



# Efecto de relaves mineros, cáscaras de yuca y desechos de cáscara de arroz en el desempeño y durabilidad de los ladrillos cocidos

## *Effect of mining tailings, cassava peels, and rice husk wastes on performance and durability of fired bricks*

Mario Alberto Saucedo-Coley <sup>a</sup>; Carlos Alberto Ríos-Reyes <sup>a</sup>; German Adolfo Díaz-Ramírez <sup>a</sup>

<sup>a</sup> Universidad Industrial de Santander, Colombia; meison122@hotmail.com

<sup>a</sup> Universidad Industrial de Santander, Colombia; carios@uis.edu.co

<sup>a</sup> Universidad Industrial de Santander, Colombia; gadiarz@correo.uis.edu.co

Correspondencia: carios@uis.edu.co

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### Resumen

Dos de las principales actividades económicas que contribuyen a los países en desarrollo son la minería y la agricultura. En Colombia, la producción de arroz y yuca constituye una de las actividades agrícolas más importantes que genera grandes cantidades de biomasa. Por otra parte, los residuos mineros pueden ser dispuestos de forma inadecuada, constituyendo una grave amenaza para el medio ambiente, principalmente para la calidad de las aguas superficiales y subterráneas. La acumulación de estos residuos industriales no gestionados ha dado lugar a una mayor preocupación medioambiental. Los residuos agrícolas y mineros tienen una aplicación restringida a pesar de su considerable valor potencial. La valorización, el reciclaje y el uso de estos residuos industriales en el desarrollo de materiales de construcción sostenibles parecen ser una solución viable no solo para mitigar el impacto ambiental sino también una opción económica para desarrollar técnicas de construcción ecológica. El objetivo de esta investigación es evaluar el efecto de la incorporación de cáscaras de yuca, cascarilla de arroz y relaves mineros sobre las propiedades físicas y mecánicas de los ladrillos a base de desechos, y así contribuir al componente de sustentabilidad de la industria de la construcción. Las materias primas fueron analizadas por difracción de rayos X y microscopía electrónica de barrido para conocer su composición mineral y química. Los ladrillos a base de residuos se fabricaron con diferentes cantidades de residuos. El comportamiento mecánico de los ladrillos propuestos se evaluó mediante la resistencia a la compresión y a la flexión. La durabilidad se probó mediante ataque químico con H<sub>2</sub>SO<sub>4</sub> y NaCl en condiciones ambientales corrosivas. Los resultados obtenidos indican que la adición racional de residuos agrícolas y mineros constituye una alternativa viable para el desarrollo de nuevos materiales de construcción.

**Palabras clave:** Minería y agricultura; Desechos; Ladrillos cocidos; Materiales de construcción; Desempeño y durabilidad.

### Abstract

Two of the main economic activities that contribute to developing countries are mining and agriculture. In Colombia, the production of rice and cassava constitutes one of the most important agricultural activities that generates large amounts of biomass. On the other hand, mining wastes may be inappropriately disposed of, constituting a serious threat to the environment, mainly on surface water and groundwater quality. The accumulation of these unmanaged industrial wastes has led to increased concern for the environment. The agricultural and mining wastes have a restricted application despite they have potentially considerable value. The valuation, recycling, and use of these industrial wastes in the development of sustainable construction materials appear to be a viable solution not only to mitigate the environmental impact but also an economical option to develop green buildings technics. The aim of this research is to assess the effect of cassava peels, rice husks, and mining tailings incorporation on the physical and mechanical properties of waste-based bricks, and thus contribute to the sustainability component of the construction industry. Raw materials were analyzed by X-ray diffraction and scanning electron microscopy to determine their mineral and chemical composition. Waste-based bricks were fabricated with different quantities of waste. The mechanical performance of the proposed bricks was assessed by compressive and flexural strength. Durability was tested by means of chemical attack with H<sub>2</sub>SO<sub>4</sub> and NaCl under corrosive environmental conditions. The results obtained indicate that the rational addition of agricultural and mining wastes constitutes a viable alternative for the development of new construction materials.

**Keywords:** Mining and agricultural; Wastes; Fired bricks; Construction materials; Performance and durability.

## 1. Introduction

Planet Earth has been affected by global warming and climate change because of the demand for natural resources, the use of fossil fuels, the agriculture, the greenhouse gases, the

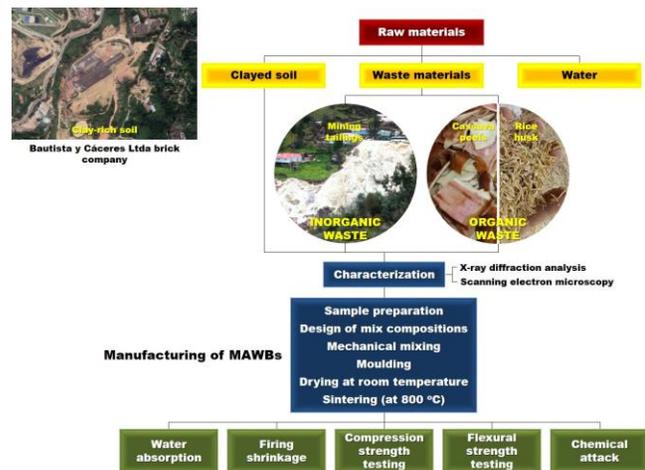
carbon dioxide emissions, the excessive consumption of energy and the uncontrolled production of organic and inorganic wastes [1-5]. The industry produces a huge quantity of solid waste, which generates significant environmental concerns in addition to occupying a large area

of land for disposal. There is interest in establishing downstream industries for recycling in order to value and reuse these solid wastes. This would incorporate them as alternative materials in the production of construction materials that are environmentally friendly, energy-efficient, and profitable, with great market potential to meet the needs of people in rural and urban areas. Organic wastes such as cassava peels (CP) and rice husks (RH) constitute biomass generated by the agriculture industry. They are lignocellulosic materials containing polymeric structures [6-7]. According to estimates from the Food and Agriculture Organization of the United Nations (FAO) in 2020, agroindustrial activity generated around 1.5 billion tons of solid waste annually worldwide, which cannot be sustainably returned to the environment. However, they that can be valued, recycled and used as sustainable and novelty construction materials, which appears to be an alternative solution not only to waste generation and landfill disposal but also to high cost of building materials. These materials are generally not used and are sometimes disposed of in the environment without undergoing any treatment, which generates a strong environmental impact [8-9]. Bricks are construction materials that are traditionally obtained from natural resources such as clay. However, both the irrational use of these resources as well as the uncontrolled emission of gases into the atmosphere is what ultimately contributes to the destruction of the environment. Colombia, like other developing countries, faces one of the most important challenges: the rational use of energy and the incorporation of industrial waste as raw materials in the production of construction materials. Clay-based bricks, which are the most widely used construction materials in buildings, dams, tunnels, and bridges around the world, are a prime example. Current research is interested in developing new construction materials that are environmentally friendly [10], and in recent years, the incorporation of industrial waste into brick production has been a focus of interest [11-12]. However, during the brick making process, there is a non-negligible percentage of losses due to contraction during drying, resulting in cracks, breaks, or tilting. Quality control during the drying process is one of the most critical parts of the manufacturing process. As a result, there are several methods focused on optimizing drying and reducing defects in brick production [13]. Understanding the drying process is critical in reducing cracking. Lean clays or degreasers can be added to the mixture, but preparing this type of mixture is not always easy. Additionally, adding degreaser is not always convenient because the clays may not be greasy enough to withstand the addition, or high plasticity may be required to prepare the bricks, and adding a little degreaser would considerably reduce the plasticity of the paste. Ecological bricks allow for the proper development of construction activity in harmony with environmental protection, using industrial waste, which allows for lower costs and energy use. As urban centers expand, the need for building materials such as bricks has progressively increased. The construction industry proposes the development of bricks with improved

properties. The design of bricks generally aims to obtain more homogeneous and porous materials with appropriate mechanical resistance [10], which is essential to ensure their performance and durability [14-15]. Several industrial by-products, such as paper and pulp waste [16-18], cigarette waste [19-20], steel slag [21-22], ash [23-25], rubber [26], mining waste [27], glass [28], rice husks [29-30], tea and coffee [31], or corn stalk fiber [32], have been incorporated as raw materials in the manufacture of bricks. The use of these industrial wastes can contribute to optimizing energy use and improving quality control in the manufacture of bricks. The main objective of this work is to assess the effect of incorporating cassava peels, rice husks, and mining tailings in the manufacture of waste-based bricks, and their performance and durability through mechanical testing, as well as chemical attack with  $H_2SO_4$  and  $NaCl$  under corrosive environmental conditions.

## 2. Materials and methods

Fig. 1 illustrates the workflow followed in the fabrication and testing of the MAWBs in this study. The raw materials used in the preparation of the bricks are described, in particular mining (tailings) and agricultural wastes (cassava husks and rice husks). Moreover, it describes the raw material characterization techniques and the protocol followed during the manufacture of the MAWBs.

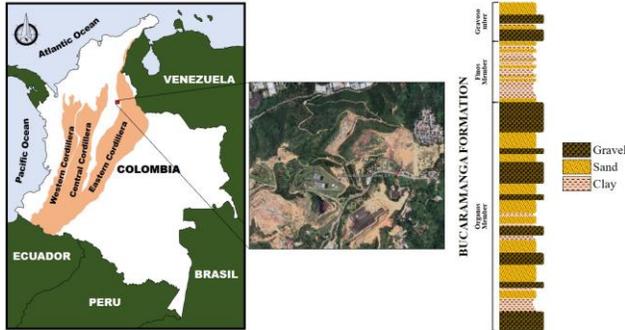


**Figure 1.** Workflow followed for manufacturing and testing of MAWBs. Source: Authors.

### 2.1 Raw materials

The materials used for the manufacture of mining and agricultural waste-based bricks (MAWBs) consisted of raw clay-rich soil, gold mining and agricultural (cassava and rice husks) wastes. The raw clay-rich soil used in this study was extracted from the Finos Member of the Bucaramanga Formation and was supplied by the Bautista y Cáceres Ltda brick company, which is located in Girón town, Santander (Colombia) as shown in Fig. 2. The gold mining tailings were supplied by the mineral beneficiation laboratory of the

Universidad Industrial de Santander, which is the leading public higher education institution in Santander (Colombia). The cassava peels were obtained from a stall in a local market place. The rice husks were supplied by LA GRANJA rice industry, located in the city of Bucaramanga, Santander (Colombia). The use of these industrial wastes should be promoted as an appropriate and alternative low cost but high-quality building technology.



**Figure 2.** Left, geographical location of the Bautista y Cáceres Ltda brick company. Right, generalized stratigraphic column of the Bucaramanga Formation. Source: Authors.

## 2.2 Characterization of raw materials

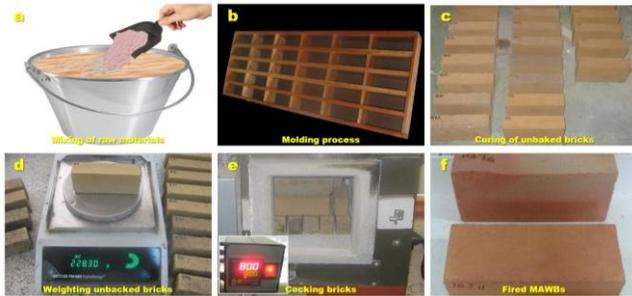
For the qualitative determination of main crystalline phases present in the clay-rich material, a powder X-ray diffractometer (PhilipsPW1710) was used, which was operated in Bragg-Brentano geometry with Cu-K $\alpha$  radiation ( $k = 1.5406 \text{ \AA}$ ) at 40 kV and 40 mA, and secondary monochromatization. Data were collected in the  $2\theta$  range of  $2\text{-}70^\circ$  with scanning steps of  $0.02^\circ$ . Crystalline patterns were compared with standard line patterns from the powder diffraction file database provided by the International Centre for Diffraction Data (ICDD) and the Joint Committee on Powder Diffraction Standards (JCPDS) files for inorganic compounds. The morphology of the agricultural residues was examined by environmental scanning electron microscopy (ESEM) (FEI Quanta 650) under the following analytical conditions: magnification = 200x, WD = 10.3-10.5, HV = 10.0-30.0 kV, HFW = 1.49 mm, Z Cont or SE mode, BSED or LFD detector.

## 2.3 Manufacturing of MAWBs

The preparation of bricks by adding mining and agroindustrial waste is not inherently new, as it has been the subject of research and development in the construction materials industry for several decades. However, the specific way in which the bricks are prepared and the combination of waste used may be novel and may offer specific advantages in terms of mechanical properties, durability, and sustainability. Furthermore, the application of this technology in different regions or contexts may be novel and valuable in addressing specific challenges related to waste management and sustainable construction. The raw materials

underwent several pretreatment steps such as spreading, drying, crushing, and screening to improve, homogenize, and clean them for sample preparation and characterization. The agricultural residues, which included cassava peels and rice husks, were sun-dried for 24 hours and then ground using a conventional mill typically used for grinding corn. The clay was spread out on cardboard and tamped with a geological hammer to break up the lumps that formed due to weathering and humidity. The mining waste was already crushed. The raw materials were then screened using a Ro-Tap sieving machine with a series of 20, 30, 60, 80, and 100 mesh screens. For the clay-rich material, the particles remaining on the #100 mesh sieve were collected, while for the mining residues, the particles were collected on the #60 mesh sieve, to ensure that the inorganic residues had a larger particle size than the clay-rich material. The size difference in the aggregates aimed to create porosity and reduce the final weight of the brick. Fig. 3 illustrates the process of preparing the MAWBs. A homogeneous mixture of clay, water, cassava, and rice husk fillers was created (Fig. 3a). The quantities were controlled to avoid any cracks or defects during the air-drying process. For the experimental campaign, six samples of each mixture were prepared, and the blocks were made in molds (Fig. 3b) that could produce thirty bricks at a time. The bricks were  $11.0 \times 5.0 \times 2.5 \text{ cm}$  and scaled down to 1:3 of the measurements of conventional “temosa” bricks ( $33 \times 15 \times 7.5 \text{ cm}$ ). In brick preparation, the size or quantity of bricks to be prepared at once may be conditioned by various factors, such as the size and capacity of the machinery used, the space available for manufacturing, and the time available for drying and curing the bricks. Logistic and production efficiency considerations may also be considered to determine the optimal quantity of bricks to be prepared in a batch or manufacturing session. The manufacturing of MAWBs followed the ASTM C62-17 [37] standard. The wastes were added to the conventional clay bricks in proportions of 5%, 10%, and 15% (wt/wt) to evaluate their influence on the compressive mechanical properties of the bricks. An additional mixing was carried out using equal amounts of the three types of residues proposed in the study, i.e., 5% of each type of residue for a total of 15% addition. The mixture proportions were based on the dry weights of the ingredients. The percentage of water used for brick manufacture was 20%, as recommended by Robuste [33]. The bricks were compacted manually, and five nominally identical samples of each mix were tested for mechanical properties and durability. Control mixtures without solid residues were also prepared. The mixtures were placed in molds and left for two days before being demolded to maintain their integrity. The shrinkage of the manufactured bricks was monitored for eight days. Air drying was carried out in a controlled environment to avoid the appearance of cracks, and the samples were spray-dried every 12 hours for eight days (Fig. 3c). The dimensions of the MAWBs were taken before and after the drying process. To remove excess moisture, the bricks were dried further before being fired. They were first weighed (Fig. 3d) and then placed in a

HERAEUS kiln at 800°C for 2 hours (Fig. 3e). The resultant MAWBs (Fig. 3f) were cooled to room temperature and measured and weighed again. During the preparation of laboratory bricks, the controls were performed by measuring and adjusting the moisture content, plasticity, and particle size distribution of the clay matrix used in the mixtures. The dimensions and weight of the molds and the resulting bricks were also checked. The error in the tests may vary depending on the specific testing method used, but in general, it is expected to be relatively low due to the controlled environment and careful measurement and adjustment of the materials.



**Figure 3.** Procedure for manufacture of reference and mining and agricultural-based bricks. Source: Authors.

The proportions of the mixtures used for the reference bricks and the mining- and agricultural-based bricks in the present study are shown in Table 1. The MAWBs were assigned designations: RB (reference brick) for the bricks without solid residues, and MAWxB for the blends, where MAW and x indicate the type of residue incorporated (MTW for mine tailings residue, CPW for cassava husk residue, and RHW for rice husk residue) and its percentage content in the clay matrix, respectively.

**Table 1.** Design of mixes for manufacture and testing of reference and mining and agricultural-based bricks. Source: Authors.

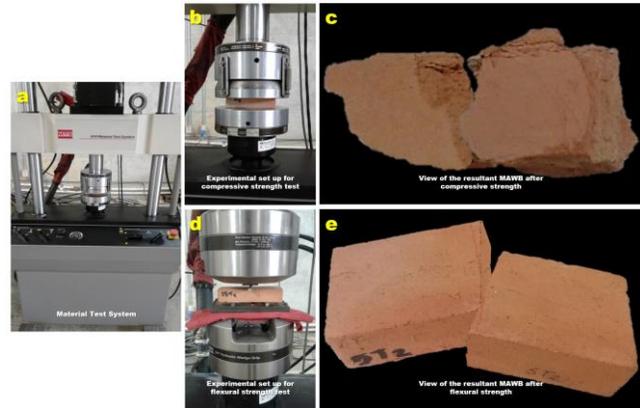
Trial (I)	Mix code	Mix proportions (%)			Water absorption				Firing shrinkage			
		CRM	MTW	CPW	RHW	H <sub>2</sub> O	W <sub>w</sub> (g)	W <sub>d</sub> (g)	WA (%)	L <sub>w</sub>	L <sub>f</sub>	FS
T1	RB	80	0	0	0	20	216.90	202.48	7.12	10.42	10.25	1.60
T2	RHW5B	75	5	0	0	20	206.98	182.88	13.18	10.48	10.28	1.91
T3	RHW10B	70	10	0	0	20	206.57	171.80	20.24	10.43	10.32	1.12
T4	RHW15B	65	15	0	0	20	179.61	138.50	29.68	10.43	10.30	1.28
T5	CPW5B	75	0	5	0	20	213.07	188.73	12.90	10.50	10.37	1.27
T6	CPW10B	70	0	10	0	20	199.49	165.00	20.90	10.32	10.30	0.16
T7	CPW15B	65	0	15	0	20	166.68	128.72	29.49	10.27	10.17	0.97
T8	MTW5B	75	0	0	5	20	219.27	206.28	6.29	---	---	---
T9	MTW10B	70	0	0	10	20	218.41	209.98	5.52	---	---	---
T10	MTW15B	65	0	0	15	20	228.22	209.62	8.87	---	---	---
T11	TMW5B	75	1.67	1.67	1.67	20	211.38	188.50	12.14	---	---	---
T12	TMW10B	70	3.33	3.33	3.33	20	199.93	173.92	14.95	---	---	---
T13	TMW15B	65	5.00	5.00	5.00	20	188.12	157.49	19.45	---	---	---

RB, reference brick; CRM, clay-rich soil; RHW, rice husk waste; CPW, cassava peels waste; MTW, mining tailing waste; 5, 10 and 15 indicates the dose of waste in bricks (B); WA, % water absorption; W<sub>w</sub>, weights of wet bricks; W<sub>d</sub>, weights of dried bricks; FS, firing shrinkage; L<sub>w</sub>, bricks before firing; L<sub>f</sub>, bricks after the firing.

### 2.4 Testing of MAWBs

The MAWBs were tested for compressive strength, flexural strength and chemical attack under corrosive conditions (Fig. 4). The tests were performed according to ASTM standards. The test was repeated 6 times for each type of specimen for proper data processing. A total of 78 MAWB were manufactured. The mechanical tests were performed according to ASTM C67-11 [34] standard. A universal

testing machine (MTS 810), Fig. 4a, with a maximum load cell of 50 kN was used in the testing procedure.



**Figure 4.** (a) Universal Testing Machine. (b) Experimental set up for compressive strength test. (c) View of the resultant MAWB after compressive strength testing. (d) Experimental set up for flexural strength test. (e) View of the resultant MAWB after flexural strength testing. Source: Authors.

The compressive strength test was performed in accordance with ASTM D 2166-00e1 [35] standard, using a speed of 0.5 mm/min. Two leveled steel plates of the same dimensions (100.0 x 40.0 x 5.0 mm) were used to set up the test (Fig 4b). The test was carried out until the specimens were brought to failure (Fig. 4c). The three-point bending strength test was performed under ASTM D 1635-00 [36] standard. A support spacing of 90 mm and a speed rate of 0.2 mm/min were used. Both the supports and the loading point consisted of steel cylinders of 5 mm diameter and 100 mm length (Fig. 4d). The equipment records the maximum load at the moment when the first crack occurs in the respective specimen, which triggers the rupture of the material (Fig. 4e). The flexural strength calculations were performed according to Eq. (1):

$$(1) R_F = \frac{3Pa}{2bd^2}$$

Where  $R_F$  is the ultimate flexural strength (MPa),  $P$  is the applied load (N),  $a$  is the support span (mm),  $b$  and  $d$  are the specimen width and thickness (mm) respectively.

Water absorption was determined according to ASTM C62-17 [37] standard by analyzing the difference in mass of fired bricks before and after the firing process. The percentage of water absorption of the bricks was obtained by applying Eq. (2):

$$(2) WA = \frac{W_w - W_d}{W_d} \times 100\%$$

Where WA represents the percentage of water absorption and  $W_w$  and  $W_d$  the weights of the wet and dried bricks, respectively.

Firing shrinkage, according to the ASTM C326 [38] standard, was obtained by measuring the length of the bricks before ( $L_w$ ) and after the firing ( $L_f$ ). The percentage of firing shrinkage was calculated from Eq. (3).

$$(3) FS = \frac{L_w - L_f}{L_w} \times 100\%$$

MAWBs with the best performance in the mechanical tests (compression and flexural) were selected for testing their resistance in 0.25 M H<sub>2</sub>SO<sub>4</sub> and 0.25M NaCl solutions for 7 days, simulating corrosive environmental conditions. The weights and measurements of each of the MAWBs were taken.

### 3. Results and discussion

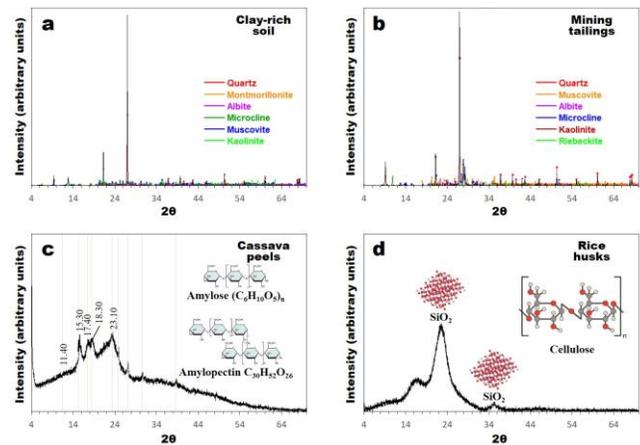
#### 3.1 X-ray diffraction analysis

The clay-rich material (Fig. 5a) used in the manufacture of bricks consists of quartz, potassium feldspar (microcline), sodium calcium feldspar (calcium albite), clay minerals corresponding to the group of phyllosilicates (kaolinite, muscovite, montmorillonite). The main minerals identified in the mining waste (Fig. 5b) were quartz, potassium feldspar (microcline), sodium calcium feldspar (calcium albite), clay minerals corresponding phyllosilicates group (kaolinite, muscovite, amphibole (riebeckite), compositionally, the mining residue is very similar to the clay sample analyzed. The XRD pattern of cassava peel (Fig. 5c) shows a broad region between 10° and 27° with major diffraction peaks at 11.40, 15.30, 17.40, 18.30 and 23.10°. It reveals that this organic waste is a semi-crystalline material [39], consisting of amorphous amylose (a linear polymer) and semi-crystalline amylopectin (a branched polymer) [40]. A similar XRD pattern on cassava peels was obtained by several authors [39,41-43]. At an industrial level, the properties of the cassava peel give rise to several uses, such as the production of ethanol, adhesive, gelling agent, binder, stabilizer, etc [44-46]. The XRD pattern of rice husk is shown in Fig. 5d, revealing an amorphous structure and a crystalline peak found around 2θ of 22.25° that confirms the presence of cellulose. The major reflection or peaks of SiO<sub>2</sub> are observed at 2θ of 22.25 and 35.00°, which were comparable with other reports [47-48]. Several rice husk by-products such as polymeric composite resins and polymeric lumber, cement-based materials or ceramic membranes can be developed [49-52].

#### 3.2 Morphology

In the micrographs, different particle sizes can be observed in the clay-rich material (Fig. 6a), with angular to rounded morphologies whose composition is also diverse. In Fig. 6b, the micrograph of the mining waste shows particles of different morphologies, including elongated tabular, angular edges, conchoid fracture, sub-rounded particles, and a porous structure. Some particles also exhibit dissemination of spots of metallic clusters. Meanwhile, other particles have very irregular shapes and fractures. On the other hand, Fig. 6c illustrates the surface morphology of cassava peel, which has

been confirmed to have heterogeneous characteristics and complex nature. It appears to be composed of several smooth to globular-shaped starch granules, similar to those found in other studies [53-54]. In Fig.6d, the micrograph of the rice husk shows that the exocarp presents a symmetrical corrugated structure with protuberances in the form of convex cells or bubbles, resembling a tortoise shell. The grooves across the grain of the rice separate these protuberances, and they are oriented in the parallel direction along the grain. Meanwhile, the internal face, called the endocarp, is composed of a concave surface with layers of a lamella structure that serve as a substrate for the rice grain. Several other studies report similar morphologies of rice husk [55-58].



**Figure 5.** XRD patterns of the starting raw materials: (a) clay-rich soil, (b) mining tailings, (c) cassava peels and (d) rice husks. Source: Authors.

Fig. 7 illustrates a SEM image and EDS spectra of the starting clay-rich soil. There are a large number of clay materials, making their classification complex. In general terms, clay is defined as a hydrated aluminum silicate, within which three major groups, such as kaolins, are recognized. Some authors consider them primary clays because they do not have impurities, except for a few that come from the mother rock, montmorillonite, which has Mg, Ca, or Fe ions in its structure, and smectite, which may have a more variable composition, but in most cases are K impurities, as is the case of bentonite.

Fig. 8 illustrates a SE image and EDS spectra of the starting mining tailings. The EDS spectrum shows the high content of Si associated to aluminumsilicate minerals (quartz and feldspar), with K being more abundant than Na. Microscopic analysis reveals the presence of sulfides, particularly pyrite, which is a mineral often associated with gold, particularly in veins through which hydrothermal fluids rich in Fe and S can circulate. Additionally, metallic elements including Mg, Mn, and Ti have been identified in association with gold, typically forming oxides that are commonly found as accessory materials or linked to the structure of silicates and carbonates.

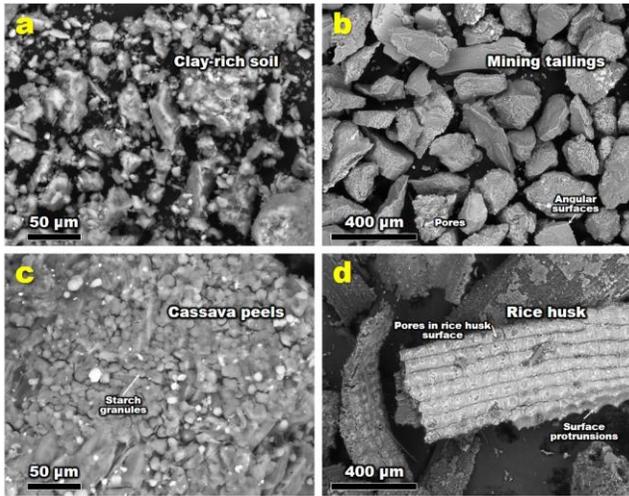


Figure 6. Secondary electron (SE) images of the raw materials used in the manufacture of bricks. Source: Authors.

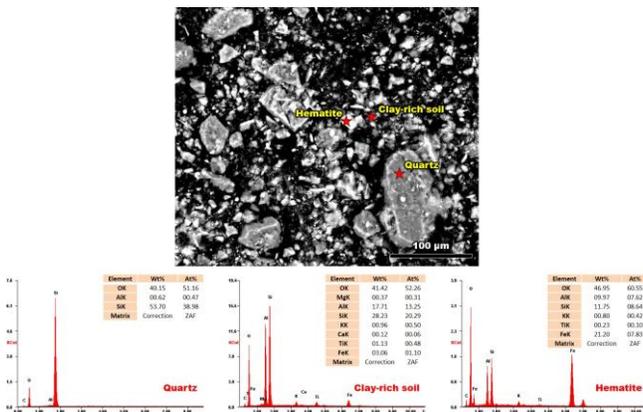


Figure 7. SE image and EDS spectra of the starting clay-rich soil. Source: Authors.

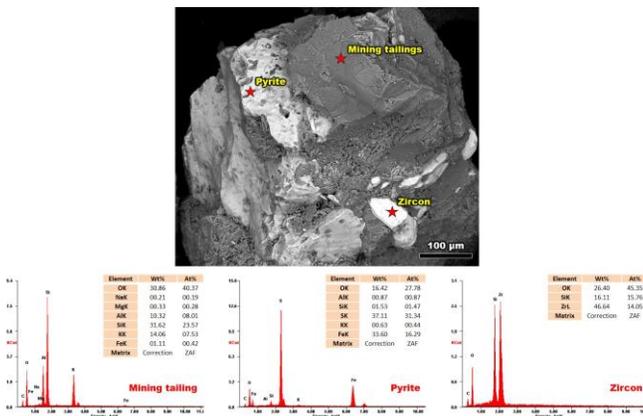


Figure 8. SE image and EDS spectra of the starting mining tailings. Source: Authors.

Fig. 9 displays a SEM image and EDS spectra of cassava peels. The EDS spectrum confirms their organic origin, as evidenced by the prominent C (42.30 wt%) and O (38.95 wt%) peaks. Other elements such as Al, Si, Mg, Fe, and K are present in the soil where the tuber grows, and they adhere

to the peel where they are absorbed by the plant as nutrients. These findings align with previous studies on cassava peels [53-54, 59-60]. Additionally, elements like Ca and Cl are present as dissolved ions of salts, generated as a result of rainwater leaching or irrigation after urea with CaCl application. According to Othman and Mohd-Asharuddin [59], the characteristic signals of Na, Ca, and Si can be attributed to their metal-binding properties. However, the analyzed cassava peels do not contain Na. The EDS spectra also reveal the occurrence of aluminum silicates, barium sulfates, and calcium phosphates. As reported by Benesi [61], starch granules in cassava peels contain 80% amylopectin and 20% amylose.

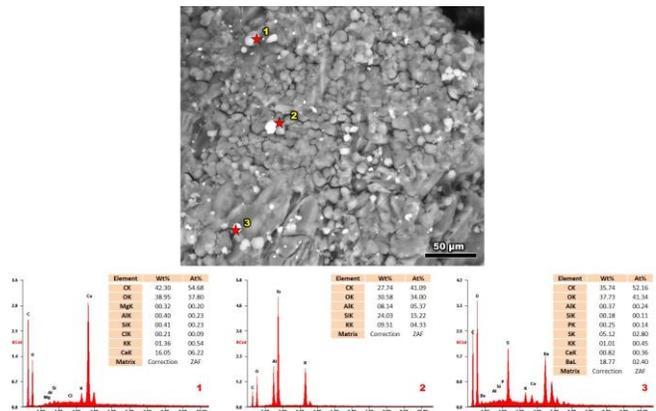


Figure 9. SE image and EDS spectra of the starting cassava peels. 1, organic C and O + Al, Si, Mg, Fe, and K introduced by soil; 2, aluminum silicate from soil; 3, aluminum silicate + barium sulfate + calcium phosphate from soil. Source: Authors.

Fig. 10 shows a SE image and EDS spectra of the initial rice husk. The EDS spectra reveal that the Si content in the outer epidermis (exocarp) of rice husk (42.92%) is higher than in the inner epidermis (endocarp) of rice husk (8.81%). Furthermore, trace amounts of other elements were detected. According to Deshmukh et al. [62], most of the Si occurs in the exocarp cells, particularly concentrated in the dome-shaped protrusions. Si is distributed in a greater proportion in the exocarp, an area that is mostly composed of inorganic material, which is consistent with the protective function of Si for the rice grain. The rice husk is also characterized by prominent C (14.11-52.18 wt%) and O (42.97-37.01 wt%) peaks, although the C content is higher in the endocarp, whereas the O content is higher in the exocarp. Therefore, the endocarp contains more organic material than the exocarp, which reveals the function of this structure as a substrate for the organic part of the rice grain. In the endocarp, aggregates containing impurities are present, with the following elements found in higher to lower proportions: K, Ca, P, S, Al, and Cl. These elements are attached to the internal structure, do not have a regular shape, and are scattered throughout the endocarp in percentages of less than 1%. Similar results have been obtained by several authors [48,63-64].

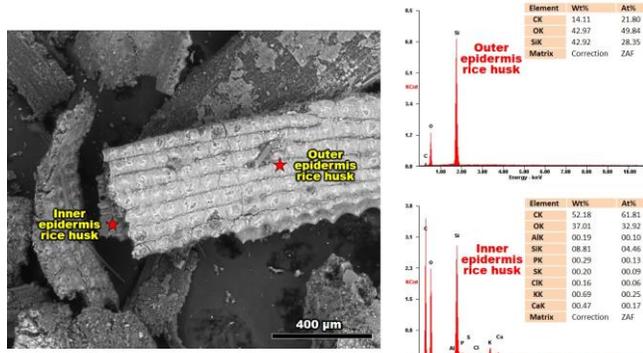


Figure 10. SE image and EDS spectra of the starting rice husk. Source: Authors.

### 3.3 Experimental tests of the MAWBs.

There were no significant dimensional alterations observed in any of the MAWBs, although their volume increased. Moreover, no defects, such as cracks or swelling, were observed after firing. Previous studies [65-66] have reported a texture characterized by the presence of black nuclei, attributed to burned organic matter that was not completely combusted during firing. However, in our study, we did not observe such nuclei in the fired bricks. In general, MAWBs have a reddish color similar to that of conventional bricks, without industrial residues. However, the color becomes lighter with the increase in the dose of residues. Table 2 presents the main physical and mechanical properties of MAWBs. The incorporation of industrial residues resulted in a slight expansion of the MAWBs at 900 oC during firing, which is a characteristic behavior of porous bodies. This can be attributed to the high content of quartz present in the clay, which is inert at the referred temperature, promoting both the reduction of brick shrinkage and the increase in its porosity

due to the high content of organic matter in the industrial waste. All MAWBs showed a contraction at this temperature. The weight loss experienced by the bricks increased with respect to the industrial waste content at 900 oC for all types of wastes. This weight loss, as well as the increase in porosity, is attributed to the combustion of organic matter in the clay during the firing process. On the other hand, the removal of water content from clay minerals is a result of dehydroxylation reactions in the clay [31]. According to Romero et al. [67], it is evident that the open porosity in MAWBs decreases when the amount of liquid phase tends to get closer to the particles. Furthermore, the porosity of MAWBs decreases with temperature. However, the addition of sawdust to the mixture produced greater changes in porosity compared to the mixtures in which cocoa husks, rice husks, and sugar cane were added, which produced smaller differences in apparent porosity. Eliche-Quesada et al. [31] have obtained similar results. There is no doubt that the addition of agricultural residues increases the porosity of the MAWBs. However, the combustion of organic matter takes place through a different mechanism in the formation of interconnected surface porosity [31]. The combustion of organic matter is a process in which organic compounds are oxidized and converted into carbon dioxide, water, and other combustion products. This process generates heat and can occur through different mechanisms, depending on the conditions under which it takes place. On the other hand, the formation of interconnected porosity in a brick is related to the elimination of water and other volatiles during its firing. This process involves the evaporation of water and other organic compounds present in the clay used to make the brick, which generates a porous structure that allows air and water vapor circulation through it.

Table 2. Average results from experimental tests of the MAWBs. Source: Authors.

Trial (T)	Mix code	Compressive strength				Flexural strength				
		P (kg)	Area (cm <sup>2</sup> )	Stress (MPa)	Strain (mm/mm)	P (kg)	L (cm)	b (cm)	h (cm)	MR (MPa)
T1	RB	1673.028	45.86	36.482	0.020	30.532	5.13	10.13	2.47	3.808
T2	RKW5B	1592.929	47.38	26.235	0.021	46.049	5.27	10.27	2.47	5.822
T3	RHW10B	1317.779	47.38	27.813	0.019	33.223	5.27	10.27	2.40	4.456
T4	RHW15B	1238.506	47.22	26.235	0.016	24.849	5.33	10.33	2.40	3.380
T5	CPW5B	1199.665	50.37	23.810	0.024	125.234	5.37	10.37	2.37	17.450
T6	CPW10B	864.179	48.91	17.667	0.017	73.938	5.43	10.43	2.33	10.620
T7	CPW15B	457.475	47.75	9.577	0.020	29.104	5.23	10.23	2.27	4.350
T8	MTW5B	1055.590	46.60	22.642	0.015	121.213	5.40	10.40	2.40	16.495
T9	MTW10B	764.318	47.45	16.103	0.014	93.852	5.53	10.53	2.47	12.153
T10	MTW15B	340.677	47.10	7.235	0.018	55.960	5.50	10.50	2.40	7.674
T11	TMW5B	1107.921	47.49	23.343	0.016	61.984	5.33	10.33	2.40	8.452
T12	TMW10B	948.183	47.10	20.134	0.011	38.575	5.33	10.33	2.37	5.364
T13	TMW15B	561.068	47.45	11.354	0.028	26.761	5.13	10.13	2.30	3.844

RB, reference brick; RHW, rice husk waste, CPW, cassava peels waste; MTW, mining tailing waste; 5, 10 and 15 indicates the dose of waste in bricks (B); P, load; L, b and h parameters for flexural strength test; MR, modulus of rupture.

It is important to note that the combustion of organic matter and the formation of interconnected porosity in a brick are different processes that occur under different conditions. Although both processes may involve the elimination of organic compounds and the release of gases, the way in which they occur is different and not directly related. Regarding the green brick model being tested, it is important to consider that interconnected porosity is an essential characteristic for the performance of the brick in terms of thermal insulation, water absorption, and mechanical strength. Therefore, it is necessary to ensure that porosity is properly formed during the firing of the brick and that it is not affected by other processes, such as the combustion of organic matter, which could alter the final properties of the brick.

### 3.3.1 Water absorption of the MAWBs

The percentage of absorbed water represents one of the main factors that control the behavior of MAWBs, as the clays, according to their physicochemical properties, are susceptible to swelling, affecting the performance and durability of constructions materials as bricks. In this way, the bricks must have an internal structure dense enough to limit the absorption of water, which is why the mining tailings was used, however, only the effect of the addition of organic wastes as cassava peels and rice husk was evaluated, considering that even though they contribute to lightening of the brick, they can also favor the water infiltration. Table 1 illustrates the water absorption data of the MAWBs. Fig. 11 reveals that the RBs, without addition of mining tailings or cassava peels and rice husk, showed the lower water absorption rate of 7.12 % while organic waste-based bricks showed higher water absorption rates (13.18-29.68% for RHW-based bricks and 12.90-29.49% for CPW-based bricks). In general, these ranges of water absorption showed very similar values independent of the organic residue incorporated in the structure of the bricks. In each case, the water absorption increased with increasing dose of cassava peels and rice husk added to the mixture. The increase in water absorption of the organic waste-based bricks shows that as the liquid phase in the paste decreases at a specific high firing temperature, there is an increase in the pore volume of the particles in the bricks [68]. MTW-based bricks showed lower water absorption rates (5.52-8.87%) than those obtained in organic waste-based bricks. The lowest water absorption value (5.52%) was obtained using 10 wt% of mining tailings. The TMW-based bricks showed water absorption rates (12.14-19.45%) higher and lower than those obtained for the reference and mining- and agricultural-based bricks, which demonstrates that the addition of the mining tailings in the mixes promoted a decrease of the water absorption, whereas the addition of cassava peel or rice husk wastes contributes to increase it. These organic wastes are capable of forming pores within the brick structures during firing due to the decomposition and dehydration of its organic part, resulting in lightened bricks [31,68-69]. As a

consequence of temperature changes associated with environmental phenomena, the demand for organic waste-based bricks with better insulation or low thermal transfer has increased [69]. Based on the results presented in this study, it seems that incorporating agricultural wastes such as cassava peels and rice husks into clay-based bricks could be a more suitable option for producing bricks with better insulation or low heat transfer. The addition of these agricultural wastes induced porosity during the firing process, which allowed for lightening of the units and potentially reducing construction costs. Furthermore, these agricultural wastes did not significantly reduce the mechanical resistance of the bricks, and the resulting compressive strength values were within the admissible limits set by Colombian regulations for specific building materials used in civil construction. On the other hand, incorporating mining tailings as aggregates did not result in significant lightening, and the mechanical resistance of the samples was reduced with the addition of this waste. Therefore, it is not recommended to use mining tailings as aggregates for manufacturing bricks. Overall, it seems that using agricultural wastes such as cassava peels and rice husks would be the most suitable option for supplying the demand for organic waste-based bricks with better insulation or low heat transfer. However, it is important to note that further research may be necessary to determine the most optimal dosage of these wastes to achieve the desired properties in the bricks.

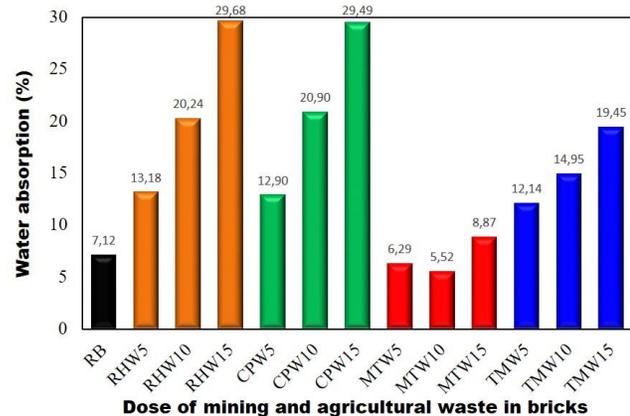


Figure 11. Results of water absorption. RB, reference bricks; RHW, rice husk waste; CPW, cassava peels waste; MTW, mining tailings waste; TMW, total mix waste. Source: Authors.

### 3.3.2 Firing shrinkage of the MAWBs

Clay dehydration is a crucial factor that influences firing shrinkage. Akinyele et al. [68] reported that during the firing process of clays at high temperatures, the particles fuse together, resulting in increased firing shrinkage due to their greater proximity. It is essential to consider this parameter to prevent problems such as cracks. Generally, it is well-known that all clays shrink during firing, and the amount of shrinkage depends on the type of clay and the firing temperature. For this study, we used the same type of clay to

make all the bricks and calibrated the furnace to minimize variations and ensure equal heat distribution. The results of the firing shrinkage of the MAWBs are presented in Table 1. Based on the results presented in Fig. 12, it can be concluded that the effect of the dose of organic waste on firing shrinkage is not consistent. The firing shrinkage decreased with increasing organic waste dose, although the lowest values were obtained by adding 10 wt% of organic waste. This could be due to the lack of homogenization of the mixture used for the preparation of bricks using this dose. Additionally, it was observed that the addition of RHW produced higher values of firing shrinkage compared with those obtained after adding CPW, indicating that RHW has a greater influence on firing shrinkage than CPW. Finally, it can be noted that the highest firing shrinkage (1.91%) was obtained by adding 5 wt% of RHW, while the lowest firing shrinkage (0.16%) was obtained when 10 wt% of CPW was added. These results suggest that the optimal dose of organic waste for minimizing firing shrinkage in the production of clay bricks depends on the specific type of waste being used, and that higher doses may not necessarily result in better outcomes. Therefore, it is advisable to check the length of the bricks as they are removed from the kiln and sorted. The variation in dimensions should be kept within certain limits and if they do not conform, the bricks should not be sold as first quality. The quality control of the bricks requires that they have a firing shrinkage of less than 8% to have a good performance [70]. The organic waste-based bricks showed firing shrinkage values of 0.97-1.27%, which are within the safety limits indicated in the ASTM C326 standard. [38]. The limits of firing shrinkage depend on the type of brick and the regulations of the country or region where they are manufactured. The dilatometry method is commonly used to measure firing shrinkage in laboratory tests, which involves measuring the dimensional variation of a brick sample before and after being subjected to high temperatures in a furnace. The difference between the dimensions before and after firing is expressed as a percentage of firing shrinkage.

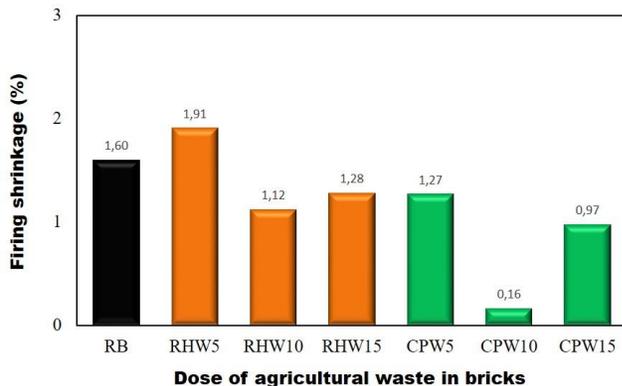


Figure 12. Results of firing Shrinkage. RB, reference bricks; RHW, rice husk waste; CPW, cassava peels waste. Source: Authors.

### 3.3.3 Compressive strength of the MAWBs

Compressive strength is a crucial parameter for quality control in building material applications [22]. Fig. 13 displays the average compressive strength of reference and waste-based bricks, and the results are presented in Table 2. Experimental data demonstrate that the RBs have a higher compressive strength than the MAWBs. Therefore, compressive strength tends to decrease with waste addition and as the dosage of waste increases. All MAWBs exhibited a linear decrease in resistance that is inversely proportional to the amount of residue added. In other words, the higher the addition percentage, the lower the compressive strength. Mining tailing waste-based bricks showed the highest values, with a higher compressive strength of 33.62 MPa using a dosage of 5 wt%, whereas rice husk waste-based bricks showed the lowest values, with a lower compressive strength of 7.24 MPa using a dosage of 15 wt% cassava peels. The presence of oil in agricultural waste can enhance compressive strength, as suggested by Eliche-Quesada et al. [31]. They suggest that oily films form between the particles, which act as lubricants during the mixture preparation and allow for more efficient packing, leading to an improvement in the mechanical properties of the MAWBs. However, a higher percentage of agricultural waste (10 and 15 wt%) can generate oil pockets that promote the generation of pores after firing and contribute to a decrease in compressive strength [71].

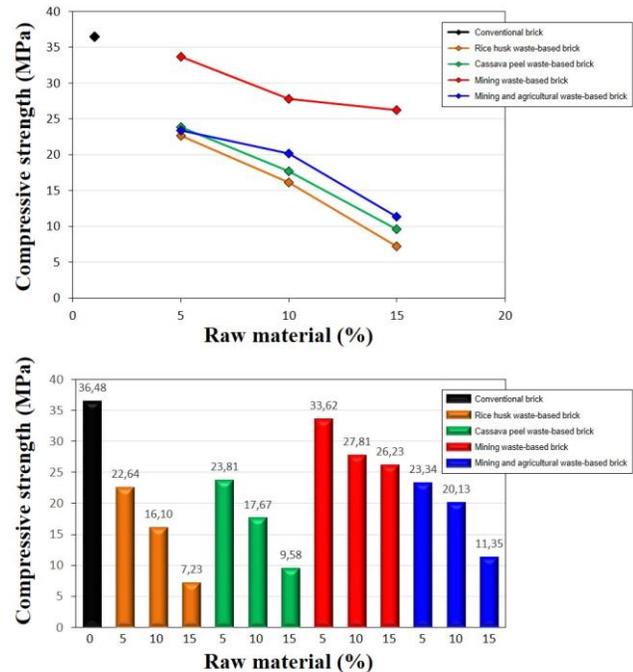


Figure 13. Average compressive strength for all MAWBs. Source: Authors.

According to the NTC 4017 [72] standard, which is equivalent to the ASTM C67-11 [34] standard, the minimum compressive strength required in a brick is 10 MPa for one unit and 14 MPa for five bricks. Most of the MAWBs meet the technical specifications for compressive strength, except for MAWB6 (9.58 MPa) and MAWB9 (7.24 MPa), which

add 15 wt% cassava peels and rice husk aggregate, respectively, and MAWB12 (11.35 MPa), which adds 5 wt% of each waste to the mix. The highest compressive strength was obtained for the RBs (36.48 MPa). However, the RBs should present the lowest apparent porosity and water absorption, as suggested by Görhan and Şimşek [13].

We conclude that additions of 15%, with the exception of mining tailings, are not favorable, and it is not recommended to replace the traditional paste in this percentage or higher. Additions of 5 and 10% of residues promote a decrease in compressive strength compared to that of the bricks in which the use of these residues was not incorporated, although they presented values within the admissible ranges. In addition, it could be also concluded that the addition of agricultural and mining waste can be a viable alternative for brick manufacturing, as most of the bricks meet the required technical specifications in terms of compressive strength. However, the amount and type of waste added can affect the compressive strength and apparent porosity of the bricks. Therefore, care should be taken when selecting and adding waste to the brick mix to avoid a significant decrease in the quality of the bricks. Additionally, the use of vegetable oils in the preparation of the brick mix as a lubricant to improve the mechanical strength of the bricks could be explored.

### 3.3.4 Flexural strength of the MAWBs

Fig. 14 illustrates the average modulus of rupture (*MR*) of the MAWBs with respect to the waste content. The experimental test results of the MAWBs are summarized in Table 2.

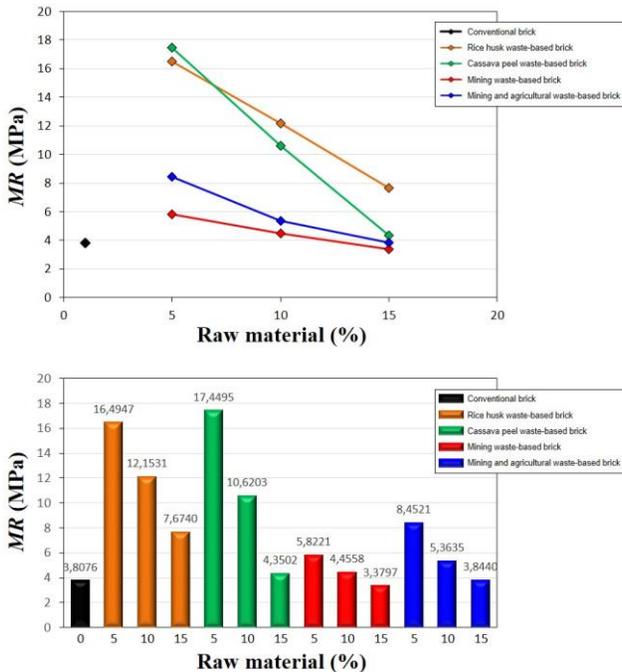


Figure 14. Average MR for all MAWBs. Source: Authors.

It can be observed that the *MR* tends to decrease with an increase in waste addition and dosage. The agricultural waste-based bricks demonstrated higher *MR* values (17.45 MPa for cassava peel waste-bricks and 16.50 MPa for rice husk waste-bricks) using a 5 wt% dosage. However, with an increase in waste dosage (10 and 15%), the rice husk waste-based bricks demonstrated higher *MR* values compared to cassava peel waste-based bricks. Conversely, mining tailing-based bricks demonstrated lower *MR* values, with a *MR* of 3.38 MPa using a 15 wt% dosage. In general, the MAWBs with organic content presented higher *MR* values. Furthermore, previous studies [73-74] have shown that the flexural strength is about 10 to 30% of the compressive strength, which establishes a minimum flexural strength interval of 1.0-1.4 MPa. Therefore, all MAWBs meet the minimum flexural strength target. These results suggest that the addition of agricultural and mining residues can be a viable alternative for brick manufacturing. However, the type and amount of waste added can significantly affect the *MR* and other mechanical properties of the bricks, which should be taken into consideration while selecting and adding waste to the brick mix.

### 3.3.5 Resistance of MAWBs to attack with H<sub>2</sub>SO<sub>4</sub> and NaCl

During immersion of MAWBs in acidic or saline environments (Fig. 15), the release of air from the pores of the test bricks resulted in the production of bubbles, rather than effervescence generated by dissolution of the bricks themselves. The test bricks that were attacked by the solution showed an increase in weight, indicating that a quantity of the solution penetrated into the bricks and remained in the pore space. However, no white spots or pitting, which are characteristic of efflorescence, were observed on the surface of the test bricks immersed in the solutions. The absence of efflorescence is promising for the use of MAWBs in construction, as it is a common problem in brick production. However, the test bricks immersed in the 0.25M H<sub>2</sub>SO<sub>4</sub> solution showed notable darkening and surface spots after 24 hours of removal, as evidenced in the image taken after 15 days. This indicates that the acidic environment could have a negative impact on the durability of the bricks. On the other hand, the test bricks immersed in the 0.25M NaCl solutions did not show any noticeable changes or affects. Based on these results, it can be concluded that the MAWBs have a good resistance to acidic and saline environments. However, it is important to note that prolonged exposure to acidic environments can lead to darkening and surface spots on the bricks, which could affect their appearance. It is also worth noting that the use of waste materials in the production of MAWBs can contribute to reducing the environmental impact of the brick manufacturing industry. Additionally, further research could be conducted to investigate the long-term durability of these bricks in different environmental conditions, as well as the potential for optimizing the composition of the bricks to further improve their resistance to wear and tear.

In addition to the structural benefits, the use of agricultural wastes as additives in clay bricks can also have significant environmental benefits. Agricultural wastes, such as cassava husks and rice husks, are abundant in many parts of the world and are often discarded as waste. By incorporating these materials into clay bricks, they can be reused and recycled, reducing the amount of waste that is sent to landfills and potentially reducing the need for virgin raw materials. Furthermore, the creation of air-filled pores in the microstructure of the bricks during the firing process, as a result of the use of agricultural wastes, has beneficial effects as thermal insulating materials.

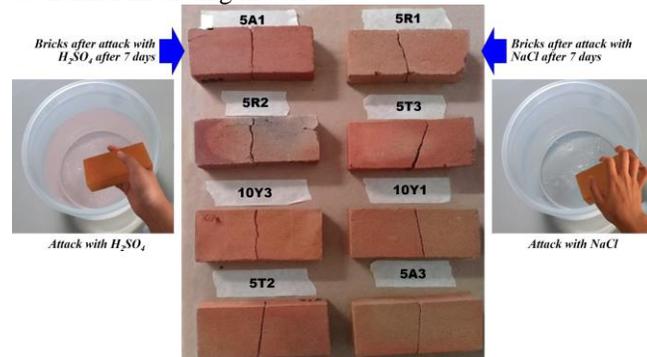


Figure 15.  $H_2SO_4$  and  $NaCl$  attack of the MAWBs. Source: Authors.

These air-filled pores act as insulators, reducing the amount of heat that is transferred through the bricks, which can lead to improved energy efficiency in buildings. This is particularly important in regions with extreme temperatures, where thermal insulation can help to reduce energy consumption and associated greenhouse gas emissions. Overall, the use of agricultural wastes as additives in clay bricks can have significant economic, environmental, and social benefits. The findings of this study contribute to the development of sustainable construction materials and provide a potential solution for the reuse of industrial wastes that are causing negative environmental impacts.

## 5. Conclusions

The present study evaluated the use of mining tailings and agricultural wastes (cassava husks and rice husks) as additives in the manufacture of clay-based bricks. The results indicate that the incorporation of these industrial wastes can be a promising alternative in the production of bricks. Among the different types of bricks evaluated, those with mining tailing waste aggregates showed higher mechanical resistance, with a maximum compressive strength of 33.62 MPa using a dosage of 5 wt%. In contrast, bricks with agricultural waste aggregates showed lower resistance, with a minimum compressive strength of 7.24 MPa using a dosage of 15 wt% cassava peels. However, all the samples met the Colombian requirements and regulations for building materials used in civil construction, which for clay bricks must meet certain technical specifications, such as a minimum compressive strength of 20 MPa, a maximum

water absorption of 20%, a maximum dimensional variation of 5%, among other characteristics. The addition of agricultural wastes to the traditional clay mix can significantly reduce the weight of the bricks by inducing porosity during the firing process. However, the use of mining tailings as aggregates is not recommended, as it does not provide significant lightening and reduces the mechanical resistance of the samples. The percentage of waste added to the mixture should not exceed 10 wt%, as higher values lead to a substantial reduction in compression and flexural resistance. The incorporation of mining and agricultural wastes as a novelty initiative for the development of alternative construction materials provides a potential solution for the reuse of industrial wastes causing negative environmental impacts. The clay-based bricks with the addition of mining and agricultural wastes are resistant under extreme acid and saline environmental conditions. Furthermore, the lightening of the bricks may reduce construction costs by requiring fewer bricks and lighter structures. This study promotes energy saving and the valorization, recycling, and use of mining tailings and agricultural wastes as raw materials in the manufacture of construction materials such as clay-based bricks. Another benefit of using alternative organic materials as agricultural wastes to lighten construction materials such as clay bricks is the creation of air-filled pores in the microstructure of the bricks, which enhances their thermal insulation properties. Thus, developing new mixtures for bricks like those presented in this study can contribute to generating products for civil construction that are both mechanically and thermally resistant and environmentally friendly.

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