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Unburned bodies of mineral carbon coming from Colmena kilns placed in the metropolitan area of San José de Cúcuta, Colombia: Possibilities of reuse

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Abstract. In this work residues from the combustion process of the mineral coal used to generate energy in the kilns of the ceramic industry in the metropolitan area of San José de Cúcuta were collected and characterized. The material collected was subjected to grain size reduction and characterized by gravimetric thermal analysis, differential scanning calorimetry, scanning electron microscopy, microstructural analysis by X ray diffraction and chemical composition from X-ray fluorescence. The results obtained show that the unburned bodies coming from Colmena kilns (which are currently discarded) still have a very high concentration of organic phase that can provide energy to the ceramic process through combustion, if they are subjected to firing temperatures above 650 °C. On the other hand, the characterization obtained shows that chemically these unburned bodies are rich in inorganic elements such as silicon, aluminum and calcium, which are present in the material as amorphous (91.9% w/w) and crystalline phase (8.1% w/w), with quartz and mullite as relevant crystalline phases. It was established that this waste can be used as a substitute of clay materials in the manufacture of construction ceramics.

1. Introduction

Within the construction area, ceramic materials play a very important role in the development of civil works of different nature. The production of this type of material is based on the use of clay and an additional set of minerals such as quartz, feldspar and limestone which, when heated to temperatures above 900 °C, allows to obtain construction elements of high mechanical resistance, resistant to environmental conditions and pleasant aesthetic appearance [1].

Around the metropolitan area of San José de Cúcuta, there are large reserves of clays which have led to the creation of a conglomerate of companies dedicated to the manufacture of ceramic construction materials [2]. Many of these companies produce masonry products, floors and unglazed roofs using processes that are not at the same technological level as the ones used in Spain, Italy or Brazil [3].

Many of the products manufactured by regional ceramics companies, (especially floors and roof coverings) are recognized nationally and internationally for the color tones obtained during the firing process [2]. These characteristic tones are obtained from the use of “inverted flame kiln”, better



known in the area as "Colmena Kiln". The Colmena kiln uses mineral coal as fuel for generating the energy required for the firing process, reaching working temperatures close to 1050 °C [2]

Although Colmena kiln can produce products with very striking color tones, its design features and materials used lead to its technology is considered very poor from the point of view of energy consumption compared to other kinds of kilns such as Hoffman or Tunnel type, used in this industry [2,4,5].

In the region, the processes of dosing mineral coal to the combustion chambers of the Colmena kilns is done manually or with mechanized devices that dose pulverized coal. Under any of the two dosing alternatives, it has been evidenced in previous studies, that the content of residues recovered from the combustion process is much higher compared to the obtained in the laboratory [6,7].

Under this scenario, this work aims to characterize these residues coming from the Colmena kilns and at the same time to find possible fields for them to be used within the same regional ceramic industry.

2. Materials and methods

2.1. Materials

The material collected (combustion residues) for this work was acquired from a brick company, located in the municipality of El Zulia, Norte de Santander, Colombia.

The clayey material for the manufacture of ceramics at laboratory scale, was collected from the mining site of the company Cerámica Murano, which is located in the Alejandra sector, jurisdiction of the El Zulia municipality, Norte de Santander (metropolitan area of San José de Cúcuta). They are red clays of the sedimentary type, which are geologically part of the "Guayabo Group" as described in the literature [8].

2.2. Methods

For microstructural analysis by X-ray diffraction (XRD), a powder diffractometer, brand BRUKER model D8 ADVANCE with DaVinci Geometry operating at 40 kV, 40 mA, step sampling with an increment of 0.02035° 2Theta and sampling time of 0.6 seconds, was used. measuring between 3.5-70.0° 2Theta, using Cu K α 1 radiation.

The qualitative analysis of crystalline phases was carried out by comparing the diffractograms obtained with the diffraction patterns PDF-2, of the International center for diffraction data (ICDD). Quantitative analyzes of the phases found were carried out by refining the observed profile with the Rietveld method, adding a known amount of an internal standard (Aluminum oxide, α -phase) close to 20% to the selected specimens of the samples.

X-ray fluorescence (XRF) was used to establish the chemical composition of the collected material. The quantitative analyzes were carried out using the QUANT-EXPRESS method (Fundamental Parameters) in the range of sodium (Na) to Uranium (U), in a sequential wavelength fluorescence spectrometer of 4 kW dispersive wavelength BRUKER model S8 TIGER. The X-ray source was a tube of Rhodium. The value of ignition losses (L.O.I) was determined by calcination of the specimens selected from the samples with a heating rate of 3.08 °C/minute up to a temperature of 950 °C, maintaining said temperature for two hours.

Thermal gravimetric analysis/Differential scanning calorimetry (TGA/DSC) was used to characterize the material collected as combustion residue, identify phases and exothermic/endothermic events. A SDT-600 equipment produced by TA Instruments was used. A heating rate of 20 °C/min and an air atmosphere with a flow rate of 100 ml/min were used. Approximately 15 mg of sample (177 μ m) were used for the test. Alumina crucibles were used to load the sample and as a reference.

Scanning electron microscopy (SEM) was used to establish morphological aspects of the waste. An energy dispersive X-ray (EDX) detector coupled to the microscope was used to establish microchemical aspects of the sample. The equipment used was a FESEM microscope, MERLIN model produced by Carl Zeiss. The samples were coated with gold for analysis.

The forming of the ceramic samples was carried out in a laboratory extruder (New Wave series 101), natural drying was carried out to eliminate the molding water, firing was carried out in an electric kiln (Gabbrielli brand, 5 °C/min) using oxidizing atmosphere. Standard ASTM C326-03 [9] was used to calculate the shrinkage of drying and cooking, and Colombian technical standards NTC 4321-3 [10] and NTC 4321-4 [11] were used to establish the percentage of water absorption and resistance mechanical to flexion, this last test in a Gabbrielli laboratory equipment.

3. Results and discussion

The results of chemical composition (XRF) and structural composition (XRD) are shown in Tables 1 and Table 2.

Table 1. Chemical composition of unburned bodies of mineral carbon coming from Colmena kilns.

Oxide	(% w/w)	Oxide	(% w/w)
SiO ₂	12.34	TiO ₂	0.20
Al ₂ O ₃	8.94	MgO	0.29
Fe ₂ O ₃	0.89	Na ₂ O	0.09
K ₂ O	0.10	SO ₃	0.77
CaO	0.33	* L.O.I	76.01

Table 2. Microstructural composition of unburned bodies of mineral carbon coming from Colmena kilns.

Phase	Card PDF-2	Name	(% w/w)
Crystalline	SiO ₂	010-75-8321	Quartz 4.8
Crystalline	Al _{4.52} Si _{1.48} O _{9.74}	010-79-1457	Mullite 3.3
Amorphous			91.9
Total			100.0

From the information shown in the Table 1, it can be seen that only 23.99% of unburned bodies of mineral carbon coming from Colmena kilns corresponds to inorganic phase, the remaining value is associated to the organic matter present and /or water present in the material (see thermal analysis in the Figure 1). Silicon and aluminum are the most representative elements of the inorganic fraction. The amount identified of each one of them shows correlation with the crystal phase analysis established by XRD and Rietveld refinement presented in the Table 2. The sulfur content evidenced is associated with the presence of pyrite mineral, it comes with mineral coal during the extraction process in the mine [12]. There is evidence of the presence of small concentrations of alkaline and alkaline earth elements that can be useful as fluxes if the unburned bodies are used as a substitute for clay in the manufacture of ceramic construction materials [13].

The amorphous fraction is likely composed of the residual organic matter from mineral coal that was not oxidized during the combustion process, as evidenced by the thermal analysis and differential scanning calorimetry results presented in Figure 1.

From the TG profile of Figure 1 it can be seen that the material does not present mass loss associated with physically absorbed/absorbed water (<150 °C) [14]. The mass loss events are located above 500 °C and are characterized by being exothermic according to the heat flow profile. This behavior of total mass loss (approximately 75%) is very similar to that obtained in the calcination losses presented in Table 1 (XRF analysis). This result leads to infer that during the process of combustion of the mineral coal in the Colmena Kiln, only a fraction of the fixed carbon is converted into a gas phase (carbon dioxide and carbon monoxide). Most of the energy currently used in the system, could be associated with the volatile fraction of the mineral coal (hydrogen, methane and other hydrocarbons), which represents more than 30% of the mass composition in the results of the proximate analysis evidenced in the literature [15].

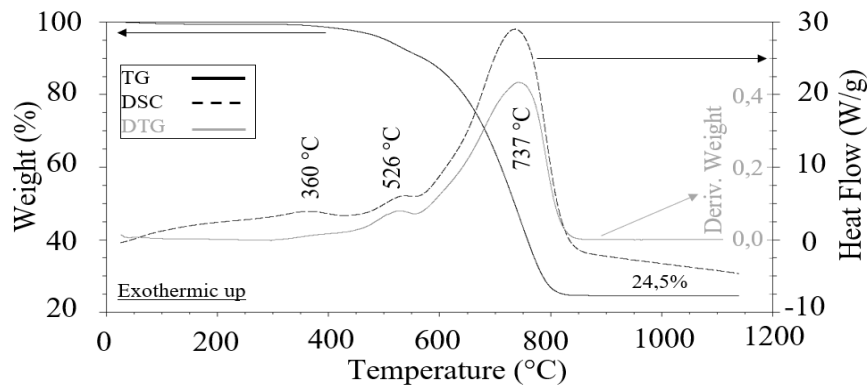


Figure 1. TGA, DTG and DSC profile of unburned bodies of mineral carbon coming from Colmena kilns (air atmosphere).

The analysis of the calorific power of a sample of the mineral coal used by the brick company, as well as of the unburned bodies obtained, gave values of 27200 kJ/kg and 15900 kJ/kg respectively, a result that corroborates what was said before. This value of calorific power of the unburned bodies can be considered as useful for the ceramic industry, since it shows similarity with other combustible materials that have been used in industry to generate heat, such as rice husk (14000 kJ/kg) and coffee husk (16000 kJ/kg) [16].

The unburned bodies collected were also characterized by SEM/EDX in order to know the morphological and microchemical aspects of the material. Two distinct differentiated morphologies were identified, which are presented in Figure 2 and Figure 3. Similarly Table 3 contains information on the microchemical composition of the regions or sites identified in the aforementioned Figures 2 and Figure 3. In the images of Figure 2 and Figure 3, it can be seen that there are two regions, which differ by the greater or lesser presence of porosity. The less porous region (Figure 3) appears to have a rounded appearance with a possible vitreous phase. The other region is quite porous (Figure 2), with pore diameters between 20 and 200 micrometers, the cause of the porosity was possibly originated by the release of gases from the interior of the mineral coal during the combustion process.

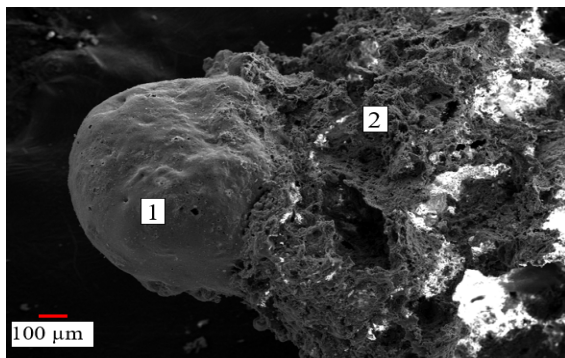


Figure 2. Micrography (SEM) of unburned bodies of mineral carbon coming from Colmena kilns (morphology type 1).

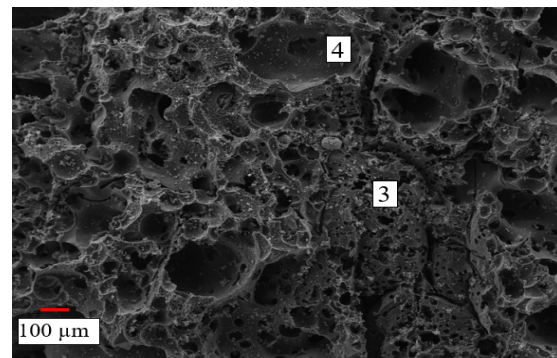


Figure 3. Micrography (SEM) of unburned bodies of mineral carbon coming from Colmena kilns (morphology type 2).

The microchemical information of the unburned bodies correlates quite well with that obtained by XRF results, in that the majority elements are oxygen, silicon and aluminum. The porous region (sites 3 and 4 in Figure 3) is characterized by the presence of sulfur and by the scarce presence of sodium and magnesium. An important aspect evidenced is that the silicon/aluminum ratio in this region is lower compared to the porous region, this fact could suggest that there is a greater presence of mullite in these areas (mullite is a phase rich in aluminum).

Table 3. Microchemistry of some particles present in the unburned bodies of mineral carbon coming from Colmena kilns (% atomic).

Chemical element	Site 1	Site 2	Site 3	Site 4
O	68.83	70.42	71.26	74.56
Na	0.37	0.22	---	---
Mg	0.42	0.19	---	---
Al	9.58	10.84	8.71	7.48
Si	16.14	16.12	12.54	8.93
S	---	---	1.70	2.83
K	0.85	0.98	0.41	---
Ca	0.17	0.12	1.26	1.83
Fe	3.30	0.44	3.64	4.36

Regarding the less porous region (site 1 and 2 in Figure 2), its microchemical composition and morphology are closely related to that evidenced in fly ash from thermoelectric plants, which show a rounded appearance with an amorphous character in most cases [17].

Finally, the results of substitution of clay by unburned bodies in the elaboration of construction ceramics are presented. Figure 4 shows a photograph of the material fired at 1000 °C with different levels of residue substitution, and Table 4 shows the physico-ceramic analysis information.

**Figure 4.** Photographic record of ceramic samples made using the unburned bodies (wastes).**Table 4.** Some properties of ceramics obtained using unburned bodies of mineral carbon coming from Colmena kilns as substitute clay material (firing temperature, 1000 °C).

Substitution (%)	Drying shrinkage (%)	Cooking shrinkage (%)	Water absorption (%)	Mechanical resistance to flexion (N/mm ²)
0	8.21	0.72	11.15	16.93
5	6.91	0.20	12.08	7.96
10	7.05	0.71	13.11	21.41
15	7.02	0.80	16.7	19.57
20	6.95	0.76	23.34	16.02

Figure 4 shows that the samples made from the addition of unburned bodies coming from Colmena kilns, once fired, have a color tone similar to that obtained with clay alone. However a process of chemical reduction of the iron present inside the ceramic samples (process known as black heart) was evidenced. This reaction is caused by the oxidation of the organic phase present in the waste used [18]. The results of Table 4 show that the substitution of clay by unburned bodies from Colmena kiln allows to obtain ceramics (firing at 1000 °C) with similar or even better technological properties to natural material, as in the case of mechanical resistance to flexion. Another important aspect to highlight is the fact that those unburned bodies to be rich in organic matter, and being present within the ceramic mass, can bring heat to the system(kiln) at the time of being oxidized at temperatures higher than 800 °C, bringing with it a possible energy saving in the fuel used in the firing stage.

4. Conclusion

The characterization process carried out on the material collected (unburned bodies) revealed that these residues are very rich in organic matter, with a calorific value close to 15900kJ/kg. This residue can still be used as fuel during the ceramic firing process, if the temperature of the kiln is above 650 °C. On the other hand, it was evidenced that the use of this residue as a substitute for clay, allows to obtain ceramics (at 1000 °C) with technological properties equal to or better than those obtained with clay alone.

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