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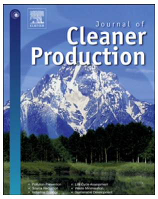

Incorporation of residues from the minero-metallurgical industry in the production of clay–lime brick

Welington L. Ferreira, Érica L. Reis*, Rosa M.F. Lima

Department of Mining Engineering, Federal University of Ouro Preto, Ouro Preto, MG, Brazil

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ABSTRACT

Industrial processes such as the extraction and processing of building and dimension stone and the manufacturing of ferroalloys generate large amounts of waste, which can cause environmental damage. Therefore, the development of new techniques for recycling and reusing industrial waste would be useful for minimizing the environmental impacts of these activities. This paper presents the incorporation of soapstone powder and Fe–Si–Mn slag in clay–lime brick as a partial substitution for agglomerate (lime) because these residues meet the standard specification for the chemical composition of a pozzolanic material. The results show that brick samples where 25% lime is substituted by waste residues achieved a compressive strength above 2.0 MPa, which is within the standard specification, after 28 days of curing (soapstone powder) or 60 days of curing (soapstone powder and Fe–Si–Mn slag). These materials were classified as class II, non-inert residues.

1. Introduction

The southeastern region of Brazil (the states of São Paulo, Minas Gerais, Rio de Janeiro and Espírito Santo) is the most developed region in the country and has intense mineral–metallurgical activity. Brazilian steel production totalled 35,162 Mt (Jesus, 2012) in 2011, and the state of Minas Gerais is responsible for 53.2% of all Brazilian mineral production (IBRAM, 2012).

The total recovery of dimension stone is very low. Gencel et al. (2012) reported that 20–30% of the marble block extracted in Turkey turns into dust during the cutting process. In Brazil, the total recovery of dimension stone in quartzite and soapstone quarries is approximately 30–40% per extracted volume (Rodrigues and Lima, 2012). It is common practice all over the world to dispose of the waste from dimension stone processing plants in landfills, which creates a high environmental impact.

In the steel industry, 0.7 to 1.7 t of slag is produced for each tonne of steel (WSA, 2013). In Fe–Si–Mn alloys, 0.9 to 2.2 t of slag is produced for each tonne of alloy (Olsen et al., 2007). For actual Brazilian steel production, 35,162 Mt (Jesus, 2012) of steel is produced along with 24,613.4 to 597,757.4 Mt of slag per year. In 2012, the Fe–Si–Mn alloy industry located in Ouro Preto, Minas Gerais produced 48,794.12 t of slag. Part of the produced slag is normally returned to the steel process; however, the majority must be stored.

Recycling has the potential to reduce the amount of waste disposed of in landfills and to preserve natural resources. Construction materials such as brick and concrete that contain waste materials can support construction sustainability and contribute to the development of civil engineering by reusing industrial waste, minimizing the consumption of natural resources and producing more efficient materials (Pelisser et al., 2011; Gencel et al., 2012, 2013). All of the above mentioned factors are important when the Brazilian habitation deficit is taken into account (Nascimento, 2007).

Clay–lime bricks are easy to manufacture and through processes that do not include burning, which avoids the environmental impacts associated with burning manufacturing processes (Figueiredo, 2011). Among other advantages, lime soil bricks reduce the usage of bedding mortar and coatings due to the quality and final appearance of the bricks, which are markedly superior to their counterparts. These advantages stem from the dimensional regularity and facial flatness of lime soil bricks compared to conventional ones. For this reason, lime soil bricks can be easily used in

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* Corresponding author. Departamento de Engenharia de Minas, Universidade Federal de Ouro Preto, Campus Universitário, Morro do Cruzeiro, S/N^{o}., CEP.: 35400-000, Ouro Preto, MG, Brazil. Tel.: +55 31 3559 1590; fax: +55 31 3559 1593.
E-mail addresses: erica@demin.ufop.br, ericalreis@hotmail.com (É.L. Reis).

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masonry, requiring only waterproofing and a finishing cover (Marino and Boschi, 1998).

In this paper, slag from Fe–Si–Mn alloy and soapstone powder produced by the alloy industry and soapstone quarries in the Ouro Preto region of Minas Gerais, Brazil, were used as partial replacements of lime for brick manufacturing. Their pozzolanic characteristics and the possibility to decrease the final price of produced bricks were evaluated in order to assess the bricks as building materials, especially for the poorest economic class of the population.

2. Materials and methods

2.1. Materials characterization

The following characteristics of the raw materials used to produce brick mixtures were previously characterized: particle-size distribution, qualitative mineralogical composition, chemical composition, density and specific surface area.

Particle-size analysis was performed by wet sieving (Tyler series–3360 to 37 μm). X-ray diffraction (total powder method) was used to identify the main minerals in slag, clay and lime. For this purpose, a diffractometer with Cu tube (PanAnalytical model Empyrean) was used. Diffraction data were collected from 2° to 72°. An ultrapycnometer (model 1200e, version 4.00) and BET (model 1200e) were used to determine the densities and specific surface areas of the raw materials, respectively. The run conditions of the ultrapycnometer were as follows: analysis temperature of 27.9 °C, target pressure of 19.0 psig, dry Helium gas, and a flow purge of 4 min (the final density was determined as the average of three determinations). The BET measurements were performed using a degasification time of 16 h at 200 °C. The determination was performed in a 30 ml/min nitrogen flux at a temperature of 77.3 K. The chemical compositions were analysed by inductively coupled plasma–optical emission spectroscopy (Spectro model Ciros/CCD). Loss on ignition was determined by gravity method. Clay Alteberg's limits were determined based on ABNT NBR 6459/84 and NBR 7180/84 standards.

2.2. Preparation of brick samples

Raw bricks were produced using one part agglomerate with 10 parts of brick clay (fraction size −4.8 mm in accordance with NBR 6457/86 standard). Clay–lime bricks (no added residue) and bricks with the addition of 25%, 50% and 75% slag from the manufacture of Fe–Si–Mn alloys or thin soapstone replacing part the lime. The amount of added water was determined based on the standard practice of the NBR 7182/86 standard, which specifies the optimum humidity. Table 1 presents the brick mixture generated from the raw materials.

Table 1
The brick mixture prepared from the raw materials.

Sample	Agglomerate			Clay – 4.8 mm	Humidity (%)
	Lime	Soapstone powder	Fe–Si–Mn slag		
RF	1	–	–	10	22
ST1	0.75	0.25	–	10	21
ST2	0.50	0.50	–	10	20.5
ST3	0.75	0.25	–	10	20.0
SL1	0.75	–	0.25	10	21.0
SL2	0.50	–	0.50	10	20.5
SL3	0.25	–	0.75	10	20.0

Obs.: RF – reference; ST – soapstone; SL – slag.

A hydraulic press (Nowak model PM 15 TON) was used to make the cylinder bricks, which were 5.00 × 10.0 cm in size. Fig. 1 depicts the process of brick confection: In the first step, the brick mixture was introduced into a sample holder and then pressed with a pressure of 2.5 MPa (Fig. 1a). After pressing, the excess material was removed, and the brick was finally removed from the sample holder (Fig. 1b). The bricks produced were introduced into a humidity chamber (EQUILAM, model SS600UMe) at a temperature of 23 ± 2 °C and a relative humidity ≥95% in accordance with the standard procedure of confection and cure-cylinder bricks (NBR 12024/92) for 28 and 60 d.

2.3. Characterization of brick samples

After the 28- and 60-day cure periods in the humidity chamber, the physical and mechanical properties of sample bricks, such as water-absorption values and compressive strength, were determined in accordance with the procedure of the NBR 8492/92 standard. For compressive strength, a press (TIME GROUP trademark model YAW-2000D) with a press strength of 500 N (50 kgf/s) was used.

Solid-residue classification was performed with bricks of lime–residue–clay, which yielded better results in terms of physical and mechanical properties, in accordance with the NBR 10.004/04 standard. Both the leaching and solubilized extracts of solid residues were analysed in accordance with the ABNT NBR 10005/04 and NBR 10006/04 standards.

3. Results

3.1. Characterization of raw materials

Fig. 2 presents the size distributions of the raw materials used (clay, soapstone powder and Fe–Si–Mn slag). As can be observed by the size distribution, the soapstone powder (~50% −37 μm) was finer than the clay (~25% −37 μm) followed by the Fe–Si–Mn slag (~3% −37 μm).

Figs. 3–6 show the X-ray powder diffraction patterns of the clay, lime, soapstone powder and Fe–Si–Mn slag. The identified minerals in the clay sample were quartz (SiO_2), kaolinite ($SiO_2Al_2O_5(OH)_4$) and muscovite ($KAl_2(Si_3Al)O_{10}(OH)_2$). The lime sample contained the phases portlandite ($Ca(OH)_2$), calcite ($CaCO_3$) and nacrite ($Al_2Si_2O_5(OH)_4$). In the Fe–Si–Mn slag sample, only the enstantite phase ($Mg_2Si_2O_6$) was identified. The identified minerals in the soapstone sample were talc ($Mg_3Si_4O_{10}(OH)_2$) and chlorite ($H_{16}\ Al_{2.78}\ Fe_{0.94}\ Mg_{11.06}\ O_{36}\ Si_{5.22}$), which is in accordance with Rodrigues and Lima (2012).

Table 2 depicts the physical properties of the raw material. The specific surface area of the clay sample was the highest, followed by the specific surface area of the lime sample. This result is likely related to the sample porosities and the presence of kaolinite in these samples (Figs. 3 and 4) as opposed to the size distribution (Fig. 2) since the soapstone powder was finer than other samples. The low humidity of soapstone compared with the other samples could be related to its natural hydrophobicity. The density of the materials varied from 2.45 g/cm^3 (lime) to 3.22 g/cm^3 (Fe–Si–Mn slag).

The chemical composition and loss on ignition (LOI) of the raw materials are presented in Table 3. The chemical composition of all analysed samples are in accordance with the main minerals identified in the diffraction patterns presented in Figs. 2 to 5. The higher LOI value of lime sample compared with the other raw samples is related to the carbonate (calcite) and hydroxide phases (portlandite and nacrite).

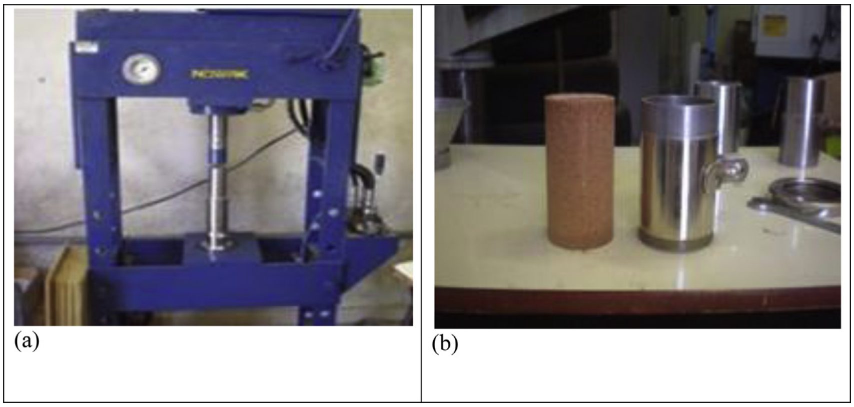

Fig. 1. Production of cylinder bricks: a) Material compaction by a hydraulic press at 2.5 MPa and b) brick removal from the sample holder.

Table 4 compares the pozzolanic material's chemical specifications with the chemical compositions of wastes (soapstone powder and Fe–Si–Mn slag). Both of the analysed wastes have chemical compositions in accordance with E class pozzolanic materials (NBR 12653/92). Therefore, it is possible to replace part of the lime in the clay–lime brick mixture.

Atterberg indices: The liquidity limit and plasticity index of the clay samples were, respectively, 43.5% and 14.7%. These values are in accordance with the specifications for clay–cement bricks (NBR 10832/89), which have limits on the maximum liquidity limit and plasticity index of 45% and 18%, respectively. In accordance with *The Unified Soil Classification Syst*em–USCS, this sample can be classified as ML (silt), which is described as inorganic silts and very-fine sand, rock alteration, fine silt or clay sand.

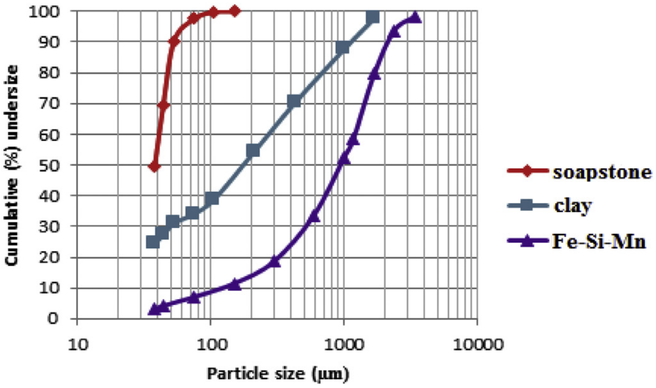

Fig. 2. Size distributions of raw materials.

3.2. Characterization of sample bricks

Table 5 presents the water absorption of brick samples after 28 and 60 days of curing in the humidity chamber at the standard specification. The water absorption for all bricks was within the standard specification (≤20%). As reported by Mahllawy (2008), the water absorption is related to the material resistance when the bricks are exposed to the environment.

Table 6 depicts the compressive strength of the produced bricks compared to the standard value (NBR 8492/84). In general, the compressive strengths of all clay–lime–soapstone bricks were higher than that of clay–lime–Fe–Si–Mn slag, which could be attributed to the finer size distribution (Fig. 2) and higher specific surface area of soapstone powder compared to Fe–Si–Mn slag (Table 2) because a higher contact area can increase the pozzolanic activity. The samples RF (clay–lime) and ST1 (25% substitution of lime by soapstone powder) achieved compressive strengths within the standard value after a 28-day curing period. The sample bricks SL1 (25% lime substitution by Fe–Si–Mn slag) demonstrated a compressive strength within the standard value after a 60-day

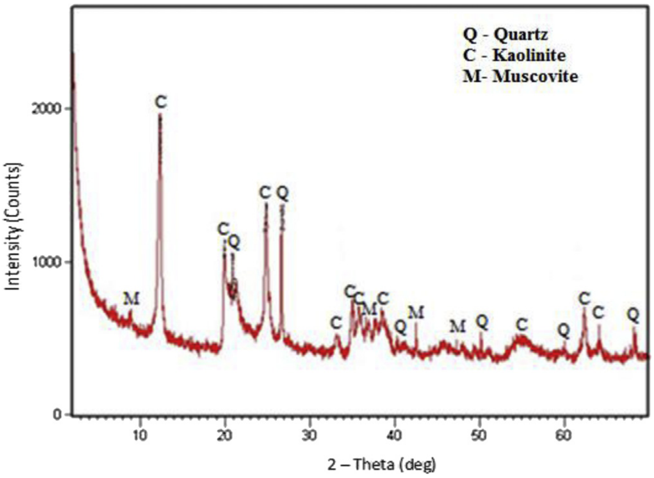

Fig. 3. X-ray powder diffraction pattern of the clay.

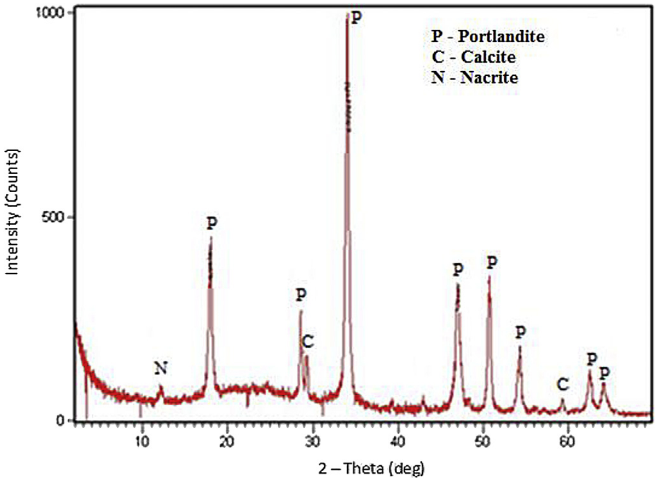

Fig. 4. X-ray powder diffraction pattern of the lime.

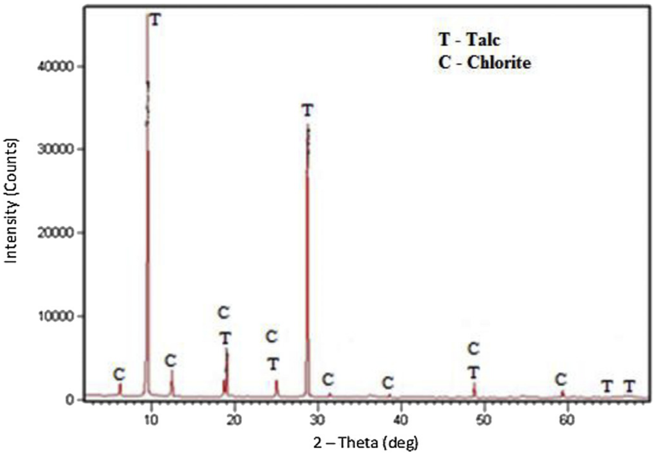

Fig. 5. X-ray powder diffraction pattern of the soapstone powder.

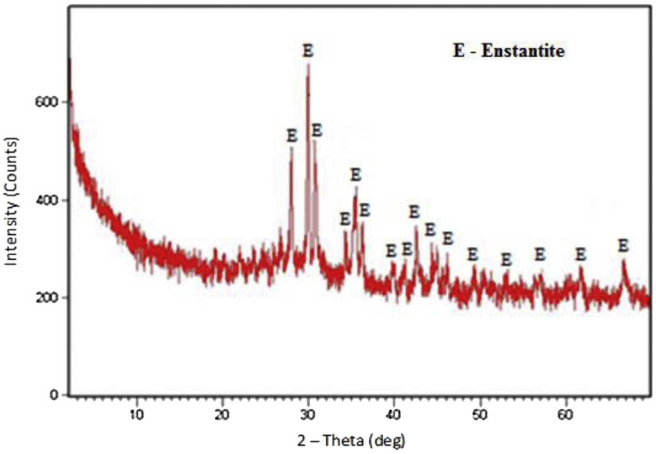

Fig. 6. X-ray powder diffraction pattern of the Fe–Si–Mn slag.

Table 2
Physical properties of the raw materials.

Sample	Specific surface area (m^2/g)	Density (g/cm^3)	Porosity (%)	Humidity (%)
Clay	32.414	2.593	1.6	12.530
Lime	11.540	2.450	0.6	0.610
Fe–Si–Mn slag	1.560	3.220	0.3	0.170
Soapstone powder	3.430	2.960	0.2	0.340

Table 3
Chemical composition and loss on ignition (LOI) of raw materials.

Grade/compound		Clay	Lime	Soapstone powder (Rodrigues and Lima (2012)	Fe–Si–Mn slag
Wt.%	SiO_2	62.62	29.99	58.91	36.57
	MnO	–	–	0.04	21.72
	Al_2O_3	28.91	0.29	2.30	15.04
	Fe_2O_3	5.96	0.11	4.99	3.56
	TiO_2	1.48	–	–	–
	K_2O	0.64	–	–	1.44
	MgO	0.14	0.92	27.80	7.66
	CaO		67.21	0.07	11.33
	SO_3	–	–	0.96	1.15
	LOI	12.0	27.1	5.1	–
ppm	Zn	36.70	7.61	–	10.96
	As	5,38	5.56	3.32	9.75
	Cu	–	–	16.93	–

Table 4
The chemical specification of pozzolanic materials of E class (NBR 12653/92) compared with the chemical compositions of wastes (soapstone powder and Fe–Si–Mn slag).

Chemical composition	E class (NBR 12653/92)	Soapstone powder	Fe–Si–Mn slag
$SiO_2 + Al_2O_3 + Fe_2O_3$, minimum Wt.%	50	66.2	55.17
SO_3, maximum Wt %	5.0	0.96	1.15
Humidity, maximum Wt. %	3.0	0.34	0.17
LOI, maximum Wt.%	6.0	5.05	–
Free alkalis as Na_2O, maximum Wt.%	1.5	0.03	0.74

Table 5
Water absorption of sample bricks and standard deviation compared with the standard specification.

Sample brick	Water absorption (wt. %)	
	28 d	60 d
NBR 8492/84 standard	≤20	≤20
RF	19.11 ± 0.16	19.25 ± 0.11
ST1	19.01 ± 0.37	19.32 ± 0.25
ST2	19.68 ± 0.53	19.37 ± 0.18
ST3	19.77 ± 0.52	19.23 ± 1.19
SL1	19.38 ± 0.60	19.17 ± 1.65
SL2	19.68 ± 0.48	19.45 ± 1.01
SL3	19.92 ± 0.12	19.52 ± 0.94

Obs.: RF – reference; ST – soapstone; SL – slag.

curing period. However, as known, pozzolanic cementation is a slow and progressive process that can take months or years to complete. Thus, the compressive strength of the bricks will likely increase with the curing time for all samples.

Based on the results presented in Table 6 and on previous discussions, it is possible to conclude that the amount of $Ca(OH)_2$ was sufficient for pozzolanic reaction only up to 25% lime replacement by both tested residues (soapstone or Fe–Si–Mn slag) because the obtained values of the evaluated parameters were similar to those measured in standard clay–lime (10:1) bricks.

The partial replacement of lime, which is most expensive component in the brick mixture, by soapstone powder and Fe–Si–Mn slag in clay–lime brick manufacturing could be useful in the Ouro Preto region because waste material is readily available and its use could decrease the final cost of the brick, providing both environmental and economic advantages.

Table 7 depicts the chemical composition of the brick leaching products, which possessed characteristics within the water absorption and compressive-strength standards (ST1 after 28- and 60-day curing times and SL1 after a 60 day of curing). The elements

Table 6
Compressive strength of brick samples after 28- and 60-day cure periods and standard deviation compared with the standard specification.

Sample brick	Compressive strength (MPa)	
	28 d	60 d
NBR 8492/84 standard	≥2.0	≥2.0
RF	2.10 ± 0.00	2.50 ± 0.01
ST1	2.10 ± 0.02	2.20 ± 0.03
ST2	1.94 ± 0.01	1.65 ± 0.08
ST3	0.64 ± 0.36	1.10 ± 0.01
SL1	1.73 ± 0.11	2.10 ± 0.01
SL2	1.53 ± 0.04	1.30 ± 0.01
SL3	0.63 ± 0.01	0.74 ± 0.06

Obs.: RF – reference; ST – soapstone; SL – slag.

Table 7
Chemical composition of the brick leaching products.

Brick sample	Content of chemical elements (mg/L)				
	As	Ba	Cd	Cr	Pb
Standard (maximum value) (ABNT 10004/04)	1.0	70.0	0.5	5.0	1.0
L28ST1	<0.004	0.085	<0.009	0.061	<0.026
L60ST1	<0.004	0.093	<0.009	0.058	<0.026
L60SL25	<0.004	0.199	<0.009	0.047	<0.026

Obs.: L28 – leaching product after 28 d cure time; L60 – leaching product after 60 d cure time; ST – soapstone; SL – slag.

Table 8
Chemical composition of the brick solubilised products.

Chemical element (mg/L)	Brick sample			
	Standard (maximum value) (ABNT 10004/04)	S28ST1	S60ST1	S60SL1
Al	0.20	26.1	22.19	28.20
As	0.01	<0.040	<0.040	<0.040
Ba	0.07	<0.001	<0.001	<0.001
Cd	0.005	<0.009	<0.009	<0.009
Cr	0.05	0.02	0.024	0.022
Cu	2.0	<0.007	<0.007	<0.007
Fe	0.3	0.981	1.075	1.399
Na	200.0	0.343	0.352	0.372
Pb	0.001	<0.026	<0.026	<0.026
Zn	5.0	<0.003	<0.003	<0.003
Mn	0.01	<0.001	<0.001	<0.001

Obs.: S28 – solubilized product after 28 d cure time; S60 – solubilized product after 60d cure time; ST – soapstone; SL – slag.

Hg, Se, Ag and fluoride were not analysed because these elements are not present in any brick mixture (Table 3). The chemical analysis, performed in accordance with the standard specification (Table 7), indicated that the sample brick residues can be classified as not-dangerous residues (residues of class II).

Table 8 presents the chemical compositions of the solubilised brick products. The compositions of the solubilised products were within the water absorption and compressive-strength standards (ST1 after 28- and 60-day curing times and SL1 after a 60 day of curing). Based on the chemical compositions presented in Table 8, both wastes can be classified class II, non-inert residues.

Table 9 summarizes the qualification parameters given by the Brazilian Technical Standards for unfired clay–lime and the clay–soapstone or Fe–Si–Mn slag residues–lime bricks tested in this work. The results of using building waste as pozzolanic agents in soil–lime bricks (Patrício et al., 2013) and grit waste from the cellulose industry as a partial replacement of Portland cement in soil–Portland cement bricks (Siqueira and Holanda, 2013) are also presented.

Table 9
Comparison of unfired bricks produced in this study and by other researchers.

Brick kinds	In this study		RF	Patricio et al. (2013)	Siqueira and Holanda (2013)
Composition of brick	Clay-lime-soapstone	Clay-lime-Fe-Si-Mn slag	Clay-lime	Soil-lime-building waste	Soil-cement-grits waste
Compressive strength (MPa)	2.20	2.10	2.50	2.26	5.55
Water absorption (%)	19.35	19.17	19.5	13.5	17.5
Cure (d)	60	60	60	90	28
% weight replaced by waste	25	25	0	25	20

As can be observed in Table 9, the compressive strengths of the bricks incorporating both studied wastes in this work were similar to that of demolition waste bricks for the same weight % of lime replaced by waste (25 wt.%). The water absorption values determined in this study were higher than the demolition waste brick. However, the curing time of the bricks manufactured with demolition waste was 50% higher than that of the bricks with soapstone powder and Fe–Si–Mn slag. The smaller compressive strengths and higher water absorptions of the studied waste bricks in this work compared to bricks of soil–Portland cement–waste grit may be explained by the use of cement and the smaller proportion (20 wt.%) of grit waste in this brick mixture despite the shorter curing time (28 d).

Based on current prices of Portland cement, lime, transportation and energy in Minas Gerais, Brazil, the cost to prepare one tonne of unfired brick mixture of soil–Portland cement and soil–lime (10:1), 25 wt.% replacement of lime by soapstone powder or Fe–Si–Mn are of $39.11 USD $33.33 and $25.33, respectively. This means that the cost of soil–lime and soil–studied wastes–lime mixtures are 17% and 32% lower compared with the soil–cement mixture, and the cost of the soil–studied wastes–lime mixture is 25% lower than the soil–lime mixture.

4. Conclusions

Based on this investigation of soapstone powder and Fe–Si–Mn slag, it was concluded that both wastes have chemical compositions useful for pozzolanic activities. The pressure strength of the bricks' clay–lime–residue (10:0.75:0.25) after 28- and 60-day cure times were within standard specifications (>2.0 MPa) for soapstone powder. For Fe–Si–Mn slag, this specification was achieved only after a 60 day of curing. In accordance with the leaching and solubilised products from sample bricks, which achieved pressure strength within the standard specification (≥2.0 MPa), both residues can be classified as class II residues, not inert.

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