Production of lightweight red ceramic floor tiles with addition of thermoelectric plant coal fly ash and its effect on physic mechanical properties

A Sarabia¹², J Sanchez¹², and R P Ramírez¹²
¹ Grupo de Investigación en Tecnología Cerámica, Universidad Francisco de Paula Santander, San José de Cúcuta, Colombia
² Centro de Investigación de Materiales Cerámicos, Universidad Francisco de Paula Santander, San José de Cúcuta, Colombia

E-mail: j_sanchezmolina@yahoo.es

Abstract. Fly ash obtained from coal combustion was used as a partial substitute of clay material for lightweight red ceramic floor tiles production by pressing. Raw materials were characterized by X-ray diffraction and X-ray fluorescence. The technique of molding by pressing was used for the manufacture of the prototypes, once firing, were evaluated their physical and mechanical properties (linear shrinkage, apparent density, water absorption, flexural strength). The results indicated that fly ash from the thermoelectric power plant at Termotasajero under the working conditions allow reduce the density of ceramic products with physic mechanical properties adequate for its use as ceramic tiles classified as BIIb and BIIIb.

1. Introduction
The use of raw materials in the industrial sector has caused an accelerated rate that compromises the resources capacity and environment quality. In this context, the circular economy presents an alternative to the linear model, and has gained importance worldwide, as a mechanism to respond to the challenges of economic and productive growth that seeks to protect the environment, based on the principles of reducing, reusing and recycling applicable in the life cycle of the product [1,2].

Currently, one of the strategies used in the European Union is to carry out a greater recycling of the residual by-products of one industry and use them as technological inputs or nutrients in another industrial sector. For the elaboration of ceramic products, it is necessary to use large quantities of clay, where different investigations have been carried out, which seek to use different raw materials in mixtures of clays, in different combinations and proportions, for the manufacture of products [3,4].

On the other hand, the massive amount of fly ash generated by coal-fired power plants worldwide becomes a major environmental problem. In the thermoelectric industry, it is stated that approximately 70%-80% of the ash present in coal is collected in the form of fly ash [5-8] and around 700 tons of fly ash per MW of installed power are produced annually [5]; which by March 2018 in Colombia would mean an estimated 961,800 tons of total annual fly ash production, being 229,600 tons from Norte de Santander, Colombia [9].

Coal fly ash has had different applications among which it stands out as a raw material for the agro-industrial sector improving soil conditions, as an adsorbent for the elimination of organic compounds, in the production of zeolites, in the synthesis of geopolymers, in the manufacture of mesoporous
materials, as an adsorbent for gases such as CO₂ and NOx, and in the manufacture of glass and ceramic products [6,10,4,11,12].

Several studies have been carried out in the ceramic sector, that have evaluated the use of fly ash in the manufacture of ceramic products such as ceramic tiles [13-17] where it has been possible to obtain products with greater mechanical strength, greater linear shrinkage after firing, lower water absorption compared to standard mixtures. In spite of the results obtained in the previous studies, it must be considered that the mineralogical and chemical composition of fly ash differ from one source to another, the type of coal and the combustion method [18,19] being a quite heterogeneous product, composed mainly by SiO₂ (43.4 - 55.9%), Al₂O₃ (21.4 - 49.8%), Fe₂O₃ (2.4-8.1%), CaO (2.5-5.2%), MgO (0.3-2.9%), Na₂O (0.3-3.4%), K₂O (0.2-1.9%), TiO₂ (0.1-1.5%) and unburned carbon (1.9% - 2.8%) [19-22], so the methodology used in the different investigations probably does not guarantee that its application is of general use in the production of ceramics.

Among the challenges demanded by the ceramic sector is to respond to the need to build and reform with criteria of sustainability and energy efficiency, which implies the optimization of the manufacturing process, waste reduction, use of energy resources, reduction of emissions, among others. In particular, for ceramic tiles, one of the trends is the manufacture of lightweight products to reduce the thickness of the material which allows better handling and placement of the product, where the product must have a high strength and comply with technical standards [23].

Considering the availability of fly ash, and its composition of alumino-silicate material, which could be considered compatible in a ceramic paste, as a degreasing actor and/or glass-phase former [19], the production of ceramic tiles is proposed, replacing in the formulation of the mixture different proportions of feldspar by coal fly ashes. Some of the main physical and mechanical properties of the final products were studied, such as linear shrinkage, density, water absorption and flexural strength.

2. Method

As in a previous investigation [24], coal fly ash (CFA) was supplied by a local thermoelectric power plant, clay, feldspar, limestone, raw breakage and cooked breakage supplied by a ceramic company in the region, were used as raw materials for the ceramic tiles. From a standard mixture (CFA0) composed of 78.5% clay, 16.5% feldspar, 2% limestone, and 3% fireclay, feldspar was replaced in proportions of 5, 10 and 100% per rice CFA with particle size less than 74 μm, maintaining the concentration of the other raw materials; the mixtures were designated CFA5, CFA10 and CFA100 respectively.

The materials were ground to diameters less than 74 μm (ASTM D 200 mesh) in a rotary hammer mill, its chemical and mineralogical composition, as well as the other raw materials was determined by the X-ray Fluorescence (XRF); Feldspar and CFA was analyzed by X-ray diffraction (XRD) technique.

The raw material mixtures for the production of the test specimens were wet milled using 400 g of dry basis solid material and 36% by weight of water using a rapid ball mill with 400 g of alumina grinding bodies for 2 minutes 45 seconds. After grinding, the mixtures were dried at 110 °C up to constant weight, and then milled to ASTM-E-11 No. 18 (mesh aperture: 1 mm) using a rotary hammer mill. From each humidified mixture to 5.6- 5.8% by weight and screened to avoid agglomeration due to moisture, 10 specimens were pressed uniaxially at 26.7 bar in a pressing machine using a steel mold of 110 x 55 x 8 mm. To form each specimen, 91.8 ± 1.7 g, 83.9 ± 1.6 g, 83.6 ± 0.7 g, 77.4 ± 0.5 g, of CFA0 (standard), CFA5, CFA10 and CFA100 mixtures were weighed, respectively.

The specimens were dried to constant weight at 110 °C and firing in an industrial roller kiln at a maximum temperature of 1120 °C with a full cycle time of 34 min. The effect of the different concentrations of CFA on the body properties of the sintered specimens was studied by measuring their linear shrinkage (C), density (T), water absorption (E₂₅), according to the criteria established in NTC 4321-3 [25] and flexural strength (R) and modulus of rupture (S) according to NTC 4321-4 [26].
3. Results and discussions

3.1. Raw material characterization

Tables 1 and Table 2 present the consolidates obtained for the analyses of XRF and XRD respectively.

| Raw Material | SiO₂ | Al₂O₃ | Fe₂O₃ | K₂O | TiO₂ | MgO | P₂O₅ | Na₂O | CaO | L.O.I. |
|--------------|------|-------|-------|-----|------|-----|------|------|-----|-------|
| Clay         | 60.07| 21.37 | 5.64  | 1.94| 0.92 | 0.73| 0.61 | 0.31 | 0.39| 7.74  |
| Feldspar     | 71.61| 15.20 | 1.02  | 5.58| 0.18 | 0.26| 0.54 | 3.08 | 0.45| 1.78  |
| CFA          | 52.85| 26.27 | 7.77  | 1.31| 1.17 | 0.65| 0.56 | 0.21 | 1.16| 7.36  |

| Crystalline Phase | Composition (%) |
|-------------------|------------------|
| Quartz            | 44.50            |
| Muscovite         | 5.10             |
| Microcline        | 19.60            |
| Albite            | 25.30            |
| Mullite           | -                |
| Magnetite         | -                |
| Total Crystalline | 94.5             |
| Amorphous and others | 5.5       |

The chemical composition correlates with the composition of the crystalline phases identified by XRD. The results of the analysis of the clay allow us to infer that it is kaolinitic-illitic clay, which provides sufficient plasticity to be able to obtain a defined shape. These provide mainly Si, Al and part of Fe, K, Ti, Mg, Ca, Na and P. The proportion of Ca and Mg is very important in the formulation of pastes, because the higher the content of these elements, the smaller the contraction in fired, since calcium and magnesium silicates are formed that increase their volume with temperature, counteracting the effect of the contraction of the silicate phases. Due to their content of Fe₂O₃, Na₂O, K₂O, MgO and CaO, the plastic raw materials can be considered suitable for the manufacture of red fired stoneware, with some variations in their tones due to the titanium oxide content, these colours are characteristic of the region, especially of the metropolitan area of San José de Cúcuta, Colombia [27]. Regarding the other calculated oxides, they are not going to be very harmful because they are in very small percentages that at the time of the process did not alter the behavior of the material.

A high silica content can be observed, which acts in the paste as a degreaser, favouring the degassing of impurities and the elimination of water during the drying process, as well as reducing dimensional shrinkage and deformations during firing. Generally the silica content of a clay varies between 45-55%, however, high silica contents such as those present in the materials analyzed, even when they are not very far from the standard, can alter the technological behavior of the clay and the physical and mechanical properties of the final product, since quartz crystals change their crystalline structure at 573 °C producing volume changes, which could generate ruptures in the final piece, so special care must be taken in the heating speed between 500 °C and 600 °C [28].

The alumina content of the raw materials analyzed is approximately 21%, enough to provide the clay, high melting temperature, low thermal conductivity, high corrosion resistance, low expansion coefficient and hardness. The concentrations of calcium and sulphur are low, and the presence of barium is observed, which decreases the probability of the appearance of efflorescences, since barium reacts with the sulphate present in the paste and forms barium sulphate which is a very stable and not very soluble compound [29].
The feldspar analyzed is alkaline potassium-sodium type, with a low proportion of sodium and traces of barium in relation to potassium; the identified fire losses are significantly high, a value that is influenced by the high sodium and potassium content.

CFA of this thermoelectric plant are silico aluminous with pozzolanic properties class F (according to standard ASTM C 618 [30]), as they have percentages in weight of Si+Al+Fe greater than 65% and of MgO less than 10%. The inorganic phases with their structures present in fly ash were: mullite (23.4%), followed by quartz with 11.9%, and, in lower concentration, magnetite with 1.9%. It was also found that the fly ash sample is made up of crystalline and amorphous phases, with a percentage of crystalline components of 37.2%, and 62.8% of amorphous phase. It is also evident that the CFA is chemically composed in its inorganic part by a high percentage of SiO$_2$, Al$_2$O$_3$, and Fe$_2$O$_3$; and in smaller percentage by K$_2$O, TiO$_2$, CaO and MgO, that make it propitious to be used as load in a ceramic paste and a 7.36% of organic material (lost by fire or unburned coal) which makes it possible to consider it a good raw material for reducing density of the final products.

3.2. Evaluation of the effect of coal fly ash incorporation on density

Figure 1 presents the apparent density results for designed mixtures, and the maximum and minimum data of each mixture. The apparent density of the fired pieces decreased with greater additions of CFA, becoming 7.9% lower than that of the standard mixture with a total replacement of the feldspar. This fact could be associated to a great extent with the morphological characteristics of fly ash, which usually contains a high surface area and porosity; likewise, the oxidation of the residual organic phase could be responsible for this result, a characteristic that does not allow for a good process of filling the pores by the glassy phase formed and/or sintering of grains, thus reducing the effectiveness of the densification process. At higher additions of CFA, the variation in the specific density of the bodies is less.

![Figure 1](image.png)

3.3. Evaluation of the effect of coal fly ash incorporation on physical mechanical properties

The results of the physical and mechanical characterization of the developed specimens are shown in Table 3, and are analyzed as follows.

| Mixture | C (%)  | LOI (%) | Eb (%) | R (N/mm$^2$) | S (N)  |
|---------|--------|---------|--------|--------------|--------|
| CFA0    | 3.42   | 5.45    | 9.87   | 605.70       | 18.33  |
| CFA5    | 2.84   | 1.32    | 11.05  | 387.92       | 13.20  |
| CFA10   | 2.26   | 5.58    | 12.89  | 257.66       | 8.63   |
| CFA100  | 3.67   | 6.62    | 8.95   | 503.80       | 18.83  |

The use of CFA in the manufacture of ceramic tiles affected the final properties of these products. The results of the evaluated properties indicate that the lower the CFA concentration, the linear
shrinkage is low; however, in a total substitution of the feldspar, the ash favors the increase of this measure, being counterproductive for the quality process of the final product. As can be seen in Figure 1, the density of the pieces decreases with greater addition of CFA; however, when observing the value of water absorption for the mixture with total substitution of feldspar for CFA, it can be seen that this is lower than the one obtained for the standard mixture (without substitution). Both behaviors could be associated to the interaction mechanisms of the phases of the CFA at high temperature, different from the one caused by the melting oxides, interaction of the vitreous phase generated by the clay with the pores of the fly ash (presents high superficial area), the role of the iron (found in greater concentration in the fly ash) in the formation of the vitreous phase, and the reactivity of the amorphous phase of the ashes with the same clay [31,32].

Ceramic tiles are commercially classified according to their water absorption capacity (Eb) and breaking strength, taking into account the requirements of the Colombian technical standard NTC 919 [33]. According to the results shown in Table 3, the standard mixture CFA0 and the CFA100 mixture are classified in group BIIb (6% > Eb < 10%, Resistance to rupture > 500 N), so they can be used in the manufacture of ceramic tiles with low or medium porosities, for pedestrian pavements and claddings; while mixtures CFA5 and CFA10 are classified as BIII (Eb>10% and Resistance to rupture> 200 N), and can be used in the manufacture of ceramic tiles for interior or exterior cladding not subject to the risk of frost, and can be produced in a wide variety of products due to the colour of the substrate (sponge), formats and ceramic surface treatments for decorative purposes.

4. Conclusions
The flying ashes of the thermoelectric plant of termotasajero, have low presence of vitreous mineralogical phases, being able to identify only vitreous phases like magnetite, quartz and mullite.

The content of unburned carbon or carbon residues affects the physical-mechanical properties of the ceramic bodies. Due to the characteristics of ash formation (presence of unburned particles that oxidize later in the ceramic process and morphologies present), the greater the addition of ash, the less dense the ceramic is obtained.

The partial substitution of 5% and 10% of feldspar by CFA has a negative effect on the properties of BIIb type tiles, resulting in a change of classification to BIIIb. While the substitution of 100% of the feldspar by ash allowed obtaining a ceramic with a percentage of water absorption and a mechanical resistance similar to that obtained with the traditional paste. The obtaining of these conditions seems to follow a different reaction mechanism to that produced by the melting oxides (high concentration in the feldspar but poor in the ash).

5. Acknowledgments
The authors express their gratitude to Colciencias and Universidad Francisco de Paula Santander for the support provided through the Young Researchers and Innovators Program.

References
[1] Prieto V, Jaca C and Ormaizabal M 2017 Memoria Investig. Ing. 15 85-95
[2] Park J, Sarkis J and Wu Z 2010 J. Cleaner. Prod. 18 1492–99
[3] Karayannis V, Spiliotis X, Domopoulou A, Ntampegiotis K and Papapolymerou G 2015 Revista Romana de Materiale 45 358-63
[4] Sarabia A, Sánchez J and Leyva J 2017 Respuestas 22 6-15
[5] Ruiz J, Santos C, Cambroner L, Corpas F, Alfonso M and Moraño A 2000 Bol. Soc. Esp. Ceram. Vidr. 39 229-31
[6] Ahmaruzzaman M 2010 Prog. Energy Combust. Sci. 36 327–63
[7] Querol X, Moreno N, Umaña J, Alastuey A, Hernández E, López A and Plana F 2002 Int. J. Coal Geol. 50 413–23
[8] Yu J, Li X, Fleming D, Meng Z, Wang D and Tahmasebi A 2012 Energy Procedia 17 3-9
[9] UPME 2018 Informe mensual de variables de generación y del mercado eléctrico colombiano: Marzo de 2018 (Bogotá: Sistema de Información Eléctrica Colombiano)
[10] Iyer R and Scott A 2001 Resour. Conserv. Recycl. 31 217–228
[11] Blissert R and Rowson N 2012 Fuel 97 1-23
[12] Yao Z, Ji X, Sarker P, Tang J, Ge L, Xia M and Xi Y 2015 Earth Sci. Rev. 141 105-121
[13] Luo Y, Ma S, Liu C, Zhao Z, Zheng S and Wang X 2017 J. Eur. Ceram. Soc. 37 1847–56
[14] Zimmer A and Bergmann C 2007 Waste Manage. 27 59–68
[15] Ji R, Zhang Z, Yan C, Zhu M and Li Z 2016 Constr. Build. Mater. 114 888–895
[16] Sokolar R and Smetanova L 2010 Ceram. Int. 36 215–21
[17] Kockal N 2012 Bol. Soc. Esp. Cerám. Vidr. 51 297–304
[18] Olgun A, Erdogan Y, Ayhan Y and Zeybek B 2005 Ceram. Int. 31 153–8
[19] Wu X, Huo Z, Ren Q, Li H, Lin F and y Wei T J. Alloys Compd. 702 442–48
[20] Luo Y, Ma S, Zhao Z, Wang Z, Zheng S and Wang X 2017 Ceram. Int. 43 1–11
[21] Martin L, Winnefeld F, Tschopp E, Müller C and Lothenbach B 2017 Cem. Concr. Res. 95 152–63
[22] Wang Q, Cui X, Wang J, Li S, Liv C and Dong Y 2017 Constr. Build. Mater. 138 35–44
[23] Promateriales 2016 Cerámica en la construcción Consulted on: https://promateriales.com/ceramica-en-la-construccion/
[24] Sarabia A, Ramirez R and Sánchez J 2017 Congreso Internacional de Innovacion y Tendencias en Ingenieria (CONIITT) (Bogota) (Bogotá: Universidad Católica de Colombia)
[25] Instituto Colombiano de Normas Técnicas y Certificación (ICONTEC) 1998 Ingeniería civil y arquitectura. Baldosas cerámicas. Parte 3: Método de ensayo para determinar la absorción de agua, porosidad aparente, densidad relativa aparente y densidad aparente, NTC 4321-3 (Colombia: Instituto Colombiano de Normas Técnicas y Certificación)
[26] Instituto Colombiano de Normas Técnicas y Certificación (ICONTEC) 2015 Ingeniería civil y arquitectura. Baldosas cerámicas. Parte 4: Método de ensayo para determinar el módulo de rotura y la resistencia a la flexión, NTC 4321-4 (Colombia: Instituto Colombiano de Normas Técnicas y Certificación)
[27] Bernal I, Cabezas H, Espitia C, Mojica J and Quintero J 2003 Revista Acad. Colomb. Ci. Exact 27 569-78
[28] Sanchez J, Sarabia A y Alvarez D 2016 Respuestas 21 48-56
[29] Gazulla M, Sánchez E, Gonzales J and Orduña M 2014 Bol. Soc. Esp. Ceram. Vidr. 53 227-34
[30] American Society for Testing and Materials (ASTM) 2012 Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete, ASTM C618 (West Conshohocken: American Society for Testing and Materials)
[31] Rodriguez G and Ortega L 2014 Ingeniería Investigacion y Desarrollo 4 14-19
[32] Gutierrez O, Pineda Y and Vera E 2015 Revista Metalurgica 51 2-11
[33] Normas ICONTEC: Instituto Colombiano de Normas Técnicas y Certificación (ICONTEC) 2015 Baldosas cerámicas. Definiciones, clasificación, características y rotulado, NTC 919 (Colombia: Instituto Colombiano de Normas Técnicas y Certificación)