revista principia Vol. 59, N. 2

REVISTA DE DIVULGAÇÃO CIENTÍFICA
E TECNOLÓGICA DO INSTITUTO FEDERAL
DE CIÊNCIA, EDUCAÇÃO E TECNOLOGIA
DA PARAÍBA

SUBMITTED January 6, 2021
APPROVED October 5, 2021
PUBLISHED ONLINE October 23, 2021
PUBLISHED June 30, 2022

ASSOCIATE EDITOR
Mariana Amorim Fraga

DOI: *http://dx.doi.org/10.18265/1517-0306a2021id5237*

ORIGINAL ARTICLE

Ecological bricks produced from scheelite residue, stone powder, and cassava wastewater for non-structural masonry

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ABSTRACT: One solution to mitigate the environmental impacts of extracting mineral and vegetable residues is to use them in the construction industry, which is considered one of the largest consumers of mineral resources on the planet. Thus, this work conducted a study on the combination of scheelite, stone powder, and cassava wastewater with the addition of cement to produce an ecological brick that can be used as non-structural masonry in aiming to use waste and reduce environmental impacts. The percentage of each residue was determined after performing chemical and physical characterizations through a packaging analysis between the particles, obtaining a formulation with the same mass percentage of each solid residue, and adding cassava wastewater and cement. The technological assays showed results by Brazilian standards for cement soil, with water absorption values below 20%, simple compression strength close to or greater than 2 MPa, and low mass loss. Cement phases were observed in the SEM and XRD analyses, highlighting the contribution of packaging between the residues and the influence of cassava wastewater due to its acidity and binding properties, providing promising results for manufacturing ecological bricks.

Keywords: cassava wastewater; ecological brick; scheelite residue; stone powder; sustainability.

Tijolos ecológicos produzidos a partir de resíduo de scheelita, pó de pedra e efluente de mandioca para alvenaria não estrutural

RESUMO: *Uma solução para mitigar os impactos ambientais da extração de resíduos minerais e vegetais é utilizá-los na construção civil, considerada uma das maiores consumidoras de recursos minerais do planeta. Assim, este trabalho realizou um estudo sobre a combinação de scheelita, pó de pedra e efluente de mandioca (manipueira) com a adição de cimento para a produção de um tijolo* *ecológico que pode ser utilizado como alvenaria não estrutural, com a finalidade de aproveitamento dos resíduos e redução dos impactos ambientais. A porcentagem de cada resíduo foi determinada após realização de caracterizações químicas e físicas através de uma análise de empacotamento entre as partículas, obtendo-se uma formulação com a mesma porcentagem em massa de cada resíduo sólido, adicionando manipueira e cimento. Os ensaios tecnológicos apresentaram resultados de acordo com as normas brasileiras para solos de cimento, com valores de absorção de água abaixo de 20%, resistência à compressão simples próxima ou superior a 2 MPa e baixa perda de massa. Fases do cimento foram observadas nas análises de MEV e DRX, destacando-se a contribuição do empacotamento entre os resíduos e a influência do efluente da mandioca devido à sua acidez e propriedades aglutinantes, apresentando resultados promissores para a fabricação de tijolos ecológicos.*

Palavras-chave: *manipueira; pó de pedra; resíduo de scheelita; sustentabilidade; tijolo ecológico.*

1 Introduction

The civil construction industry has consumed more than half of the planet's natural resources (CBCS, 2014), generating significant pollution through solid waste and gases, with carbon dioxide emissions of about 0.9 to 1.1 tons emitted into the atmosphere for each ton of cement produced (EL-ATTAR; SADEK; SALAH, 2017).

Using soil-cement bricks is suggested among the alternatives for more sustainable construction, which is composed of a compact mixture of soil, cement, and water in varying proportions, promoting cement hydration chemicals and combinations of minerals and soil compounds. These bricks have several advantages over conventional ceramic bricks due to their practicality in production and because it is not necessary to burn clay minerals from the soil in sintering. After curing, there is a considerable increase in mechanical strength, wear, and impermeability, mainly due to cement hydration chemicals (ACCHAR; MARQUES, 2016).

A disadvantage of using soil for bricks is its removal, which can generate environmental impacts such as silting up rivers, deforestation, and damage to fauna, in addition to it being necessary in some cases to improve the soil because it is a heterogeneous material.

Another issue is the use of clean water, as it is considered a precious and essential asset for life, scarce in the northeast of Brazil, which is widely used in the construction industry and can be replaced by some liquid waste.

Recent studies have used residues in soil-cement bricks, obtaining satisfactory results. Examples of this can be found in the works of Silva *et al*. (2014), Paschoalin Filho, Storopoli and Dias (2016), and Ferreira and Cunha (2017), demonstrating that the product has a facility to receive additives and substitutes which do not impair technical properties, and in some cases provide improvements in those properties. There is a significant amount of research on residues from mineral and vegetable extraction among the different waste sources used, probably due to the large amount of waste produced, the environmental impacts caused, and the satisfactory characteristics and technical properties presented by the new materials resulting from processing these residues.

Given the above, a study on the combinations between scheelite, stone powder, and cassava wastewater residues with the addition of cement was conducted through a correlation between their microstructure, properties, and performance with the justification of producing an innovative ecological brick to promote greater sustainability and economy by using waste and eliminating the use of soil and water.

2 Theoretical reference

It is possible to verify the use of residues in soil-agglomerating bricks as partial substitutes for agglomerates, partial or total substitutes for hydration water and or soil, highlighting in this work the study for residues in substitution for hydration water and substitution to the soil.

Due to the environmental impacts caused by the extraction of soil, research has been carried out on soil-agglomerating bricks with partial or total replacement of the soil, contributing to the use of the large amount of waste arising from various industrial activities.

Rodrigues and Holanda (2015) used waste from a water treatment plant as a partial substitute for soil in soil-cement bricks, obtaining satisfactory results in mechanical properties. The waste from the water treatment plant proved to be viable to replace the soil since it has plasticity from kaolinite particles.

Acchar and Marques (2016) used the oil well drilling gravel residue from drilling onshore wells in total replacement of soil. This residue demonstrated properties suitable for soil replacement, such as plasticity and mechanical resistance, since it is composed of mixtures of small fragments of rocks impregnated with the fluid used to cool and lubricate the drill bit during the drilling of the well (LEONARD; STEGEMANN, 2010).

Paschoalin Filho, Storopoli, and Dias (2016) incorporated PET (polyethylene terephthalate), from PET bottles, into the soil. The residue was ground and mixed with the soil to be added cement and water and the compaction assay was carried out. For the best formulation, the brick used approximately 300 g of PET powder, equivalent to 6 PET bottles of 2 L, obtaining satisfactory results for soil-cement bricks without structural function.

Siqueira *et al*. (2016) produced soil-cement bricks with the incorporation of eggshell residues and welding slag, and it was established that up to 15% by weight of welding flux slag residue and up to 30% by weight of eggshell residue can be added to the soil-cement brick as a loading material, obtaining satisfactory results in technical properties.

2.1 Scheelite residue and stone powder

Brazil's scheelite production corresponds to only 0.5% of world production (DNPM, 2017), but this country still has the largest reserves in Latin America. These reserves are found in the Scheelífera Province of Serido in the states of Rio Grande do Norte and Paraíba.

The generation of waste through the scheelite beneficiation process represents a high amount. This process generates 99.2% of residues, leaving only 0.8% of the tungsten concentrate (processed scheelite ore). An example of the large amount of waste generated in the scheelite beneficiation process is the largest scheelite mine in Latin America, the *Brejuí* mine, which has about 7 million tons of scheelite waste (GERAB, 2014).

The use of scheelite residue in construction materials has shown satisfactory results in addition to ceramic mass in the work of Machado *et al*. (2012), in the replacement of sand in mortars in the work of Gerab (2014) and Medeiros (2016), and in soil-bricks cement for floors in the work of Santandrea, Meira and Oliveira (2017).

In 2016, the gross production of gravel and gravel declared by the Annual Report of Crops (RAL) was 202.2 million tons with the benefited production reaching 185 million (DNPM, 2017), accumulating large amounts of stone powder.

This residue has been used as a substitute for sand for concretes and mortars as researched in the works of Campos (2015) and Machado *et al*. (2016), making it necessary to add plasticizer to the concrete due to the lamellar morphology of the stone powder, making workability more difficult.

2.2 Cassava wastewater

The cassava wastewater (*Manihot esculenta* Crantz) is a milky and yellowish liquid that flows from the fleshy roots of cassava by pressing them to obtain the starch or cassava flour (FERREIRA *et al*., 2001; PONTE, 2006). To take advantage of the effluent and reduce the environmental impacts caused by it, applications of *manipueira* as natural fertilizer, pesticide, vinegar, alcohol, soap, and civil construction materials have been made (SEBRAE, 2015).

Due to a large amount of organic matter in suspension, it is possible to use the effluent to cultivate aquatic microorganisms of great protein value as performed in the work of Borghetti (2009) who evaluated the growth of microalgae in a culture medium with different concentrations of cassava wastewater, obtaining satisfactory results.

3 Methodology

The experimental procedure started by collecting and characterizing the materials, followed by their homogenization, compacting, and molding to perform the technological water absorption and simple compression strength tests.

After breaking the specimens in the compressive strength test, samples were selected for analysis of the phases formed by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

The scheelite residue was collected from an open stock at the *Brejuí* mine in Currais Novos, Rio Grande do Norte state in Brazil, using only fine residue, and the stone powder was obtained from a mining operation in Itapevi in Bahia, Brazil, obtained by crushing granite rocks. The cassava wastewater was obtained from a flour mill in Lagoa Nova City, Rio Grande do Norte State in Brazil, being conditioned in an open tank for more than 48 hours to volatilize most of the free cyanide, as recommended by other studies such as in Silva *et al*. (2017). After the free cyanide evaporation, the cassava wastewater was stored in gallons to avoid biochemical degradation of the product.

CP II F-40 cement (Portland cement with limestone filler) which has properties recommended by the Brazilian Portland Cement Association (ABCP, 2004) was used to produce soil-cement compositions, being purchased in local stores.

The applied raw materials were selected by the statistical method of quartering according to NBR 10007 (ABNT, 2004), with the chemical and physical characterizations subsequently performed. The tests regarding the granulometric and density characteristics were carried out in the soil laboratory (UFRN), following the NBR 7181 (ABNT, 2018b), NBR 6457 (ABNT, 2016a), and NBR 6508 (ABNT, 2016b) standards.

X-ray diffraction (XRD) with a SHIMADZU XRD 7000 device and X-ray fluorescence with an EDX-720 (XRF) device were used for mineralogical and chemical characterization, being performed at the Materials Characterization Laboratory of the Federal University of Rio Grande do Norte (UFRN).

The cassava wastewater characterization was carried out in several laboratories starting with the cyanide determination test in the Bioagri laboratory in Paulista-PE. Acidity tests, hydrogen potential, electrical conductivity, the solids content in suspension, and staining were performed at the Federal Institute of Education, Science and Technology of Paraíba (IFPB) at the LANANO Laboratory – Nanomaterials Laboratory. Macronutrient and micronutrient, chloride, sulfate, and phosphate assays were carried out in the EMPARN laboratory (Agricultural Research Corporation of Rio Grande do Norte).

A compaction test performed in the soil laboratory (Post-Graduation in Civil Engineering-PEC/Federal University of Rio Grande do Norte-UFRN) was carried out following the NBR 7182 (ABNT, 2016c) standard to define the formulations and liquid content in the mixture. All the applied formulations are described in Table 1 and used a combination of scheelite residue and stone powder at the same mass percentage, due to be the best packing between the particles. This formulation had the addition of 11% of cassava wastewater, a value determined as the optimum humidity of the compaction test of this mixture of residues.

Table 1 ▶ Nomenclature of the formulations produced. *Source: research data*

Formulation	**Percentage (approximate) in total brick mass (g)**		
	R (%)	C (%)	CW (%)
F1	86	5	9
F2	83	8	9
F3	81	10	9

Note: F - Formulation; R - Solid residues; C - Cement; CW - Cassava Wastewater

Homogenization was performed in a concrete mixer, starting with a mixture of scheelite residue and stone powder to be added to the cassava wastewater and the cement. A Sahara Hobby press was used to manufacture type A bricks (5 cm thick, 10 cm wide, and 20 cm long) according to the NBR 8491 Standard regarding Soil-Cement Brick Requirements (ABNT, 2012a). Molding and curing followed the precepts of standard NBR 10833 (ABNT, 2012b), and water spraying to maintain humidity during the curing period was replaced by cassava wastewater, avoiding changes in the bricks' composition.

The water absorption assay was performed using a tank and an appropriate dryer in the soil laboratory (Post-Graduation in Civil Engineering-PEC/Federal University of Rio Grande do Norte-UFRN), following the Brazilian standard NBR 8492 (ABNT, 2016d). For this test, three samples were used for each formulation, being presented with the average of the results at 7 days of cure, totaling 9 bricks.

The samples were weighed and placed in an oven until they reached constant mass. Soon after, they were weighed again and immersed in water for 24 hours, then removed from the immersion and weighed.

The simple compressive strength assay (SCS) was performed at the Construction Materials Laboratory at UFRN using a universal AMSLER machine according to the Brazilian standard NBR 8492 (ABNT, 2016d). Three samples were used for each formulation at each curing time, with the average of the results being presented, totaling 27 bricks, as shown in Table 2.

Table 2 ▶
Number of samples for the simple compressive strength essay. *Source: research data*

	Cure days			
Formulation	**7**	**14**	**28**	**Total**
F1	3	3	3	9
F2	3	3	3	9
F3	3	3	3	9
		Total		27

The modified durability assay was carried out according to the NBR 13554 standard (ABNT, 2012c) with the brushing step being removed, as this step is not necessary for some researchers such as Silva *et al*. (2014), since requirements for surface abrasion for masonry bricks are less rigorous than those found for road purposes. Mass loss by immersion and drying is evaluated in this essay, starting after 7 days of curing. Six cycles were carried out with 5 hours of immersion in a tank with water and 42 hours of drying in an oven at a temperature of 71 ± 2°C, lasting 12 days.

After the brick ruptured in the simple compressive strength test, formulation samples with the best results were sent for microstructural surface analysis by SEM and verification of the phases formed by XRD at the Materials Characterization Laboratory at UFRN using the X'pert tool to analyze the XRD peaks.

4 Results and discussion

This topic presents the results of waste characterization, packaging analysis between waste particles, technological tests, and analysis of phases formed by SEM and XRD.

4.1 Residue characterization

The specific mass result for the scheelite residue presented 2.90 g/cm^3, which is close to the specific mass value of calcite which is 2.71 g/cm^3, and 2.65 g/cm^3 for the stone powder, as well as to the specific mass of the quartz which is 2.65 g/cm^3 (KLEIN; DUTROW, 2012). These data are probably due to the high calcite levels found in the scheelite residue, as verified in the works of Machado *et al*. (2012) and Medeiros *et al*. (2019), while the specific mass value of the stone powder is probably due to the high amount of quartz contained in this waste, as found in the work by Machado *et al*. (2016).

Figure 1 shows the granulometric analysis results of the scheelite residue (SR) and stone powder (SP). The difference between the two curves can be seen, with the scheelite residue having more than 65% of its particles passing through the 0.075 mm diameter, sieve # 200. This is characteristic of powdery material, while the greatest distribution for stone dust particles is found in 0.60 mm to 0.30 mm, sieves #30 to #50.

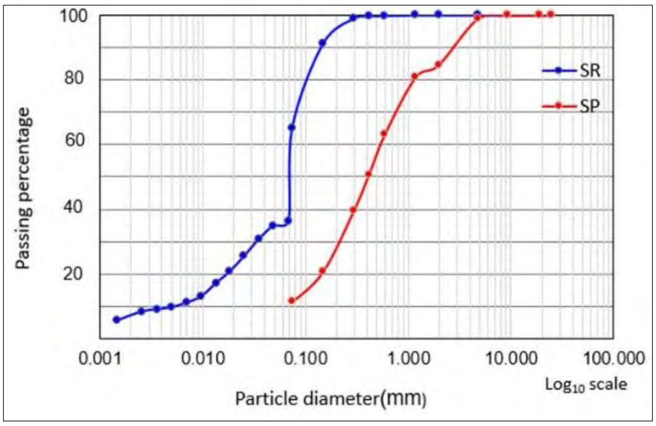


Figure 1 ▶
Curves of the granulometric analysis of solid residues. SR: Scheelite residue; SP: Stone powder. *Source: research data*

According to the NBR 6502 Standard (ABNT, 2018a) which defines terms for rocks and soils, the scheelite residue mostly presents granulometry of fine sand (particles between 0.06 mm and 0.2 mm) and the stone powder has an average sand size of 0.20 mm and 0.60 mm, indicating that there are coarse sand particles and levels of powdery material estimated at 11%. It is worth mentioning that the combined residues tend to form more efficient packing between particles, since most of the stone powder particles are larger than the scheelite particles, thereby filling voids according to the particle packing theory (OLIVEIRA *et al*., 2000).

The granulometric analysis results of the residues are consistent with the beneficiation process since the scheelite residue is thinner because it is obtained after washing the water used in the vibrating tables to separate the scheelite from the coarse residue. However, the stone powder is obtained by cutting rocks and obtaining larger pieces together with a fine powder gathered at the end of the crushing process.

Table 3 presents the XRF and XRD analysis results of scheelite residues and stone powder, highlighting the main constituted elements and their phases formed by the X-ray diffractogram data of waste samples.

Table 3 ▶
Solid waste characterization. *Source: research data*

Elements	Scheelite residue (%)	Stone powder (%)
Ca	53.37	4.87
Fe	17.99	26.99
Si	12.25	36
Al	4.99	0,00
K	0.00	13.59
Zr	0.00	9.49
Others	11.40	8.72
Formed phases	Calcite, quartz, almandine	Quartz, albite, microline
SEM analysis	Spherical particles	Lamellar particles

High calcium levels are noted in the scheelite residue, which is characteristic of limestone rocks and scheelite itself ($CaWO_4$), with significant amounts of iron and silicon, representing more than 80% of the sample. The X-ray diffraction result shows calcite, quartz, and almandine, which is a mineral that contains iron, aluminum, and silicon ($Al_2Fe_3O_{12}Si_3$). These characterization results for scheelite residues are similar to the results found by Machado *et al*. (2012) and Medeiros *et al*. (2019), since they were derived from the same mine, reinforcing that there was no considerable variation in the collected waste.

As the stone powder comes from granite rock, as stated by the mining company from which the sample was collected, it has a high amount of silicon with relevant amounts of iron and potassium, with chemical characterization values close to those found by Machado *et al*. (2016) who also used stone powder derived from granitic rock.

As seen in Table 4, the cassava wastewater was classified as a colloidal solution with an acid pH of 4.5, yellowish in color, consisting of a solution with total solids of 14,563 mg/L and 2,373 mg/L solids in suspension with free cyanide content found of 5.62 mg/L, which is even lower than the value obtained by Chisté and Cohen (2011) in their study on the cyanide content in tucupi (indigenous food derived from cassava wastewater).

Table 4 ▶
Some cassava wastewater characteristics.
Source: research data

Variable	Value
Total solids	14,563.00 mg/L
Suspended solids	2,373.00 mg/L
Free cyanide	5.62 mg/L
Total cyanide	8.92 mg/L
pH	4.50
Electric conductivity	7.62 mS/cm

The chemical composition analysis by macronutrient and micronutrient, chloride, sulfate, and phosphate results are shown in Table 5, with potassium (1.456 mg/L) being highlighted. Potassium is also found at high levels in the work of Neves *et al*. (2014) and Nasu, Formetini, and Furlanetto (2015). According to Heydt *et al*. (2015) in their study on anaerobic biodigestion of starch residues, different values in the cassava wastewater composition were found for at least 3 authors, attributing that the characteristics of this residue vary according to the cassava processing, with the raw material quality and the destination of the final product having the acid pH and high organic matter and cyanide concentration as their main characteristics.

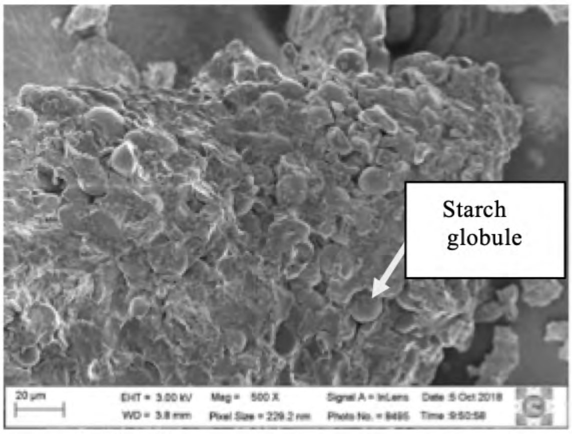
The value of cassava wastewater electrical conductivity was similar to the work of Duarte *et al*. (2013), which was 6.8 mS/cm, and Barreto *et al*. (2013), which was 7.81 mS/cm. These electrical conductivity values indicate the presence of free ions in the solution that can facilitate ionic exchanges with waste and cement.

Table 5 ▶
Chemical elements in the cassava wastewater.
Source: research data

Elements	**Value (mg/L)**
Potassium (K)	1.456
Nitrogen (N)	1.121
Sodium (Na)	351
Magnesium (Mg)	219
Phosphorus (P)	132
Iron (Fe)	117
Calcium (Ca)	93
Zinc (Zn)	20
Manganese (Mn)	15
Copper (Cu)	9

The morphology of the cassava wastewater particles is seen in a 500x magnification in Figure 2. There are spherical clusters of different sizes similar to the starch globules found by Vieira *et al*. (2010) and Garcia *et al*. (2016) in their work with cassava starch.

Figure 2 ▶
SEM of cassava wastewater.
Source: authors' archive



4.2 Particle packaging analysis

The analysis of the packaging tests among the solid residues is shown in Table 6, which presents the values of maximum specific mass and optimum humidity obtained in the compaction test of the scheelite residue and stone powder formulations at mass percentage.

Table 6 ▶
Result of the compaction test for 3 waste formulations.
Source: research data

Property	**Mass percentage of scheelite residue / stone powder**		
	60/40	**50/50**	**40/60**
γsmáx (g/cm³)	1.8	1.94	1.89
Hot (%)	12.8	11.5	11.8

Subtitle: $\gamma_{smáx}$ – maximum specific mass; H_{ot} (%) – optimum moisture percentage.

The mixture with many fines (60% of SR) provides an increase in the specific surface of the particles, requiring more water to close the smaller voids. In the mixture with few fines, there will be a greater amount of larger voids, as seen in the compaction with 40% of SR. Therefore, the best result is the compaction with 50% scheelite residue and 50% stone powder, without excess fines or large particles.

It is possible to visualize this packaging between the particles of the residues in Figure 3, which presents the SEM of formulation F1 in the magnitude of 500x for 28 days of curing. In this Figure, lamellar particles of about 100 µm are noted, which due to the size and shape are stone dust and smaller spherical particles that may be stone dust smaller or scheelite residue.

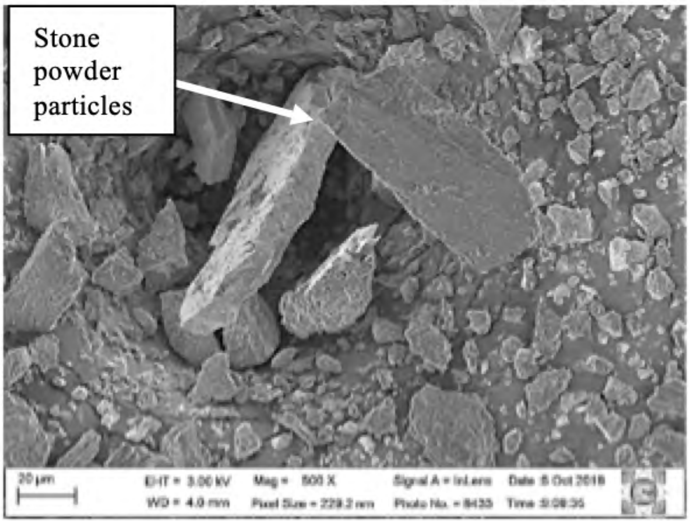


Figure 3 ▶
SEM of formulation F1 for 28 days.
Source: authors' archive

The compaction test performed in the 50% solid residue mixture (R) for each is shown in Figure 4, with a curve of the residues without cassava wastewater (with water) and another curve of the residues with cassava wastewater. Both tests show a normal dry density distribution curve concerning moisture, representing good packing between the particles both in terms of size and morphology, with the most spherical and smallest scheelite residue particles filling the voids between the larger, lamellar stone powder particles, as according to the study of particle packing by Oliveira *et al.* (2000).

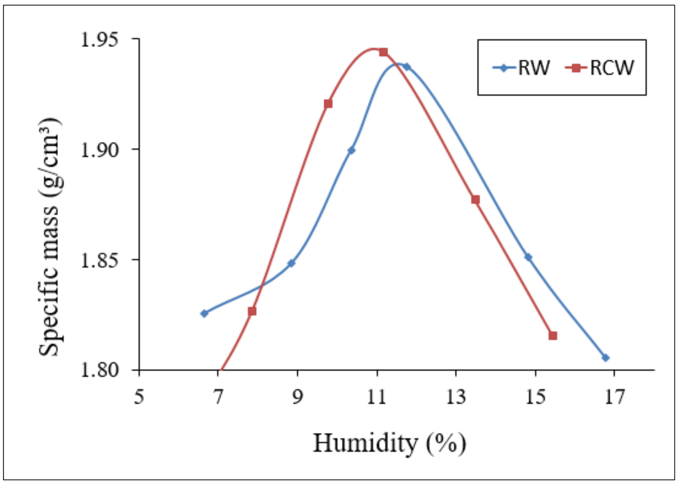


Figure 4 ▶
Compaction essay of residues with water (RW) and residues with cassava wastewater (RCW).
Source: research data

It is noticed that the residues with cassava wastewater promoted an increase in the specific mass and a decrease in the optimum humidity, which is justified by the high amount of solutes in the effluent facilitating the void filling between the solid residue particles, as studied in the works of Akindahunsi (2019) who investigated the influence of cassava and corn starch as an additive in concrete and Abraham and Ransinchung (2018), who studied the influence of fine asphalt aggregates recovered in mortar, facilitating the void filling.

4.3 Technological essays

It is observed in Figure 5 that there was no considerable variation in the water absorption value for the formulations even with the increase in the cement content which promotes greater densification of the mixture due to cement reactions. This can be justified by the effect of cassava wastewater present in all formulations, promoting void filling between solid residue particles, as verified in the work of Singh *et al*. (2003) in mixtures of mortars modified with polymers.

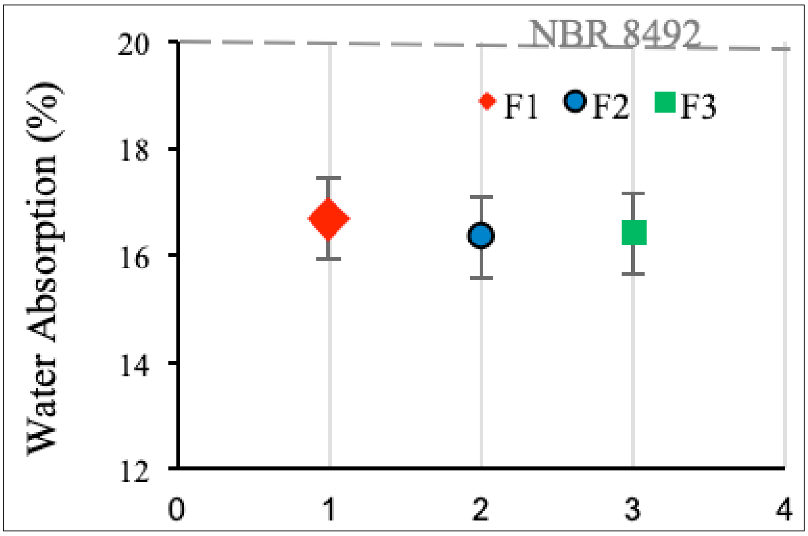
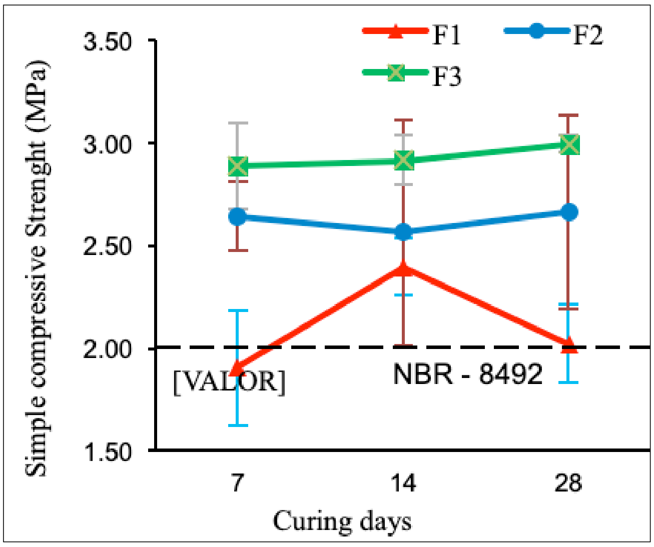


Figure 5 ▶
Water absorption of formulations.
Source: research data

Figure 6 presents a simple compressive strength graph of the F1, F2, and F3 formulation samples in the curing times of 7, 14, and 28 days. It is noted in the graph that the results follow the NBR 8491 standard (ABNT, 2012a), being above 2 MPa, except for the F1 formulation for 7 days of curing. It is also worth noting that the minimum binder percentage recommended for chemical soil stabilization according to Sherwood (1993) is only 6% of cement.

Figure 6 ▶
Simple compressive strength of the formulations.
Source: research data



In working on incorporating PET (polyethylene terephthalate) into the soil for manufacturing soil-cement bricks, Paschoalin Filho, Storopoli, and Dias (2016) also obtained some simple compression strength values less than 2 MPa. However, the authors considered the brick to be suitable for masonry without structural function, since this compression test is only performed on one brick, with a considerable increase in the mechanical simple compression strength for a brick wall.

In comparing the curing times of 7, 14, and 28 days, it is observed that there were no significant variations in the formulations, unlike the work of Silva *et al*. (2014) in which there was an increase of approximately 0.5 MPa in the formulation with the addition of 12% cement from 7 to 28 days, due to pozzolanic reactions.

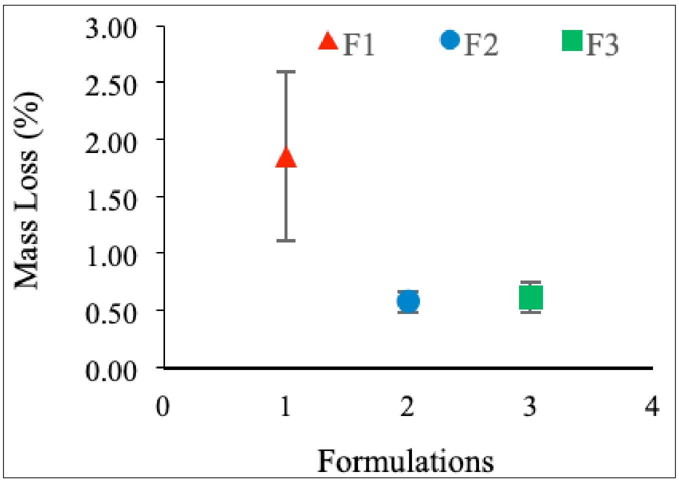
Strength in 7 days of curing can be justified with values close to the values of 28 days of curing mainly due to the influence of cassava wastewater, which promotes acceleration in the hydration reactions of cement and with solid residues since the acidity of cassava wastewater facilitates forming ions in the solution. According to Mehta and Monteiro (2014), the accelerating additive should promote dissolution of the cationic or anionic components of cement, with preference to the dissolution of the constituent which has the lowest dissolution speed during the initial hydration period.

In a study on the effects of hydroxyethylcellulose and oxalic acid, Singh *et al*. (2003) evaluated the changes in cement hydration in both acceleration and delay in curing time, evaluating the influence of pH on reactions with anhydrous cement.

It is also possible that the finer solid particles contained in all residues accelerate the cement hydration by the filler effect as occurred in some works with fine particles of carbonates or other aggregates in cement paste such as in the work of Irassar *et al*. (2015) and Rocha, Cordeiro, and Toledo Filho (2013). In addition to the contribution of cement reactions to the increase in cement compressive strength, there may also be an increase in strength due to the formation of calcium carboaluminate from the carbonate dissolution in an acid medium, reacting with the calcium aluminates of the cement as shown by Bonavetti, Rahhal e Irassar (2001), Chatterjee (2002) and Ipavec *et al*. (2011).

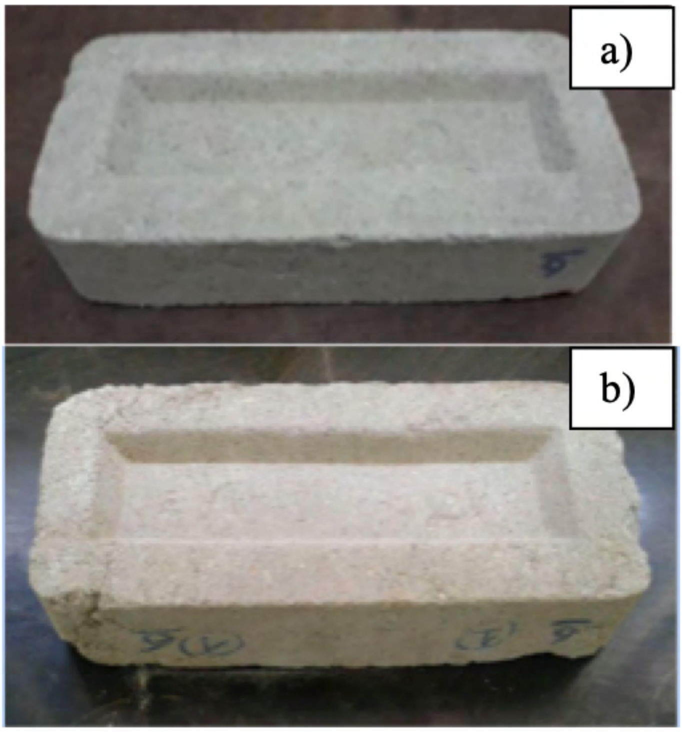
The results of the modified durability test (shown in the graph in Figure 7) presented equivalent mass loss to the results by Silva *et al*. (2014), who performed the modified durability in soil-cement bricks without brushing. The formulation with a 12% addition of cement to the soil by Silva *et al*. (2014) presented 0.45% of mass loss, being close to the F2 formulation value (addition of 9% cement), indicating that the mixture of residues together with their packing contribute to the brick's durability.

Figure 7 ▶
Mass loss of the formulations.
Source: research data



The difference between the mass loss of the formulation with 5% cement (F1) for the others stands out in the graph, and there was also a superficial breakdown of some bricks of this formulation during their handling in the test as shown in Figure 8.

Figure 8 ▶
View of the F1 formulation brick surface before (a) and after (b) the durability test.
Source: authors' archive



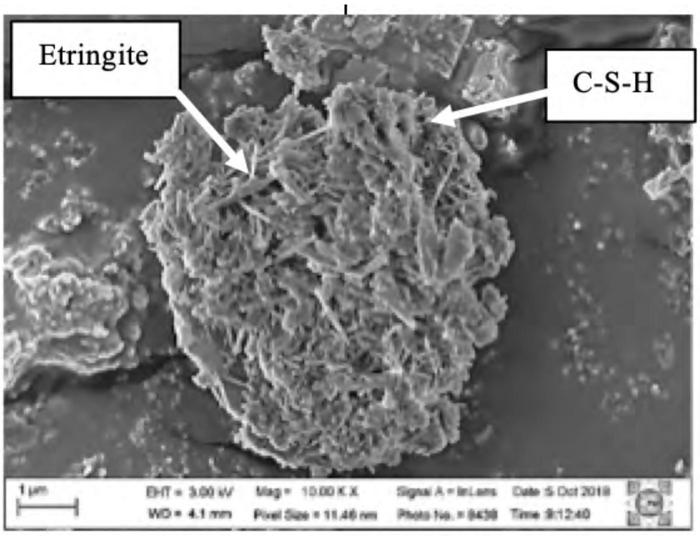
As was verified in the simple compressive strength test, this formulation is less resistant than the intermediate formulation (F2) which obtained values closer to the simple compressive strength of the F3 formulation.

4.4 Analysis of the formed phases

As there was no significant variation in the morphology of the particles and phases formed between the formulations from 7 to 28 days of curing, the most significant morphologies are presented in order from smallest to largest scale

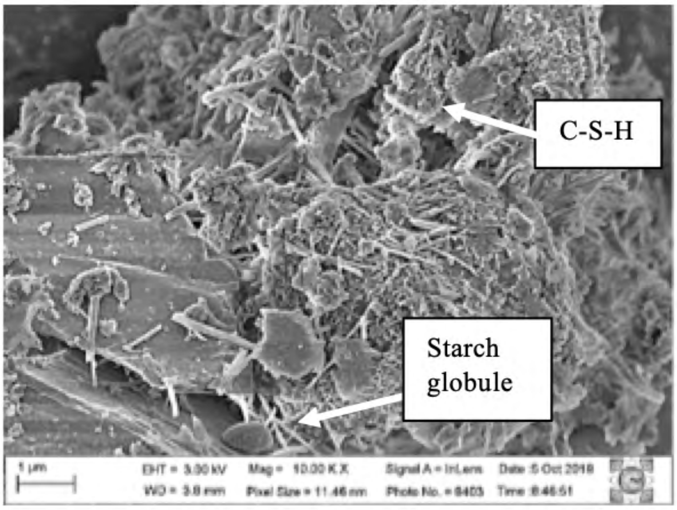
In Figure 9, at the magnitude of 10,000X, referring to the SEM of formulation F3, it is possible to identify structures similar to hydrated calcium silicate (C-S-H) and long plates similar to ettringite as seen in the research by Mehta and Monteiro (2014).

Figure 9 ►
SEM of formulation F3 within 28 curing days.
Source: authors' archive



In Figure 10, with a greater magnification (20,000x) for the F1 formulation within 7 days of curing, it is possible to verify, in addition to the characteristic morphology of hydrated calcium silicates, globules similar to those seen in the SEM of the *manipueira* of this work, indicating that they can be starch globules as seen in the studies by Vieira *et al*. (2010) and SEM analysis of cassava wastewater in Figure 2 of this work.

Figure 10 ►
SEM of formulation F1 within 7 curing days.
Source: authors' archive



At a higher magnitude, of 40,000x in SEM, as seen in Figure 11 of formulation F3 within 28 days of cure, it is possible to better visualize the fibrous and spongy structures of C-S-H, also verified in the works by Braz *et al*. (2019) and Mehta and Monteiro (2014).

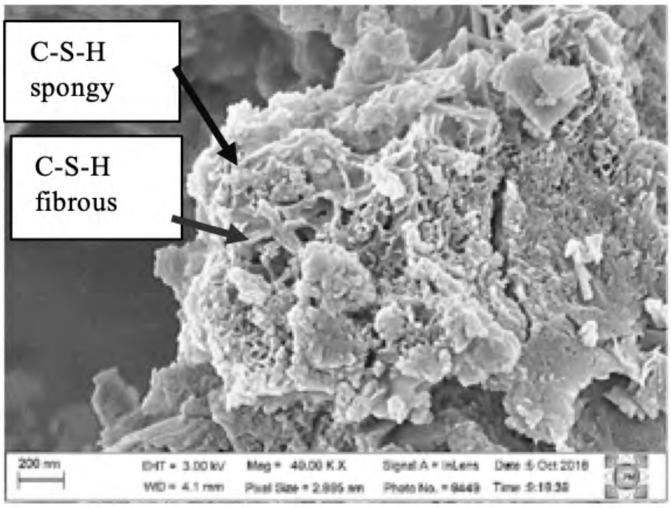
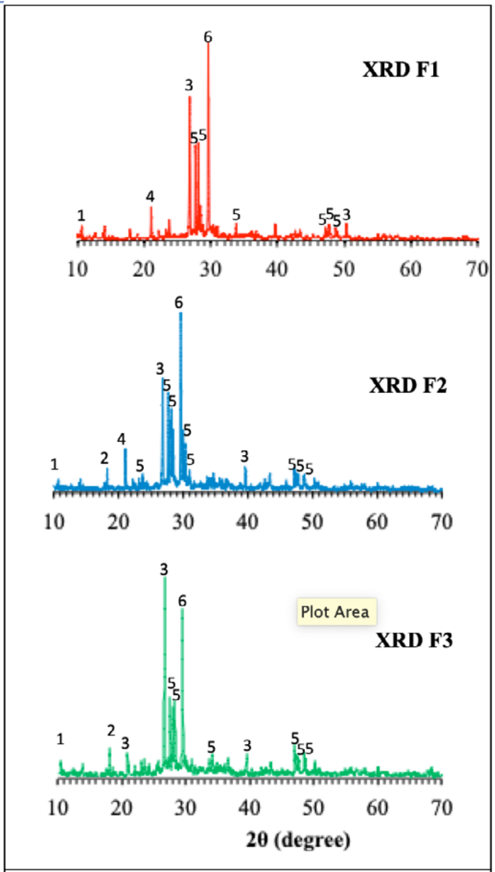


Figure 11 ▶
SEM of formulation F3 within 28 curing days at 40,000x.
Source: authors' archive

The result of the analysis of phases formed by cement reactions and residues is analyzed using XRD at 7 curing days. All formulations presented phases resulting from cement hydration such as C-S-H and crystals from residues such as quartz and calcite, becoming similar to the diffractogram of formulation F1 shown in Figure 12 with the codes of the crystallographic charts.



Subtitle - element (reference code):
1 - Grossular (98-002-8300); 2 - Portlandite (98-004-6333); 3 - Quartz low (98-002-3116); 4 - Calcium Potassium Silicon Oxide Hydrate (98-009-1650); 5 - Clinotobermorite (98-005-6942); 6 - Calcite (98-000-5342).

Figure 12 ▶
XRD of the formulations.
Source: research data

In this diffractogram, it is important to note the presence of portlandite and C-S-H phases that are similar to the minerals clinotobermorite and tobermorite of formula $Ca_5(Si_6O_{16})(OH)_2$. The kinetics of the reactions of tobermorite formation depends on the fineness of the starting materials, the nature of the siliceous materials, the hydrothermal curing conditions, and the CaO/SiO_2 molar ratio (KIHARA, 1991).

The minerals tobermorite and clinotobermorite were also found by several authors who studied the formation of cement phases such as Braz *et al*. (2018) who used aluminum recycling residues, and sugarcane bagasse ash and zeolite in mortars. Fernández, Ruiz, and Cuevas (2016) in their study on concrete bentonite, and Cuesta *et al*. (2018) analyzed the reactions of hydrated tricalcium silicate in a multiscale.

The C-S-K-H phase named Calcium Potassium Silicon Oxide Hydrate ($CaK_4(H_2O)_8Si_{16}O_{38}$) was also verified in formulation F2, which should represent the reaction of the potassium ion (K^+) present in the acid handling with the anionic constituents of cement and Ca^{2+} in medium aqueous. This phase is common in cementitious compounds that contain alkalis (Na, K), having a structure analogous to tobermorite. C-(N,K)-S-H can incorporate an alkali content of up to 20%, which decreases as a direct function of the Ca/Si ratio.

5 Conclusions

Based on the analysis of the packing between the particles, water absorption, compression strength, microstructural analysis, and verification of the formed phases, it can be concluded that:

- The scheelite, stone powder, and cassava wastewater residues proved to be viable for incorporation into bricks to replace soil and water, having comparable properties to soil-cement bricks;
- The high packing between the waste particles together with the formed cement reactions contributed to the satisfactory mechanical properties;
- The cassava wastewater contributed to better cohesion between the solid waste particles, filling voids between solid particles due to the filler effect, and also activating chemical reactions with cement and waste;
- All formulations (F1, F2, and F3) showed satisfactory mechanical properties for use in sealing masonry, highlighting the F2 formulation with the best cost-benefit ratio, because it uses less cement, still having results close to F3;
- The SEM and XRD analysis showed high mechanical strength phases such as the C-S-H, highlighting the presence of C-S-K-H by the action of the cassava wastewater, as well as the presence of starch particles in SEM images.

The production of this ecological brick promotes environmental, social, and market advantages due to its low cost and ease of production.

Acknowledgments

The authors would like to thank the Post-graduate Program in Materials Science and Engineering (PPGCEM) at the Federal University of Rio Grande do Norte (RN), the Federal Institute of Education Science and Technology of Paraíba (IFPB), and the *Coordenação de Aperfeiçoamento de Pessoal de Nível Superior* (CAPES), financing code 001.

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