabricación cerámica y del vidrio reciclado en el proceso cerámico integral". Boletín de la Sociedad Española de Cerámica y Vidrio. Vol 51, 2, 139-144.

[17] Caligaris, R., Quaranta, N., Caligaris, M y Benavidez. E., "Materias primas no tradicionales en la industria cerámica". Bol. Soc. Esp. Cerám. Vidrio, 39 [5] 623-626