Environmental Engineering and Management Journal April 2020, Vol. 19, No. 4, 565-576
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu

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MICROSTRUCTURAL AND PHYSICAL CHARACTERIZATION OF SOLID WASTES FROM CLAY BRICKS FOR REUSE WITH CEMENT

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Abstract

This study aims to evaluate the properties of different wastes obtained from four red ceramic brick industries in the northern region of Santa Catarina, Brazil. The characterization of the clay brick waste (CBW) was performed using the XRD techniques, XRF, FTIR, DTA and SEM. Techniques to determine the pozzolanic activity, particle size, B.E.T. surface area and specific mass were used. The consumption of calcium hydroxide (CH) in the cementitious pastes with the CBWs was also measured. An application in mortar is also analysed. The results indicated that the CH consumption was a function of the large surface area of the waste particles. The CBW reactivity is favoured by firing temperature adequate (about 800 ºC), low presence of K_2O and impurities and higher kaolinite content. CBW-B showed the highest consumption of calcium hydroxide in the cement pastes tested (remaining 0.40% CH). Morphological analysis showed that microcrystals of halloysite was smaller than those of kaolinite and have more elongated profile. These differences provide the larger surface area observed for halloysite and this has an influence on the reactivity. The reference paste presented CH content of 2.37%. The compressive strength of the mortar with CBW improved comparing to reference, in 28 days (from 2.45 to 5.65 MPa), and in 90 days (from 5.72 to 10.39 MPa). The use of these wastes could reduce solid waste discards in many regions. Besides reducing CO_2 emissions and saving natural resources from the manufacture of cement.

Key words: brick waste reuse, burned clay microstructure, clay brick waste, solid waste characterization, sustainable building materials

Received: May, 2019; Revised final: August, 2019; Accepted: October, 2019; Published in final edited form: April, 2020

1. Introduction

World cement production reached 4 million tonnes in 2013 (Cement Org, 2019). In China, the world's largest cement producer, production reached 2,300 million tonnes in 2013. The installed capacity for cement production in Brazil exceeds 100 million tons per year in 2019 (Cement Org, 2019). Portland cement production consumes large quantities of non-renewable natural resources (limestone, phyllite, quartzite, magnetite), but also requires a lot of energy. The production of one ton of cement consumes about 1.6 tons of natural resources (Jennings and Bullard, 2011). A modern cement plant consumes about 100 kWh per ton of cement produced (Gartner and Macphee, 2011). Moreover, cement manufacturing is responsible for the emission of various gases, particularly carbon dioxide (CO_2). Brazil has an emission factor of about 610 kg CO_2/ton cement, below countries such as Spain (698 kg CO_2/ton cement) and England (839 kg CO_2/ton cement); China reaches 848 kg CO_2/ton cement. This is due to differences in types of plant and differences of raw materials (Cement Org, 2019). Policymakers and engineers should have the focus in strategies for low carbon development (Cai et al., 2019).

Due to this growing need for new natural resources and energy, many initiatives have been

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proposals for thermal ceramic materials (Effting et al., 2006), for the use of wastes, and for the partial replacement of cement by cementitious materials that exhibit pozzolanic properties. Industrial and mineral wastes such as blast furnace slag, fly ash, silica fume (Targan et al., 2002), polymer waste and ceramics (Deschner et al., 2012; Nadeem et al., 2013; Rodríguez et al., 2013; Snellings et al., 2012; Silva et al., 2016) have been used as cementitious materials in partial replacement of Portland cement. The use of ceramic brick-red ground waste as binder materials (Baronio and Binda, 1997; Bolouri Bazaz and Khayati, 2012; Demir et al., 2011; Lin et al., 2010a, 2010b; Naceri, 2009; Subasi et al., 2017) has had an advantage from the point of view of sustainability, since the combustion of these products, usually in the range of 600 to 900 ºC produces a ceramic body with considerable concentrations of metakaolin (Demir et al., 2011). The red ceramic brick waste from industries were mainly caused by raw materials homogeneity and processing problems, such as the drying and firing stage, resulting in cracks and breaks (Murmu and Patel, 2018).

Generally, these wastes are not reused in the process because the change of the ceramic mass plasticity. However, they have the advantage of having a low cost compared with metakaolin. Previous studies refer to materials with different characteristics of clays of the region evaluated due to geological differences found in these countries in and the northern of the State of Santa Catarina, Brazil. In many cases, metakaolins are produced from pure kaolin, very expensive and difficult to be found in some locations. Furthermore, process conditions and production waste of these aforementioned studies are distinct from those used in the region, so there is the need to perform investigations with the materials of the region, given their differences in mineralogy and microstructure yet little investigated. This large amount of clay brick wastes could be used instead of being disposed of in the environment.

The objective of this work was to evaluate the properties of four different types of clay brick wastes, for use as cementitious material in replacement of Portland cement. The influence of metakaolin in partial replacement of Portland cement depends on the physical, chemical and microstructural characteristics of the metakaolin (particle size, mineralogy, crystallinity, order and structural disorder) and temperature conditions and heating rate. Further, to identify which source has the greatest potential for pozzolanic activity and investigate the effect of clay brick waste on the compressive strength of mortars for a practical application.

2. Material and methods

2.1. Materials

The particulate clay brick wastes (CBW) were collected from four ceramic industries in the northern region of the State of Santa Catarina, Brazil; specifically, the cities of Joinville (industries A and B), Garuva (industry C) and São Bento do Sul (industry D). The wastes were parts (bricks) not sold because of size problems, cracks and other (Fig. 1).

Other information about the four ceramic industries such as the time of firing, the annual production, the amount of waste and the main defects observed in the bricks are in Table 1. The Portland cement used was type CPII-Z-32, compound with 6 to 14% pozzolan, has a particle size <41 µm and surface area of 0.37 m^2/g (Blaine fineness). The fine aggregate (sand) used in the pozzolanic activity test consists of a standard sand formed by four granulometries, 150, 300, 600 and 1180 µm. The river sand used to make the mortars had a fineness modulus of 2.44 and a maximum particle diametre of 2.36 mm.

2.1.1. Chemical characterization of clay brick wastes

The Table 2 shows the chemical composition of CBWs. According to the NBR 12653 and ASTM C618-19 (ABNT, 2014; ASTM, 2019), the calcined clays belong to the class of natural pozzolanic materials and must have, among other requirements, chemical composition of at least 70% of ($SiO_2 + Al_2O_3 + Fe_2O_3$), loss on heating maximum of 10% and the amount of available alkali maximum of 1.5% Na_2O.

Fig. 1. Clay brick wastes and clay brick powder after milling (45 µm)

Table 1. Information about the industries suppliers of the clay brick wastes

	Industry A	*Industry B*	*Industry C*	*Industry D*
Firing Temperature	700-800 ºC	800-900 ºC	1100 ºC	800 ºC
Firing Time	36 h	30 h	48 h	40 h
Annual production	7 million of bricks	1.4 million of bricks	2.16 million of bricks	3 million of bricks
Amount of ceramic bricks waste discarded	1 at 5% (6000 to 30000 pieces / month)	1% (1200 pieces / month)	5% (9000 pieces / month)	2% (6000 pieces / month)
Main defects of bricks discarded	Failures in dimensions, cracks	Bricks breaking because they are too moist Failures in dimensions, cracks	Failures in dimensions, cracks	Failures in dimensions, cracks

The results presented in Table 2 show that the CBW-A reaches the pozzolanicity requirements because presented 94.15% of (SiO_2 + Al_2O_3 + Fe_2O_3). The CBW-B had 93.32% of (SiO_2 + Al_2O_3 + Fe_2O_3), that is above the minimum of 70% indicated by the NBR 12653 and ASTM C618-19 (ABNT, 2014; ASTM, 2019). The CBW-C and CBW-D had 96.00% and 92.33% of (SiO_2 + Al_2O_3 + Fe_2O_3). The CBW-D showed significantly higher alkali content, > 1.5% (Na_2O + K_2O). The Na contributes to the so-called alkali-silica reaction impairing the durability of mortar and concrete. The most important component increasing the pozzolanic activity of a pozzolan is SiO_2, but Al_2O_3, Fe_2O_3, MgO and K_2O decrease the pozzolanic activity (Ahmet and Sukru, 2007).

Table 2. Chemical composition of clay brick wastes (expressed as % oxides) and physical properties

Chemical composition	*CBW-A*	*CBW-B*	*CBW-C*	*CBW-D*
SiO_2	66.72	64.66	64.85	64.42
Al_2O_3	21.21	22.15	22.48	20.54
Fe_2O_3	6.22	6.51	8.67	7.37
TiO_2	1.37	1.44	1.28	0.94
K_2O	0.67	0.81	0.53	3.56
CaO	0.21	0.20	0.16	0.09
MgO	0.48	0.31	0.34	1.03
Na_2O	0.18	0.15	0.11	0.16
P_2O_5	0.09	0.13	0.10	0.14
MnO	0.06	0.05	0.11	0.07
Loss on ignition (%)	2.78	2.58	0.15	1.14
$SiO_2 + Al_2O_3 + Fe_2O_3$ (%)	94.15	93.32	96.00	92.33
Physical Properties	**CBW-A**	**CBW-B**	**CBW-C**	**CBW-D**
Surface area B.E.T. (m^2/g)	34.36	35.16	20.21	31.80
Average particle diametre (μm)	8.07	6.04	9.83	5.34
Specific mass (g/cm^3)	2.64	2.56	2.83	2.61

2.1.2. Physical characterization of clay brick wastes (particle size, B.E.T. surface area and specific mass)

The Table 2 shows the physical characteristics of the clay brick wastes. The results of the surface areas of the ceramic studied were presented in general close to the results found by other authors. Some literature results reached 0.77 m^2/g (Samet et al., 2007), 19 m^2/g (Cordeiro and Désir, 2010), 31 m^2/g (Fernandez et al., 2011) and 47 m^2/g (Herek et al., 2011). The mean particle diameter values were consistent with the respective fineness of each waste, as expected, that is, larger particle diameter results in less surface area. The fineness (particle size) of particulate brick waste is one of the determining factors for reactivity of the material (have pozzolanic activity). It is known that the material passing the sieve 45 μm is more reactive. The specific mass for CBW-A was 2.64 g/cm^3. For the CBW-A, the average particle diameter was 8.07 μm and the result to B.E.T. was 34.36 m^2/g. The specific mass for CBW-B was 2.56 g/cm^3, the lowest among CBWs. For the CBW-B, the average particle diameter was 6.04 μm, and the result to B.E.T. was 35.16 m^2/g. Compared to the equivalent CBW-A, the lowest average diameter corresponds to a higher surface area.

The average diameter of the particles of CBW-C and CBW-D were 9.83 and 5.34 μm. For CBW-C and CBW-D, the B.E.T. results were 20.21 and 31.80 m^2/g. Compared with other equivalent CBWs, although the average diameter in CBW-D is the smallest of all, the surface area is not the highest, but the differences are not significant. The specific mass was higher for CBW-C because of the higher temperature of 1300 ºC, which sintered and grouping the particles.

Fig. 2 shows the particle size distribution of the clay brick wastes studied (after passing in sieve 45 μm).

2.2. Methods for characterization of clay brick waste

2.2.1. Sample preparation

Samples for characterization were removed from burned bricks, which were obtained from the discarded waste that contain cracks and dimensional faults. For each industry ceramic samples were obtained containing several pieces. Reducing the size of the sample is given by quartering, to the extent necessary for milling. For XRD tests, XRF, FTIR and SEM, samples of ceramic bricks disposed by industries were ground in a dry ball mill for 1 hour. A powder by sieving in the sieve of 45 μm was obtained. The mill used was the Servitech CT-241 model, and used a ceramic coated jar and ceramic coated spheres. For samples of CBWs analysed in the SEM, the powder obtained after sieving was dried for 24 hours in an oven at 103 ºC. The powders were then deposited on the specimen holder on tape carbon and coated with carbon, and remained in the desiccator until the time of analysis in the microscope. For the pozzolanic activity test, consumption of calcium hydroxide (*CH*) test, laser granulometry, B.E.T. and specific mass, the CBW samples were milled in one dry ball mill for 1 hour and sieved in the sieve 45 µm.

2.2.2. Characterization techniques and equipment

To identify the physicochemical, mineralogical and microstructural characteristics of clay brick wastes the following techniques of characterization were applied:

a. Characterization by XRD, XRF, FTIR and SEM

For phase analysis was used a diffractometer X-ray Shimadzu XRD 6000 (using Cu Kα), with a range of diffraction at 2θ. The equipment used for the chemical analysis was an X-ray spectrometer model Philips PW 2400. Analysis by infrared spectroscopy (FTIR) was performed on a Perkin - Elmer Spectrum One, with a range of 4000-560 cm^{-1}. The equipment used for the images of microstructures of clay brick waste was a scanning electron microscope Hitachi SU-70.

b. Thermal analysis (DTA/TG)

DTA/TG tests were performed in a differential thermal analyzer Setaram Labsys DSC16, at a heating rate of 10ºC/min under an air atmosphere in the 25-1100ºC temperature range.

c. Pozzolanic activity

To determine the pozzolanic activity in cement according to NBR 5752 (ABNT, 2012) five mortars were prepared, one mortar for each of the four types of CBW (through the material in the sieve 45 µm) and a reference mortar only with cement (without CBW). The amounts of materials are given in Table 3 and Table 4. In Table 3, "X" and "Y" are the quantities of water and are determined when the mortar has a consistence of 225 ± 5 mm. So are made attempts to adding water until this consistence. After finding consistence, three cylindrical specimens (5 cm x 10 cm) were moulded in 4 layers, with 30 strokes per layer. After 24 hours, the specimens were removed from the moulds and placed in a tank with water saturated with calcium hydroxide per 28 days. The activity index pozzolanic is determined by (Eq.1).

After 24 hours the bodies of tests were removed from the moulds and placed in a tightly sealed container that stayed in an oven at 38 °C until the break date for 28 days. The activity index pozzolanic is determined by (Eq. 1).

$$\frac{f_{cb}}{f_{ca}}.100(\%) \qquad (1)$$

where:

f_{cb} = Average resistance in 28 days of the specimens with cement and material to be tested (mortar with CBW).

f_{cA} = Average resistance, in 28 days, the bodies of the test with cement only (reference mortar).

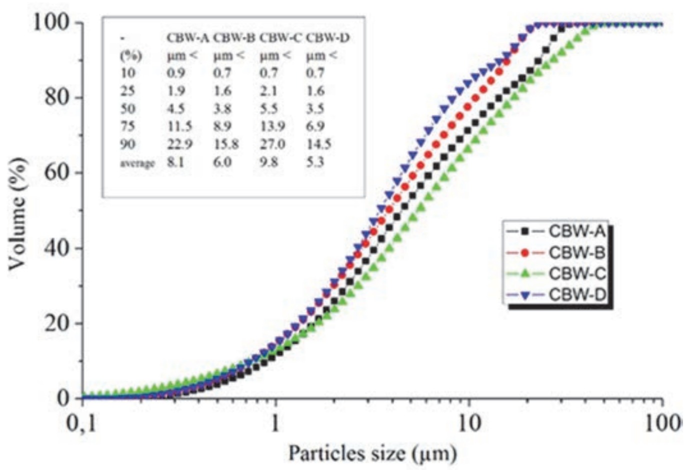

Fig. 2. Particle size distribution of the clay brick wastes.

Table 3. Information for calculation of the masses of pozzolan city test

Material	*Materials mass (g)*		
	Reference mortar	*Mortar with pozzolanic material*	
Cement	312.00	202.80	
Pozzolanic material	-	$109.2\frac{\delta_{poz}}{\delta_{cim}}$	δ_{poz} e δ_{cim} are respectively specific mass of the pozzolanic material and cement
Sand	936.00	936.00	
Water	X	Y	X and Y are the quantities of water necessary to produce consistency rates of 225 ± 5 mm (flow table test).

Table 4. Calculated masses for pozzolanic activity tests

	Amount of materials (g)	
	Reference mortar	*Mortar with pozzolanic material*
Cement	312.00	202.80
Pozzolanic material	-	88.82 (for each CBW)
Sand	936.00	936.00
Water	X =169.15	Y = 174.15 (to CBW-A)
		Y = 197.53 (to CBW-B)
		Y = 169.15 (to CBW-C)
		Y = 195.15 (to CBW-D)

The water required is a relationship that can be expressed in percentage by equation (Eq. 2)

$$\frac{P}{R}.100(\%) \tag{2}$$

where:
P and R = quantity of water necessary to obtain a normal consistency index (225 ± 5) mm for mortars P (with pozzolanic material) and R (reference), respectively.

d. Particle size analysis, B.E.T. surface area and specific mass.

The analysis of the clay brick wastes particle size was determined by laser using a particle analyser equipment of the type Beckman Coulter LS-230, which analyses sizes between 0.04 and 2000 µm. The specific surface areas of CBWs were determined by the B.E.T. (Brunauer- Emmett-Teller) in a Micromeritics Gemini surface area analyser V2.00 equipment. The specific mass of CBWs was measured with a helium pycnometer Multipycnometer Quantachrome.

e. *CH* consumption (by DTA/TG)

A control paste (cement and water) with water to cement ratio of 0.5 was prepared for *CH* (calcium hydroxide) consumption test. Another four pastes were prepared similarly, but with the substitution of 40% of cement by the four types of CBW (fineness of 45 µm). After 14 days, the pastes were milled in porcelain bowl and each resulting powder was sieved in the 45 μm sieve. Each sample was subjected to DTA/TG analysis to determine the consumption *CH* by weight loss at peak between 460-600 ºC. The measurements were performed with a differential thermal analyser Setaram Labsys DSC16, at a heating rate of 10 ºC/min under an air atmosphere in the 25-1100 ºC temperature range.

2.3. Design of mortar mixtures and properties measurement

To evaluate the effect of CBW in a common application in constructions, mortars without CBW and with 40% (grain size < 45 µm) of CBW-A were tested. The choice of CBW-A was due to the fact that it performed well in initial tests (very similar to CBW-B) and because the ceramic industry A has the highest production and consequently has the largest amount of waste. The initial proportion of materials adopted for mortars was, by volume, 1 : 1.5 : 6 (cement, lime and sand) commonly used in construction. This proportion was transformed from volume to mass.

The preparation of the mortars was carried out according to NBR 13276 (ABNT, 2005a). First, the quantities of sand, lime and water were mixed for 4 min in the mortar mixer (model I3010 – Pavitest Contenco). This mixture was left to stand for 16 to 24 hours. Then the amount of evaporated water (mass) was adjusted (after 16-24 hours) and cement and RPT, already mixed, were added. The mixture remained for a further 4 minutes in the mortar mixer. The amount of CBW replacing the cement added to each mixture was calculated relative to the mass of the cement.

The compressive strength test was performed according to NBR 13279 (ABNT, 2005b). Prismatic mortar specimens of 40 x 40 x 160 mm were moulded to perform the compressive strength tests. The densification was performed through 30 drops in each of the two layers on the automatic density table. Six prismatic samples of 40 x 40 x 160 mm were tested for each mortar at each curing age (28 and 90 days). For the compressive strength test, a hydraulic press, connected to a computer, model Emic PC200I with a mortar test device was used.

The samples of hardened mortars and pastes for the analysis of XRD and FTIR were removed from a mortar and a paste denominated M0 and P0, (without CBW) and a mortar and a paste with 40% (by mass) of cement replacement by CBW (M40 and P40) after 28 days of cure. The pastes used (without sand) had the W/C ratio of 0.5.

3. Results and discussion

3.1. Characterization of clay brick wastes

3.1.1. Mineralogical analysis by X-ray diffraction

According to Fig. 3a, the majority crystalline phase present in the samples was the α-quartz. Only CBW-D sample showed muscovite, probably due to the larger amount of potassium (*K*). At the temperatures used, the clay mineral kaolinite and halloysite had dihydroxylation and transformed into metakaolin, predominantly amorphous, justifying the isolated presence of quartz in other samples (Shvarzman et al., 2002).

3.1.2. Analysis by infrared spectroscopy

In the FTIR spectrum of CBWs of Fig. 3b, in 695, 779 and 797 cm^{-1} are bands associated with Si-O deformations, while the band at 1039 cm^{-1}

corresponds to the perpendicular vibration of Si-O. A significant change in the Si-O vibration 1002 cm^{-1} in the spectrum of ceramic samples in nature (kaolinite, unburned) to a higher frequency in the range of 1039 cm^{-1} in the spectrum of CBWs (with metakaolin) (Fig. 3b) is attributed to the amorphous material (Frost et al., 1997).

3.1.3. Analysis by infrared spectroscopy

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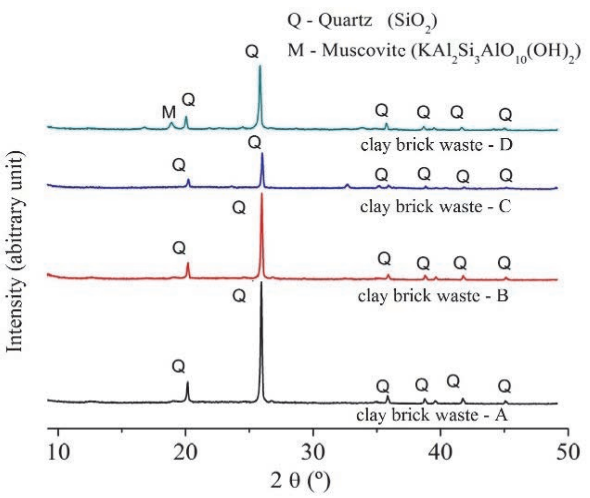
3.2. Morphological characterizations of clay brick wastes

The micrograph CBW-A (Fig. 4a) shows the morphology to metakaolin and the meta-halloysite, similar to an unburned sample. The SEM image of the CBW-A shows the diametre of pseudo-hexagonal particles of metakaolin is in the micrometer range. Microcrystals of halloysite are smaller than those of kaolinite and have more elongated profile. These differences in morphology influence the larger surface area observed for halloysite (Zatta, 2010). Consequently, it remains to metakaolin and metahalloysite in calcined clays.

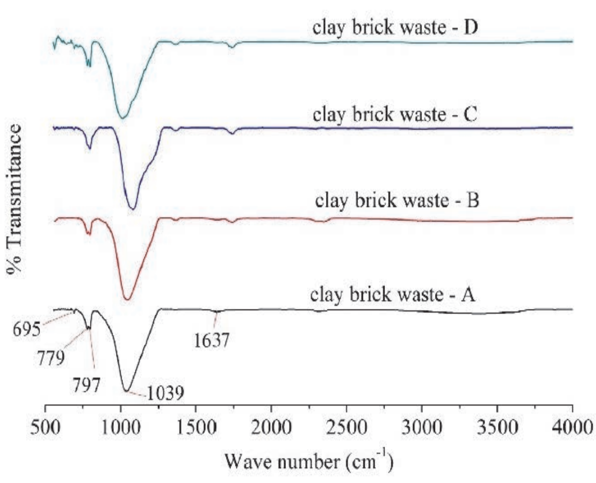
The micrograph of CBW-A appears to have small microcrystals metahalloysite. That, and also the fact that they are more disintegrated and irregular particles in relation to CBWs C and D, may have contributed to the higher specific surface area of this sample (34.36 m^2/g), compared to CBWs C and D.

When the morphology of the clay particles changes after the heat treatment, a morphology containing flakes corresponds to part of the amorphous material. Consequently, in clays containing minor amounts of kaolinite and high amounts of impurities such as quartz, calcite and muscovite, heat treatment has much less influence on the morphology (Selmani et al., 2015). The characterization of flakes indicative of amorphous material is not as visible in CBW-A. The micrograph of CBW-B (Fig. 4b) shows that the crystal metakaolin and metahalloysite have the same morphology of the starting crystals (which are found before the calcination). The micrograph of CBW-B presents microcrystals metahalloysite and more disintegrated and irregular particle, which may have contributed to the higher specific surface area of this sample (35.16 m^2/g), among all CBWs. The CBW-B also shows the morphology containing flakes indicating the presence of amorphous material (Selmani et al., 2015).

A large amount of kaolinite results in a larger amount of amorphous material, after heat treatment. Therefore, CBW-B (before firing) has a larger grain's consolidation ability, suggesting a greater strength of the final product burned. The micrograph of CBW-C (Fig. 4c) shows that the metakaolin plates seem more grouped (and larger). The Fig. 4c shows the CBW-C has slightly larger pseudo-hexagons that CBWs A and B resulting in lower surface area. The CBW-C showed the lowest value for surface area (20.21 m^2/g), between the CBWs.



(a)



(b)

Fig. 3. XRD patterns of clay brick wastes ranging from 10° to 50° at 2θ (a), FTIR spectra of the clay brick wastes in the range of 500-4000 cm^{-1} (b)

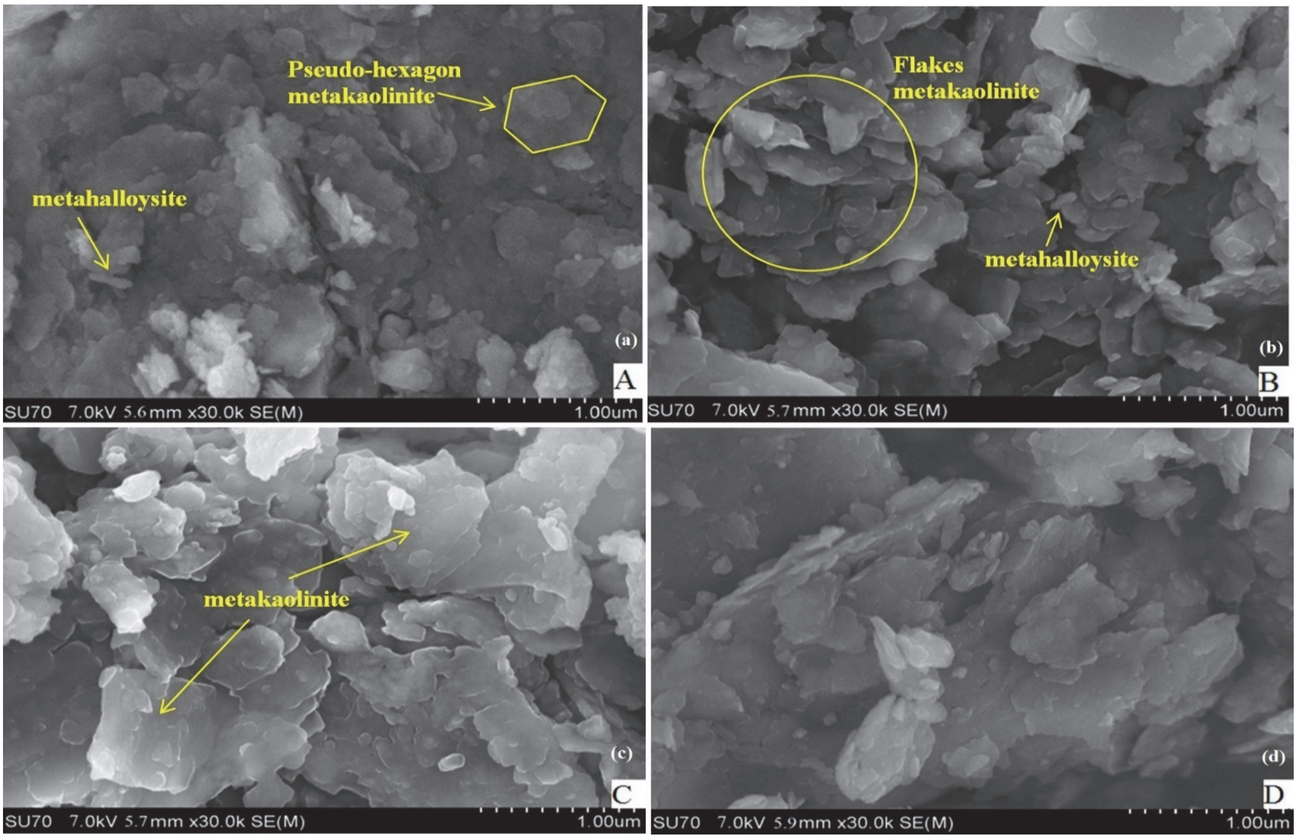


Fig. 4. Micrograph obtained by SEM SE (secondary electrons) of CBW-A (a), CBW-B (b), CBW-C (c) and CBW-D (d)

The image also shows a more homogeneous appearance, possibly due to sintering caused by higher firing temperature, 1100 ºC, the highest temperature among the studied CBWs. The characterization of flakes corresponding to the amorphous material is more visible in CBWs B and C. The micrograph of the CBW-D (Fig. 4d) shows that the CBW-D also has slightly larger pseudo-hexagons that CBWs A and B, resulting in a smaller surface area. The CBW-D showed the lower value for surface area (31.80 m^2/g), than CBWs A and B.

3.3. Comparative analysis of potential of clay brick wastes for use as pozzolanic material

The pozzolanic activity of CBWs was measured in two ways: first, according to NBR 5752 (ABNT, 2012); after through the calcium hydroxide content in cement pastes with and without CBWs. The paste with lower contents of *CH* indicates that the CBW in this paste consumed more *CH*, improving the matrix with the formation of more *C-S-H* (calcium silicate hydrated).

3.3.1. Determination of pozzolanic activity rates of clay brick wastes

For a material be considered pozzolanic, a ratio, expressed as a percentage of compressive strength relative to the reference mortar should be greater than 75% according ASTM C618-19 (ASTM, 2019). The required water must be maximum 115%, also relative to the reference mortar. The CBW-A had 75% of pozzolanic activity. The pozzolanic activity measured for the CBW-B was 86%, the highest among the ceramic studied, even if the water is a little above the 115% limit. The pozzolanic activity measured for the CBW-C was 71% and the pozzolanic activity measured for the CBW-D was 69%. The minimum requirement to be considered pozzolanic material changed from 75 to 90% on NBR 12653 (ABNT, 2014) in the last update in 2014. All samples presented pozzolanic activity below that specified by NBR 12653 (ABNT, 2014). This may have happened because they are not pure clays but clayey ceramic masses that contain impurities such as quartz. The impurities have crystalline structure where no dehydroxylation occurs and thus does not contribute to generate amorphous material. The CBW-A and CBW-B can be considered pozzolanic materials according ASTM C618-19 (ASTM, 2019).

3.3.2. Determination of the calcium hydroxide consumption by clay brick wastes

Another way of measuring burnt clays pozzolanic activity is by quantification of calcium hydroxide (*CH*) present in cement and ceramic pastes. The amount of calcium hydroxide present may be calculated from the loss in mass peak between 450-600 ºC (corresponding to calcium hydroxide) in the curve of DTA/TG sample (Marsh, 2004 apud Fernandez et al., 2011). The Fig. 5a-e displays the curves DTA/TG of the pastes containing cement and CBW and the control paste, with only cement, after 14 days of curing.

Fig. 5a illustrates the thermal phenomena occurring, indicated in points (1) to (4), according to the literature (Barger et al., 2001; Bazaldúa-Medellín et al., 2015; Singh and Garg, 2006). The loss of mass that extends from 90-130 ºC, point (1) corresponds to the decomposition of *C-S-H* and ettringite. Between 180 and 200 ºC, point (2), occurs decomposition of tetracalcium aluminate hydrate (C_4AH_{13}). At about 470-500 ºC occurs the *CH* decomposition, point (3). The peaks were marked in Fig. 5 with an arrow. At peak between 750-800 ºC, point (4), there is the decomposition of calcium carbonate ($CaCO_3$). It can be seen that the greatest weight loss at peak between 450-600 ºC occurred in the control paste, as expected. Based on the results of DTA/TG, it was calculated the calcium hydroxide content in five pastes after 14 days of curing (Fig. 5f). The *CH* content was calculated relative to the initial mass of the cement sample (was not considered cement + clay brick waste, just the amount of cement). In all pastes with CBW, calcium hydroxide content was lower than that calculated for the control paste without CBW. Among the pastes with CBWs, the paste with the CBW-B had the lowest content of *CH* indicating that the CBW-B had the best performance and the CBW-C the highest content. Therefore, CBW-C had the worst performance.

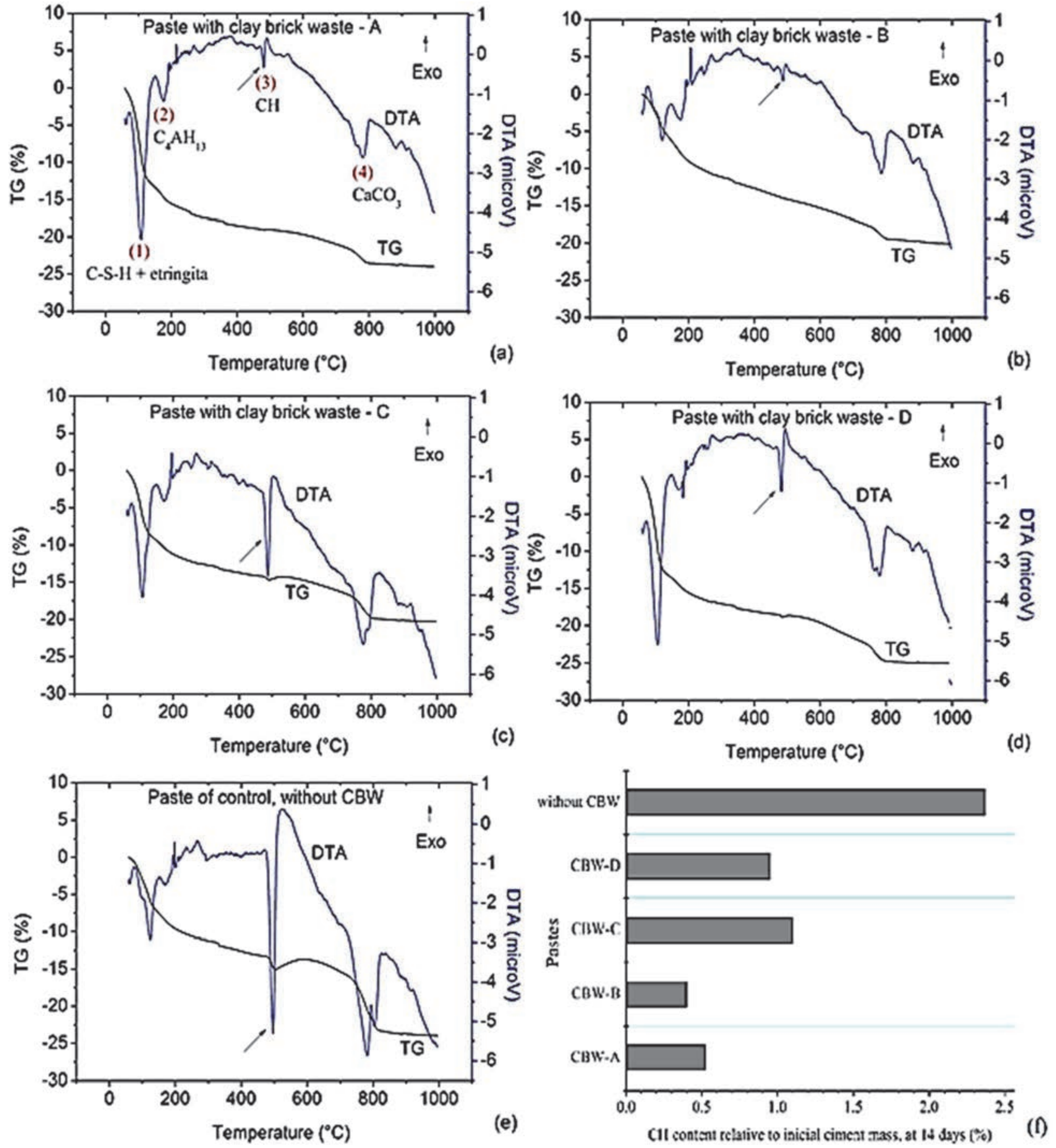


Fig. 5. Curves of DTA/TG analysis, after 14 days, of pastes with cement and CBW (a-d), of the paste of control (e), and calcium hydroxide content present in the pastes (f)

These results are consistent with the results for B.E.T. of CBWs (34.36 m^2/g for CBW-A, 35.16 m^2/g for CBW-B, 20.21 and 31.80 m^2/g for C and D). The CBW-C had the lowest surface area and the CBW-B, the biggest. The larger surface area of the CBW-B contributed to higher reactivity. All CBWs had significantly greater surface areas than the Portland cement CP-Z-II-32 (0.37 m^2/g), which certainly contributes to the pozzolanic effect of addition of CBW. The pozzolanic activity of natural clays has a significant correlation with the kaolinite content (metakaolin), with the inverse of the structural order and the specific surface of calcined clays (Tironi et al., 2011).The main factors influencing the pozzolanic action are the amorphous silica content and the distribution of particle sizes (Bolouri Bazaz and Khayati, 2012).

The CBW-C did not show good performance in consumer *CH* in pastes (remaining 1.10% of total cement paste). This may possibly be due to a higher crystallinity of the kaolinite in the ceramic mass before firing, or due to the fact that their firing was 1100 ºC, which certainly will have reduced the amount of amorphous material, or because the CBW-C has the lowest surface area (20.21 m^2/g) and the largest average particle size (9.83 µm). Comparatively, the CBW-B was fired at 800 ºC, it has an average particle size of less (6.04 µm) and higher surface area (35.16 m^2/g), and presented the best performance (remaining 0.40% of the total cement paste). The firing temperature influences the reactivity of the calcined clays, due to the different degree of crystalline material disorder (Cordeiro and Désir, 2010). The CBW-D showed low *CH* consumption (remaining 0.95% of total paste cement), which can be explained by a larger amount of impurities and small amount of kaolinite likely. The CBW-A showed *CH* consumption higher than the CBW-D (remaining 0.52% of cement paste). The CBW-A has a higher surface area than CBW-D. The control paste presented *CH* content of 2.37% of total cement paste.

The final qualitative rating, after chemical, mineralogical and microstructural analysis is shown in Table 5. The last column of Table 5 shows the sum of ”+” of each clay brick waste and classification. The rating order, the most suitable clay brick waste for use as a supplementary cementitious material to the least suitable was: CBW-B, CBW-A, CBW-D and CBW-C.

3.4. Properties and microstructure of mortar containing clay brick waste

The consistence index reduced, as expected, as the residue absorbs water from the mixture (Table 6). Even with the reduction of consistence (201 mm) the mortar can be considered workable. The compressive strength of the mortar with CBW practically doubled comparing to M0, from 2.45 to 5.65 MPa in 28 days, and from 5.72 to 10.39 MPa in 90 days.

The increase in compressive strength can be explained by the pozzolanic reaction. Calcium hydroxide, which is a product of the cement hydration reaction, reacts with the metakaolin particles to form the *C-S-H* phase. This phase is responsible for increasing the strength in the cementitious matrix. One possible reaction can be proposed to represent the phenomena (Eq. 3) (Siddique and Klaus, 2009).

$$Al_2O_3.(SiO_2)_2 + 6CaO.H_2O + 9H_2O \rightarrow (CaO)_4.Al_2O_3.(H_2O)_{13} + 2CaO.SiO_2.H_2O$$

$$AS_2 + 6CH + 9H \rightarrow C_4AH_{13} + 2CSH_1 \qquad (3)$$

3.4.1. XRD analysis of mortars

The phases (Fig. 6a) of mortar without CBW (M0) were α-quartz ($2\theta = 26.6°$), calcite ($CaCO_3$, $2\theta = 29.5°$), gibbsite ($Ca(SO_4)$, $2H_2O$, $2\theta = 20.7°$), brucite ($Mg(OH)_2$, 2θ = 38.0 º), calcium hydroxide ($Ca(OH)_2$, 2θ = 18.1, 47.25 and 50.90º) and the hydrated calcium silicate with crystalline predominance (*C-S-H*, 2θ = 28-29.8º) (Gameiro et al., 2012; Lin et al., 2010a; Serry et al., 1984). The mortars with CBW had very similar hydration products, as expected. The peaks for the *CH* do not appear for the M40 indicating their consumption by the reaction with the CBW. This resulted in the homogeneous and dense system and a considerable increase in resistance.

3.4.2. FTIR analysis of pastes

The pastes provide information similar to that of mortars. The presence of calcium hydroxide in the pastes without CBW (P0) can be confirmed by the band at 3642 cm^{-1} referring to the hydroxyl vibrations of *CH* (Shi et al., 2015) in the FTIR spectrum of Fig. 6b-c. It can be seen that the peak corresponding to calcium hydroxide does not appear in the paste P40, as expected.

Table 5. Performance summary of the main characteristics and qualitative classification of clay brick wastes

	Clay brick wastes				
	Average particle diametre	***Surface area B.E.T.***	***CH consumption***	***Pozzolanic activity***	***Classification by performance***
CBW-A	+++	++++	+++	+++	2º (13 +)
CBW-B	+++	++++	++++	++++	1º (15 +)
CBW-C	++	+	+	++	4º (6 +)
CBW-D	++++	+++	+	+	3º (9 +)

Table 6. Components (to prepare 2.5 litres), and properties of mortars

Mortar	***CBW (%)***	***W/C ratio (mass)***	***Consistence (mm)***	***Compressive strength 28 days (MPa)***	***Compressive strength 90 days (MPa)***
M0	0	2.50	285	2.45 ± 0.30	5.72 ± 0.48
M40	40	2.50	201	5.65 ± 0.81	10.39 ± 0.33
Mortar components	Cement (g)	CBW (g)	Lime (g)	Sand (g)	Water (g)
M0	394	-	409	3305	986
M40	205	136	450	3636	854

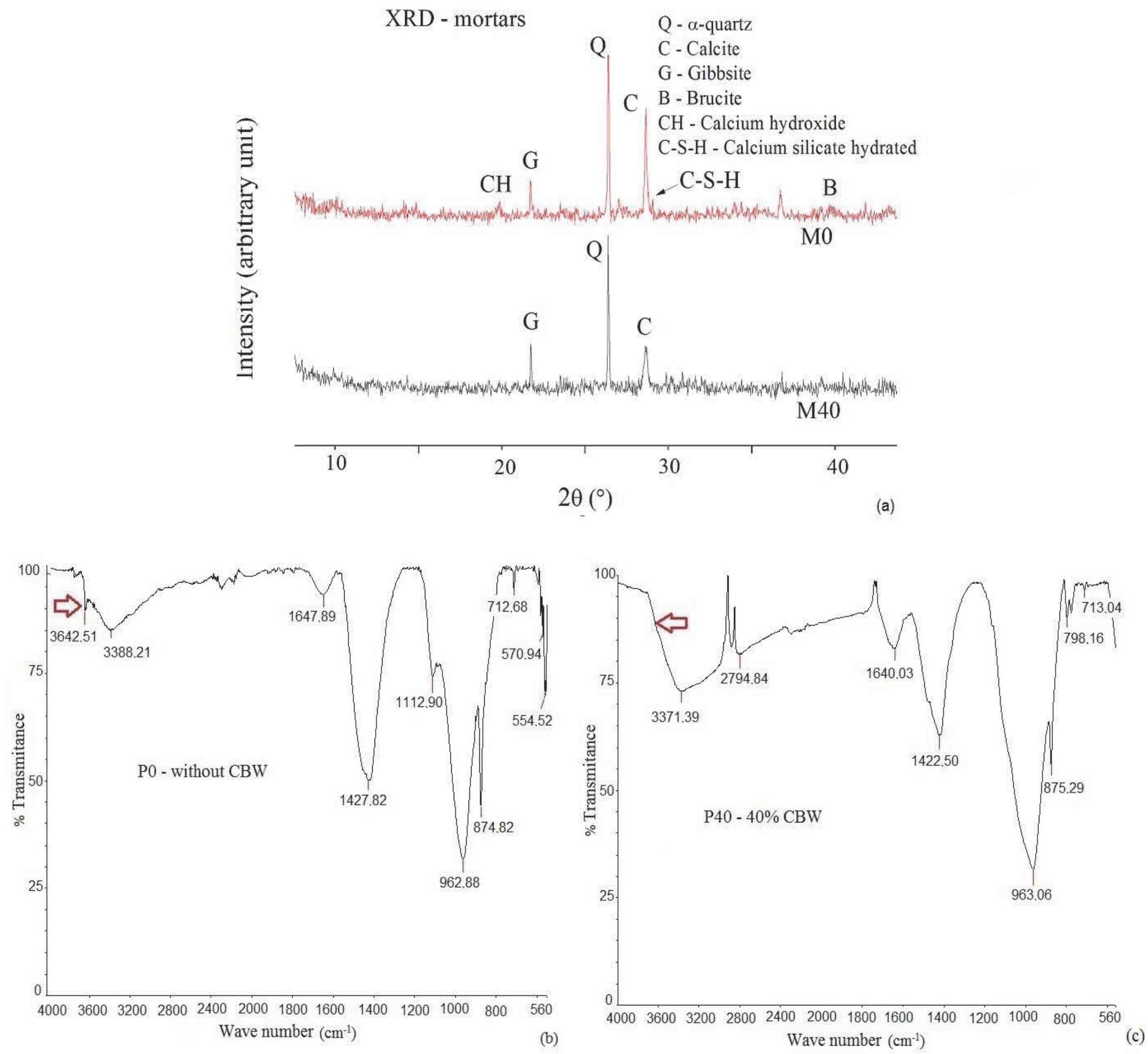


Fig. 6. X-ray diffractograms of mortar (a), and FTIR spectra in the range of 560-4000 cm^{-1} of pastes (b-c).

This result is further evidence of *CH* consumption by CBW. The bands at 713, 875 and 1428 cm^{-1} correspond to the calcite present. The band in the range of 950 to 1000 cm^{-1} refers to the vibrations of the *C-S-H*. The band at 1647 cm^{-1} can be attributed to *O-H* vibrations. And the band at 1112 cm^{-1} can be attributed to Si-O-Si vibrations (Somna et al., 2010).

4. Conclusions

The particulate clay brick waste from the ceramic industry B (CBW-B) can be deemed the most suitable for use as supplementary cementitious materials in mortars or concrete for construction. The higher burning temperature leads to a loss of potential of the waste for recycling as supplementary cementitious material. The CBW-A and CBW-B showed better pozzolanic reactivity, mainly because the firing temperature was adequate and did not present high K_2O and impurity content and showed higher kaolinite content. CBW-A and CBW-B presented the largest surface area and adequate morphology for higher pozzolanic reactivity. The CBWs A and D have little content of kaolinite, but the surface area results were higher than the CBW-C, which showed the smallest surface area. The main result to qualify the use of clay brick wastes as a supplementary cementitious material was certainly test evaluated the consumption of calcium hydroxide (*CH*). The final classification by performance may be considered as B, A, D and C. The CBW-B showed the highest consumption of calcium hydroxide in the cement pastes tested (remaining only 0.40% in the cement paste). The control paste presented *CH* content of 2.37%.

In the SEM images it was possible to verify the presence of amorphous material, such as metahalloysite and metakaolinite. In clays containing smaller amounts of kaolinite and large amounts of impurities such as quartz, calcite and muscovite, the heat treatment has much less influence on morphology. Only the CBW-A and CBW-B can be considered pozzolanic materials according ASTM C618-19. The compressive strength of the mortar with CBW (particle size < 45 μm) improved significantly (130.61% in 28 days and 81.64% in 90 days) comparing to reference mortar.

The use of CBW in partial replacement of Portland cement could result in an environmental gain by reducing CO_2 from cement production, by saving natural resources and by the use of a waste that would be discarded in nature.

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