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Usage potential of fly ash an metakaolin in cementitious materials for 3D printing

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ABSTRACT

The technology of 3D printing has been studied by different researchers, due to the possibility of producing solid objects swiftly, time reduction, labor with fewer failures the construction process. One of the challenges to be overcome is related to the development of mixtures promising. Thus, research aimed at the technology of cementitious materials is necessary to develop extrudable and sustainable mixtures. This article aimed to investigate the potential use of (FA) and (MK) in cementitious materials for application in three-dimensional printing (3D) by checking the aspects of constructibility. In the first stage, tests of normal consistency and initial and final setting time were carried out on pastes, with calcium oxide 4% and addition of (FA) and (MK) in the percentages of 8%, 10% and 15% in relation to the cement mass, in order to establish an ideal water / cement ratio. In the second stage, given a pre-determined trace of 1: 1.5, in mass, the viscosity, yield stress, extrudability and verticality tests were carried out on the cementitious materials developed in the first stage. It was observed that for the aspects related to the normal cement consistency and initial and final setting time, the paste with 15% substitution (FA) presented a longer initial setting time when compared to pastes with (MK) added. yield stress, materials with 15% substitution (FA) and without superplasticizer additive showed favorable results in the relation of the initial and final yield stress, as the mixture of 15% (MK) with 0.4% superplasticizer additive. and, therefore, they were considered promising because they were subjected to extrudability and verticality tests. Thus, it is concluded that considering the constructibility applied to prototyping, cementitious materials with 15% substitution (FA) and (MK) in relation to the cement mass present results considered relevant for the application in 3D printing.

Keywords: Cementitious materials, mineral additions, disruptive technology, additive manufacture.

1. INTRODUÇÃO

In recent years, civil construction has undergone several transformations, this due to several factors, including the insertion of three-dimensional technology (3D). Born with the promise of liberating forms in architecture using digital manufacturing, the growing interest in 3D printing is also driven by time and cost saving opportunities, on-site safety and environmental concerns to optimize material and waste reduction [1]. With the continuous development of technology, new opportunities and challenges are presented in the construction industry. Digital manufacturing techniques have rapidly developed and made possible, without future, a replacement of traditional formwork construction technology [2]. This technology the 3D printing has supported changes in the automotive, aerospace and health sectors, also in general industries and in the civil construction. [3, 5, 6].

The constructions that adopt the conventional system of construction using concrete and masonry use an expressive quantity of molds to make possible the concreting of elements. Associated to the constructive process, it is allied the high cost, waste and longer time of labor for the preparation and mounting of the molds [4].

At the 1st RILEM International Conference on Concrete and Digital Fabrication, held in 2018, there was a considerable increase in publications related to digitally manufactured concrete [6]. One of the examples is the printed concrete by extrusion, led by Prof. Khoshnevis, [3] and other research groups present different lines of study, for example, Apis Cor and Win Sun introduced reinforcement in its printed elements producing a permanent 3D printed formwork and placing it inside it the rebar [7].

To attend the necessary requirements for the use of 3D printing, a number of studies are related to the development of special concretes that attend the necessity of pumping and extrusion through nozzles and rheological characteristics of the materials used [12]. Printability is controlled by many factors, including

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flowability (workability), extrudability, buildability, interlayer bonding and open time. Flowability and extrudability are interrelated, while flowability and buildability are opposed to each other [2]. These researches have indicated that there is not a unique mixture that attends the requirements of 3D printing. Thus, this fact leaves room for innovation concerning the use of different materials that combined may present the necessary characteristics for the construction of elements with this technology [8].

According to [9] the challenge still seems to be the transformation of available high-quality cementitious materials, specifically also concrete materials complying with valid structural concrete codes, to printable materials, so that we can move from formwork-based technologies to more automated additive manufacturing approaches. It is noticed that the mixture must present gain of resistance relatively quick and yield stress sufficient for the inferior layers not to be deformed when receiving the loads of the superior layers [13]. For the mix to be printable, it should be capable of being pumped, extruded and deposited in layers within an optimized duration of time. The printing time-gap between layers is complicated by the scale and complexity of the geometry [8]. These characteristics were reached through tests performed abroad using, in most cases, the sulfo-aluminous cement as binder [4].

The according to [4] sulfo-aluminous cement it presents some characteristics favorable to its applicability in 3D printing, among they can be mentioned: initial setting time, high resistance in the first few ages and continuous development of resistance over time. Since this cement is not commercialized in Brazil, its use is not viable. Thus, it is important to study the substitution or adequation of the commercial cements to obtain characteristics that make possible the application of 3D printing. One of the possibilities of developing cements with characteristics similar to sulfo-aluminous cement is through additions, such as (FA) and (MK), this is due to the fact that enables a pozzolanic reaction, and that, through silicates, provide the production of secondary calcium silicate (C-S-H) [10, 27].

The addition of (FA) in the mixtures for 3D printing allows changes in terms of shear stress similar to the use of plasticizers making it extrudable and printable, and yet, it can result in greater adhesion strength and adhesive energy for these binders when compared to conventional binders cement-based [11]. Already the inclusion of (MK) due to its high pozzolanic activity, physical and chemical specification improves the mechanical strength and durability, [10]. However, pozzolanic additions can delay or start the process of capturing the mixture, a property that is undesirable for 3D printing. This occurs due to changes in the cement hydration process and the release of hydrogen from calcium, being one of the solutions for reversing or increasing the calcium oxide in the mixture [34].

According to [9] in the technology 3D printing, the challenge still seems to be the transformation of available high-quality cementitious materials, specifically also concrete materials complying with valid structural concrete codes, to printable materials, so that we can move from formwork-based technologies to additive manufacturing approaches. This article focused on the study of cement mixtures with sustainable additions through analysis of the characteristics considered promising for applications in 3D printing. Thus, the objective to comparatively investigate the potential of cementitious materials with substitution of fly ashes (FA) and metakaolin (MK) in terms of buildability.

2. MATERIALS AND EXPERIMENTAL METHOD

2.1 Materials

The materials used in this study were the cement Portland of high initial resistance CP V – ARI; fine aggregate – medium quartz sand; fly ash (FA); metakaolin (MK); calcium oxide and water provided by the local supply company.

According to the NBR 16697:2018 [14] the cement CP V – ARI is the purest cement commercialized in Brazil, that being the reason why it was chosen to be used in this research. The characteristics of the cement CP V – ARI are specified in Table 1.

Tabela 1: Mechanical and physical properties of the cement CP V - ARI.

RESISTANCE TO COMPRESSION (MPA)				BLAINE FINENESS (CM^2/G)	SETTING TIME (MIN)	
24 HOURS	3 DAYS	7 DAYS	28 DAYS		INITIAL	FINAL
27	27	42	48	5330	160	265

Source: [15]

The characterization of the fine aggregate was performed through analysis of granulometry, specific mass, unitary mass and content of powdery tests, these following the normative procedures of the NBR 248:2003 [16], NBR NM 52/2009 [17], NBR NM 45/2006 [18], and NBR NM 46/2003 [19], respectively. In Figure 1, it is possible to observe the granulometric curve of the fine aggregate.

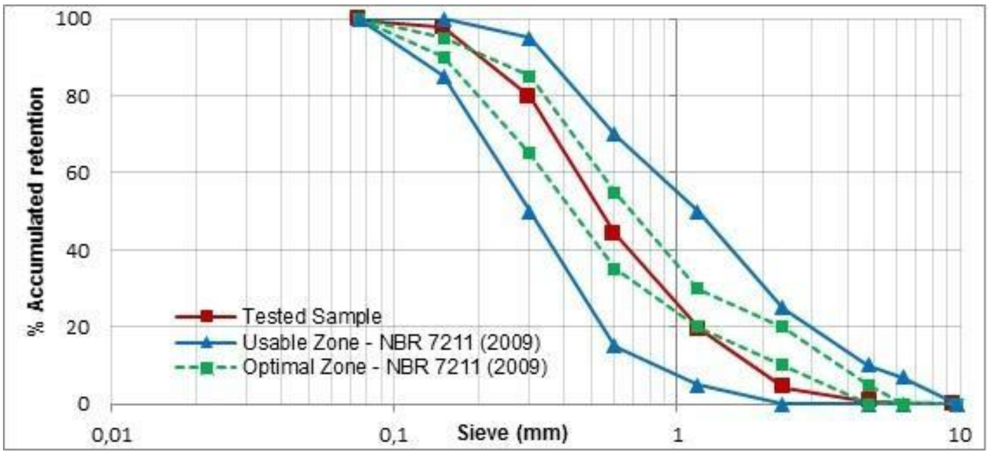


Figure 1: Granulometric curve of the fine aggregate

It is noted that the sand presents granulometric curve within the limits stablished by the NBR 7211:2009 [20]. Given the maximum dimension that attends the conditions imposed for the materials used in 3D printing as 2.4 mm. [21, 4], reported that the aggregate must present an average dimension of 2 to 3 mm. The sand applied in the test presents fineness module equals to 2.45 what classifies it, within the limits, as an average quartz sand, specific mass of 2.65 g/cm^3; unitary mass without compacting of 1.63 g/cm^3 and content of powdery material of 0.47%.

Approximate values were obtained by [2], when developing a study with mortars and analysis of their respective deformations during the 3D printing process. The researchers used sand with a fineness module and apparent density of 2.1 and 2.6 g/cm^3, respectively. According to [4], in the process, the 3D printer will be fed by material through a pump, high pressure pipe and a nozzle, the smallest diameter in this route could is the nozzle diameter. Hence, and in order to ensure proper flow of material the maximum size of aggregate cannot exceed the nozzle diameter.

Regarding the (FA) these are considered pozzolan, obtained through the calcination of coal in the fluidized bed boilers, what are part of the process of energy production. According to [22], an (FA) is produced through the combustion of coal in boilers, in a high temperature process and is commonly used as a main component of cement or concrete components.

The (FA) presents high fineness of the grains, the particles may vary from 1 μm to 100 μm of diameter with vitreous mineralogical composition, with 60% to 85% of amorphous silica [23, 24]. According to [25], the production of fly ash is only in the state of Rio Grande do Sul are around 1.5 million tons/year and worldwide annual production is estimated at 500 million tonnes, which corresponds to 75 to 80% of the total ash generated [26].

Fly ash established among the main mineral additives, due to its pozzolanic characteristics, that is, they must be effectively rehabilitated with a portlandite to produce the C-S-H gel, whose structure is similar to the C-S-H gel used by hydrogen. Thus, it may be that pozzolans can contribute to the development of concrete properties [27]. The main characteristic associated to the pozzolanas is the reaction caused by the combination with calcium hydroxide $Ca(OH)_2$, forming stable products with binding properties, given that these reactions result in the formation of calcium silicates more stable than these originally formed by the hydration of Portland cement [28].

According to [24], the cohesion and viscosity of the concretes and cementitious material in the fresh state are influenced by the minerals addition, mainly for the additions that present average diameters (specific surface) inferior to these of the cement, as the (FA). Furthermore, the lower specific mass of these materials when substituting the cement causes the elevation of the volume of binders, influencing the rheological properties of the cementitious materials. For [29] the addition of (FA) in concretes is responsible for the alteration of its performance in the fresh and hardened state, modifying its mechanical properties and durability.

The choice of substituting the mass of cement by (MK) had as basis scientific researches as [30], who studied the incorporation of (MK) as substitute for the Portland cement in 23 concretes and observed that it promoted reduction of retraction by drying, and therefore may result in a greater geometric stability for the cementitious material; [31] studied the influence of substituting the Portland cement by (MK) in concretes in the percentages of 8% and 10% and [32] in concretes of high performance in the percentages of 5%, 10%, 15% and 20% and concluded that the percentages that presented the best results in the fresh and hardened states are 8%, 10% and 15% as substitution for the cement mass.

CASTRO *et al*. [33], described the (MK) as clays that in process of calcination, originate the metakaolinite of non crystalline structure and elevated fineness. Concerning the chemical composition of the (MK) when compared to the sulfoaluminous cement (SAC), commonly used in 3D printing, it is observed similar proportions of the chemical compounds Al_2O_3 and Fe_2O_3, given that in terms of percentage in mass, regarding the Al_2O_3, the (MK) contains 40.18% and the (SAC) 35.17%, Fe_2O_3 (MK) contains 1.23% and (SAC) 1.53% [4].

Concerning cementitious materials applied to 3D printing with substitution of (FA), that may reduce the quantity of calcium hydroxide $Ca(OH)_2$ in the mixture, since its release is related to the cement hydration. The smaller quantity of $Ca(OH)_2$ in the mixture decreases the reactivity of the pozzolanic additions, since besides remaining inactive until the cement hydration, the release of $Ca(OH)_2$ in the mixture will be even lower due the substitution of (FA). As a method to accelerate the reaction during the initial hours, the addition of calcium oxide will cause alteration in the setting time [34].

DONATELLO *et al.* [35] performed studies regarding the pozzolanic activity of different additions when used in substitution for the Portland cement. It was observed that in the sample with (FA) addition, after the complete hydration of the cement mass, only 25% resulted in $Ca(OH)_2$, it occurs due the fact that the (FA) consumes $Ca(OH)_2$ for its own hydration. A solution for its consumption is adding a quantity of $Ca(OH)_2$ equivalent to the quantity removed, in other words, 25% of the quantity in cement mass. In this article, there were added 4% in relation to the cement mass of calcium oxide for all the pastes and cementitious materials developed in the experimental program.

2.2 Experimental Method

The experimental method was divided in two study stages: pastes and cementitious materials, the mixtures developed were named according to the materials used, as example, for the paste and cementitious material without additions, it was adopted as p_reference and mat_reference, respectively, and for the others, the nomenclature was given through the percentage and the type of addition - (FA) or (MK). In Figure 2, it is possible to obtain the flowchart referred to the experimental stages.

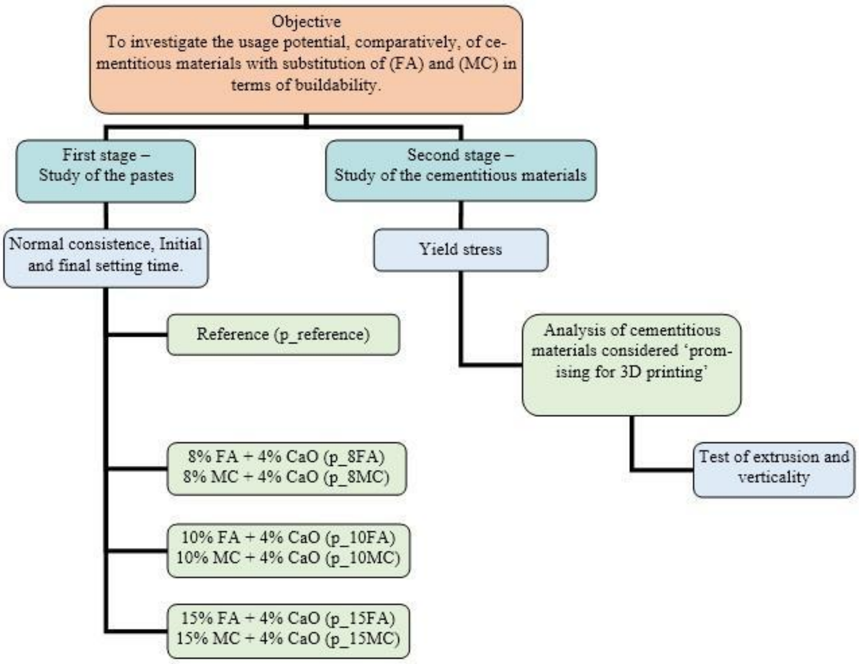


Figure 2: Flowchart of the experimental program

In the first stage, denominated study of the pastes, there were performed tests of normal consistence of cement according to the NBR 16606:2018 [36] and of initial and final setting time according to EN - UNE 196-3:2016 [37], with Vicatronic device of the Matest enterprise.

The test of normal consistence of the cement presented as purpose to define the ideal ratio water/cementitious for the development of pastes to be submitted to the test of initial and final setting time. For the test of normal consistence there were used the quantities of materials according to proportions presented in Table 2, given that the volume of water was gradually determined during the test until reaching the mold depth of 5 to 7 mm according to normative recommendations.

Table 2: Proportionality of materials in pastes.

PASTES	BINDERS			
	CEMENT CPV - ARI	MK	FA	CAO
p_reference	1	0	0	0
p_8FA	0,92	0	0,08	0,04
p_8MK	0,92	0,08	0	0,04
p_10FA	0,9	0	0,1	0,04
p_10MK	0,9	0,1	0	0,04
p_15FA	0,85	0	0,15	0,04
p_15MK	0,85	0,15	0	0,04

After the definition of the relations water/cementitious for each paste, it started the test of initial and final setting time, in order to stablish the minimum initial setting time for each paste with and without substitution (FA) and (MK), so afterwards it is possible to relate these with the results for yield stress obtained in the second stage - study of cementitious materials. This fact is justified, since after the initial setting time the cementitious materials tend to cause greater resistances in a fine pellicle between the layers leading to difficulty in the verticalization, as the stacking and adherence [38].

In the second stage there were performed tests of yield stress, extrudability and verticality in cementitious material developed through the pastes stablished in the first stage, with binding relation and sand of 1:1,5 and ratio water/cementitious of 0.4, according to quantities of materials disposed in Table 3.

Table 3: Trace of the cementitious materials.

CEMENTITIOUS MATERIALS	BINDERS					ADDITIVE
	CEMENT CPV - ARI	FA	MK	SAND	CAO	
mat_reference	1	0	0	1,5	0	0
mat _8FA	0,92	0,08	0	1,5	0,04	variable
mat _8MK	0,92	0	0,08	1,5	0,04	variable
mat _10FA	0,9	0,1	0	1,5	0,04	variable
mat _10MK	0,9	0	0,1	1,5	0,04	variable
mat _15FA	0,85	0,15	0	1,5	0,04	variable
mat _15MK	0,85	0	0,15	1,5	0,04	variable

Sequentially, in all cementitious materials there was alteration in the quantity of superplasticizer in the range recommended by the manufacturer, of 0 to 0.5% in relation to the mass of cement, so that these were analyzed regarding the gain of yield stress in function of time, given that the ones that obtained the best results were submitted to tests of extrusion and verticality, characteristics considered necessary for the application in 3D printing according to the study of [13].

2.2.1 Evaluation of Yield Stress

For the determination of yield stress through the test with the Vicat device, [39] stablishes a relation between the radius R of the Tetmajer sounder, equals to 0.5cm, and the height of penetration h in the cementitious material, where 0 cm represents the moment when the sounder touches the cementitious material, according to equation 1.

$$T_0 = \frac{3}{(2\pi R h)} \quad (1)$$

For the determination of height of penetration h, it was opted to stablish the measure of 0 cm in the height where the sounder touches the surface of the cementitious material in the mold. When leaving the sounder, it is measured the number of centimeters that the sounder penetrates in the mass. [40] in its study affirms, by evaluating the yield stress for cementitious materials applied to 3D printing, that it is necessary for the final (45 min) and initial (10min) relation stress to be in the interval between 25 and 150. Thereafter, besides the graphics of yield stress by time, in this article there were determined the relations between final and initial stresses to verify if any of the cementitious materials were presented within the interval proposed. The cementitious materials that presented the best evolution in yield stress were submitted to tests of extrudability and of verticality.

2.2.2 Evaluation of Extrudability

For the extrusion evaluation of the cementitious materials, it was performed a test using a silicone pistol. For that, the pistol nozzle was cut in order to maintain an opening of 2 cm, as [21], suggests being ideal for 3D printings with circular nozzle, according to Figure 3.

Figure 3: Silicone pistol.

The extrusion of the cementitious materials was evaluated visually and based on the following premises:
- workable mixture capable of going through the pistol nozzle;
- mixture with yield stress such that it does not flow through the exit opening due its own weight;
- mixture that flows without segregation or filtration (exit only of the cream);

After the verification of the extrusion capacity, it began the verticality test.

2.2.3 Evaluation of Verticality

For the test of verticality, since there is no normative that evaluates this characteristic, the study performed by [13] was used as reference. Thus, it is considered a wall of 0.20 m of width and 3 m of height, it was decided to impose a horizontal scale of 1:10 and a vertical scale of 1:20. Therefore, there was printed a 3D wall of 2 cm width and 15 cm height.

The decision for a vertically greater scale occurred, since it is believed that a scale of 1:10 would be integrating an elevated neatness in the element, thus the collapse of the element would be a possibility – not necessarily for not attending the characteristics of a 3D printing – but due its elevated neatness and this property will not be evaluated in this article.

For the determination of the time between the printing of each layer, it was considered the time that the combination presented the greatest gain of yield stress, according to [13].

3. RESULTS AND DISCUSSION

3.1 Study of the pastes

In table 4, there are presented the different results obtained in relation to the ratios water/cementitious for each of the pastes with and without substitution (FA) and (MK).

Table 4: Results of ratios water/cementitious from the test of normal consistence

PASTES	RATIOS WATER/CEMENTITIOUS
p_reference	0,32
p_8FA	0,34
p_8MK	0,37
p_10FA	0,34
p_10MK	0,37
p_15FA	0,35
p_15MK	0,39

As it is observed in Table 4, from the test of normal consistence, the pastes with substitution of (FA), when compared to the pastes with (MK), obtained lower values of relations water/cementitious, it possibly occurs due the fact that the (MK) presents specific surface are of 327000 cm²/g [41] and (FA) of approximately 190000 cm²/g [42] what influences the demand of kneading water of the pastes produced.

For the stage 2 – study of cementitious materials, considering that the p_15MK needed a factor water/cementitious of 0.39 it was conducted an adjustment to 0.40 so the paste attains a greater value of consistence. In Figure 4, it is possible to observe the results concerning the initial setting time for the paste of reference and with substitution of (FA).

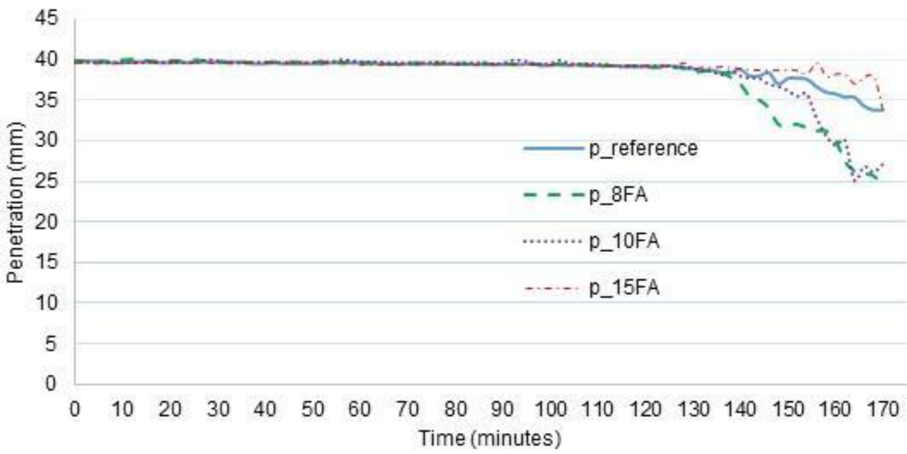


Figure 4: Results of initial and final setting time of the reference and (FA) pastes.

In Figure 4, it is verified that all pastes without and with substitution of (FA) have its beginning of penetration decay approximately at the same moment, between 130 and 140 minutes, indicating the moment when the reactions of hydration are intensified in the paste. It is verified that for all the pastes with substitution of (FA) when compared to the p_referência, the presence of calcium oxide in addition did not accelerate the hydration reactions of the cement.

It is observed that the paste with substitution of 15% of (FA), p_15FA, presented a greater retard in the initial setting time when compared to the other percentages. Thus, the p_15FA is the paste that requires the longest period of time until the initial setting time, what for the process of printing will present as benefit the increase of the execution time without compromising the link between the layers. It is also possible to verify from Figure 3 that after 170 minutes none of the pastes had concluded the setting time.

Regarding the obtained results in the pastes with and without substitution of (MK), in Figure 5, it is observed that when compared to the pasta_referência, the (MK) accelerated initial setting time in approximately 30 to 40min. This acceleration occurred, mostly, in detriment of the elevated thickness of the (MK), what causes the increase on the velocity of hydration reactions of the cement.

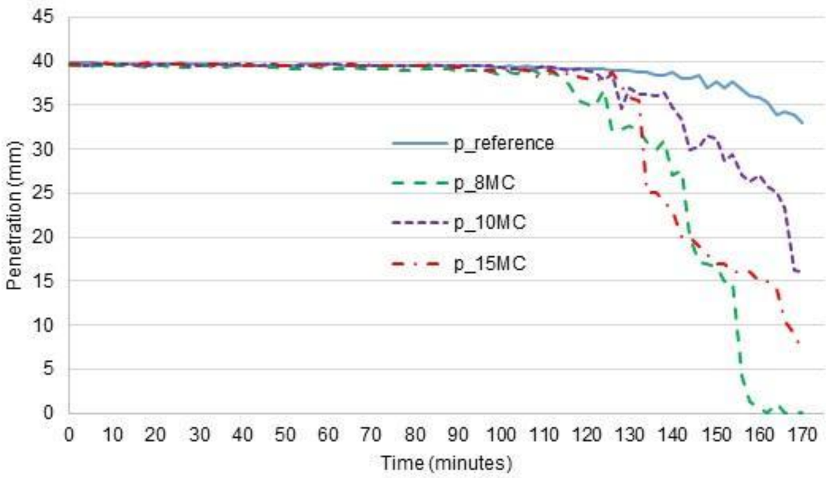


Figure 5: Results of initial and final setting time of the (MK) and reference paste

However, it is important to note that the presence of calcium oxide in addition maximized the velocity of the hydration reactions of the cement and, consequently, the pastes began to set in advance. In the studied pastes it was verified that only the ones with 8% of (MK) substitution presented final setting time within the 170 minutes of test. The others did not conclude the setting time during the experiment.

Based on Figure 5, it is verified that differently from the pastes without and with substitution of (FA), the pastes without and with substitution of (MK) do not present the same time for the beginning of penetration decay between these, given that the p_8MK had its initial setting time in approximately 110 minutes and the p_10MK and p_15MK between 120 and 130 minutes.

Thus, it is concluded that considering only the tests with setting time it is not possible to determine which of the substitutions (FA) or (MK) present the best performance to be applied in 3D printing. For that it was necessary to analyze the yield stress, in order to guarantee that when the second layer is executed the first presents an adequate yield stress and the mixture is not in setting time, guaranteeing the adherence between these.

3.2 Study of the cementitious materials

In this second stage, yield stress test was initially carried out. It is important to note that during the test of yield stress, in the cementitious materials, there were added the superplasticizer additive in order to obtain promising results of stress for the application in 3D printing. According to WANGLER, *et al* [40], the yield stress varies proportionally in relation to the total height of the layers inserted and the height of only one layer. In other words, the authors affirm that for a cementitious material to be considered vertical for 3D printing, the evolution of the yield stress must occur within the interval of 25 to 150.

For the obtainment of the final results related to the analysis of yield stress, the values referred to the final yield stress, obtained at 45 minutes, are divided by the value of initial stress obtained at 10 minutes.

KHALIL, *et al*. [13] produced cementitious materials with 93% of Portland cement, 7% of sulfo-aluminous calcium cement, sand, ratio water/cementitious of 0.35 and 0.2% of addition of superplasticizer additive and obtained a relation between final and initial stress of 35, in other words, cementitious materials considered applicable for 3D printing according to the limits proposed by WANGLER, *et al* [40].

In Table 5 there are the results of the relation initial and final yield stress for each cementitious material produced with and without substitution of (FA) and (MK).

Table 5: Relation between initial and final stress of the materials with substitution of (FA) and (MK)

	RATIO INITIAL/ FINAL YIELD STRESS	SUPERPLASTICIZER ADDITIVE (%)	TEST TIME (MIN)
mat_reference	9,13	0	45
mat_8FA	10	0,2	45
mat_10FA	8,25	0,1	45
mat_10FA	1,22	0,2	45
mat_15FA	13,8	0,1	45
mat_15FA	16,5	0	45
mat_8MK	20,67	0,2	45
mat_10MK	8	0,2	45
mat_10MK	8	0,3	45
mat_15MK	25	0,4	30

From Table 5 it is possible to observe that the result of the ratio initial/final stress obtained by the mat_referência, was of 9.13 and, therefore, does not meet the limits proposed by [40], of 25 to 150. The greatest relation obtained for the cementitious materials produced with substitution of (FA) was of the mat_15FA with 0% of addition of superplasticizer additive, it occurs due the fact that the water added to the cementitious material may cause a decrease on the relation initial/final yield stress. Thus, a reduction on the relation water/cementitious of the mat_15FA could approximate the result for the interval proposed by [13], of 25.

The time when the greatest yield stress was reached for the cementitious material with substitution of (FA) is of considerable importance for definition of the interval of deposition between the layers – verticality test. In Table 5 it is possible to observe that at 45 minutes the mat_15FA reached the greatest raio initial/final stress of 16.50. [13], when studying cementitious materials, obtained the ratio initial/final stress of 35, at 20 minutes, this result was constant until 45 minutes. Thus, since there was no evolution of the ratio initial/final stress over time, it was set the interval of layers deposition as 20 minutes.

Thus, for the result obtained in the mat_15FA, it is necessary 45 minutes of waiting, so that one layer is deposited over another, since only after this period the inferior layers present a greater value of yield stress and, therefore, greater resistance to deformations that would compromise the vertical structure.

Concerning the cementitious materials with substitution of (MK) it is noted that only the composite with 15% of (MK) substitution meets the minimum limit of 25, proposed by [40]. For mat_15MK with 0.4% of superplasticizer, the results of the ratio initial and final stress were constant from 30 to 45 minutes, concluding that the time of deposition between layers must be of at least 30 minutes.

It must be noted that among the concepts of 3D printing, the ideal material for this technology must present itself with elevated fluidity in the first minutes, so the pumping pipe does not clog. And during the posterior minutes, it must present a greater evolution regarding the yield stress so it supports the load of the other deposited layers. From these concepts it is possible to observe that the cementitious materials with 15% of (FA) and (MK) substitution are adequate for 3D printing, since these presented evolution in the yield stress.

Thus, based on the test of yield stress it was possible to define which cementitious material are considered promising to be submitted to extrudability and verticality tests. These being the 15% of (FA) substitution without superplasticizer additive and with 15% of (MK) with 0.4% superplasticizer additive.

The extrusion test of the materials was performed before the verticality test, using the test performed by [12] as reference. In Figure 6 it is possible to observe the cementitious materials being extruded in the silicone pistol with opening of 2 cm and overlapping of its layers.

(a)

(b)

Figure 6: Extruded materials with substitution of 15% of (FA) and (MK) (a) Cementitious material with substitution of 15% (FA) without superplasticizer additive; (b) Cementitious material with substitution of 15% (MK) with 0.4% of superplasticizer additive

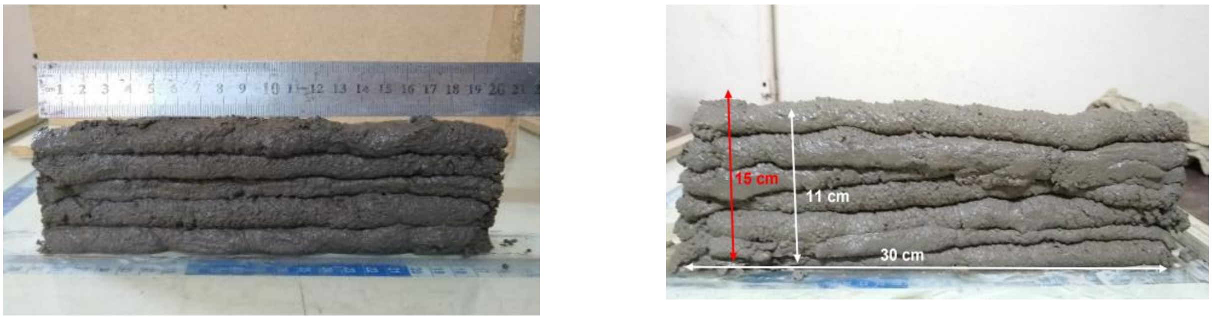
The extrudability can be observed in Figure 6, where Figure 6.a corresponds to the cementitious material with substitution of 15% (FA), where it is verified a continuous filament and an adequate consistence, it neither presents segregation and flux with its own weight, in other words, the cementitious material was only capable of exiting the pistol with the application of force, that being considered promising for the extrusion process, even considering that it did not reach the interval of yield stress proposed by [40].

Comparatively, the cementitious material with 15% of (MK) substitution and 0.4% superplasticizer additive, Figure 6.b, presented itself workable enough to not clog or block the nozzle exit and demonstrated adequate consistence to maintain itself geometrically stable when extruded. However, the difference between both material typologies is notorious, given that the substitution of (MK) presents a rougher aspect when compared to the cementitious material with substitution of (FA).

In terms of verticality, the time of execution between the layers occurred according to the period of time stablished in the test of initial and final setting time, that being of 45 minutes for the cementitious material with substitution of (FA) and of 30 minutes for the cementitious material with substitution of (MK). It is verified, therefore, that the test of yield stress and initial and final setting time is of considerable importance, since it facilitates the test of verticality, given that if the waiting time is superior to the time of initial setting time, the verticality process will be compromised, given that after the cementitious material initiates setting time, there will be the appearance of the surface pellicle affecting the adherence between layers.

The deposition of layers occurred similarly to the process used by [13], in other words, through the silicone pistol without the assistance of any other device. In figure 7.a it is possible to observe that for the cementitious material with substitution of (FA) the process of layers deposition occurred qualitatively, since the first layer did not present excessive deformations, maintaining its geometry, even supporting the weight of the superior layer and its own, enabling the deposition of 5 layers.

Regarding the verticalization of the layers with substitution of (MK), according to Figure 7.b, there is a greater deformation between the layer deposited and a greater capacity of overlapping, that being a total of 7 layers.



(a) (b)

Figure 7. Verticalization test of the cementitious composite with 15% of (FA) substitution. (a) Cementitious material with 15% of (FA) substitution without superplasticizer additive and (b) Cementitious material with 15% of (MK) substitution with 0.4% of superplasticizer additive.

Comparatively, regarding the verticalization of the layers with substitution of (FA) and (MK), it is verified a greater deformation between the layers and a greater capacity of stability of the layers deposited in the cementitious material with substitution of (MK) when compared to the cementitious material with substitution of (FA), such as differences related to the consistence between the two materials, given that the material with substitution of (FA) presents smooth appearance and without segregation and the (MK) presents aspects of roughness.

4. CONCLUSIONS

In this article, regarding the application of (FA) and (MK) substitutions in pastes and cementitious materials of 3D printing applied to the prototyping, it is possible to conclude that:

- Concerning the normal consistence of the cement in pastes with substitution of (FA), compared to these of (MK), it obtained lower values of ratio water/cementitious, since the (MK) presents elevated surface area, what influences the greater demand of kneading water in the produced pastes, making necessary the use of superplasticizer additive.
- Regarding the initial and final setting time, the p_15FA presented a greater value of retard in respect of the initial setting time when compared to the p_15MK.
- The p_15FA demanded a longer period for the formation of surface pellicle enabling a longer printing process without compromising the adherence between layers when compared to the p_15MK.
- It was obtained a greater relation of yield stress in the mat_15MK when compared to the mat_15FA, without additive of superplasticizer, with results of 25 and of 16.50, respectively.
- In terms of extrudability and verticality, the cementitious materials with substitution of 15% (FA) and (MK) were considered promising, given that these obtained capacities of continuous flow, without blockage along the nozzle and, did not present segregation and exudation.

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