



Mortar with refractory waste for passive fire protection

Resíduos refratários para argamassa para proteção passiva contra incêndio


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Abstract

Passive fire protection (PFP) is a field of study applied to the civil construction industry. Refractory brick waste contains elements that can contribute to the properties necessary for PFP. Therefore, this study developed a mortar with refractory brick waste for use as PFP. The authors proposed four formulations with compressive and flexural strength, bulk density and apparent porosity, thermal conductivity, and linear variation that were evaluated before and after heat treatment at 600 °C and 1100 °C. The density did not show significant differences between the formulations. The porosity increased after the heat treatment. The mixture that showed the highest shrinkage at 1100 °C was the one with the highest gypsum content, and all the other ones had shrinkage values lower than the maximum allowed by the C195 standard. The mixture that used the highest amount of gypsum was the one that obtained the lowest thermal conductivity. Therefore, it is concluded that using refractory waste is viable for the development of PFP mortars because they meet the regulatory requirements.

Keywords: Refractory waste. Recycled raw materials. Passive protection. Fire.

Resumo

A proteção passiva contra incêndio (PPCI) é um campo de estudo aplicado à indústria da construção civil. Os resíduos de tijolos refratários contêm elementos que podem contribuir para as propriedades necessárias à PPCI. Diante disso, o trabalho desenvolveu uma argamassa com resíduos de tijolos refratários para utilização como PPCI. As 4 formulações propostas tiveram a resistência à compressão e flexão, densidade e porosidade aparente, condutividade térmica e variação linear avaliadas antes e após tratamento térmico a 600 °C e a 1100 °C. A densidade não apresentou significativas diferenças entre as formulações. A porosidade aumentou após o tratamento térmico. A mistura que apresentou maior contração a 1100 °C foi aquela com maior teor de gesso e todas as demais apresentaram valores de contração menores que o máximo permitido pela C195. A proporção que utilizou maior quantidade de gesso foi a que obteve a menor condutividade térmica. Portanto, conclui-se que a utilização do resíduo refratário é viável para PPCI, uma vez que atendem aos requisitos normativos.

Palavras-chave: Resíduos refratários. Matérias-primas recicladas. Proteção passiva. Incêndios.

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Introduction

The purpose of passive fire protection (PFP) is to keep the ambient temperature below the critical temperature and contain the fire at the place of origin for a limited period of time (MRÓZ; HAGER; KORNIEJENKO, 2016). One way to obtain a material that provides this protection is to add substances to the formulation that can absorb heat when the temperature of the material increases. Gypsum is frequently used for this purpose because of its endothermic capacity (CIUDAD *et al.*, 2011). However, materials that are based on this compound usually have low strength due to their high water consumption to improve workability. To solve this problem, other components are added to the gypsum, such as vermiculite, mica and alumina (MARTIAS; JOLIFF; FAVOTTO, 2014). One type of material containing these components is refractory waste. Refractory wastes are post-mortem materials; i.e., they still have the potential to be applied in categories less noble than the ones from their initial processes (DA SILVA; BRAGANÇA, 2012). Worldwide refractory production is very high, approximately 35 to 40 million tons per year (HORCKMANS *et al.*, 2019), consequently leading to a very large amount of refractory waste, approximately 28 million tons per year (COPPOLA *et al.*, 2020).

PFP materials must have low density, low thermal conductivity and adequate strength. Among the various types of PFP materials, hydrated cementitious materials stand out. Hydrated cementitious materials, such as mortars and concretes, have free water in their pores and hydrated crystals, so they contain a large amount of bound water. This water contributes to slow down the fire process. In addition, the decomposition processes of portlandite and calcium silicate hydrate (CSH) are endothermic, and thus contribute to the reduction of temperature in the event of a fire (MRÓZ; HAGER; KORNIEJENKO, 2016). Therefore, the work developed cementitious composites with refractory waste. For this purpose, the waste was chemically and physically characterized, and four different ratios of refractory waste were tested. The composites with different rates of refractory waste were subjected to tests of compressive strength, bulk density, thermal conductivity and linear variation.

Materials and methods

Silica-alumina refractory waste was physically, chemically and mineralogically characterised. Physical characterisation included particle size tests (ABNT, 2015a), loss on ignition, density and moisture. The loss on ignition was determined gravimetrically using a muffle furnace. The result was obtained by the difference in mass of a 1 g sample at room temperature and the mass of that sample after calcination at 1100 °C for 1 h. The density was determined using the Archimedes principle. First, the temperature of the water used in the test (approximately 23 °C) was recorded. Afterwards, the empty pycnometer was weighed (m_1) and then approximately 4 g of the sample was weighed in a beaker (m_2). Posteriorly, the pycnometer was filled with water, dried on the outside with soft paper and weighed (m_3). After that, the sample was transferred to an empty pycnometer with a funnel. Then, the pycnometer with the sample was filled with water and dried and weighed (m_4). The density was calculated using Equations 1 and 2:

$$v = \frac{m_4 - m_3}{d_w} \quad \text{Eq. 1}$$

$$d = \frac{m_2}{v} \quad \text{Eq. 2}$$

Where:

v is the volume of the sample;

m_4 is the weight of pycnometer with water and the sample;

m_3 is the weight of the pycnometer full of water;

m_2 is the sample's weight;

d_w is the water density; and

d is the density of the sample.

Moisture was measured by Mettler Toledo Moisture Analysis HB43 at a temperature of 110 °C with 5 g of sample.

The chemical composition was determined using a sample that was grounded inside a tungsten

capsule in a Shatter-Box mill until a particle size less than 75 μm was obtained, melted in platinum crucibles and later moulded into the test pellet by means of Magic Pro PW254 Philips equipment. The chemical and physical characterisation of the refractory waste is shown in Table 1. According to the particle size analysis shown, the waste can be classified as a small aggregate, according to NBR 7211 (ABNT, 2005); however, the material was slightly finely ground because 90% of the fractions were below 600 μm ; thus, the smaller particle size implies a greater specific surface of the material, which favours reactivity (JUENGER; SIDDIQUE, 2015), but requires more mixing water (GHAFARI *et al.*, 2014). The waste had values of density, loss on ignition, and moisture of 3.20 g/cm^3 , 2.36% and 0.35%, respectively. The chemical analysis indicated the presence of the following chemical elements: aluminium, silicon, iron and manganese.

The mineralogical characterisation was performed using a Philips X'Pert MPD diffractometer with a scan range of 5 to 65°, a gradual advance of 0.05° in each 1 s interval, a 40 mA current in the filament and an electron acceleration voltage of 40 kV. The diffractogram was analysed using a demo version of Match! and the Crystallography Open Database (Revision 204654 from January 2018). Peaks of mullite - $3(\text{Al}_2\text{O}_3) \cdot 2(\text{SiO}_2)$ (code 9001567), periclase - MgO (code 9006747), magnetite - Fe_3O_4 (code 9002327), corundum - Al_2O_3 (code 9007496), quartz - SiO_2 (code 9005019), cristobalite - SiO_2 (code 1010954) and lime - CaO (code 9006744) were identified in the analysis of the diffractogram (Figure 1).

To develop the mortar for passive protection, four compositions were tested, which are presented in Table 2. Sodium citrate was added to increase the workability of the mixtures. The mortars were prepared using a mechanical mixer, manually compacted into 40 x 40 x 160 mm^3 moulds and vibrated on a vibrating table. In the fresh state, the mortars were subjected to setting time tests (ABNT, 2015b) and a normal consistency (ABNT, 2015b). The test specimens remained in the moulds during the first 24 h of curing and were removed from the moulds after this period and left in contact with air until the date of the assays. After 28 days, some of the samples were heated at a rate of 100 °C/h to 600 °C and 1100 °C for 5 h. Afterwards, assays were performed to evaluate the properties of specimens before and after heating.

Table 1 - Chemical and physical characterisation of the refractory waste

Chemical composition by XRF (wt%)	
SiO_2	25.23
Al_2O_3	49.90
Fe_2O_3	10.03
CaO	1.74
MgO	9.31
P_2O_5	0.13
Na_2O	0.30
K_2O	0.28
TiO_2	2.30
Cr_2O_3	0.23
MnO	0.35
ZrO_2	0.09
Loss on ignition (%)	2.36
Moisture (%)	0.35
Particle density (g/cm^3)	3.20
Particle size distribution	
D_{10} (μm)	45
D_{50} (μm)	125
D_{90} (μm)	600

Figure 1 - Diffractogram of the refractory waste

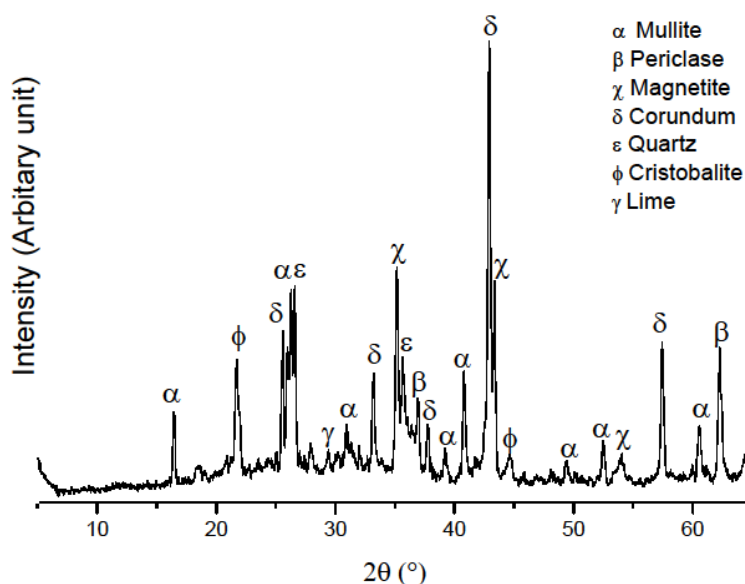


Table 2 - Composition of the mortars

Material	A	B	C	D
	% by weight			
Clay	3.93	5.32	3.43	3.43
Aluminous cement	0.00	10.64	11.43	0.00
Portland cement	0.00	0.00	0.00	11.43
Sodium citrate	0.03	0.03	0.03	0.03
Newspaper scrap	3.27	2.66	2.86	2.86
Vermiculite	3.93	5.32	3.43	3.43
Refractory waste	16.36	26.59	21.71	21.72
Microsilica	0.65	0.53	0.57	0.57
Gypsum	37.29	2.13	13.71	13.72
Water	34.54	46.80	42.84	42.81

The bulk density and apparent porosity were determined according to ABNT (2017) standards, and the flexural strength and compressive strength tests were performed at 28 days in a 100 t Kratos hydraulic press, model 100 ECC – 100 MP, with a load rate of 800 N/s, according to ABNT (2010). Linear variation was evaluated in thermally treated samples according to ABNT (2013). The elastic modulus was determined using the ultrasound technique (AMERICAN..., 1996) in bar-shaped specimens measuring 40 x 40 x 160 mm³, which were cured for 28 days. For this assay, James Instruments Ultrapulse C8901 "V" Meter 150 KHz ultrasound equipment was used.

Results

Refractory waste showed low moisture, equal to 0.35%, therefore, possibly this material does not have a high moisture absorption rate from the environment. This low level of moisture presented by the waste has little effect on its density and reduces the formation of hydrated oxides at room temperature. The waste density, 3.02 g/cm³, is within the range of 2.1 and 3.3 g/cm³, which is considered suitable for refractory materials (SMITH; HASHEMI, 2010). The density is related to the thermal conductivity, since the higher the density, the greater the thermal conductivity (CARABBA *et al.*, 2019). The waste refractory also showed low loss on ignition, which leads us to believe that it has considerable thermal stability and little presence of organic matter. Peaks of mullite - 3(Al₂O₃).2(SiO₂) (code 9001567), corundum - Al₂O₃ (code 9007496), and lime - CaO (code 9006744) were identified by analysing the diffractogram (Figure 2), maintaining consistency with the raw materials used.

Regarding the properties in the fresh state, Table 3 presents the results for the setting time, consistency and

adherence. All formulations exhibited a setting time less than 150 min (ABNT, 2015b). The faster setting time occurred for mixture A due to the high percentage of gypsum added to it, which contributed to the rapid formation of hydrated crystals (CARVALHO *et al.*, 2008). It can be observed that even the mixture A presenting a setting time shorter than the others, when analysing the consistency, all mortars presented approximate values, that is, the material presents initial workability similar to the others. This could be explaining for the sodium citrate presence in all formulations with the same proportion. The sodium citrate influences the workability of calcium sulfate cements due to the increase of citrate ions in the cement hydration solution (DIMA *et al.*, 2019). Sodium citrate can also improve the compressive strength as it forms a denser structure (QI, 2011). Bearing in mind that the application time would be shorter, in view of the setting time inferior to the others, an interesting use of the material of the A formulation could be given with the projected mortar method, in which the water insertion would be directly in the application nozzle. Therefore, more rapid hardening is required to guarantee adherence to the substrate. Regarding the consistency, all mortars had approximate values.

The physical and mechanical properties of the mortars are presented in Table 4. Compositions A and C obtained better results of compressive and flexural strength. This performance could be explained in the A composition by the high presence of gypsum, which is considered a fire resistant material and in the C composition for the presence of aluminous cement. Formulation B obtained lower results due to the higher percentage of water added (ABRAMS, 1925) and the low presence of gypsum. However, the compressive strength of all mortars meets General Services Administration AIA/SC/GSA/07811 (> 0.0359 MPa), even after heating at 600 and 1100 °C. Regarding the elastic modulus, it can be noted that compositions A and C had the highest values, accompanied by the highest strength, among the compositions evaluated. Regarding bulk density, they met the requirements of General Services Administration AIA/SC/GSA/07811 ($> 0,240$ g/cm³) and showed no significant differences between the formulations. This can be attributed to the addition of equal percentages of the raw materials, which would most likely alter the density of the structure. For the tests performed after heat treatment, there was a considerable loss of strength. This can be attributed to the thermal expansion that occurs in the cement paste, causing cracks in the microstructure of the material (COSTA; FIGUEIREDO; SILVA, 2002). As observed, 1100 °C was insufficient for the sintering effect to be higher than the expansions in the four compositions tested (MILANEZ *et al.*, 2010). In the density parameters, there were no major changes in the results between the heated and unheated structures. Regarding porosity, there was a considerable increase in pores in all compositions, possibly due to the dehydration of the specimens during burning (COSTA; FIGUEIREDO; SILVA, 2002) and growth of cracks. Composition A had the highest shrinkage at 1100°C, and the behaviour of the other compositions was very similar to each other, ranging from approximately 1% to 2% at 600 °C and between 2% and 3% at 1100 °C. The mortars showed shrinkage smaller than international standards, except the mortar A which contents the higher gypsum content (AMERICAN..., 2013). The volume variation of cemented composites is expected. At temperatures up to 100 °C, there is evaporation of the free water present in the mortar. After this temperature, the paste itself shrinks due to the loss of water contained in the material structure. Between 600 °C and 800 °C, shrinkage occurs due to the decomposition of cement hydration products (COSTA; FIGUEIREDO; SILVA, 2002). In addition, the contraction may be associated with the presence of gypsum, as the greatest contractions occur in the traces with greater presence of this constituent. This is due to the intrinsic moisture of the gypsum because approximately 20% of the hydrated gypsum corresponds to the chemically bound water (MRÓZ; HAGER; KORNIEJENKO, 2016).

Figure 2 - Diffractogram of the mortars

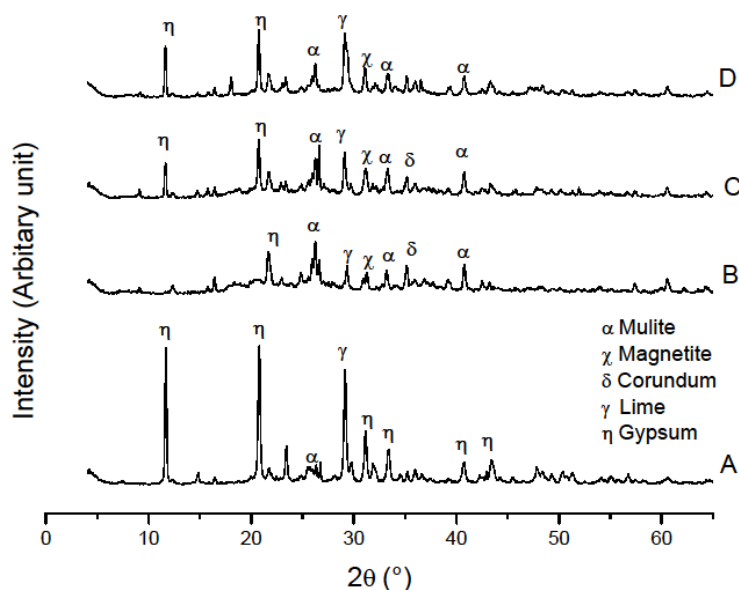


Table 3 - Characteristics in the fresh state

	A	B	C	D
Setting time (min)	25	80	105	120
Consistency (mm)	125	121	134	128

Table 4 - Properties of mortars

Condition	Properties	Mortar			
		A	B	C	D
20°C	Bulk density (g/cm ³)	1.16	0.85	0.96	0.88
	Apparent porosity (%)	47.3	63.90	55.30	61.30
	Compressive strength (MPa)	4.73	1.10	4.46	2.04
	Flexural strength (MPa)	2.40	0.70	2.20	1.20
	Elastic modulus (GPa)	2.71	0.62	1.56	1.14
600°C	Bulk density (g / cm ³)	1.00	0.80	0.80	0.80
	Apparent porosity (%)	64.10	71.60	70.80	70.30
	Compressive strength (MPa)	0.40	0.30	0.30	0.20
	Flexural strength (MPa)	0.90	0.30	1.00	0.30
1000°C	Linear variation (%)	-1.40	-1.50	-1.60	-1.60
	Bulk density (g / cm ³)	1.10	0.80	0.80	0.80
	Apparent porosity (%)	62.80	72.40	70.90	70.40
	Compressive strength (MPa)	2.00	0.00	0.70	0.00
	Flexural strength (MPa)	0.70	0.20	0.30	0.10
	Linear variation (%)	-5.10	-2.60	-3.20	-2.50

Conclusion

The refractory waste used in the present study exhibited peaks of mullite and alumina, which are compounds that contribute to the increased strength of materials for passive fire protection that use gypsum in their composition. All the mortars containing refractory waste and gypsum met the requirements for the setting time, according to the Brazilian standards. The mortar consistency was close to each other and at values suitable for use. At the international level, all mortar formulations met the parameters of compressive strength, even after being subjected to high temperatures. The bulk density values of the mortars containing refractory waste met the international recommendations. In addition, the importance of the relationships

between water/cement ratio and strength, and between porosity and bulk density was confirmed once again. In addition, the importance of the relationships between porosity and thermal conductivity, between water/cement ratio and strength, and between porosity and bulk density was confirmed once again. The synergy between refractory waste and gypsum led to mortars within the studied parameters. Using refractory waste proved to be effective and is ecologically correct for adding value to refractory waste, generating a differentiated product.

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