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Evaluation of coal fly ash in cementitious matrices

Avaliação de cinza volante de carvão mineral em matrizes cimentícias

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Abstract

The addition of ash, initially classified as waste in cement matrices, is essential to achieve the requirements of National Policy of Solid Waste. However, technologies that enable such applications should be sought, especially when the material has adequate pozzolanic activity. The aim of this study was to verify the pozzolanic activity of fly ash from coal burning, from the aluminum manufacturing process, such as mineral admixture in mortars and conventional concrete. For that, physicochemical characterization of the ash sample and the mechanical behavior of mix dosage of mortar and commercially used concrete tests were carried out. Results showed the ash in evaluation has pozzolanicity as relevant standards employed and when inserted in the studied cementitious matrices, showed the expected performance for this type of addition (higher mechanical strength at older ages).

Keywords: fly ash, concrete, mortar, waste, aluminum.

Resumo

A adição de cinzas em matrizes cimentícias é essencial para se alcançar os requisitos da Política Nacional dos Resíduos Sólidos. Entretanto, deve-se buscar tecnologias que viabilizem tais aplicações, principalmente quando o material apresenta adequada atividade pozolânica. O objetivo deste trabalho foi verificar a atividade pozolânica da cinza volante proveniente da queima de carvão mineral, proveniente do processo de fabricação de alumínio, como adição mineral em argamassas e concretos convencionais. Para isso foram realizados ensaios de caracterização físico-química da amostra de cinza e do comportamento mecânico de traços de argamassas e concretos comercialmente empregados. Os resultados demonstraram que a cinza em questão possui atividade pozolânica conforme normas ABNT empregadas e quando inserida nas matrizes cimentícias estudadas, apresentaram o desempenho esperado para este tipo de adição (maior resistência mecânica em idades mais avançadas).

Palavras-chave: cinza volante, concreto, argamassa, resíduo, alumínio.

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1. Introduction

Increasing mechanical efficiency and lifetime of concretes and mortars without increasing their environmental impact is an incessant search for construction materials researchers. And, under this perspective, the use of pozzolanic activity waste has been a great tool in this segment, considering the potential for substitution of clinker [1] [2]. However, the wastes available with characteristics by pozzolans requires physicochemical processes to achieve this characteristic, according to describe of the current standards, which demand high energy consumption [3].

Generally, the fly ash is already commercially used as mineral admixture in cementitious matrices due to high proportions of oxides in their chemical compositions [4]. However, there are types of ashes that have not yet been fully studied, for example, the ones from fly ash mineral coal burning (FAMC), from the manufacture of aluminum.

According to the standards ABNT NBR 12653:2014 [5] and ASTM C618:2012 [6], the pozzolanic material is defined as siliceous or silico-aluminous that has little binder activity. However, when finely ground and exposed to water and calcium hydroxide, they chemically react with the calcium hydroxide and made biding compounds. Thus, the direct addition of pozzolans to the concrete or mortar, besides reducing the consumption of cement, can raise the mechanical performance, give greater efficiency of cement Portland and to provide greater durability [7]. Furthermore, the FAMC can be used to production of concretes with greater durability because when the pozzolanic materials react with the hydroxides, present in cementitious matrices, they can prevent alkali-aggregate reaction [8]. This is because the FAMC are easily soluble and reactive with aggregates that have high silica content.

PACHECO et al [9] describe that cementitious matrices with fly ash provide slower hydration chemical reactions, but, this addition is indicated to reduce clinker consumption, with the replacements in the cement between 40% and 50%.

The use of fly ash combined with new production technologies can contributes to reducing CO_2 emissions, the main environmental liability of the cement industry. In this scenario, Brazil has been a place of prominence on the use of fly ash in Portland cement production, mainly in the South of the country, where there is higher production of this waste due the high consumption of coal for thermal power plants installed there.

In this context, there is need researches about other types of ash, for example, the one from the use of coal in the bauxite processing for primary aluminum production (FAMC). Current data report that every 100 t of coal used in boilers, 10 t of ashes are generated, where 90% is fly ash and 10% is known as heavy ash, which is deposited on the boiler bed [10]. In Brazil, use of energy coal is approximately 8 million tons per year [11].

Bauxite processing uses boilers of type “dry combustion with artificial draught” in steam generation for the BAYER process [10]. According to RAMOS [12], the operation of this boiler (reactor) has basically four stages. The first stage is the ignition and the second is the addition of inert material (sand) that guarantees the fluidization and recirculation of materials. The third is the addition of fuel – “coal,” and the fourth is the addition of a limestone mixture to minimize fumes. Therefore, the fly ashes generated in this process are very different from those generated by electrothermal boilers.

Therefore, there is need to evaluate the potential of this waste added in concretes and mortars. Standard ABNT NBR 12653:2014 [13], which sets out the requirements to identify the pozzolanic activity of mineral waste, classifies the pozzolans into three groups:

- class N: volcanic origin and artificial from industrial by-products;
- class C: finely ground fly ash from thermoelectric power plants;
- class E: other pozzolans (fly ash, ash from plant waste).

It should be noted that the international standard ASTM C618:2012 [6] specifies the same limits of chemical compounds of the Brazilian standard [Table 1].

The high volume of waste in question and the potential pozzolanic activity, proven by several researchers in similar waste [8, 9, 10, 12, 14.15], indicate the appropriateness of using the coal fly ash burning in cementitious matrices. Menendéz et al. [14] evaluated the mechanical behavior of heavy ash and fly ash, from the production of aluminum, in replacement of cement in mortars in 10%, 25% and 35% contents. The results indicated 20% content of fly ash as ideal, considering the compressive strength of specimen standards (without fly ash).

Other authors evaluated concretes with replacement of cement for fly ash in 20%, 30% and 40% contents. The results obtained by these authors reached 91%, 82% and 67% of the strength of the standard ratio, respectively to contents indicated, considering 28 days of cure. To 112 days, the concretes with additions reached strength 87% higher than standard concrete, showing that the growth rate of concretes with high content of fly ash is late the higher is the addition rate [16]. This study highlights the need to

Table 1
Chemical compounds that must be present in materials with pozzolanic activity according to current standards

Compound (%)	ABNT NBR 12653:2014	ASTM C 618:2012
$SiO_2 + Al_2O_3 + Fe_2O_3$	≥ 70.0	≥ 70.0
SO_3	≤ 5.0	≤ 5.0
Moisture content	≤ 3.0	≤ 3.0
Loss on ignition	≤ 10.0	≤ 10.0
Alkalis available in Na_2O	≤ 1.5	≤ 1.5
Material retained on 45-µm sieve	≤ 20%	≤ 34%

Table 2
Traces of the concretes produced and related materials

Materials	Executed traces for slump of 130 mm (values in kg/m³)				
	Reference	FAMC			Metakaolin
		5%	10%	20%	10%
Cement CP V ARI RS	300	300	300	300	300
Addition	0	15	30	60	30
Aeolian sand (M F: 1.40)	819	804	789	759	789
Gravel basalt (# 19 mm)	1130	1130	1130	1130	1130
Admixture (lignosulfonate-based)	1.8	1.8	1.8	1.8	1.8
Water/binders ratio	0.617	0.587	0.597	0.564	0.606

evaluate the pozzolanic material inserted to the cementitious system that will be applied, in addition to the tests that verify the pozzolanic potential.

There are properties, intrinsic to the mortars and concretes, that impact on the development of pozzolanic reactions and resulting mechanical performance, among them, the granular structure and the gaps caused by the incorporation of air due to the combination of chemical additives. In this context, this study evaluated the behavior of a sample of fly ash of the mineral coal from aluminum production (FAMC) incorporated to the central dosed concrete and industrialized mortars.

2. Materials and experimental program

2.1 Pozzolanic activity of fly ash of mineral coal from aluminum production

The Pozzolanic activity of FAMC sample was determined according to NBR 12653:1992 [5], in the presence of cement and lime, standard used when this study was initiated. Workability of the mortar was determined according to parameters defined by the Flow Table method [17], considering a 225 ±5 mm spreading, whose water/binders ratio varied according to the FAMC content.

The material under analysis in this study was obtained in the capture of filters subsequent to the boilers where coal is burned. The collected material was tested "*in natura*", without any processing for its employment.

To analyze the efficiency of the fly ash of the mineral coal burning (FAMC) applied in concretes and mortars, traces occurred with reference to the proportions applied by DAMINELLI et al. [18], which determined the indicator of technical performance of binders by m³ of concrete.

2.2 Concrete

For concrete recipes with incorporation of FAMC, a cement consumption of 300 kg/m³ was used and replacement contents of 5%, 10% and 20% [14, 16]. All recipes had the addition of 10% of Metakaolin HP (Metakaolin from Brazil) and the water/cement ratio varied according to the content of FAMC and slump set at 130±20 mm, following standard ABNT [19] and survey data about the characteristics of concretes produced by central batchers in the region of Campinas, São Paulo (Table 2). Two specimens of 100 x 200 mm were molded for evaluation of the axial compressive strength in each age, taking the higher value of the pair as indicated by ABNT NBR 12655 [20].

Table 3
Trace of structural laying mortars produced

Materials	Traces of the laying mortar (kg/tonne)			
	Reference	FAMC	FAMC 10%	FAMC 20%
Cement CP V ARI RS	155	155	155	155
Ash addition	0	8	16	31
Cal CH III	37	37	37	37
Phyllite	37	37	37	37
Fine sand	431	423	415	400
Medium sand	340	340	340	340
Water retainer 15,000 m.Pa.s	0.090	0.090	0.090	0.090
Water (% of mixture mass)	15%	15%	15%	15%
Water/binders ratio	0.968	0.922	0.880	0.806

Table 4
Traces of the lining mortars produced

Materials	Traces of the lining mortars (kg/tonne)			
	Reference	FAMC	FAMC 10%	FAMC 20%
Cement CP V ARI RS	125	125	125	125
Ash Addition	0	6	13	25
Cal CH III	44	44	44	44
Phyllite	60	60	60	60
Fine Sand	771	765	758	746
Air-entraining agent	0.030	0.030	0.030	0.030
Water retainer (15,000 m.Pa.s)	0.027	0.027	0.027	0.027
Water (% of mixture mass)	15	15	15	15
Water/binders ratio	1.200	1.143	1.091	1.000

2.3 Mortar

For FAMC additions in mortars, two types were produced: for laying of structural masonry and for lining (Tables 3 and 4). The quantity of recipes was considered in relation to the ton (t), measure unit adopted for the industrialized dry mortars. Properties in the fresh and dried state mortars were determined according to ABNT NBR 13281:2005 [21]. Contents of FAMC additions followed the premises indicated for the production of concrete for the pair evaluation of its performance. Three specimens of 40 x 40 x 160 mm were molded for each test age, according to ABNT NBR 13279 [22].

3. Results and discussions

3.1 Characterization of pozzolanic activity of the ash

The results obtained for the sample of FAMC [Table 5] confirm its Pozzolanic activity according to current standards [Table 1] and the version of the standard by which the test was performed [5]. Such rules prescribe that the sum of oxides must be ≥ 75%, which was achieved for the waste studied (73%), for the material retained on the 45 µm sieve. Only the loss to ignition (13.7%) was higher than the limit imposed by the standards (10%). The values are also consistent with fly ash commercially used and by other researchers [23], showing that the temperatures employed in BAYER type ovens can impact on this property. When relating the results according to the NBR 12653:1992 [5], which was considered during the tests of this study (Tables 6 and 7), were attended the requirements respecting the minimum of

Table 5
Physicochemical properties of the ash (ABNT NBR 12653)

SiO_2	52.8%	72.4%
Al_2O_3	15.6%	
Fe_2O_3	4.0%	
Waste on 45 µm sieve		9.4%
Specific mass (g/cm³)		2.46
Specific area (cm²/g)		8.630
Loss on ignition		13.7%

Table 6
Results of the pozzolanic activity test with cement – ABNT NBR 5752:1992

Samples	Compressive strength (MPa)	Index of pozzolanicity	Water content required
100% Cement CP II F 32 (A)	28.2	–	–
65% CP II F + 35% Fly Ash (B)	24.8	87.9%	108.4%

Table 7
Results of the pozzolanic activity test with lime – ABNT NBR 5751/92

Test specimen 1	Test specimen 2	Test specimen 3	Mean	Maximum relative deviation
7.2	7.1	7.3	7.2	1.4%
* Values in MPa				

Table 8
Results obtained with the concretes produced

Addition	Relation	Cement	Addition	Water	Slump	Axial compressive strength (MPa)*			
(kg/m³)	water/ binder effective	(kg/m³)	(kg/m³)	(L/m³)	mm	3 days	7 days	28 days	ECM**
–	0.617	300	0	185	130	31.2	37.3	44.5	6.7
Ash (15.0)	0.587	300	15	185	130	33.1	38.3	46.1	6.8
Ash (30.0)	0.597	300	30	197	130	32.5	37.9	46.4	7.1
Ash (60.0)	0.564	300	60	203	130	31.7	37.7	47.2	7.6
Metakaolin (30.0)	0.606	300	30	200	130	32.5	40.1	45.5	7.3

* test according to ABNT NBR 5739. Indicating greater value of the pair molded to every age according to ABNT NBR 12655;
**ECM: Efficiency of Cementitious Material, corresponds to [binders/fc28] according to [18].

75% in cement tests (replacement) and 6.0 MPa for compressive strength with lime. The results are also similar to those obtained in the literature consulted [24, 25].

MEDEIROS et al. [24] studied the reactivity of some materials according to the reaction and interaction with calcium hydroxide by X-ray test. These authors commented that the indirect method to assess the strength developed in mortar with lime has influenced the composition of the matrix. Since the morphology and granulometry of materials can affect the workability required, being necessary to vary the water content of the composition. Still, the contrast of the test with the lime makes similar performance in the reactivity analysis with Portland cement. When obtaining 87.9% pozzolanic activity on replacement of 35% of cement mass, the material FAMC fits as pozzolanic material, but does not have high reactivity in face of other artificial pozzolans marketed [24] [25].

3.2 Results obtained with the concretes

With the addition of FAMC to concrete, there was varying the content of water to maintain the slump, it was possible to identify the water consumption because the increase in the fine content [Table 8]. Considered the reduce water consumption, the Metakaolin (reference material) showed the highest mechanical strength, compared with the fly ash [Figure 1]. Thus, there is a linear correlation between the strength and the factor water/binders, which demonstrate an efficiency of the FAMC sample up to the content of 10%. The higher strength of the Metakaolin in the early ages is expected, since its higher fineness in relation to the FAMC. In addition, the higher content of aluminates justify this performance because are responsible by increase of the strength in the early ages [24] [25].

To quantify the efficiency of the FAMC sample in question, the method identified as ECM (Efficiency of the Cementitious

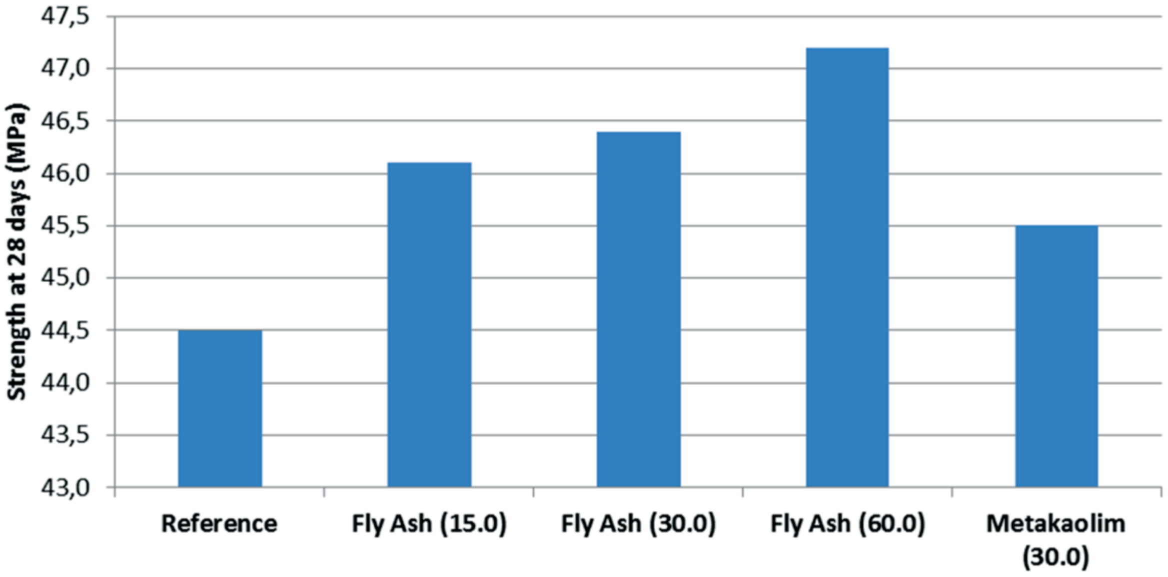

Figure 1
Results of concretes strength at 28 days according to the type and content of addition in kg/m³

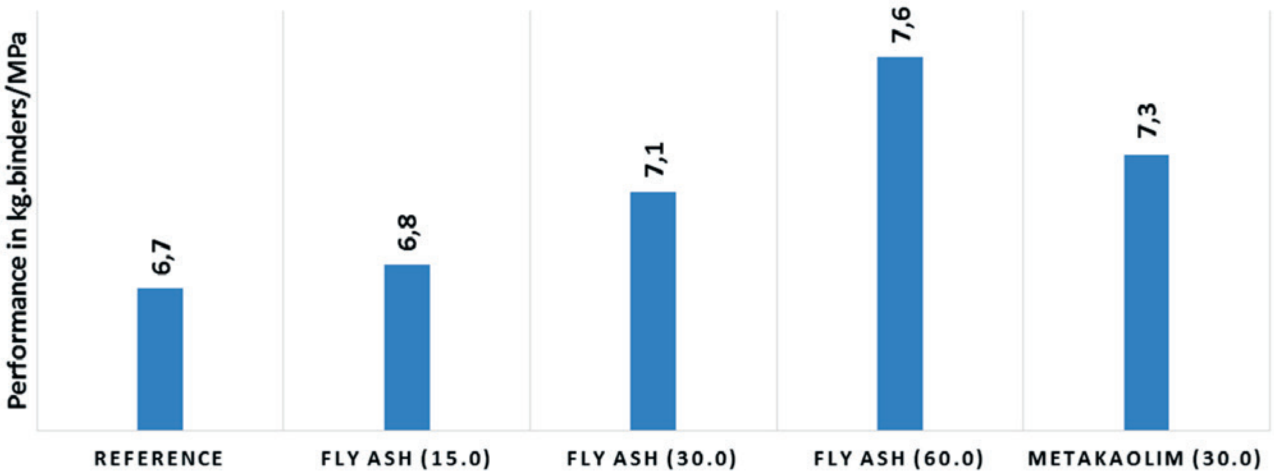

Figure 2
Results of Efficiency of the Cementitious Material (ECM) according to the levels of addition in kg/m³

Material) was applied, which is the ratio of the binders (cement + mineral admixture) by the strength obtained at 28 days old (Figure 2), by DAMINELLI et al. [18]. These authors demonstrated there is total viability in the industrial production of concrete with ECM of the 3.0 and 4.0 kg/MPa. Other researchers [26] identified that the concretes produced with commercial cements presents performance, in relation to the binder consumption/strength, in the range of 7 to 9 kg/MPa. These values are close to those obtained in this study (6.7 to 7.6 kg cementitious materials/MPa).

The analysis of results shows that the incorporation of FAMC increased compressive strength at 6.0% to the content of 20%. However, under the ECM indicator analysis, the increase in strength is smaller than for the contents below 20%. When using this type of mineral admixture, changes may occur in the microstructure of concrete and, consequently, compromise its durability [25]. This can occur due to reduction of the slump index with increase of fine material, because there is greater exposure area and rheological interaction, one of the points that must receive attention when adopting these materials in the production of concretes.

Therefore, in addition to considering the classification of the Pozzolanic Activity Index (PAI), from the regulations in force, there is a need to assess the performance of the waste at the end of application systems (mortars and concretes). If on the one hand the reference material (Metakaolin) presents greater PAI than the FAMC sample [25], on the other hand the two types of mineral admixtures feature the same performance when considering the ECM index.

3.3 Results obtained with the mortars

The results of mortars, developed for the different applications and therefore having different matrices and granulometric structures are presented in Table 9. The behavior of fresh mortars was similar for over all mineral addition types, considered NBR 13281:2005 [19]. This it shows almost identical recipes with FAMC and metakaolin. Although, studies show negative impact

Table 9
Results obtained with the mortars produced

	Addition of ash	Flow-table (mm)	Density (g/cm³)	Water retention (%)	Compressive strength		Tensile flexural strength	
					7 days	28 days	7 days	28 days
Lining mortar	0%	249	1640	88	3.8	5.0	1.1	1.4
	5%	254	1650	90	4.3	5.2	1.1	1.5
	10%	261	1660	86	4.0	5.4	1.3	1.6
	20%	2156	1590	87	4.4	6.0	1.4	1.6
Laying mortar	0%	258	2020	90	13.1	14.6	2.7	3.3
	5%	256	2080	88	15.4	17.0	2.9	3.3
	10%	251	2085	90	14.7	17.6	2.8	4.1
	20%	262	2090	91	14.5	17.6	3.0	3.7

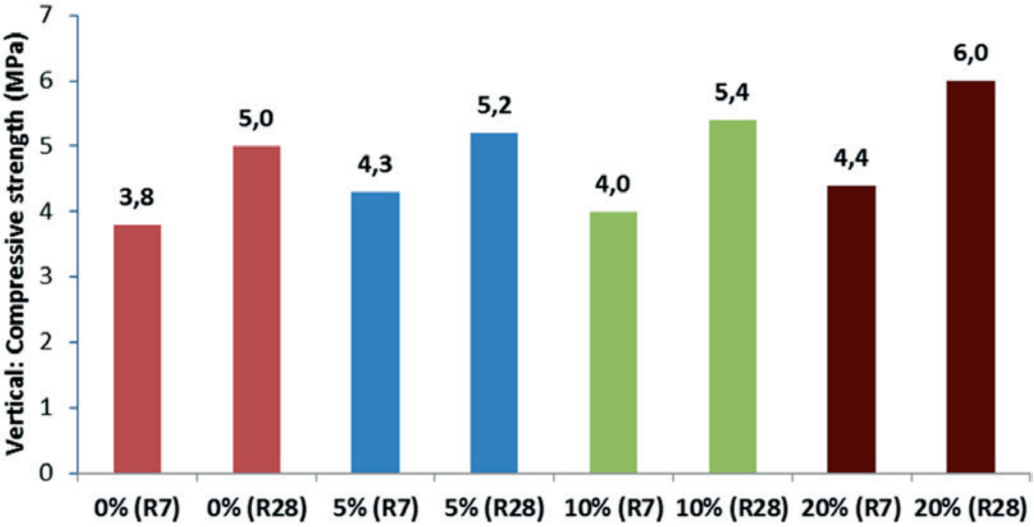

Figure 3
Compression results of lining mortars according to percentage of addition to the cement and test age

on fresh mortars with coal ash [28], the use of admixtures (air-entraining agents and water retainers) can contribute to reducing this impact, unlike the results of concrete. Water retainers admixtures, commonly applied in mortars, are chemicals that change the viscosity, acting in the lubrication, allied to greater air content in the cementitious matrix, caused by air-entraining admixtures. This incorporation of air can mitigates the impact of increased fine content found in the analysis of concrete.

The mechanical behavior was improved with the increased incorporation of FAMC (Figures 3 and 4). However, because the structure of the cementitious matrix of the lining mortars has significant air incorporation (25%), it is justified that its mechanical performance is lower than the performance shown by the mortar for structural laying. Thus, it is understood that densification of the cementitious matrix due to formation of secondary calcium silicate (pozzolanic activity) provides smaller effect on lining mortar matrices, given the necessity for greater incorporation of voids needed to confer higher elastoplastic deformation.

When employing the ECM index for results obtained at 28 days with both types of mortars, it was found that such performance assessment method gives adequate applicability only for laying mortars. The values for lining mortars were 25.0; 25.2; 25.5 and 25.0 for the admixtures of 0%; 5%; 10% and 20% of FAMC, respectively, in function of the high vesicular structure, thus the formation of new compounds does not manage to densify the matrix to confer such better effect. For the line of structural laying mortars, the ECM values were consistent with the literature [18] [26] [29]. These values confirm the increase of mechanical strength due to interaction between admixtures and the structure of compound materials by cementitious materials [30]. These authors studied the mechanism of chemical reactions and the speed of these samples with metakaolin, which concluded that as the increase in the rate of replacement of cement by mineral admixture, the relation between the calcium hydroxide (CH) and cement quantity available decreases, the optimal point for the presence of CH being 10% of replacement content. This level

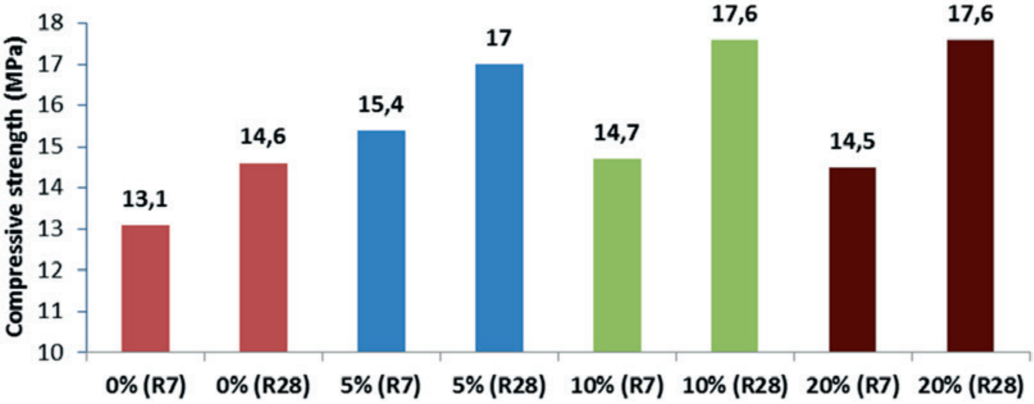

Figure 4
Results from compression of laying mortars according to percentage of addition to the cement and test age

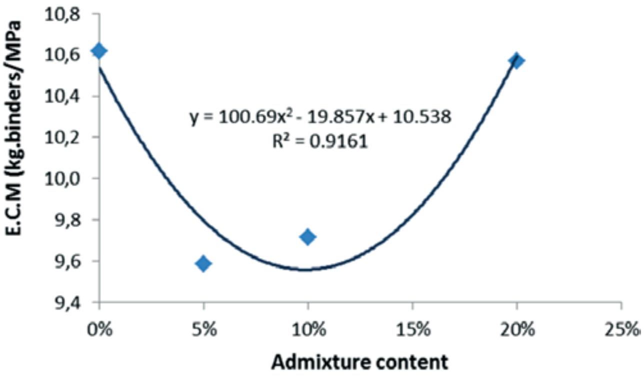

Figure 5
Results of efficiency of the cementitious material (EMC) of laying mortar samples at 28 days of age

was also observed for this sample of FAMC, highlighting once again the same pozzolanic performance compared with commercial pozzolans and ECM index (Figure 5).

4. Conclusions

1) From the point of pozzolanic material classification, the sample of fly ash of the mineral coal (FAMC) fulfilled the regulatory requirements in force, except the material content in the loss to ignition, which should be followed in new samples and actions to fitness indicated during the industrial process.
2) Addition of 5% FAMC in traces of concrete and industrialized dry mortars presents 16% increase in compressive strength in relation to the reference traces. For the traces studied, there was a reduction in the consumption of binders, with the addition of 1.0 kg/m³ of FAMC.
3) As for the analysis of efficiency of the cementitious material (ECM), the concrete performance, with maintenance of index kilograms.binders/MPa, remained until the content of 10% FAMC.
4) The analyzed waste showed better performance than the sample of commercial pozzolan (Metakaolin HP), a fact that reinforces the need to assess the pozzolan in the cementitious system (because of its structure), and not only from the pozzolanic activity index, given by ABNT standards.

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