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Use of industrial boiler ash as partial replacement for Portland cement in mortars

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ABSTRACT: Civil construction has sought alternatives for cost reduction with the insertion of new products and techniques that ensure better performance of buildings. In this context, this work analysed properties of mortars produced with partial replacement of Portland cement by ashes from the burning of eucalyptus and grevíllea wood in boilers of a footwear company. To conduct this research, mortars with mixtures of 1:3 and 1:6 were produced including partial substitutions of Portland cement by the boiler bottom ash (BBA) in proportions of 0, 5, 10 and 15%. Tests of axial compressive strength, tensile strength by diametrical compression, absorption of water by both immersion and capillarity were performed. It was observed that the use of BBA resulted in improvements in the analyzed properties of mortars with increasing ash content, leading to significant increments in compressive strength and reduction of water absorption.

KEYWORDS: Industrial Ash. Portland Cement. Mortar.

RESUMO: A construção civil tem buscado alternativas para redução de custos com a inserção de novos produtos e técnicas que garantam melhor desempenho das edificações. Nesse contexto, o presente trabalho baseia-se na análise do comportamento de argamassas, produzidas com substituição parcial do Cimento Portland (CP) por cinzas provenientes da queima de lenha de eucalipto e grevílea nas caldeiras de uma indústria calçadista. Para realização dessa pesquisa, foram produzidas argamassas com traço 1:3 e 1:6, com substituições parciais do CP pelas cinzas residuais de caldeiras (CRC) nas proporções de 0, 5, 10 e 15%. Foram realizados ensaios de resistência à compressão axial, resistência à tração por compressão diametral, absorção de água por imersão e por capilaridade. Observou-se que o uso das CRC resultou em melhorias nas propriedades analisadas nas argamassas com o aumento do teor de cinzas, levando a significativos incrementos na resistência à compressão e redução da absorção de água.

PALAVRAS-CHAVE: Cinzas Industriais. Cimento Portland. Argamassa.

1. Introduction

According to the National Union of the Cement Industry (SNIC) [1] Portland cement is a hardly substitutable commodity. Data from the Brazilian Association of Portland Cement (ABCP) [2] indicate that, in 2020, 60.8 million tons of Portland cement were sold in Brazil. The world production in the same year was estimated at 4.1 billion tons [3]. Portland cement is present in all types of construction, from the simplest house to the most complex infrastructure work, and is the main binder used in concrete production. The cement industry has been considered one of the biggest polluters of the environment, both due to the large consumption of limestone deposits and its high rates of CO_2 emissions [4, 5, 6 and 27].

According to SNIC and ABCP, cited by CETESB [7], on a global scale, approximately 90% of CO_2 emissions from cement production occur during clinker production, either in the calcination or decarbonation of raw materials, or in the burning of fuels inside the kilns. As a result, for each ton of clinker produced, it is estimated that the same amount of CO_2 is released into the environment [8].

In this scenario, an alternative sought by many researchers in the construction industry is promoting the use of many wastes as partial replacement for Portland cement, including biomass, such as algaroba ash [9]; sugar cane bagasse [10, 11], biomass ash from the cocoa agro-industry [12], green coconut shell ash [13], industrial by-products [14, 15], and even residue from the production of metallic silicon [16].

The feasibility of using industrial wastes, especially the inorganic ones from combustion, is favored by the similarity between these wastes and mineral additions already commonly employed. According to Mehta and Monteiro [17], mineral additions are

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finely divided siliceous materials that present either pozzolanic activity or cementing properties, which can be added to mortars or concretes to improve their properties. According to NBR 11172:1990 [18], mineral additions can be classified according to their physical-chemical action into three types: inert, cementing and pozzolanic.

Portland cement is a hydraulic binder whose silicate-based compounds (C2S and C3S) react with water (H) producing calcium silicate hydrate (C-S-H) and calcium hydroxide (CH), i.e., CxS + H → C-S-H + CH. Among the compounds produced in the hydration of Portland cement, only the C-S-H contributes significantly to the mechanical strength of cementitious matrices, refines the pores reducing permeability and is insoluble in water with pH above 7. The CH contributes to the alkalinity of the matrix, stabilizing the passive layer of the reinforcement that hinders the corrosion process. In this context, as long as the CH content does not fall below 9.0, calcium hydroxide can be converted into new C-S-H molecules to improve the mechanical properties and durability of matrices. Pozzolanic materials fulfill this role, i.e., they react with CH in aqueous medium, forming secondary C-S-H (Pozzolan + CH + H → C-S-H) [19].

The mineral additions of the inert/filler type are essentially fine and uniform materials, whose action is purely physical, and do not possess any chemical activity, in the sense of producing calcium silicate hydrate (C-S-H). These additions promote the effect of granulometric packing and act as a nucleation point for the hydration of cement grains. When present in small quantities (usually less than 15% of the cement mass) they improve to mortar properties such as: workability, specific mass, porosity, reduced exudation and cracking tendency [20, 21, 22, 23].

According to several authors [24, 25, 26], inert mineral additions generally promote three physical effects, essentially on the hydration of Portland cement, which are: cement dilution; granulometric redistribution; and heterogeneous nucleation.

The dilution effect is related to the partial replacement of cement by the mineral addition, decreasing the amount of cement and consequently causing an increase in the water/binder ratio. The higher the content of substitution, the lower the amount of Portland cement in the matrix is, causing a lower content of hydrates generated over time, if the addition does not present cementing or pozzolanic activity [24, 25].

The granulometric distribution efefct depends on the fineness of the addition and the amount of aggregate used, which, in turn, promotes changes in the porosity of the mixture [25]. This effect occurs due to the filling of micropores by aggregate particles, promoting an increase in the contact area between cement and water, thus contributing to the cement hydration speed and the formation of C-S-H [26].

The packing is related to the correct selection of the proportion and the adequate size of the particulate materials, so that the larger voids are filled with smaller particles; the remaining voids will be filled again with even smaller particles and so on. This influences the paste consumption and several mortar properties, both in fresh and hardened states. Thus, the fines occupy the voids between the sand grains, tending to increase the compactness of the set and, consequently, may contribute to the gain of strength and decrease the porosity of the matrix [27].

The heterogeneous nucleation gains importance the greater the fineness of the material inserted. Lawrence; Cyr and Ringot [25] define heterogeneous nucleation as a physical process that promotes the activation of Portland cement. Therefore, it is a catalytic phenomenon in which a material reduces the activation energy of a chemical reaction without consumption of the chemical species, functioning only as a surface where hydration occurs.

If the addition helps the agglomerative property that forms the cementitious materials, it is said that such material has pozzolanic activity. According to NBR 12653:2014 [28], pozzolanic materials are defined as siliceous or silicoaluminous materials that, by themselves, have little or no binder activity, but which, when finely divided and in the presence of water, react with calcium hydroxide at room temperature to form compounds with binder properties. To form stable silicates that have cementitious properties, the pozzolana must be finely subdivided, as only then can silica combine with calcium hydroxide in the presence of water. The silica must also be in its amorphous state, i.e., glassy, as its reactivity is very small in crystalline state[23].

There are numerous advantages of mineral additions to concrete, since they can improve resistance to thermal cracking due to the reduction in the heat of hydration, being able to increase the watertightness of the matrix by refining the pores. Thus, it provides a greater durability to chemical agents, such as alkali-aggregate expansion and attack by sulfate, as a result of alkalinity reduction (in the case of pozzolanic mineral additions), besides decreasing the cost and improving its workability in fresh state [17].

The ashes are types of additions widely used for partial replacement of clinker. Its composition varies a lot, as it depends on genetic characteristics of the plant to the operational conditions of the boiler in which the burning is performed. However, it is possible to verify pozzolanic characteristics, which explains the use of mineral solid waste in civil construction [29].

The use of ashes as addition reduces the environmental impact and the cost of preparation of cementitious materials, because it replaces compounds of higher cost, avoiding, at the same time, the deposition of ashes in the environment, thus making the manufacturing process of cementitious materials more sustainable.

França et al. [30] used ashes from burning eucalyptus chips at levels of 10%, 20% and 30% of Portland cement replacement to evaluate the feasibility of this reuse through the analysis of the properties of mortars in fresh state. The authors concluded that the eucalyptus ashes has physical characteristics suitable for addition and contributes to higher packing density of the system that contains them due to its particles are smaller than those of cement. Moreover, it was also observed that due to the fact that the ashes has a larger specific surface area than cement and consequently require a greater amount of water for wetting mortars that contain it have lower initial workability, a fact observed through tests on the consistency table (flow table).

Gluitz and Marafão [31] developed a research to evaluate the eucalyptus wood ashes (EWA) as partial replacement for Portland cement in mortar. Its pozzolanicity index was evaluated, besides physical and chemical characteristics. To achieve this goal, specimens of mortar were molded with additions of 0, 5, 10, 15 and 20% of EWA and, from performed tests, it was concluded that ashes promoted a fall in mortar strength as the content of substitution of Portland cement by EWA increased. This drop was expected due to the result of the pozzolanic activity test, in which ashes did not show pozzolanic potential.

In this study, ashes from burning eucalyptus firewood and grevillea in boilers of the company Dass Calçados were used as mineral addition. Tests of consistency, mechanical strength and permeability were performed, from samples with different percentages of the boiler bottom ash (BBA) in partial replacement of Portland cement in the production of mortars. In addition to reducing the use of cement, it offers a new destination for the waste generated by another industry.

2. Methodology

2.1 Materials

To perform the tests, CP V – ARI, with a specific mass of 3.08 g/ml was used. This cement was chosen for not having pozzolanic mineral additions, and also presenting a maximum of 5% of carbonate materials as specified by NBR 16697:2018 [32] – the lowest content among the other cements available in the region of Cruz das Almas, state of Bahia, Brazil. The water used for the production and curing of the specimens came from the municipal water supply system.

Medium washed sand was used as fine aggregate, with a fineness modulus of 2.92 and maximum characteristic size of 2.4 mm, determined according to the procedures of NM 248:2003 [33]. **Figure 1** depicts the granulometric distribution graph. It shows the distribution curve of the fine aggregate grains and the limits of the usable and optimum zones, established by NBR 7211:2009 [34].

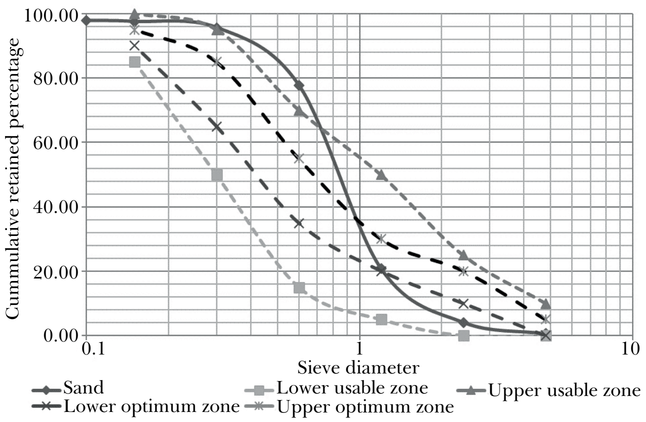

Fig. 1 - Granulometric distribution of fine aggregate and the zones defined by NBR 7211:2009 [34]. Source: The authors.

Ashes were supplied by the company Dass Calçados, located in the city of Vitória da Conquista, state of Bahia. They were obtained by the burning of eucalyptus and grevillea firewood in the boilers of the company. Then they were air cooled, stored in a sealed and impermeable container and taken to the laboratory for drying in an oven at (105 ± 5) °C for 24 hours. Afterwards, they were passed through a sieve of 0.075 mm to obtain a granulometry close to that of the cement.

The pozzolanic performance index of BBA with Portland cement at 28 days was determined at 77% based on the procedures of NBR 5752:2014 [35]. According to NBR 12653:14 [28], materials with pozzolanic activity index (PAI) higher than 90% present pozzolanic potential. This means that such materials do not present the potential to produce secondary C-S-H by the interaction between ash compounds and the hydroxides of the cementitious matrix.

2.2 Method

Two mixtures were chosen for the study (binder:aggregate ratio), observing the behavior of ashes in the rich mixture (1:3) and poor mixture (1:6) of Portland cement with water/binder ratio (w/b) fixed at 0.54 and 1.05, respectively. Ashes were used as a partial replacement of Portland cement in the percentages of 5%, 10% and 15%, and the applied formulations are presented in **Table 1**. In general, Portland cement replacements at levels higher than 15% tend to reduce the properties of cementitious matrices, due to the dilution effect of cement. In previous research, growth up to 15% in the evaluated properties justifies the advance of dilution to higher levels [36]. However, this was the first research with this residue. Therefore, it was decided to evaluate the replacement with Portland cement at levels up to 15% of BBA.

Tab. 1 – Proportions of materials in mortars.

Mix-ture	b/agl	Ash content (%)	Cement (g)	Ash (g)	Sand (g)
1:3	0.54	0	624.0	0.0	1872.0
		5	592.8	31.2	1872.0
		10	561.6	62.4	1872.0
		15	530.4	93.6	1872.0
1:6	1.05	0	367.1	0.0	2202.4
		5	348.7	18.4	2202.4
		10	330.4	36.7	2202.4
		15	312.0	55.1	2202.4

Source: The authors.

The molding of the specimens followed the procedures of NBR 7215:2019 [37]. They were kept in the molds for the first 24 hours, and then destined for curing submerged in water saturated with lime for 28 days. The produced mortars were analyzed in fresh state by consistency test, governed by NBR 13276:2016 [38] and in the hardened state by axial compressive strength tests, according to NBR 7215: 2019 [37]; tensile strength by diametrical compression, according to NBR 7222:2011 [39] and tests regarding the durability of the matrix, as follows: water absorption test by immersion and by capillarity, according to NBR 9778:2005 [40] and NBR 9779:2012 [41], respectively.

Results, with the exception of the consistency index, followed the sampling procedures of NBR 7215:2019 [37] with subsequent statistical analysis of variance (ANOVA) with ash replacement content as a factor of variation. The mean values obtained were compared to each other by the Tukey's test at the 5% significance level.

The statistical interpretation was by comparing F and F-critical values provided by the variance analysis, having as hypothesis the significant influence of the cement replacement by BBA in at least one of the groups in the analyzed property. The confirmation of the hypothesis occured for F values higher than the

F-critical. The result of the Tukey's test was identified by letters next to the mean values in the results tables, and groups with equal letters show no significant differerence from each other at 5% probability.

3. Results and discussion

3.1 Consistency index

Consistency is one of the most relevant properties of mortar in the fresh state. This property is linked to the fluidity of the mixture and represents the tendency of the mortar to deform. The greater the spread of the mortar on the test table, the lower is its yield strength and thus, the higher is its fluidity. The results are presented in **Table 2**.

It could be observed that, with the increase in the replacement content of Portland cement by BBA, there was a progressive decrease in the mortar consistency index, an effect directly linked to the increase in water demand due to the insertion of finer particles than cement with a larger specific surface, forming less workable mortars.

Tab. 2 – mortar consistency index.

Mixture	Ash content (%)	Consistency index (mm)
1:3	0	320
	5	318
	10	295
	15	282
1:6	0	268
	5	262
	10	258
	15	254

Source: The authors.

Tab. 3 – axial compressive strenth.

Mix-ture	Ash content (%)	Compressive strength (MPa)	Standard deviation. (MPa)	Variation of coefficient (%)
1:3	0	28.8^{A}	0.6	2.0
	5	28.0^{A}	0.4	1.3
	10	30.6^{AB}	1.4	4.5
	15	33.8^{B}	1.8	52
	F	11.836	**F-critical**	4.346
1:6	0	8.7^{A}	0.2	2.0
	5	8.2^{AB}	0.5	6.2
	10	8.1^{AB}	0.2	2.9
	15	7.5^{B}	0.4	5.8
	F	5.555	**F-critical**	4.066

Source: The authors.

3.2 Compressive strength

Table 3 shows results obtained for the axial compressive strength of mortars at 28 days, along with the F and F-critical values from the analysis of variance. For the 1:3 mixture, it was observed that the replacement of Portland cement by BBA showed a tendency to increase the axial compressive strength starting at 10%, with a resistance 17.3% higher than the reference in which 15% of ash was used. Based on the results of the Tukey's test, there was no variation in strength for 5% substitution. In the 1:6 mixture, the use of BBA showed a tendency to reduce the strength, although it did not significantly affect the parameter until 10% of replacement content, with mean 13.8% lower than the reference at 15%.

Observing the behavior of the compressive strength of mortars as a function of ash content, we note that the higher the quantity of Portland cement replacement by BBA in richer mixtures (1:3), the higher is the compressive strength. Such behavior can be explained through the ideas of Castro and Pandolfelli [24] and Lawrence, Cyr and Ringot [25]. According to these authors, the dilution effect of Portland cement can be compensated in the pore refining process, which causes greater densification of the matrix, reinforcing the granulometric skeleton, thus increasing compressive strength. The water absorption reinforces this interpretation. The dilution effect of Portland cement tends to decrease the amount of C-S-H produced by hydration and, consequently, both the porosity of the matrix and the the water absorption are higher. However, results indicated that the higher the replacement content of Portland cement, the lower is the rate of water absorption. Thus, it can be inferred that the residue is clogging the pores, i.e., increasing the filling of voids by water in matrices with lower contents of BBA [42].

Gluitz and Marafão [31] observed a reduction in compressive strength as the content of Portland cement replacement by waste increased. The results of this research pointed to an increment in compressive strength with increasing substitution content.

Although the two wastes did not present pozzolanic activity index, the difference in behavior is probably associated with the differences in format, size and distribution of particles between wood ash and BBA. The effects of particle packing resulting in increased compressive strength were observed by Karadumpa and Pancharathi (2021) [42].

For the 1:6 mixture, there was maintenance of the axial compressive strength for replacement contents up to 10%. As it is a mortar with lower cement content, the dilution of the binder may not be compensated when this limit is exceeded, since there are more voids to be filled by the ash particles. Moreover, the lower amount of cement results in lower production of calcium hydroxide, fundamental for the activation of the pozzolanic potential of the BBA.

Tab. 4 – Tensile strength by diametrical compression.

Mixture	Ash content (%)	Tensile strength (MPa)	Standard deviation. (MPa)	Variation of coefficient (%)
1:3	0	2.7^{A}	0.1	2.2
	5	2.7^{A}	0.2	5.7
	10	3.0^{B}	0.04	1.3
	15	3.3^{B}	0.2	5.3
	F	17.682	**F-critical**	3.862
1:6	0	0.9^{A}	0.0	0.0
	5	0.9^{A}	0.1	6.7
	10	10^{B}	0.1	5.6
	15	1.0^{B}	0.1	6.0
	F	7.615	**F-critical**	3.862

Source: The authors.

3.3 Tensile strength in diametrical compression

Results shown in **Table 4** indicate that in both mixtures the replacement of cement by BBA promoted significant variations in the tensile strength of mortars, and also that use of BBA in up to 5% did not affect the parameter, while higher values led to increases in resistance. Replacing Portland cement with 5% BBA diluted the cement, reducing the C-S-H content produced due to the hydration of Portland cement; however, this dilution effect was offset by the BBA increase in granular density. For the 15% replacement content, an increase of 22.2% was recorded for the 1:3 mixture and 11.1% for the 1:6 mixture. Vaske [43] concluded that eucalyptus ashes showed a high number of peaks in the X-ray diffractogram, typical evidence of crystalline phases which, according to the author, would indicate a low reactivity of the material. Thus, the probable pozzolanic influence of the grevillea ashes is highlighted. At the conclusion of the study, Vaske [43] indicated the viability of Eucalyptus ashes as a filler material.

Tab. 5 – Coefficient of water absorption by immersion.

Mix-ture	Ash content (%)	Coefficient of water absorp-tion (%)	Standard deviation. (MPa)	Variation of coefficient (%)
1:3	0	9.12^{A}	0.22	2.38
	5	9.03^{A}	0.17	1.87
	10	8.18^{B}	0.12	1.47
	15	7.96^{B}	0.09	1.19
	F	70.367	**F-critical**	3.238
1:6	0	11.18^{A}	2.1	1.44
	5	10.48^{A}	3.6	3.23
	10	9.64^{B}	2.2	1.62
	15	9.46^{B}	1.6	0.99
	F	72.727	**F-critical**	3.238

Source: The authors.

3.4 Water absorption by immersion

Table 5 presents coefficients of water absorption by immersion obtained. In the 1:3 mixture, mortars showed significant reduction in absorption coefficients from the 10% content on, and values 10.3% and 12.7% lower for the 10% and 15% replacement levels, respectively. Similar behavior was observed in the 1:6 mixture, in which the reduction was 13.8% and 15.4% in the 10% and 15% contents, respectively.

Such results point to a reduction in the open porosity of the matrix, probably due to the better packing of grains and refinement of pores. Similar phenomena were observed by Londero, Klein and Mazer [27, 42] in a study of the effect of particle packing on concrete properties.

3.5 Water absorption by capillarity

Table 6 show the replacement of cement for BBA resulted in significant variations in the capillary absorption coefficient at all levels of replacement observed in both mixtures. For the 1:3 mixture, there was a reduction of 42.8%, 44.7% and 56.5% for the 5%, 10% and 15% replacement levels respectively.

For the 1:6 mixture, the observed reduction was 39.4%, 46.3% and 58.1% for the 5%, 10% and 15% of BBA, respectively. Based on the Tukey's test, it is observed that there is no significant variation between the 5% and 10% substitution content despite both are significantly diverse from the reference for reductions greater than 40% of the absorption coefficient.

Thus, water absorption by capillarity reduced by increasing the ash content in the cementitious matrix. Probably the reduction of capillaries occurred by the buffering of pores amid the production of new binder substances and due to the influence of ash grains on the granulometric distribution, densifying the matrix and reducing its open porosity.

Tab. 6 – Coefficient of water absorption by capillarity.

Mix-ture	Ash content (%)	Capillary absorption coefficient (g/cm²)	Standard deviation. (MPa)	Variation of coefficient (%)
1:3	0	1.61A	0.22	2.38
	5	0.92B	0.17	1.87
	10	0.89B	0.12	1.47
	15	0.70C	0.09	1.19
	F	93.998	**F-critical**	3.238
1:6	0	2.03A	0.10	4.99
	5	1.23B	0.09	7.63
	10	1.09B	0.10	8.85
	15	0.85C	0.02	2.86
	F	139.264	**F-critical**	3.862

Source: The authors.

4. Conclusion

Based on the observed results, it can be affirmed that the replacement of Portland cement by BBA significantly influenced and progressively improved the analysed and observed properties of mortars with the addition of ash contents, and some behaviors were more evident in the 1:3 mixture, richer in binder. In addition, it can be stated that:

- The studied BBA cannot be classified as a natural pozzolan and, as such, improvements on the properties examined came from from its physical influence on the matrix densification.
- Replacing Portland cement with up to 15% BBA increased axial compressive strength by up to 17.3% in the 1:3 mixture.
- The use of BBA favored the tensile strength of mortars, producing increases of 22.2% in the 1:3 mixture and 11.1% in the 1:6 mixture when 15% replacement was used.
- In both mixtures studied, the use of BBA made the mortars progressively less permeable, reaching reductions of more than 50% in the absorption of water by capillarity at the level of 15% of substitution, which indicates the potential of its use to improve the durability of cementitious matrices.

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