Characteristics of refractory bricks used in the coke production kilns in Colombia

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Abstract. A study has been carried out on the main physicochemical characteristics of the refractory bricks that are currently used in traditional coke-making kilns in Colombia. Two classes of material (brick) used in this industry were collected, which come from a geographical area of the country that supplies brick to many kiln builders. These materials were characterized by X-ray diffraction and fluorescence, scanning electron microscopy, dilatometry, thermal conductivity, pyroscopic resistance, and percentage of water absorption. The results obtained show that these materials have had very low firing temperatures in the factory, which is evidenced in the dilatometry, microscopy and water absorption percentage data. This characteristic brings with it high firing shrinkages when subjected to high temperatures (> 4% at 1,200 °C). There is a high presence of quartz in the material (40% or more), an aspect that increases the risk of fissure formation. Chemically there is a limited aluminum content (between 22% and 23%) compared to other reference refractories. The onset of fusion of these materials occurs around 1,360 °C. The thermal conductivity obtained can be considered moderate (between 0.634 W/mK and 0.760 W/mK), thus demonstrating limited applicability as an insulator.

1. Introduction
The energy mining sector represents for Colombia a great source of wealth generation, employment generation and income for the state through the royalty tax [1]. Within this great mineral wealth, coal is one of its greatest references, with exploitation areas in the region of Guajira, Cesar, Norte de Santander, Santander, Boyacá, and Cundinamarca [1].

Due to their good characteristics (high fixed carbon content, high calorific value, low ash, and sulfur content) the coals from the departments of Cundinamarca, Boyacá and Norte de Santander have the potential to be used to obtain coke, the which has a great reception in international markets [1]. Due to this situation, the demand for Colombian coke has increased in recent years reaching production levels above 5 million tons per year, being Norte de Santander the department with the highest growth rate, going from producing about 250,000 tons in the year 2010 to 1,000,000 tons in the years 2019 and 2020. The production of coke in the country is still a very traditional process and characterized by batch manufacturing, with about 144 processing plants and just over 6,400 processing kilns, of which 90% are known as “colmena” kilns [1].

In this kind of furnace (colmena) of the coking industry, the operating temperatures can be close to 1,000 °C in the interior zone of the kiln, but in the tunnels that carry the vapors towards the chimney this temperature increases due to since these receive gaseous fractions from the entire kiln assembly.
called "battery", at the end of the tunnels these vapors and gases, still rich in combustible phases, are oxidized (combustion), increasing the temperature of the walls to values above 1,300 °C. In addition to having to withstand these high temperatures, the kiln bricks are in direct contact with the material (coal) and its vapors, a fact that can bring about reactions that can affect the structure of the refractory brick, especially due to reduction phenomena of elements present such as the iron and in turn having to be exposed to thermal shock processes due to the addition of water to quench the coke and exposure of the outside air during the knockdown of doors once the cycle is finished. These very aggressive working characteristics require the use of materials (bricks) with good technological properties such as high mechanical resistance to compression, high pyroscopic resistance, low expansion, low contraction, low thermal conductivity, good resistance to thermal shock and good resistance to attack chemical [2,3].

Due to the little knowledge about the technological properties of the materials (bricks) that are currently used for the construction of this kind of kilns (colmena), the present work aims to recognize the advantages and disadvantages that these materials have for said industry through of a characterization process of its main technological properties.

2. Materials and methods

Refractory brick samples were collected from two manufacturing companies that have their operation centers in the area near the road that leads from Zipaquirá to Ubaté, in the department of Cundinamarca, Colombia. These materials were coded as S1 and S2.

In the case of X-ray diffraction (XRD), a BRUKER brand, D8 ADVANCE diffractometer with DaVinci geometry was used, which works with Kα1 type copper radiation, scanning step by step, with a step of 0.01526°, counting time of 0.4 s, nickel filter, voltage 40 KV and 30 mA. The qualitative analysis of the present phases was established through the diffraction patterns reported in the PDF-2 database of the International Center for Diffraction Data (ICDD).

The quantitative analysis was performed by using Rietveld refinement, using an internal standard (20% corundum) to determine the amorphous phase. The chemical composition was determined with X-ray fluorescence (XRF), using a BRUKER spectrometer model S8 TIGER. The study of the morphology and chemical microanalysis was carried out in a JEOL-JSM 6490LV electron microscope. Coating of the samples was done using gold as reference material.

The dilatometry test was performed on a NETZSCH model DIL 402C dilatometer. A heating rate of 10 °C/min (air atmosphere) was used, from room temperature to 1,200 °C. A cut and polished 25.0 mm × 6.5 mm × 6.5 mm specimen was made from the original material in order to perform the test.

The thermal conductivity was performed in a Hot Disk model TPS 500 S thermal constant analyzer from Thermtest -Thermal conductivity instruments which works with the transient plane source method (TPS) that is carried out in accordance with the ISO 22007-2 standard [4].

The pyroscopic resistance, or pyrometric cone (PCE) equivalent (PCE), was established according to the guidelines of the ASTM C24-09 standard [5]. A Terrigeno brand kiln, model D8 was used in the process. The conforming of the cone was carried out using only water and subsequently a natural drying.

The mechanical resistance to compression was determined following the guidelines of the NTC 682 [6]. Gilson Company brand equipment, MC-250P model was used to collect information. Specimens cut from the original brick were used to perform the test. The dimensions of the specimens were 5.0 cm × 7.0 cm × 2.9 cm. The load was applied on the “bed face” of the sample, because in this position in which the refractory bricks are usually placed to form the walls of the “colmena” kiln. Finally, the percentage of water absorption was established by the guidelines of the ASTM C20-00 standard [7].

3. Results and discussions

The XRF and XRD results are presented in Table 1 and Table 2, respectively. From the chemical information shown in Table 1, it can be seen, that materials currently used in the region have a predominance of silicon in their composition, very different from what is usually found in alumina-silica refractory bricks manufactured by large companies. (for use in industrial kilns), where the minimum
aluminum content is higher than 40% [8]. The information shown in Table 2 corresponds to the quantitative data made from Rietveld refinement. In this type of materials, it is appreciated that aluminum is the reference material, since it has been shown in the literature that some phases of this element (alumina, corundum, mullite and cordierite) show good behavior as a refractory [3].

The results in Table 1 show that for both samples the aluminum does not exceed 24%, a value that is almost half of the minimum found in specialized refractory bricks [8]. Regarding the other elements present in Table 1, it is evident that S2 has a higher iron content, which is manifested in the redder tone of these bricks. Along with iron, sodium and potassium should be highlighted due to their role as fluxing elements that can have some effect on the technological properties of the brick, among them a possible greater contraction effect after being placed on the job stands out.

By adding the mass content of these three elements, it can be established that S2 has a greater risk of favoring the fusion of the brick when working at high temperatures. In the same way, the high iron content can be detrimental to the stability of the brick, especially when working in reducing environments, such as obtaining coke. Under oxygen deficit environments and the presence of carbon, the reduction of iron from Fe3+ to Fe2+ and finally Fe0 can occur, although there is also the case of the reaction of carbon with iron to form iron carbide [3]. In any case, these modifications can lead to loss of mechanical resistance and the spalling of the brick on the exposed faces or in contact with the coke, a risk that is more significant in the S2 material.

The magnesium and calcium contents also tend to play a relevant role as refractories when they are present as calcium oxide and magnesium oxide [3], however, the concentration of these elements is very low in the two samples analyzed, making the effect less relevant of these possible phases.

### Table 1. XRF results.

| Phase | S1 (% weight) | S2 (% weight) |
|-------|---------------|---------------|
| SiO2  | 67.19         | 65.53         |
| Al2O3 | 23.67         | 23.62         |
| Fe2O3 | 4.10          | 5.65          |
| K2O   | 2.29          | 2.19          |
| Na2O  | 0.32          | 0.30          |
| CaO   | 0.26          | 0.27          |
| MgO   | 0.69          | 0.71          |
| TiO2  | 1.06          | 1.06          |
| P2O5  | 0.08          | 0.08          |
| SO3   | 0.06          | 0.23          |
| BaO   | 0.09          | 0.10          |
| ZrO2  | 0.03          | 0.03          |
| CuO   | 0.03          | 0.05          |
| ZnO   | 0.03          | 0.04          |
| MnO   | 0.00          | 0.02          |
| SrO   | 0.02          | 0.03          |
| Cr2O3 | 0.03          | 0.03          |

### Table 2. XRD results.

| Phase      | Card Number PDF-2 | S1 (% weight) | S2 (% weight) |
|------------|--------------------|---------------|---------------|
| Quartz     | 010872096          | 39.70         | 37.60         |
| Berlineite | 010751072          | 1.10          | 0.00          |
| Mullite    | 010748549          | 1.50          | 0.00          |
| Hematite   | 010764579          | 0.70          | 0.80          |
| Rutile     | 010707347          | 0.40          | 0.70          |
| Sillimanite| 010847719          | 3.00          | 1.20          |
| Muscovite  | 010703754          | 3.00          | 9.20          |
| Amorphous  | -                  | 50.60         | 50.40         |
When observing the microstructural composition data in Table 2, it can be seen, that the presence of the alumina phase is not evident in its composition and that the contents of mullite and silymanite are also low (< 5%), a fact that shows a possible low pyrosopic resistance of these materials.

Among the refractory phases that could be formed under the current chemical composition, mullite would be the one with the highest probability of formation, theoretically, up to 33% by weight of mullite could be formed, a value that is very far from that quantified by XRD. This low concentration of mullite could be explained by low firing temperatures of the bricks or because the mechanism that facilitates its production is not being promoted.

In the case of quartz, it is evident that both samples contain a high content of this phase (> 39%). Although silica bricks are manufactured as very high-temperature refractories, they are characterized by their high purity and because their use forces them to always be at very high working temperatures; which does not usually happen in “colmena” kilns, because they are seen subjected to heating and cooling cycles. Under this circumstance, having a high content of quartz in the mineralogical composition of “colmena” kiln's refractory brick could become counterproductive since during these heating-cooling cycles phase changes are generated from the alpha quartz to the beta phase, generating an expansion of the unit cell which can generate cracks in the material if good temperature management is not done [3]. In the same way, it is probable that due to the high working temperatures that some areas of the furnace battery reach (ducts and volatile oxidation zone) the formation of the cristobalite phase is caused, which is also recognized for generating dilatometric changes very significant that they can arrive by affecting the integrity of the refractory brick [3].

An interesting fact from the mineralogical analysis is the presence of the muscovite phase and the high content of amorphous phase. The presence of muscovite suggests that the firing temperature of these bricks has not been very high, but sufficient for the transformation of the clay phases (possibly kaolinite) to an amorphous phase. This amorphous phase is rich in aluminum according to the stoichiometry and concentration of the crystalline phases identified in Table 2.

The presence of hematite, rutile and berlinite make sense due to the presence of iron, titanium and phosphorus evidenced in the chemical composition of Table 1. Of these elements, only iron plays a significant role in the refractory bricks of the area, it contributes changes in the color of the brick and can affect its mechanical resistance, as has already been mentioned before. Complementary to the chemical and mineralogical information, the dilatometry results presented in Table 3 allow corroborating some of the statements proposed so far.

Table 3 shows that the S2 material is more sensitive to dilatometric changes. About expansion effects, this last material reaches an expansion of 0.683%, 27% more compared to S1, and at a much lower heating temperature. The maximum operating temperature of the test was 1,200 °C, showing that at this temperature, shrinkage effects are being generated in the material, a product of high-temperature reactions (formation of a glassy phase and/or recrystallizations), again this effect is more marked on material S2. Once the cooling was finished, additional contractions were observed, obtaining definitive shrinkage values higher than 4%. This result reveals two important issues, the first is to corroborate that indeed the firing of these bricks in the factory is still low in accordance with the proposed XRD analysis, this statement is established from the high shrinkage obtained in both materials.

| Sample | Maximum expansion achieved | Shrinkage to 1,200 °C | Final shrinkage (%) |
|--------|---------------------------|----------------------|---------------------|
| S1     | 0.539                     | 2.817                | 4.292               |
| S2     | 0.683                     | 3.281                | 5.900               |

The second issue is related to the effects that these materials can generate once they are put into operation in the kiln or in the evacuation ducts, such high shrinkages can be a risk for the stability of the kiln, especially on the roof of the “colmena” kiln. In the same way, large spaces can be generated
between the brick and mortar whereby heat losses and excess air entering the kiln can be increased, which is not convenient, since the combustion of coal is favored.

The first derivative analysis of both materials has made it possible to recognize expansion/contraction events of the material with greater clarity. Typical quartz dilation events between 575 °C and 580 °C were identified in both materials, a very significant contraction event was evidenced in the profile of S2 at 968 °C, this event is most likely associated with the transformation of metakaolinite to spinel or primary Mullite consistent with the results of previous studies [9]. Small dilatometric changes were evidenced at 1,162 °C, 1,170 °C, and 1,188 °C in both materials, possibly associated with recrystallization events of the glass phase [9]. The pyroscopic resistance is the most relevant data used to determine the quality of the refractory by the kiln builders, the results obtained for the two collected materials are presented below in Table 4.

| Sample | Lower cone | Softening temperature (°C) | Upper cone |
|--------|------------|----------------------------|------------|
| S1     | 13         | 1,360                      | 14         |
| S2     | 13         | 1,370                      | 14         |

According to the ASTM C27-98 [10] standard, Fireclay bricks (category of this class of refractory materials analyzed) present 5 classification categories, being the “low duty” class the one that presents the lowest operating temperature, supporting a PCE of at least 15 according to the standard. When observing the information presented in Table 4, it is evident that none of the materials studied reaches this category, that is, S1 and S2 cannot be considered as refractory bricks. It is important to consider the softening temperature exposed in this work to define the use of these materials in the construction of “colmena” kilns due to their limited pyroscopic resistance. The characterization of the thermal properties of these bricks is presented in Table 5.

| Sample | Thermal conductivity (W/mK) | Thermal diffusivity (mm²/s) | Water absorption (%) | Compressive strength (MPa) |
|--------|-----------------------------|-----------------------------|----------------------|---------------------------|
| S1     | 0.7602                      | 0.4971                      | 12.68                | 45.04                     |
| S2     | 0.6346                      | 0.4853                      | 13.84                | 33.77                     |

Table 5 shows that the S2 material has lower thermal conductivity compared to S1, this difference is close to 20%. Even so, both results can be considered as high in comparison with brick references used as insulators and with a traditional masonry ceramic brick [8,11]. Fortunately, thermal conductivity is strongly influenced by porosity, which can be generated through different routes, among which the addition of unburned from the same burning process (using coal or firewood) could be an alternative for these entrepreneurs, this is if a detailed study of the process is necessary, since the addition of porosity (decrease in thermal conductivity) also brings a sacrifice in the mechanical resistance of the brick. Regarding thermal diffusivity, the results go in the same direction, a traditional brick has values close to 0.520 mm/s [12], a fact that is not far from the value reported in this work. This fact shows a high rate of heat transfer to the medium.

Finally, emphasis is placed on the other data on technological properties that have not yet been described and that are present in Table 5, that is, the mechanical resistance to compression and the percentage of water absorption. Regarding this last property, a slight difference between S1 and S2 is evident, this variation could be associated with the lower firing temperature of this last material. This property is directly associated with open porosity and must be carefully analyzed depending on the use that is given to the firebrick. A high or low value of porosity can be advantageous (or not) in firing kilns made with this class of bricks. An increase in porosity could be beneficial since it allows a decrease in thermal conductivity (see Table 5) and therefore hence the heat losses to the medium, which would be a small advantage of S2 material. However, greater porosity also brings with it a decrease in mechanical
resistance and a greater probability of accumulation of carbonaceous residues in said pores, which can react with the elements of the brick affecting its integrity, with iron being the element with the highest risk of being attacked, here S1 is the material that has the advantage.

Regarding mechanical resistance, the results obtained correlate quite well with the other data obtained, the lower firing temperature of S2 and therefore its greater open porosity makes it have less mechanical resistance. The last topic of this characterization is the analysis by means of scanning electron microscopy, the results obtained are presented in Figure 1, as well as in Table 6 for the microchemical information.

The SEM images reveal a low degree of sintering, there is not a noticeable presence of vitreous phase with the naked eye in either of the two materials. This last fact is reflected in the presence of open porosity, whose size can reach up to 10 micrometers. Large grains are also evident in both materials, which, according to the microchemistry presented in Table 6 (site 1), is associated with the presence of quartz, phase previously identified by XRD. The morphology and microchemistry of site 2 evidenced in S2 could be associated with the presence of sulfate efflorescences, typical in ceramics, with the particularity that this case would be barium sulfate instead of calcium sulfate (gypsum); site 2 and site 4 appear to have a greater association with the amorphous phase identified by XRD. The microchemistry reveals a slightly lower Si/Al ratio with respect to that presented in the data in Table 1.

![Figure 1](image_url)

**Figure 1.** Micrographs (SEM/SE) of samples analyzed. (a) S1 material; (b) S2 material.

**Table 6.** Microchemical analysis.

| Element | Site 1 (%) atomic | Site 2 (%) atomic | Site 3 (%) atomic | Site 4 (%) atomic |
|---------|------------------|------------------|------------------|------------------|
| O       | 55.44            | 54.43            | 36.69            | 44.96            |
| Si      | 44.56            | 35.90            | 22.70            | 37.78            |
| Al      | -                | 7.89             | 8.97             | 12.94            |
| Fe      | -                | 0.60             | 2.67             | 1.92             |
| K       | -                | 1.17             | -                | 1.79             |
| Ti      | -                | -                | -                | 0.61             |
| S       | -                | -                | 6.38             | -                |
| Ba      | -                | -                | 22.60            | -                |

4. Conclusion

The characterization of the refractory bricks that are usually used in the construction of “colmena” kilns for the manufacture of coke allowed to establish that this class of materials does not contain or have a very low concentration of the phases that are traditionally evidenced in silicoaluminous refractory materials (alumina and mullite). The low firing temperature is one of the variables that explain many of the characterization data obtained, especially in the S2 material.
The pyroscopic resistance data show that these materials are not classified as refractory bricks according to the ASTM C27-98 standard. It is necessary to improve the insulating properties of the refractory brick, the current data on thermal conductivity (0.634 W/mK and 0.760 W/mK) do not contribute to reducing heat losses to the environment.

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