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ORIGINAL ARTICLE

Synergic effects between mineral admixtures on strength and microstructure of concretes

Efeitos sinérgicos entre adições minerais na resistência e microestrutura de concretos

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Abstract: The present research aims at evaluating the physical, chemical and synergistic effects of substitution 25% cement in mass by limestone filler (LF), fly ash (FA) and rice husk ash (RHA), in similarity of physical condition (near grain size curves), and to compare the different binary and ternary mixtures of concrete after 28 days of wet curing, keeping the ratio water/cement (w/c) constant. The concrete samples were characterized in relation to the axial compressive strength and their microstructure using TG/DTA and MEV/EDS techniques. The CCA in the binary mixture was the one that obtained bigger compressive strength among the investigated mixtures, but when combined with a less reactive mineral addition in ternary mixtures, an overlap of chemical and physical effects occurred which resulted in better resistance and higher C-S-H formation in the hardened cement paste.

Keywords: synergistic effect, limestone filler, fly ash, rice husk ash, concrete.

Resumo: A presente investigação tem o propósito de avaliar os efeitos físicos, químicos e sinérgicos da substituição de 25% de cimento em massa por fíler calcário (FC), cinza volante (CV) e cinza de casca de arroz (CCA), em similaridade de condição física (curvas granulométricas próximas), e comparar as diferentes misturas binárias e ternárias de concreto após 28 e 91 dias de cura úmida, mantendo-se constante a relação água/aglomerante (ag/agl.). As amostras de concreto foram caracterizadas em relação à resistência à compressão axial e quanto à sua microestrutura com uso de técnicas de TG/DTA e MEV/EDS. Os resultados indicam que uma adição mineral mais reativa como a CCA quando aliada à uma adição mineral menos reativa em uma mistura ternária, proporciona uma sobreposição de efeitos químicos e físicos que se traduz em melhores resistências e maior formação de C-S-H na pasta de cimento endurecido.

Palavras-chave: efeito sinérgico, fíler calcário, cinza volante, cinza de casca de arroz, concreto.

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1 INTRODUCTION

In recent years, climate change has concerned society and has been the subject of negotiations among world leaders to restrict greenhouse gas emissions. According to the The Intergovernmental Panel on Climate Change (IPCC) Synthesis Report [1], it is likely that the Earth's surface temperature will increase by more than 1.5 °C throughout the 21st century if pollution levels do not stop growing.

In the construction industry, the replacement of cement by mineral admixtures remains a solution with great potential for reducing the environmental impacts from the production of Portland cement. The consequence of this substitution is not negative in the sense that these additions generally improve technical properties, such as mechanical strength and durability of concrete, especially at more advanced ages. Scrivener and Nonat [2] point to the future importance of seeking an understanding of the factors that control the reaction rate of Supplementary Cementitious

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Materials (SCM), as well as the changes that occur in the calcium silicate hydrates (C-S-H), aiming at a higher use of these materials when replacing the use of Portland cement in ternary mixtures.

SCM are generally silica rich materials, largely present in the amorphous state, which influences the kinetics of cement hydration, the amount and type of hydrates formed, and consequently the volume, porosity and durability of cementitious systems [3].

These materials result in concrete physical, chemical and synergistic effects when used in ternary mixtures. The physical effect is characterized by the provision of additional nucleation points for the products of cement hydration and a change in particle packing [4]. The chemical effect is dependent on the type of mineral admixture used in the cementitious mixture and the mineralogical composition (crystalline and amorphous phases) [5].

The synergistic effect occurs when two pozzolans are combined, or when a pozzolan is combined with an inert material together with the cement in a ternary mixture, characterized by the overlapping of physical and chemical effects of one or another admixture resulting in better mechanical and microstructure properties. Isaia et al. [6] found that mixing a less reactive pozzolan with a more reactive pozzolan produces a synergistic effect between these two, which translates into a greater compressive strength. Antiohos et al. [7] carried out a study on pastes and mortars and found that the effect of ternary mixtures of different fly ash improved the mechanical properties of the mixtures compared to binary mixtures (with only one type of fly ash) due to the synergistic effect between them. Ha et al. [8] studied the synergic effect between FA and RHA in self-compacting and high performance concretes (with water/cement ratio 0,26), and observed that those pozzolans combination in ternary mixtures increased the compressive strength at the most advanced ages (56 days) in relation to the reference mixture (only Portland cement) and to the binary mixture with FA.

Limestone filler (LF) is a material considered practically inert, with little chemical activity; its preponderant effect on the concrete is the physical nucleation of new sites of hydration and closure of the pores. The presence of LF in the hydrated cement paste leads to the presence of monocarbonates in the system, which promotes the transformation of monosulfoaluminates into monocarboaluminates, inducing the conversion of monosulfoaluminate into ettringite due to the release of the sulfate during the carbonate replacement in the reaction [9]. The stabilization of ettringite in the presence of calcite leads to an increase in the total volume of hydrated phases, reducing the porosity of the system [10]. This active presence of the LF in the hydration process leads to an increase in initial compressive strength in concretes [10], [11].

Fly ash (FA) is SiO_2 rich material in its chemical composition but may also contain significant amounts of Al_2O_3. According to Lothenbach et al. [3], the mixture of Portland cement with FA results in a reduction in the amount of Portlandite (CH) and, if Class F ash (containing between 15 and 35% alumina [12]) is used, the greater are the amounts of hydrated phases rich in alumina. Under normal conditions of cure, these ashes are known to have little influence on the initial strength (up to 28 days), but they provoke a development of strength at more advanced ages, above 28 days [13].

In relation to the rice husk ash (RHA), both the low silica content (content less than 20%) and the high silica content (content higher than 80%) have a strong consumption of $Ca(OH)_2$ due to the pozzolanic reactions leading to the reduction of the C/S ratio in the C-S-H of the cementitious compound [14]. In terms of mechanical strength, RHA is known to have similar performance to silica fume, increasing mechanical strength at early ages [15]. The higher reactivity of RHA is due to the high content of amorphous silica and high specific surface of its grains [16].

A synergistic effect occurs between LF and FA that leads to better mechanical properties in the ternary concretes, attributed to the interaction of the limestone with the aluminates of the cement hydration, leading to the formation of carboaluminates. These additional aluminates brought to the system by fly ash during their pozzolanic reaction amplify the aforementioned effect of the limestone filler [17]. The bonding of LF with the RHA in the ternary mixture improves chemical and morphological properties that lead to greater compression strength and reduction of permeability in the cementitious system [18]. Vance et al. [19] studied hydration and strength increase in cement binary and ternary mixtures with LF, FA and metakaolin and verified that, for a certain substitution rate (20%), ternary mixtures (containing fly ash or metakaolin with limestone filler) had greater strengths than their correspondent binary mixtures.

The aim of this study was to analyze the behavior of ternary concrete mixtures containing LF, FA and RHA up to 28 days of wet curing, and to compare them with the respective binary mixtures at levels up to 25% cement mass replacement. The concrete samples were analyzed by means of axial compressive strength, scanning electron microscopy (SEM/EDS) and thermogravimetry (TGA/DTA).

2. MATERIALS AND EXPERIMENTAL PROGRAM

2.1 Binder materials

The type of cement used in the preparation of the mixtures was the CPV-ARI 32 [20] manufactured by a Brazilian industry. In order to replace the cement, a limestone filler (LF) from the region of Santa Maria (RS, Brazil), a fly ash (FA) from the Candiota thermoelectric plant, RS, Brazil, class C [21], and a rice husk ash (RHA) from rice industries also in the region of Santa Maria, burned without temperature control, class E [21].

The grain size distributions were approximated in order to allow admixtures to be compared to each other in the binary and ternary mixtures, without the physical effect influencing the synergic effect, that is, in similarity of physical condition. Thus, the three admixtures were milled in a ball mill at different milling times, being the LF milled for three hours, the FA for two hours and the RHA for one hour. The grain size distribution curves of the mineral admixtures obtained in the laser granulometer, using the PO-GT-1043 method, with dispersed using anhydrous alcohol and ultrasound for 60 seconds are presented in Figure 1. In Table 1 are shown the average diameters of the mineral admixtures.

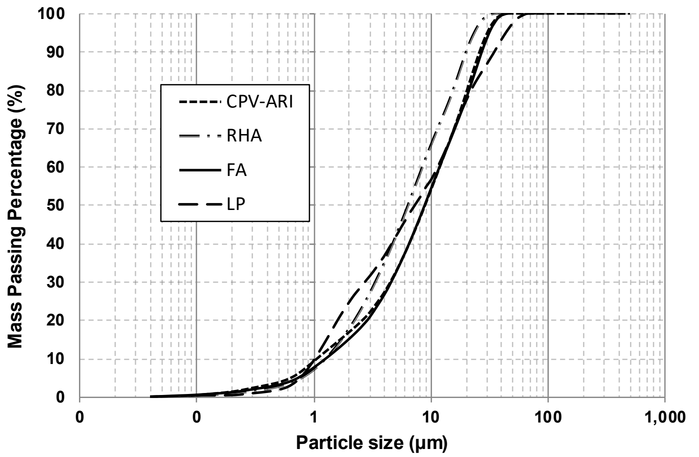

Figure 1. Particle size distribution of cement and mineral admixtures.

The mineral admixtures were statistically compared to the particle sizes (Table 1), with a 22.5% dispersion for larger grains (diameter < 90%) and a trend towards lower values for the finer grains, respectively, of 17.8% for diameters less than 50% and 10.7% for diameters smaller than 10%, which are the ones that most influence the physical effect of the reactions, the synergy and the packaging of the particles. Thus, it can be considered that, in relation to grain size, the mineral admixtures are fairly close, with a dispersion classified as medium to low, according to the granulometry range considered.

Table 1. Average Diameters of Mineral Admixtures.

Material	10% Diameter (μm)	50% Diameter (μm)	90% Diameter (μm)	Average Diameter (μm)
CPV-ARI 32 Cement	1.07	8.9	26.01	11.54
RHA (1h milled)	1.26	6.35	19.98	8.73
FA (2h milled)	1.25	8.74	26.93	11.75
LF (3h milled)	1.02	9.89	34.72	7.28
Average	1.15	8.5	26.91	9.83
Standard Deviation	0.123	1.512	6.051	2.185
Variation Coef. (%)	10.7	17.8	22.5	22.2

In Table 2 it is shown the results of the tests of the physical and chemical characteristics of the binder materials.

Table 2. Physical, mechanical and chemical characteristics of binders.

Physical properties	CP-V	LF	FA	RHA
Specific mass (g/cm^3)	3.09	2.92	2.36	2.18
Specific area BET (m^2/g)	1.14	2.64	1.04	19.67
Residual #0.075 mm (%)	0.82			
Initial setting time (min)	234			
End setting time (min)	270			
Normal consistency (%)	29.0			
Performance index with cement Portland	-	85	92	107
Compressive strength				
3 days (MPa)	27.6			
7 days (MPa)	36.2			
28 days (MPa)	42.8			
Chemical (%)				
Loss on the ignition	3.16	34.44	0.10	0.25
SiO_2	20.40	14.18	68.81	94.84
Al_2O_3	4.37	1.54	23.51	0.39
Fe_2O_3	2.64	0.87	4.70	2.58
CaO	62.90	28.89	1.00	1.32
MgO	2.70	18.28	2.16	0.40
SO_3	2.20	-	-	0.01
Na_2O	0.13	0.34	-	0.11
K_2O	0.95	0.39	0.39	1.45
MnO	0.05	-	0.68	-
TiO_2	0.29	-	0.16	-
P_2O_5	2.05	-	-	-

In the case of pozzolans tested, FA and RHA reached the chemical requirements given by the Brazilian standard NBR 12653 [21]. In relation to the performance index with Portland cement (evaluation of pozzolanic activity) at 28 days (Table 2), executed with mortars according to Brazilian standard NBR 5752 [22], it can be observed that the RHA obtained an index greater than 100%, that is, the compressive strength of the mortars with RHA were greater than the strength of the control mortar at 28 days of age, indicating good chemical activity through the pozzolanic reactions in the early ages. In spite of reaching the chemical parameters, FA did not achieve a performance of more than 90% in the performance index, as recommended by NBR 12653 [21]. It is observed that the LF with 3 hours of milling had a performance index of 85%, an index considered satisfactory since the material is an inert fine.

In relation to the specific BET surface of the cement, it is verified that the value of 1140 m^2/kg is in the expected range, considering that the cement used is a thin and low porous material. RHA presented a high BET specific surface area of 19670 m^2/kg, reflecting its highly porous internal structure with a large specific surface area, with the presence of voids, resulting in a higher demand for water (or chemical admixtures) when partial replacement of cement by this mineral admixture in the concrete. FA and LF presented values close to that of cement in the BET specific surface analysis, 1040 and 2640 m^2/kg, respectively, indicating a more spherical structure and smaller specific surface area of this admixture.

In Figure 2 it is shown the pozzolans, FA and RHA, and limestone filler (LF) diffractograms. The X-ray diffractogram of the LF shows calcite peaks ($CaCO_3$), and large peaks of dolomite carbonate ($CaMg(CO_2)_2$). The RHA X-ray diffractogram exhibits few crystalline peaks of cristobalite revealing predominantly amorphous silicon oxides in the composition. The behavior with some crystalline peaks of cristobalite and quartz indicates that the RHA was burned without temperature control. In the FA diffractogram it is observed the presence of quartz (Q), mullite (M) and hematite (H). In the comparison between the pozzolans, it is verified that the amorphization halo (between 15 and 30º 2Θ) of the RHA is broader than that of the FA, configuring greater pozzolanic activity.

2.2 Aggregates

Aiming at better packaging, the composite particles, four natural river sands with different granulometries were used, named: sand 1, sand 2, sand 3 and sand 4. The selected sands were strained in a 6,30 mm mesh strainer for the removal of stone grains, washed, taking the necessary measures in order to avoid wasting the fine grains, leaving it to decant before draining the water, and dried in an oven at 110 °C and then stored in an appropriate place (in closed boxes). Two types of diabase stones were used as coarse aggregates: gravel 0, with maximum characteristic size (MCS, [23]) of 12.5 mm, and gravel 1 with MCS of 19.0 mm. The coarse aggregate was washed, air dried and finally stored in closed boxes. The granulometric size distribution of the aggregates is shown in Figure 3. In Table 3 it is presented a summary of the characterization results of the aggregates.

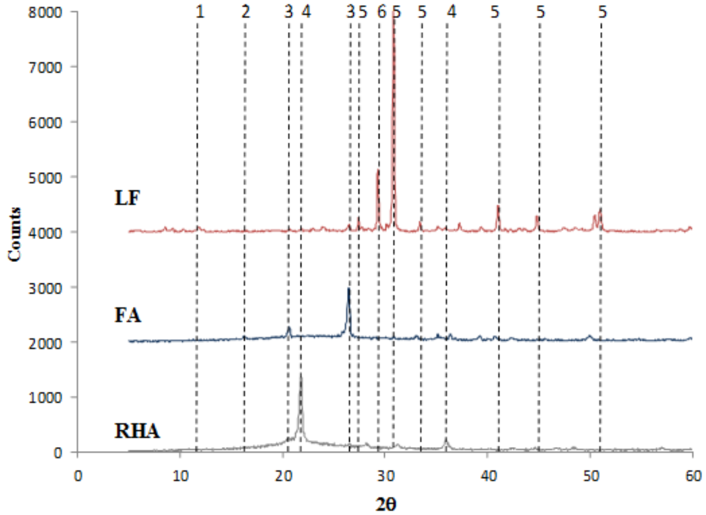

Figure 2. FA, RHA and LF diffractograms. (1) – Kaolinite; (2) – Mullite; (3) - Quartz; (4) – Cristobalite; (5) – Dolomite; (6) – Calcite.

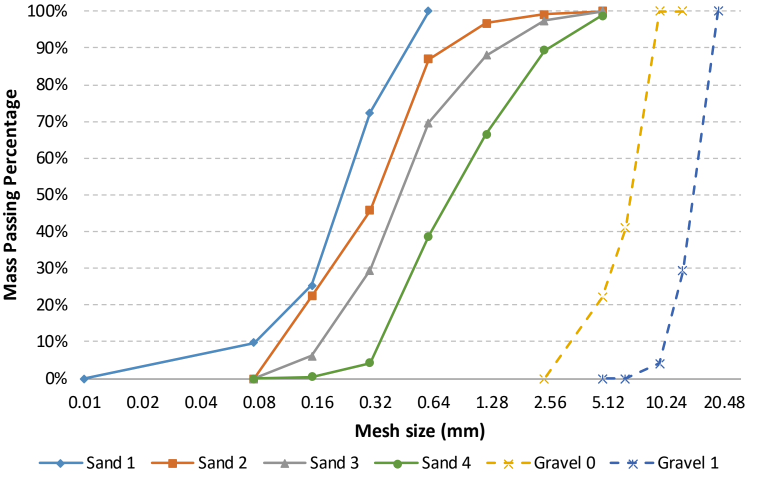

Figure 3. Particle size distribution of aggregates.

Table 3. Physical properties of aggregates.

Properties	Sand 1	Sand 2	Sand 3	Sand 4	Gravel 0	Gravel 1
Modulus of fineness	1.14	1.49	2.04	3.02	5.75	6.96
Characteristic maximum diameter (mm)	0.60	1.20	2.40	4.75	12.50	19.00
Specific mass (g/cm^3)	2.65	2.65	2.66	2.66	2.44	2.50
Unit mass (g/cm^3)	1.53	1.63	1.65	1.69	1.36	1.46
Loss of mass in Los Angeles abrasion (%)	-	-	-	-	11.04	15.20
Form index	-	-	-	-	-	2.80
Water absorption (%)	0.33	0.35	0.38	0.40	3.16	2.36
Powdery material (%)	5.50	3.00	2.80	-	-	-

2.3 Mixtures tested

The ideal mortar content was determined according to the method proposed by Helene and Terzian [23], the content of 51% was found for the chosen materials and kept constant in all mixtures. In the mixtures with mineral admixtures, the increase in paste volume was counterbalanced by reducing the volume of sand. The correction of sand amount for maintaining the paste volume in binary and ternary mixtures ensured a constant binder volume between the mixtures.

After the materials were prepared and the mortar content established, the water/binder ratio (w/b) was defined as 0.50 and cement substitution content as 25%, the best composition among the smaller amount of voids, through the analysis of the packing of particles of the constituent materials of the concrete. Thus, the binary and ternary mixtures had the aggregates varied so as to result in maximum packing. Figure 4 exemplifies the packing curve of the materials constituting Mixture 3 (binary) with 25% RHA. The attempt was to approximate the curve of the mixtures with the modified Andreasen Curve [24] by means of the variation in sand and coarse aggregate proportions. The coefficient of distribution used was 0.25, as it favors the densification of composite ceramic materials [25].

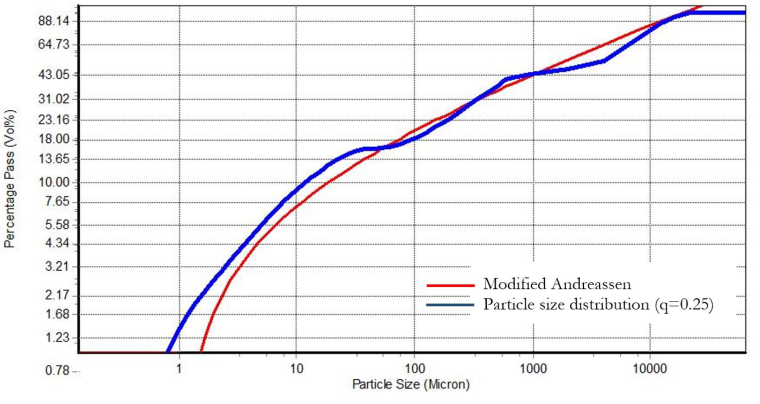

Figure 4. Example of packing curve, RHA25 mixture.

In Table 4 it is shown the unitary proportions for mixtures tested, and in Table 5 it is presented the material consumption per cubic meter of concrete. The correction in the amount of sand to maintain the paste volume in the binary and ternary mixtures ensured a constant volume of cement for all the mixtures.

For the axial compressive strength test on concrete, four cylindrical specimens were molded for each age, with a diameter of 10 cm and a height of 20 cm, according to Brazilian standard NBR 5738 [26]. The mixtures were performed in conventional inclined-axis concrete mixer, and the consistency of the concrete was kept constant for all mixtures, adopting a slump between 100 ± 20 mm. The chemical admixture used was a hyperplasticizer based on ether polycarboxylate, compatible with Portland cement. In general, the chemical admixture content remained between 0.1 and 0.2% of the mass of the binder. The specimens were densified on a vibrating table and held in the molds in a humid chamber (relative humidity of 100% and temperature of 23 ± 1 °C) for 24 hours, after which they were demolded and cured in a tank filled with lime-saturated water at a temperature of 23 ± 2 °C to date of the tests.

For the axial compressive strength data, an Analysis of Variance (ANOVA) was conducted in order to verify the statistical significance in the axial compressive strength results obtained for 7, 28 and 91 days. As a complementation of the analysis, a *post hoc* Tukey's Test was conducted, for comparing, two to two, the normal distribution data averages. The significance level adopted was 95% ($\alpha = 5\%$).

The samples for SEM were obtained after the removal of slices from the cylindrical test specimen after 28 days of curing. The slices were reduced to a maximum size of 5 mm in thickness and 20 mm in diameter. The concrete fragments were immersed in isopropanol for 7 days to stop the hydration reactions, and dried in an oven at 45 °C for a period of 48 hours. After drying, the samples were separated in closed containers and identified until they were taken to the laboratory, where they were analyzed by SEM with backscattered electrons (BSE) to shot images with the approximation of 3000x of the transition zone (ITZ) also, in the energy dispersive X-ray detector (EDS).

For each zone delimited in the BSE image, three EDS determinations were made, and with these three determinations average it was possible determine the amounts of Si, Ca e Al. It was settled that the sum of the Si, Ca and Al amounts of each of the samples correspond to the C-S-H amount, for that it was possible to accomplish a more effective comparison between the samples, basing such analysis in the studies of Durdzinski et al. [27] and Jung et al. [18].

Table 4. Unitary proportion of the studied mixtures.

Mixtures	w/b	Cement	LP	FA	RHA	Sand	Gravel	Chemical admixture
REF	0.50	1.00	-	-	-	2.06	2.94	0.0005
LF25	0.50	0.75	0.25	-	-	2.05	2.94	0.0010
RHA25	0.50	0.75	-	-	0.25	1.98	2.94	0.0030
FA25	0.50	0.75	-	0.25	-	2.00	2.94	0.0006
LF10FA15	0.50	0.75	0.10	0.15	-	2.02	2.94	0.0010
LF10RHA15	0.50	0.75	0.10	-	0.15	2.00	2.94	0.0020
FA12.5RHA12.5	0.50	0.75	-	0.125	0.125	1.98	2.94	0.0025

Table 5. Consumption of materials per m^3 of concrete (kg/m^3).

Mixture	Portland cement	LF	RHA	FA	Sand 1	Sand 2	Sand 3	Sand 4	Gravel 0	Gravel 1	Water	Chemical Admixture	Slump
1	358	-	-	-	-	-	737	-	-	1053	179	0.2	120
2	358	90	-	-	183	183	183	183	526	526	179	0.4	105
3	358	-	90	-	177	177	177	177	526	526	179	1.1	110
4	358	-	-	90	179	179	179	179	526	526	179	0.2	120
5	358	36	-	54	181	181	181	181	526	526	179	0.4	100
6	358	36	54	-	179	179	179	179	526	526	179	0.4	110
7	358	-	45	45	177	177	177	177	526	526	179	0.7	120

For the TG tests, the paste samples were prepared separately in a mechanical mixer and, after 28 days of wet curing, were ground and strained in the strainer #100 (0.15 mm mesh). For the stoppage of the hydration reactions, the paste powder was immersed in isopropanol for 15 minutes, and then filtered and washed with diethyl ether. Soon after, the samples were dried in an oven at 40 ºC for 10 minutes and stored in closed containers. During the test, portions of 15 ± 1 mg were placed in alumina melting pot and heated under inert nitrogen atmosphere, at a flow rate of 50 mL/min. Heating started from natural temperature and increased until reaching the temperature of 1000 °C, at a heating rate of 20 °C/min.

The curves resulting from the TG/DTA test on hydrated cement paste samples can be separated into bands or zones. Up to 105 ºC, evaporable water is lost, and between 105 ºC and 300 ºC, chemically combined water (BW) is lost from the decomposition of C-S-H and hydrated carboaluminates [28]. The amount of portlandite ($Ca(OH)_2$) can be calculated based on the loss of mass between the temperatures of 400 ºC and 500 °C and the calcite ($CaCO_3$) through the loss of mass above 600 °C [29].

3. RESULTS

3.1 Axial compressive strength

In Figure 5 it is presented the results of axial compression strength of the different mixtures at the initial ages, at 7, 28 and 91 days. The standard deviations resulted from each sample were indicated by the columns. The strength increased with the curing period, as expected, and at 7 days only the CCA25 mixture had a higher strength than the reference concrete, and at 28 days most of the mixtures with cement substitution by mineral additions had strength close or higher that of reference concrete. At 91 days, only the strength of the FC25 mixture was not higher than that of the reference concrete.

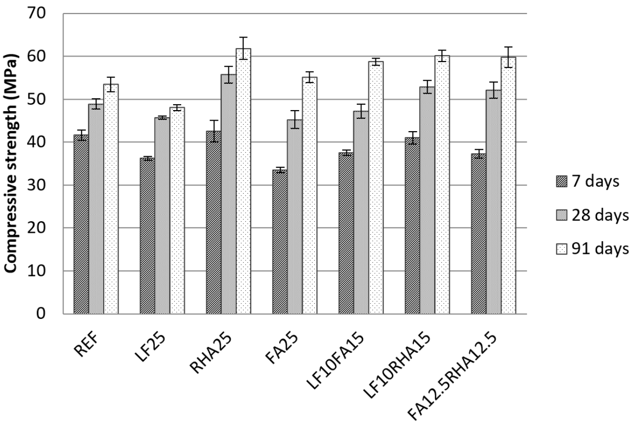

Figure 5. Compressive strength results for 7, 28 and 91 days.

Based on the Analysis of Variance *(*ANOVA*)* of the compression strength results at 7, 28 and 91 days (Table 6), it was possible to verify that there was a substantial strength difference between the evaluated mixtures. The "p" values smaller than 0,05, or $F_{calculated}$ values bigger than $F_{critical,}$ indicate that the relation between variables is statistically significant for 7, 28 and 91 days for a 95% significance level. The higher the F value, the more significant is the difference, thus at 91 days the difference was more significant than at 7 and 28 days.

In Tables 7, 8 and 9 it is presented the "p" values results obtained from the Tukey's test of comparison of compression strengths averages between mixtures at the ages of 7, 28 and 91 days, respectively. "p" values result smaller than 0,05 indicates that the strength variation between the two analyzed mixtures was significant. In those tables the significant differences were hatched with gray to facilitate identification.

Table 6. ANOVA analysis for compressive strength results at 7, 28 and 91 days.

Compressive strength at 7 days						
Variation source	**SQ***	**DF****	**AS*****	**$F_{calculated}$**	**P-value**	**$F_{critical}$**
Between mixtures	260.33	6	43.39	25.57	0.00000001	2.572712
Inside mixtures	35.63	21	1.70			
Total	295.96	27				
Compressive strength at 28 days						
Variation source	SQ	DF	AS	$F_{calculated}$	P-value	$F_{critical}$
Between mixtures	416.83	6	69.47	27.52	0.00000001	2.572712
Inside mixtures	53.01	21	2.52			
Total	469.84	27				
Compressive strength at 91 days						
Variation source	SQ	DF	AS	$F_{calculated}$	P-value	$F_{critical}$
Between mixtures	554.40	6	92.40	32.53	0.00000000	2.572712
Inside mixtures	59.65	21	2.84			
Total	614.05	27				

*SQ = the sum of the squares; **DF = degree of freedom; ***AS = average of the squares.

Table 7. Tukey's test results (p-value) for compressive strength at 7 days.

	REF	**LF25**	**RHA25**	**FA25**	**LF10FA15**	**LF10RHA15**	**FA12.5RHA12.5**
REF		0.0001	0.9454	0.0000	0.0038	0.9955	0.0020
LF25	8.2610		0.0000	0.0878	0.7842	0.0006	0.9044
RHA25	1.4320	9.6920		0.0000	0.0004	0.6667	0.0002
FA25	12.4600	4.2030	13.9000		0.0040	0.0000	0.0074
LF10FA15	6.2490	2.0110	7.6810	6.2150		0.0153	1.0000
LF10RHA15	0.8714	7.3890	2.3030	11.5900	5.3780		0.0083
FA12.5RHA12.5	6.6330	1.6280	8.0650	5.8310	0.3839	5.7620	

Table 8. Tukey's test results (p-value) for compressive strength at 28 days.

	REF	LF25	RHA25	FA25	LF10FA15	LF10RHA15	FA12.5RHA12.5
REF		0.1454	0.0001	0.0126	0.8017	0.0226	0.0896
LF25	3.8270		0.0000	0.8934	0.8364	0.0001	0.0002
RHA25	8.9160	12.7400		0.0000	0.0000	0.1521	0.0413
FA25	5.4980	1.6710	14.4100		0.2094	0.0000	0.0000
LF10FA15	1.9640	1.8630	10.8800	3.5340		0.0010	0.0044
LF10RHA15	5.1230	8.9500	3.7920	10.6200	7.0870		0.9935
FA12.5RHA12.5	4.1890	8.0160	4.7270	9.6870	6.1520	0.9347	

The Tukey's Test results confirm that cement substitution for mineral admixtures in binary and ternary mixtures may result in significant strength variations at the early ages. In the binary mixtures at 7 days (Table 7), only the 25% RHA substitution (*RHA25*) did not result in a significant compression strength decrease, but in an increase, showing the excellent performance in the early ages of CCA. In the ternary mixtures, the *LF10FA15* and *FA12.5RHA12.5* also resulted in significantly smaller strengths than the *REF* mixture at 7 days.

From the results presented in Table 8 it is noticed that cement substitution for 25% of RHA (*RHA25*) resulted in a significant compression strength increase at 28 days. The mixtures that exceeded 50 MPa at 28 days were binary with 25% RHA (*RHA25*) and the ternaries LF with RHA and FA with RHA, mixtures *LF10RHA15* and *FA12.5RHA12.5*, respectively. These were the same mixtures that outperformed the reference concrete (*REF*), yet only in the *RHA25* and *LF10RHA15* they resulted in a significant compressive strength increase. The 25% cement substitution for fly ash *(25FA)* resulted in a significant compressive strength decrease at 28 days in relation to the reference concrete. The other mixtures did not result in significant variations in relation to the reference mixture.

The binary concretes of LF (*LF25*) and FA (*FA25*) obtained very close compressive strengths. The mixture with 25% FA reached 45.2 MPa at 28 days and at 25% LF reached 45.7 MPa, indicating that the FA acts predominantly through the physical effect in the early ages, since the mixture with the limestone filler resulted in almost the same strength, that is, there was no significant difference between results.

At 91 days (Table 9), the increase in compressive strength in relation to the reference concrete was significant for most mixtures with mineral admixtures: *RHA25*, *LF10FA15*, *LF10RHA15* and *FA12.5RHA12.5*, which reached strengths of 61.8 MPa, 58.7 MPa, 60.1 MPa and 59.7 MPa, respectively. In the case of the LF25 mixture, there was a significant reduction in strength, with an average value of 48.0 MPa, and the reference concrete had an average strength of 53.4 MPa.

Table 9. Tukey's test results (p-value) for compressive strength at 28 days.

	REF	LF25	RHA25	FA25	LF10FA15	LF10RHA15	FA12.5RHA12.5
REF		0.0028	0.0000	0.9995	0.0036	0.0003	0.0050
LF25	6.4320		0.0000	0.0011	0.0000	0.0000	0.0000
RHA25	9.9650	16.4000		0.0000	0.1736	0.7753	0.1346
FA25	0.5844	7.0160	9.3810		0.0093	0.0006	0.0127
LF10FA15	6.2780	12.7100	3.6880	5.6930		0.8982	1.0000
LF10RHA15	7.9300	14.3600	2.0350	7.3460	1.6520		0.8403
FA12.5RHA12.5	6.0790	12.5100	3.8860	5.4940	0.1988	1.8510	

Figure 6 shows the average compressive strength indexes at 7, 28 and 91 days for the tested mixtures. The strength index is the relationship between the strength of the mixture with SCM and the reference mixture, for equal age and ag/agl ratio. From these results, it is possible to note, with greater evidence, the effects of mineral admixtures in the increase of the compressive strengths of the investigated mixtures with increasing age, based on the evolution of the average strength indexes.

In the comparison between binary and ternary mixtures it is noticed that the *LF10FA15* mixture achieved a slightly higher compressive strength than the respective binary mixtures *LF25* and *FA25*, as also verified by De Weerdt et al. [17], significantly higher at 91 days. For the *LF10RHA15* the strength increase was significant at 91 days in relation to the mixtures REF, *25LF* and *25FA* and ternary, *LF10FA15,* which demonstrated that there is sinergy between those two mineral admixtures, as also observed by Jung et al. [18]. In the case of the *FA12.5RHA12.5* mixture, it obtained significantly greater strength than the respective binary mixture with FA.

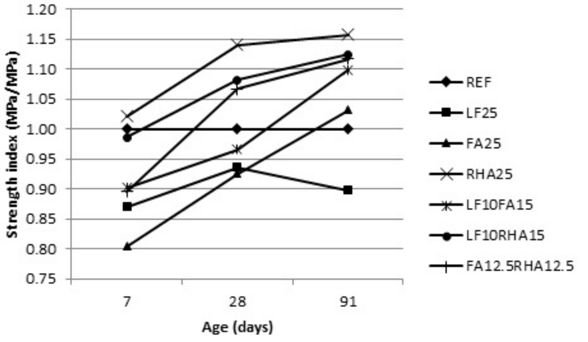

Figure 6. Strength index of the investigated mixtures.

The mixtures *RHA25*, *LF10RHA15* and *FA12.5RHA12.5* were the ones that obtained the best performances in the studied conditions in relation to the reference concrete, showing that the use of a more mineral admixture like RHA together with a less reactive one like LF or FA is effective for strength gain.

Assuming that mineral admixtures were analyzed in similarity of physical conditions, that is, with little difference between curves in all size ranges (Figure 1), so that it enables a more homogenous analysis between the binary and ternary mixtures with regards to their chemical and synergic effects, it is possible to observe a better performance of ternary mixtures in relation to the respective binary mixtures with less reactive mineral additions (LF e FA), indicating an overlapping of chemical effects (synergic effect) of those less reactive additions when they are used together with a more reactive addition (RHA) in ternary cementitious systems.

3.2 Scanning Electron Microscopy (SEM/EDS)

The microscopy images collected by BSE and EDS characterize the compounds formed in the hydrated cement paste in the concrete samples. These results allowed to make a qualitative analysis of the transition zone (ITZ) based on the images collected in the BSE with a 3000x approximation, and a quantitative analysis in terms of percentage of the compounds (Si, Ca, Al and C-S-H) present in the fragments of concrete with EDS after 28 days of wet curing. In the images presented in Figures 7, 8, 9 and 10, a region corresponding to the square indicated on the image was selected for collecting the EDS spectra shown next to each image.

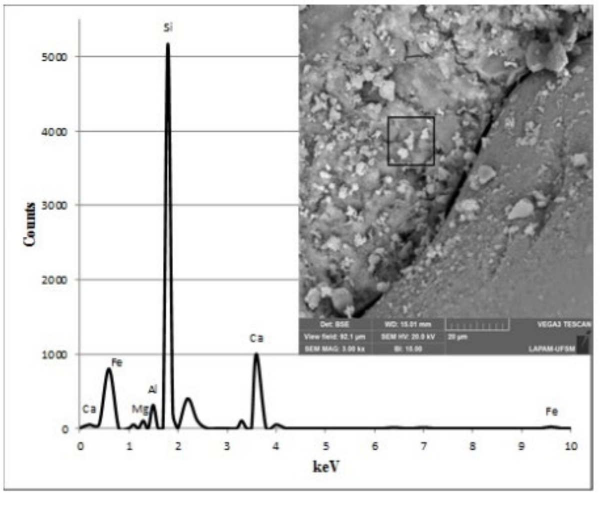

Figure 7. SEM/EDS image for REF mixture.

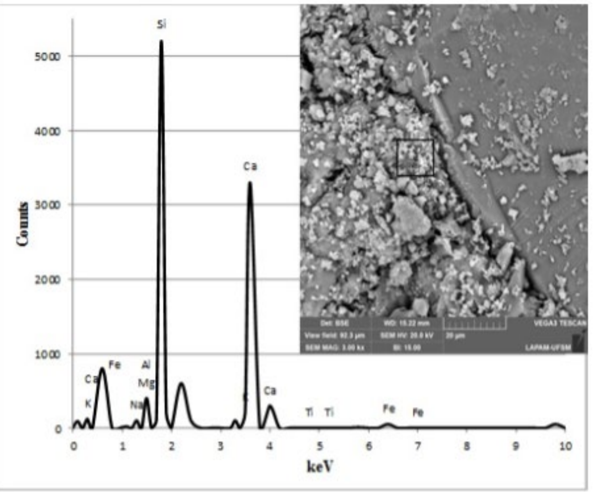

Figure 8. SEM/EDS image for LF10FA15 mixture.

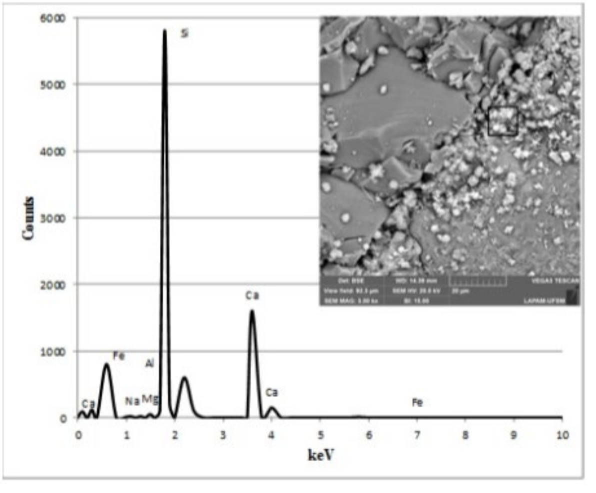

Figure 9. SEM/EDS image for LF10RHA15 mixture.

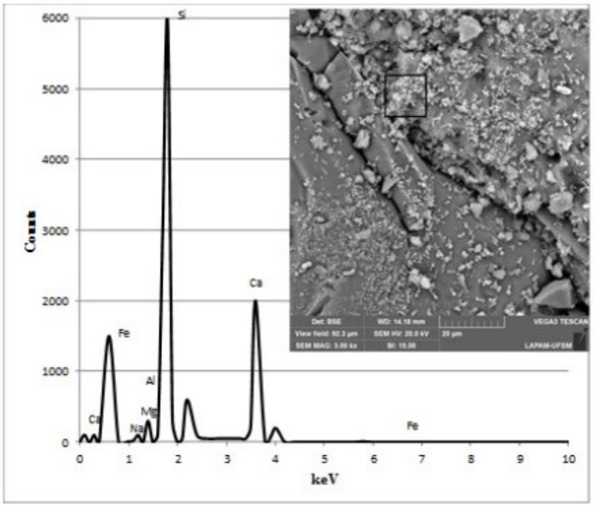

Figure 10. SEM/EDS image for LF12.5RHA12.5 mixture.

It can be seen in Figure 7 that the reference concrete (*REF*) has a porous transition zone and with fewer C-S-H microcrystals. In contrast, in Figures 8 (*LF10FA15*), 9 (*LF10RHA15*) and 10 (*FA12.5RHA12.5*), it is notable the increase in the amount of C-S-H agglomerates around the aggregate in the transition zone and a less porous and more uniform concrete in ternary mixtures than in the reference one (*REF*), as pointed by Mohammed et al. [30].

In Figure 11, it is possible to observe the mass percentages of Si, Ca, Al and C-S-H, and the value of C-S-H corresponds to the sum of the three compounds found in the EDS of the concrete samples.

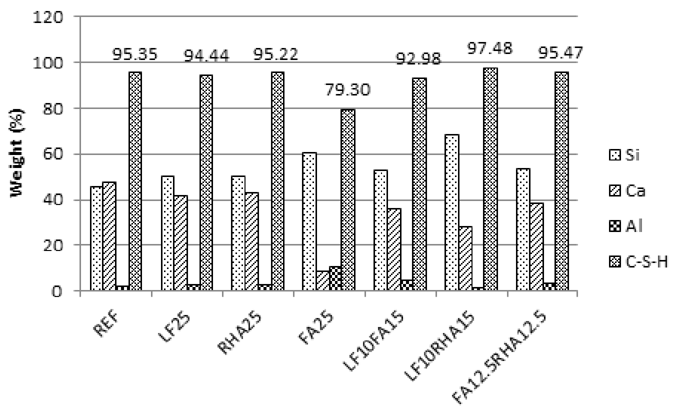

Figure 11. Percentage of weight of Ca, Si, Al and C-S-H obtained from the EDS spectrum.

The sample with the lowest amount of Ca and Si was with 25% FA (*FA25*), and the one with the highest Ca and Si amount was the ternary mixture of LF with RHA (*LF10RHA15*), revealing a synergy between these two additions in cementitious mixtures. All the mixtures with mineral admixtures showed higher Si contents than the reference concrete (*REF*). The mixture with higher presence of Al was the binary *FA25*, due to the chemical composition of the FA class F, with high content of alumina. The mixture that presented the highest content of C-S-H was *LF10RHA15*, evidencing a higher formation of hydrated calcium silicates in the ternary mixtures with LF and RHA.

3.3 Thermogravimetric analysis (TGA/DTA)

In Figures 12 and 13 it is shown the thermogravimetric curves TGA and DTA of the seven mixtures studied, respectively. A summary of the mass losses corresponding to the compounds formed in the cement paste is in Table 10.

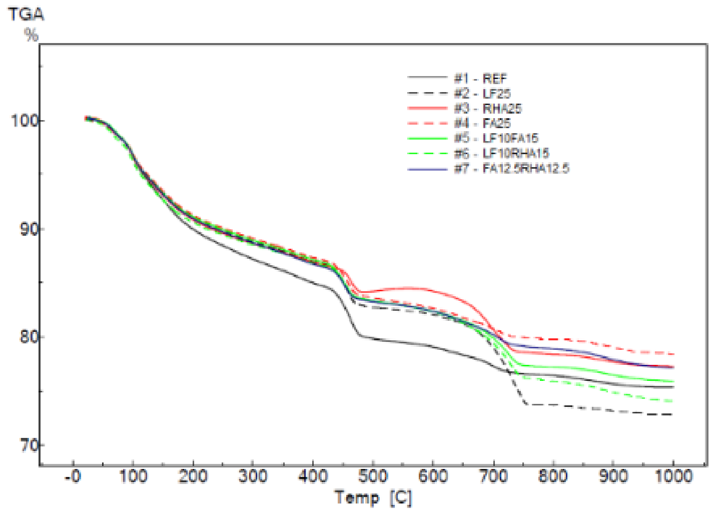

Figure 12. TGA curves for concrete mixtures tested.

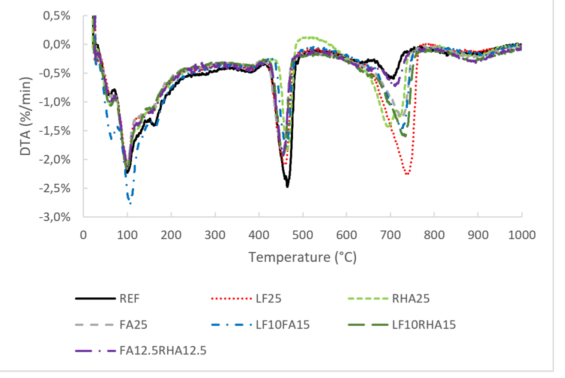

Figure 13. DTA curves for concrete mixtures tested.

Table 10. TGA/DTA results.

Mixture	BW (%)	Ca(OH)₂ (%)	CaCO₃ (%)
REF	8.91	5.16	0.78
LF25	7.46	4.23	8.38
RHA25	7.50	2.67	5.84
FA25	7.35	3.73	2.85
LF10FA15	7.34	3.79	5.14
LF10RHA15	7.16	3.48	6.37
FA12.5RHA12.5	7.54	3.47	3.47

The results of the thermogravimetric analysis at 28 days indicate that there was reduction of the remaining calcium hydroxide (CH) with the use of mineral admixtures in concrete. The mixture in which there was the highest consumption of CH was the binary mixture with 25% of RHA (*RHA25*), and in the ternary mixtures of LF and RHA (*LF10RHA15*) and FA and RHA (*FA12.5RHA12.5*), there was a very approximate consumption of CH of 3.48% and 3.47%, respectively. The reduction of the percentage of portlandite in the binary and ternary mixtures indicates the consumption of CH in the pozzolanic reaction and consequent formation of the secondary C-S-H [3].

The water content was lower in the mixtures with mineral admixtures than the reference concrete. In the mixtures with admixtures the values were very close, between 7 and 7.5%. In mixtures with 100% cement (*REF*) and *LF25* there is clearly a higher peak around 180 ºC relative to the formation of monosulfate e hemicarbonate [31]. On the other hand, there is a greater formation of $CaCO_3$ in all mixtures with mineral admixtures in comparison to the pure-cement mixture.

A better evaluation of the relative performance of the mineral additions is done through a unitary analysis, i.e., relating the results with the consumption of cement (per kg of cement) for each mixture. Thus, it was possible to obtain a comparative graph (Figure 14) between the unitary compressive strength and the contents of calcium hydroxide (CH), bind water (BW) and calcite ($CaCO_3$). The unitary contents are obtained by calculating the result by mass of cement of the mixtures.

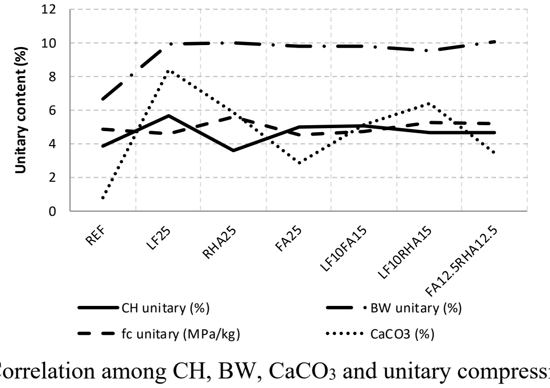

Figure 14. Correlation among CH, BW, $CaCO_3$ and unitary compressive strength.

In relation to the unitary content of CH, the inversely proportional relation between the axial compression strength and the CH amount is evident. The consumption of CH and consequent formation of secondary C-S-H in mixtures with mineral admixtures resulted in increased strength at 28 days of age.

There was a higher formation of calcium carbonate ($CaCO_3$) in the binary and ternary mixtures with LF. There is also a correlation between carbonate formation in the presence of RHA, in both binary (*RHA25*) and ternary (*LF10RHA15*) mixtures. There was a higher carbonate formation in the mixtures with the presence of mineral admixtures than in the reference mixture (*REF*), and the presence of the carbonate is directly proportional to the compressive strength in the ternary mixtures (Mixtures *LF10FA15* and *LF10RHA15*). The same occurred for unit bind water, which was higher in mixtures with mineral admixtures than in the reference mixture.

4 CONCLUSIONS

The conclusions based on the results of compressive strength and analysis of the microstructure of concrete samples with substitution of cement by LF, FA and RHA in binary and ternary mixtures, are as follows:

1. The use of RHA in binary and ternary mixtures increases the compressive strength of concrete mixtures in relation to the reference concrete, mainly at 91 days.
2. RHA is the most reactive mineral admixtures in the study, due to the presence of amorphous silica in its composition and the high specific surface of its particles. RHA was also the mineral admixture that resulted in the highest CH consumption and the highest unitary combined water content (per kg of cement).
3. The ternary mixture with LF and RHA (*FC10CCA15*) resulted in bigger compressive strength and formation of C-S-H compared to the reference mixture and the other mixtures with LF and FA, evidencing a synergic effect between these two mineral admixtures. The synergistic effect on ternary mixtures with LF is directly related to the higher carbonate formation in these mixtures.
4. When a less reactive pozzolan, such as FA, or even a non-reactive addition, such as LF, is used together with a more reactive one, such as RHA, a synergy occurs between them due to a chemical interaction, resulting in an increase in secondary C-S-H content and lower porosity at the paste-aggregate interface zone.

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