

REPLACEMENT OF CEMENT BY FILLER TO REDUCE CO₂ AND NANO-SILICA TO ENSURE HIGH-PERFORMANCE COMPOSITES

Igor da Silva Brito^{1,2}, Sandro Martini¹, Ricardo Jorge Espanhol Andrade^{2,3} and Bruno Luis Damineli*⁴

¹Dept of Civil Engineering, Sao Judas Tadeu University, Sao Paulo, Brazil

igor.brito@usjt.br, prof.martini@gmail.com

²Engineering School, Mackenzie Presbyterian University, Sao Paulo, Brazil

³MackGraphe - Mackenzie Institute for Research in Graphene and Nanotechnologies, Brazil

ricardo.andrade@mackenzie.br

⁴Institute of Architecture and Urbanism, University of São Paulo, Sao Carlos, Brazil

bruno.daminelli@usp.br

ABSTRACT

High-performance cementitious composites (HPC) represent a class of materials known for higher mechanical strength compared to traditional ones. Incorporating nanomaterials like metakaolin (MK) and microsilica (MS) can lead to greater improvements in mechanical properties. However, these materials, and mainly cement, entail environmental impact as they require high-temperature transformation processes. So, even high-strength concretes must address environmental concerns, necessitating innovative approaches. The replacement of cement with inert fillers has emerged as a strategy for reducing cement content and environmental impact, since their production involves grinding rather than high-temperature processes, resulting in lower CO₂ emissions. However, their inert nature limits reactivity, compromising the performance. This study seeks to evaluate the feasibility of producing HPC by partially replacing cement with quartz fillers (QF). This substitution was accompanied by the addition of small quantities of nano-silica to evaluate if losses in rheology and strength, caused by increased filler content, could be compensated. It was developed 5 mixtures: M0 (reference); and M1 to M4, with cement replacement by contents of 4 to 16% of NS and QF. It was measured rheological and mechanical performance. Results show that nano-silica's high surface area enhances hydration reactions, contributing to the mechanical performance, and can increase the packing of particles due to its very fine particle size distribution, contributing to rheological performance. Nevertheless, these benefits are restricted to a maximum content: after the limit where voids between coarser particles are fully filled by NS, it does not contribute to packing anymore, but the surface area continues to grow directly proportional to NS increase, with negative impacts on final rheological performance.

KEYWORDS: Inert filler; Cement replacement; Nano silica; CO₂; High-performance concrete

I. INTRODUCTION

High-performance cementitious composites (HPC) are a class of composites that exhibit mechanical resistance capabilities (both in compression and flexion) much higher than traditional cementitious composites. Using nanomaterials such as metakaolin (MK) and micro silica (MS), even more expressive improvements can be obtained in the mechanical capabilities, durability, and composition of the microstructure [1-3]. However, they are all materials with a considerable environmental impact since to be reactive, they are subjected to chemical transformation processes that involve high temperatures. Cement is calcined at 1400°C and releases around 1 ton of CO₂ per ton of clinker; MK is manufactured at 800°C, therefore also releasing considerable CO₂. MS is a waste from the production process of ferrosilicon and silicon metal and thus comes from a production chain that also has high energy consumption and releases CO₂ [4-5].

Even high-strength concretes must be designed to reduce their environmental impact [4, 6]. The replacement of cement by inert fillers has already proven to be a viable technology for reducing the cement content, with a concomitant reduction in the environmental impact – its production process does not include the use of processes at high temperatures, but only grinding, therefore releasing a much lower amount of CO₂. These materials are inert precisely because they are not subjected to burning processes under extreme temperatures. If this reduces their environmental impact, on the other hand, it gives them a low or zero contribution to reactivity, which may reduce the performance of cementitious compounds.

This work aims to analyze the feasibility of producing high-performance cementitious compounds with partial replacement of cement by inert fillers, in this case, quartz fillers (QF). To ensure that the technical characteristics will be maintained, this replacement will be accompanied by the inclusion of small amounts of nano-silica (nSiO₂), a nanomaterial capable of compensating the losses in rheology and resistance brought by the increase in the filler content [7-9]. The high surface area of nSiO₂ influences the reactivity as it introduces pozzolanic additions on a nanometric scale, which promote the acceleration of hydration reactions, generating densification of the matrix and gain in resistance to bending and compression [10-12]. Studies on the addition of nSiO₂ on durability properties have shown an increase in compactness and tightness of the matrix [8, 10]. When used together with MS and MK, nSiO₂ led to increased mechanical capacities and modifications in the microstructures of mortars with different levels of NS addition [11], with higher amounts of Hydrated Calcium Silicates (C-S-H) at advanced ages [12-14]. However, NS, at high levels, causes a reduction in the fluidity of the mixture, since the high-surface-area causes the water molecules to be adsorbed on the surface of the nanomaterial, causing a reduction in the free water available for lubrication of the rest of the particles, an issue that can be mitigated through the use of dispersing additives (superplasticizers – SP) [11-12].

This paper is structured into four sections: 1) this introduction; 2) experimental planning (which describes compositions, mixing procedures, and analysis methods); 3) results and discussions (divided into rheological and mechanical performance tests); and 4) conclusion.

II. EXPERIMENTAL PLANNING

In this study, the following binder materials were used: 1) a Brazilian Portland cement (OPC) CPV-ARI manufactured by ABNT NBR 16697 [15]; 2) metakaolin (MK) according to ABNT NBR 15894-1 [16]; 3) 920U micro silica (MS) according to ABNT NBR 15894-1 [16]; and 4) nano-silica (nSiO₂) in colloidal aqueous solution (solids content 30%). A quartz filler was used, an inert material that was included in the composition of the matrix due to its particle size distribution compatible with cement. Figure 1 shows the morphology of the materials from micrography performed in a Scanning Electron Microscope (SEM), equipment Jeol Jsm-6510.

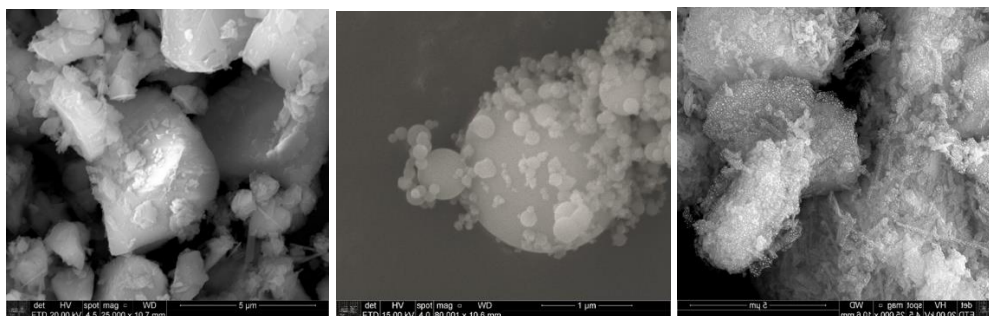


Figure 1. Surface morphology of base materials using SEM: (a) OPC; (b) MS; (c) MK.

It is possible to observe the high degree of roughness of the cement and metakaolin; the micro silica particles, on the other hand, have a more rounded shape and less roughness, which contributes to the mobility of the compositions in the fresh state. The chemical composition, shown in Table 1, obtained through the analysis of X-Ray Fluorescence (XRF) brand Oxford Instruments, model X-Supreme 8000,

shows the almost absence of CaO and the high content of SiO₂ and Al₂O₃ present in the MS, MK, and in NS when compared to OPC.

Table 1. Chemical Composition of the binder's materials.

Chemical composition	Content (%)			
	Portland Cement CPV	Micro silica 920U	Metakaulim	nSiO ₂
Calcium Oxide (CaO)	51.94	0.05	0.01	0.03
Silicon Dioxide (SiO ₂)	35.77	99.67	62.92	99.89
Aluminum Oxide (Al ₂ O ₃)	3.55	0	30.25	0
Ferric Oxide (Fe ₂ O ₃)	4.32	0.02	1.62	0.02
Sulphur Trioxide (SO ₃)	2.68	0	0.01	0.06
Magnesium Oxide (MgO)	0.57	0.11	3.79	0
Potassium Oxide (K ₂ O)	0.57	0.1	0.59	0
Alkalis (Na ₂ O - eq.*)	0	0.03	0.19	0
Titanium Dioxide (TiO ₂)	0.07	0	0.6	0

For structuring the design of the granular skeleton, natural or industrial quartz sand (almost pure SiO₂) was used, with granulometry varying between 100 and 1200µm. They are characterized and distributed as fine (60-200 µm), medium (200-600 µm), and coarse sand (600- 1700 µm), by ABNT NBR 6502 [17].

2.1 Composition of mixtures

The compositions were planned in such a way as to keep the content of all components constant, except for cement, gradually replaced by contents of 4, 8, 12 and 16% of nano-silica and quartz filler (~40% of nano silica and ~60% of quartz filler in each replacement). Table 2 presents the combinations of the studied compositions.

Table 2. Composition of micro concrete mixtures.

Material (Kg/m ³)	M0 (Ref) (m/m)	M0 (Ref) (kg/m ³)	M1 (kg/m ³)	M2 (kg/m ³)	M3 (kg/m ³)	M4 (kg/m ³)
Cement	1	593.3	563.6	533.9	504.3	474.6
Nano silica		0.0	9.4	18.8	26.5	39.9
Filler quartz		0.0	14.8	29.7	44.5	59.3
Metakaolin	0.43	255.1	255.1	255.1	255.1	255.1
Micro silica	0.11	65.9	65.9	65.9	65.9	65.9
Sand #100	0.73	437.5	437.5	437.5	437.5	437.5
Sand #50	0.69	413.5	413.5	413.5	413.5	413.5
Sand #30	0.45	269.7	269.7	269.7	269.7	269.7
Sand #16	0.33	194.8	194.8	194.8	194.8	194.8
Water	0.3	274.3	265.4	256.5	247.6	238.7
SP	0.043	25.8	24.2	23.0	21.7	20.4
w/b (m/m)		0.30	0.30	0.29	0.29	0.29
w/c (m/m)		0.46	0.47	0.48	0.49	0.50

where: w/c = water/cement ratio; w/b = water/binder ratio (all fines excluding filler quartz, which is inert); sand#100, sand#50, sand#30, and sand#16 are the sieves (sizes in mesh) where each sand is retained, indicating the particle size distribution.

The compositions had variations in their compositions with the main objective of reducing the amount of cement in contents by 5, 10, 15, and 20% about the reference (593Kg/m³). The water/binder (w/b) and superplasticizer ratios were kept fixed.

The composition of the mixtures was based on the reduction of the environmental impact from the replacement of cement by inert fines, and on the optimized distribution of particles (packaging) seeking to densify and reduce the porosity of the final material. The inputs were understood primarily through their granulometric distributions, so that it could be possible to identify the best arrangement among the available materials to obtain the lowest cement consumption and the lowest demand of water for manufacture, arriving at compositions in the category of high-performance cementitious matrices preserving the characteristics of high fluidity, consistency and high mechanical performance.

2.2 Execution of mixtures and storage of samples

To manufacture the pastes, all anhydrous materials were homogenized using a mechanical mixer at slow speed (140 RPM), divided into two sets: fine (binders and quartz filler) and coarse inert (sand). After homogenization, with only the fines in the mixer, the manufacturing process (Figure 3) was started at a slow speed (140 RPM) for 2 minutes, with the addition of 2/3 of the water and dispersing additive (commercially known as super-plasticizer). Afterwards, mixing was performed at a higher speed (285 RPM) for 2 minutes. In the third step, inert materials (pre-homogenized quartz sand) were added at slow speed (140 RPM), increasing speed (285 RPM) after insertion, and mixing in this condition for another 2 minutes. Finally, nano silica (nSiO₂) was included at 140 RPM speed and mixed for 3 minutes at 285 RPM.

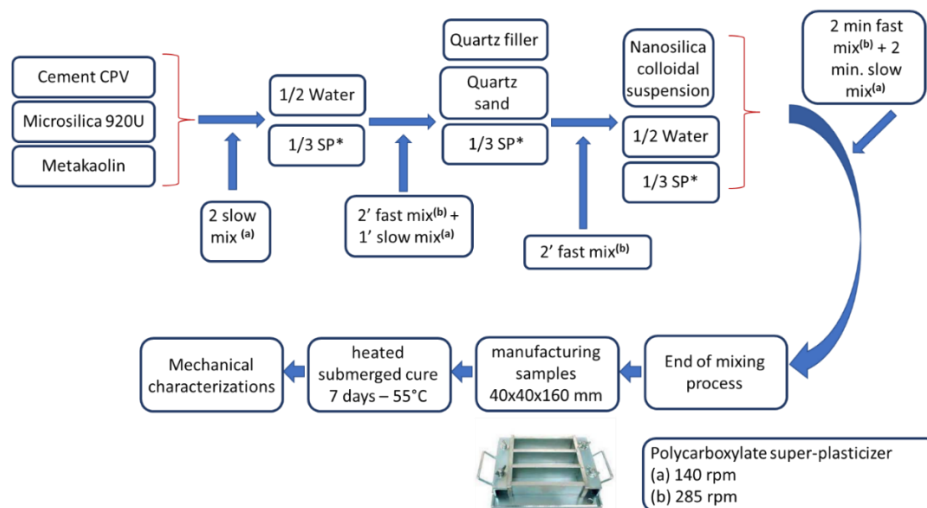


Figure 3. Micro concrete manufacturing process chart flow

The specimens were demolded after 24 hours and then subjected to submerged curing at 55°C for 7 days. In the case of samples for 28-day tests, they remained in humid curing, but at room temperature, until the date of the test.

In this study, changes in rheological, chemical, and physical properties were studied about the reference mix when performing partial replacement of the cement mass by nano-silica (nSiO₂) and quartz filler (FQ). The experimental procedures carried out are presented below.

2.3 Rheological characterization

The evaluation of the rheological behavior of the micro concrete consisted of the mini-slump test, as well as the evaluation of the stability (resistance to segregation) performed through visual inspection. Its execution took place immediately after the stage of mixing the components for the manufacture of

micro concrete, aiming to evaluate the modifications caused by the inclusion of ultrafine (FQ) and nanomaterial ($nSiO_2$). See images in Figure 4.

As it is a self-compacting material, the volume necessary to fill the cone was poured directly into the mold without the aid of a spatula, except for composition M4.

For the execution of the spreading and consistency analyses, part of the total volume produced was used to manufacture the specimens. The composition in a fluid state was poured into the conical mold immediately at the end of the mixing process, to fill the entire volume of the cone (approx. 2.2 l) [18]. Without the aid of a socket, except for the M4 composition, an interval of 30s was waited before the cone was lifted, and after 1 minute the scattering measurements were carried out. The evaluation of stability and consistency (resistance to segregation) was performed through visual inspection.

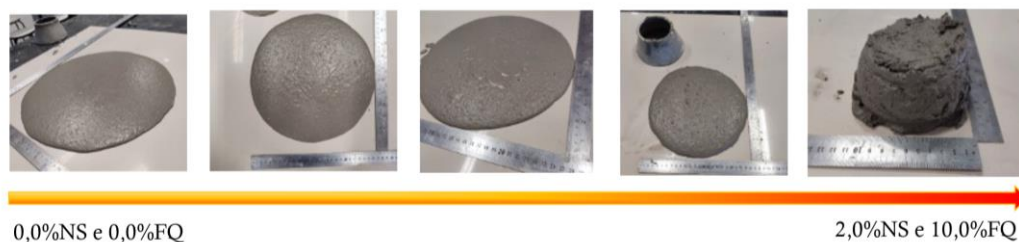


Figure 4. Spreading of compositions (a) M0; (b) M1; (c) M2; (d) M3 and (e) M4, respectively

2.4 Characterization of mechanical performance under bending and compression

For each mixture studied, 3 prismatic specimens measuring 40x40x160mm were molded. Due to the high fluidity of the compositions, there was no need for vibration, just small manual adjustments so that the mixture, almost self-compacting, filled the mold.

The bending tests were performed in a Zwick Z010 press with a capacity of 10KN and a displacement rate of 0.50 mm/min, using the BS EN 196-1 [19] standard, which provides for a test with 3 points (2 sides of support and a superior central one, to carry out the flexion effort). This test was carried out on the 3 specimens of each mixture.

After the bending test, each specimen resulted in 2 specimens of 40 x 40 mm to carry out the compression tests (6 specimens for each mixture). Compressive strength tests were carried out at 7 and 28 days, 3 specimens for each age. In this test, a Solotest 100Tf press was used, with a capacity of 100 tf and an applied load speed of 50 kgf/s. All samples were dried at a temperature of 40°C for 3 hours before mechanical characterizations, both bending and compression.

2.5 Chemical Characterization by Differential Thermogravimetry (TG)

To understand the chemical changes in the compositions, thermogravimetric analyses (TG/DSC) were planned. To ensure that they were representative, without interference from the sand, the pastes (fines, water, and dispersant) referring to the previously studied compositions were molded separately, without the inclusion of sand.

The tests were carried out in STA 449 F3 equipment, Netzsch brand. The samples were heated from 40 to 1000 °C with a heating rate of 10 °C/min in a nitrogen atmosphere (N₂). At their analysis ages (7 or 28 days), the samples were frozen, lyophilized, and comminuted to particles with granulometry passing through a #200 sieve, and being stored in a desiccator until the test.

2.6 Density, Porosity, and Water Absorption

The analysis of the Void Index and Water Absorption allows the evaluation of properties such as the compactness of the matrix and its tightness. A cylindrical 50×100 mm mortar sample was used for testing as per the specifications given by ABNT NBR 9778 [20] at 7-day age. For each mixture, the average values of water absorption, density, and porosity were evaluated from three samples. These parameters were determined by Eq. (1)-(3). Details of measurements of the water absorption, density and porosity were given in [21, 22].

$$\text{Density (g/cm}^3\text{)} = \frac{W_d}{W_w - W_{ssd}} \quad (1)$$

$$\text{Porosity (\%)} = \frac{W_{ssd} - W_d}{W_{ssd} - W_w} \times 100 \quad (2)$$

$$\text{Water Absorption (\%)} = \frac{W_{ssd} - W_d}{W_d} \times 100 \quad (3)$$

Where:

W_d: weight of the oven-dried specimen

W_w: weight submerged in water.

W_{ssd}: saturated with dry-surface weight

Other studies have employed this method of porosity determination for cementitious composites [21, 23].

2.7 Scanning Electron Microscopy

After the axial compression analysis, samples of approximately 1 cm² were taken for investigation by scanning electron microscopy (SEM), equipment Jeol Jsm-6510. Samples were oven-dried at 45 °C for 24 hours and coated with 10 nm gold to increase conductivity and improve analysis efficiency. 25 kV of accelerating voltage was used.

III. RESULTS AND DISCUSSIONS

3.1 Fluidity and Consistency

When performing the inclusion of ultrafine materials with high surface area in the composition of the cementitious matrix, the water available in the system is, in large part, used to cover the surface area of these particles, thus reducing the amount available to fill the voids and effectively move the grains, with a consequent reduction in their mobility capacity [8, 9, 12]. In the case of the present study, there is also the fact that the SP additive content was kept fixed (4.3%) calculated only on the cement content for reasons of economy – thus, it is verified in Table 2 that the total additive content (kg/m³) progressively decreased between M0 (Ref) and M3, as cement was gradually replaced by increasing levels of QF and NS. The water content was kept constant about the total fine content (shown by the water/binder ratio, w/b). Therefore, the expectation would be that the fluidity of the systems would gradually decrease due to both factors combined (increase of ultrafine content with high surface area and decrease in the total superplasticizer content).

However, on the contrary to these expectations, a comparison between the rheological behavior determined by the spreading test of all samples demonstrated that it was possible to replace cement by QF and nSiO₂ and with a decrease in the total superplasticizer content without significant damage to fluidity (see Figure 5), since, for the test setup used, all spreads over 240mm are self-compacting. This is generally not seen in simple replacements of cement by fine fillers – the tendency is always that, with the maintenance of water content, increase in total surface area, and decrease in SP content, there is a rapid and considerable decrease in fluidity. This demonstrates that the addition of nSiO₂ in a system replacing cement with fillers (in this case, QF) can decisively influence the increase in the degree of

particle packing. The increase in packing decreases the volumes of spaces between particles, reducing the demand for water needed to fill these spaces. By maintaining the water content, a system with a lower volume of spaces between the particles manages to leave more water to separate the particles, which would increase the fluidity. In the case of the experiments carried out here, this increase did not happen because this excess of water was used to cover the surface area of the particles, which also increased. In any case, the use of ultrafine particles from NS was able, through increased packing of the paste, to allow more water available to move the grains to compensate for the increase in the surface area of the system (and the water demand to cover it) and also the decrease in the SP additive content. This strategy seems, therefore, to be of fundamental importance for the strategy of replacing the cement content by fillers without significant losses in the rheological behavior.

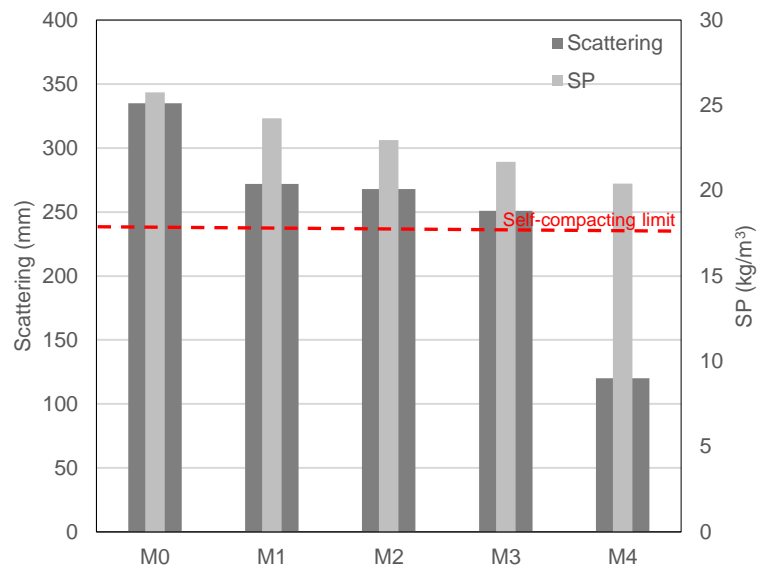
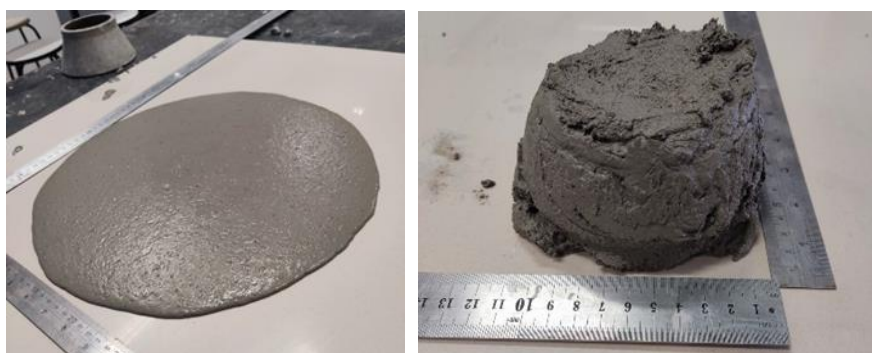


Figure 5. Scattering and total SP content of compositions studied

However, it has been noted that there is a limit to this strategy. After a certain point, the increase in the ultrafine content becomes no longer so important for the increase in particle packing, but it continues to increase proportionally to the surface area of the system. This causes a rapid loss of fluidity, as seen in composition M4. Figure 6 shows that, for high levels of cement replacement by ultra fines, especially NS (M4), there was a sharp drop in fluidity compared to the reference composition (M0). Similar effects have already been reported in the literature [24, 25].



(a) M0 - scattering 335mm

(b) M4 - scattering 120mm

Figure 6. Consistency of micro concrete

The pozzolanic effect of materials based on amorphous silica, associated with their nano sizes, leads to the rapid formation of ettringite, the crystalline phase responsible for the resistance of cementitious materials at shortages. This effect is potentiated due to the nano dimension of the NS, already occurring in the first minutes after its inclusion in the matrix system and, therefore, liable to influence the rheological behavior of the mixture already at the initial stage [26-30].

3.2 Mechanical resistance to compression and bending

In general, mixtures containing the replacement of cement by inert fines, such as the QF used in the present research, result in hardened compounds with lower compressive strength, when the water content is maintained. Figure 7. a presents the results of resistance to flexion and compression at 7 days of age, and the cement content of the mixtures studied.

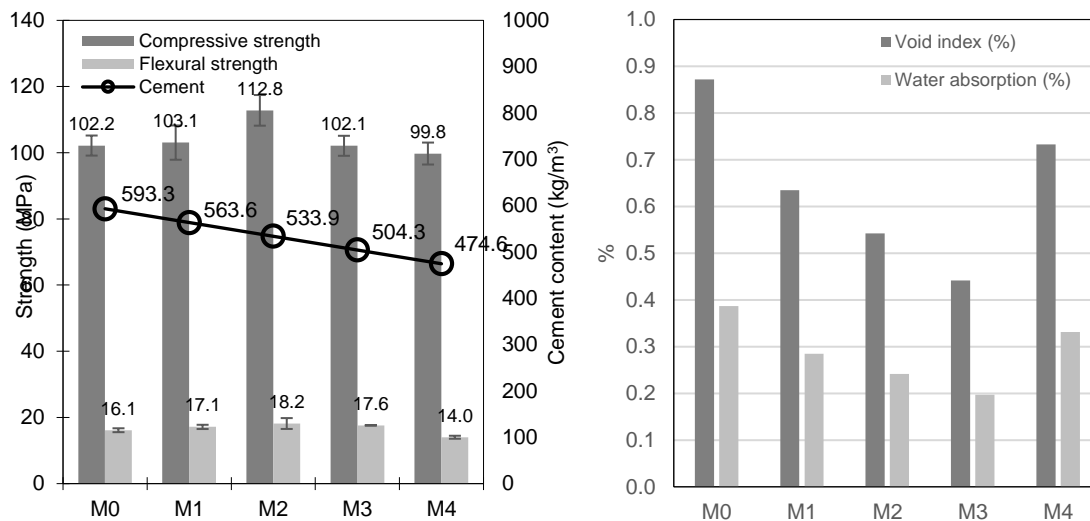


Figure 7. a) Mechanical performance (compression and bending) of mixtures compared to cement content; b) Water absorption and void index of compositions.

Considering the variation of the results, also expressed in Figure 7. a through the bars of dispersion of the results, it is observed that there was no significant change in resistance, both to compression and to flexion. This demonstrates that, regarding the most important parameter in the hardened state of cementitious materials – mechanical strength – the inclusion of nSiO₂ at reduced levels made it possible to reduce the cement content and include fillers in the composition without losing mechanical performance.

This would even be relatively easy to do if there had been a reduction in the total water content of the mixtures, with the consequent maintenance of resistance but a decrease in fluidity, or the SP additive content had been increased, which would also make it possible to increase fluidity with less water content and therefore strength maintained. However, in the present experiment, these were not the dosing assumptions. On the other hand, emphasis was placed on maintaining the water content, reducing the cement content, increasing the filler content, and decreasing the SP additive content (since this followed its dosage about the cement content, which, as seen progressively decreased). All the alternatives adopted would arrive, under normal conditions, at compounds with lower fluidity (since it was used the same water content but materials with a higher surface area and lower SP content) and lower mechanical resistance (since it was used the same water content but the cement amount was reduced by replacing it with partly inert materials, with an increase in the effective water/cement ratio). In the case of fluidity, as previously discussed, the packing brought about by the ultrafine grains of the nSiO₂ was able to compensate for the increase in the surface area of the system, as it generated a smaller volume of voids between the particles to be filled by water, allowing the fluidity to remain even without increasing the water content and even with a decrease in the SP additive content. In the case of

mechanical strength, the addition of $n\text{SiO}_2$ managed, in turn, to compensate for the lack of contribution to strength from QF (which is inert and therefore does not react to generate hydrated compounds) through its pozzolanic properties, with high reactivity due to the high surface area, which exposes a large area to enable hydration reactions. Therefore, in a joint analysis of fluidity and resistance, which is the most common and necessary in cementitious products, the $n\text{SiO}_2$ inserted up to the point where it contributed to the packing, made it possible to obtain mixtures with a decrease in the cement content. Moreover, its replacement by inert fillers without resulting losses of mechanical performance and fluidity, was also observed.

Figure 7. b shows the water absorption and the voids index [20] of the manufactured compositions. There was a trend towards a decrease in the void content and water absorption in the progression from M0 to M3, demonstrating that the maintenance of resistance even with a decrease in the cement content and an increase in the inert fine content was due to an increase in the packing of the materials. This higher packing, in the case where the water content is maintained, ends up generating denser pastes, with a higher concentration of solids and lower void content and therefore lower final porosity. In this way, the previous statement is proved that the use of NS in combination with QF made it possible to obtain materials with higher packing, which is responsible for maintaining the resistance in systems with the replacement of cement. It should always be remembered that this occurs up to the limit at which the increase in surface area brought about becomes much more influential than packing, as this packing stops increasing when enough fines are already available to fill all the voids between the coarser particles. This is seen in M4, as previously discussed, and it is also the factor responsible for bringing higher water absorption and void ratio to this composition, with a reversal of the trend observed up to M3.

The reduction in absorption and the void index indicates a dense and compact arrangement between the constituent particles, having as a binding element a high resistance matrix, which is a product of both the granular skeleton optimization technique and the use of SCMs that produce additional hydration compounds. The Interfacial Transition Zone (ITZ) is the intermediate region between coarse and fine particles, being responsible for a large part of the mechanical capacity since it is, in general, the zone with the highest concentration of voids (and therefore the lowest resistance) of mortars and concretes [31]. With the use of nanomaterials such as $n\text{SiO}_2$, this region, which is conventionally porous and fragile, presents increased densification already in the early ages of the hydration process, with increased adhesion of the matrix to the aggregate due to the better use of CH and, consequently, of Ca^{+2} available [12, 32]. A similar effect is expected when using QF in the composition, and for this material, the increase in compactness comes from its nucleating effect, when occupying interstices left by larger particles [12, 32-34].

Figure 8 presents SEM images of samples produced under thermal curing at 7 days of age. It is observed the existence of products with morphologies correlated to the hydrated phases reported in the literature: C-S-H, portlandite (CH), and hydrated calcium monosulphoaluminate (AFm), as well as phase-like ettringite (AFt) [2, 35]. The higher density suggested in the absorption and voids analyses can be seen qualitatively in the SEM images. The use of high proportions of supplementary materials (SCMs) allowed to fill spaces previously inaccessible to larger particles. In Figure 8. (a)-(b), referring to samples M0 and M1, respectively, it is possible to observe a microstructure filled with C-S-H gel. In Figure 8. c, monosulphoaluminate phases (AFm) can be seen as, a product of the conversion of ettringite (AFt), indicating, as suggested by [12], that the use of supplementary materials (MK, MS, and NS) together with submerged curing at elevated temperature causes the AFt to be converted into (AFm) and C-S-H gel since it occurs the acceleration of the initial period of hydrate formation [27-29]. In general, when carrying out the mechanical characterization, the rupture of all samples occurred not in the paste but in the aggregates, which can be partially explained by the denser transition zone observed in the SEM figures and already commented on.

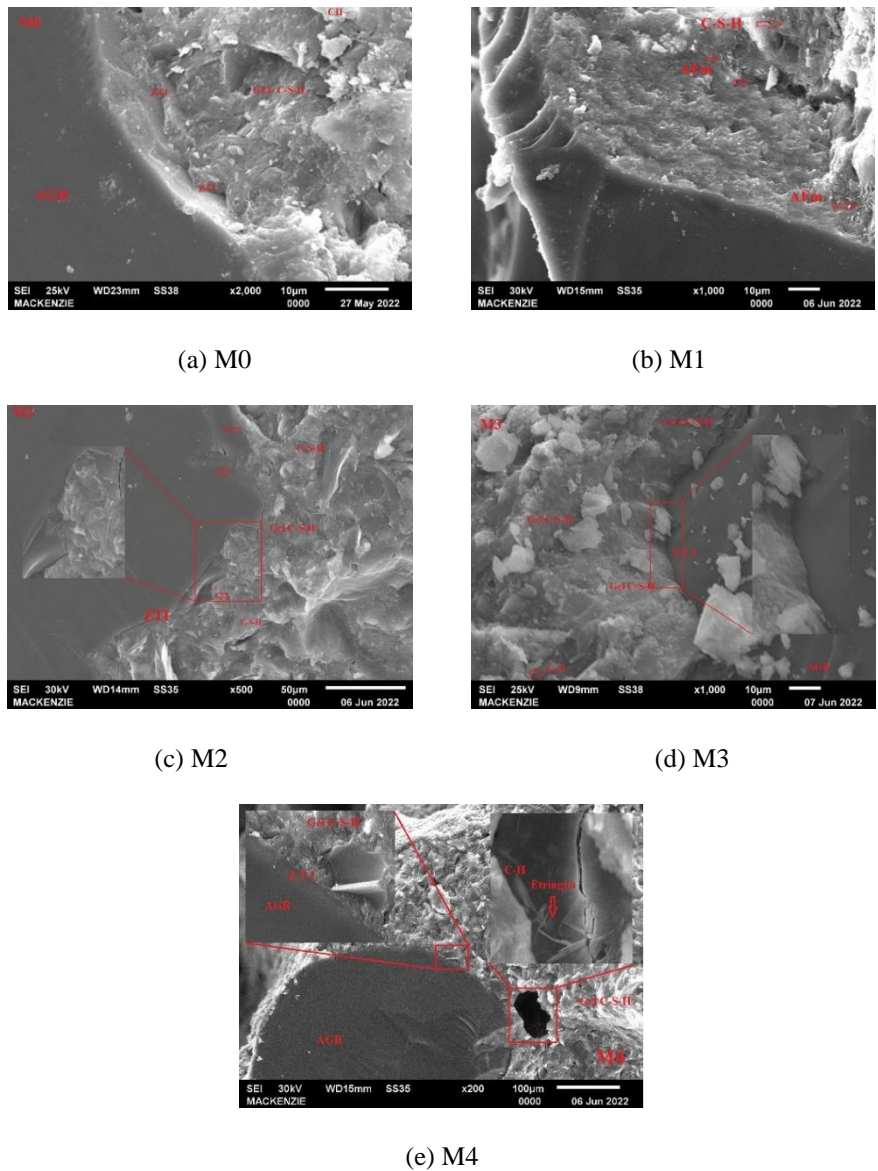


Figure 8. SEM images of the fractured surface of compositions (a) M0; (b) M1; (c) M2; (d) M3; (e) M4.

Sample M4 (Figure 8. e) presented non-hydrated supplementary materials, which may be directly related to the lack of adequate mixing of the same due to its rheological characteristics, and the lack of water available for the reaction since, as already seen, the high surface area of the system made a good part of the available water to be adsorbed on the particles. Thus, less water was available to react and to move the particles. For this reason, M4 also presented a larger volume of large pores, as shown in Figure 8. e and Figure 9, data that corroborates with those obtained in the analysis of water absorption and voids index. In M4, the maximum quantity of nSiO₂ was achieved and surpassed.

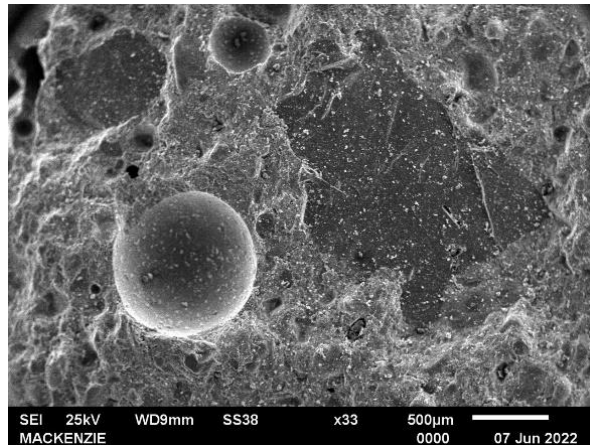


Figure 9. SEM micrograph of the M4 matrix.

The thermogravimetry (TG) analyses of the samples present important data about the chemical phases formed and present. During the test, there is mass loss at different temperatures. Mass losses in the temperature range between 150 and 300°C are related to chemically combined water (C-S-H, AFt, AFm) [6, 18, 20]; between 400°C and 550°C, the decomposition of calcium hydroxide (Portlandite – CH) occurs; between 600°C and 1000°C, carbon dioxide (CO₂) is released. More specifically, in the initial interval the decompositions of C-S-H (115°C to 125°C), gypsum (145°C to 165°C), and hydrated aluminates, ettringite (135°C to 140°C), and calcium monosulphoaluminate hydrated phases (185°C to 200°C) are reported [35, 36].

Figure 10 presents the main hydrated compounds found in thermal analysis.

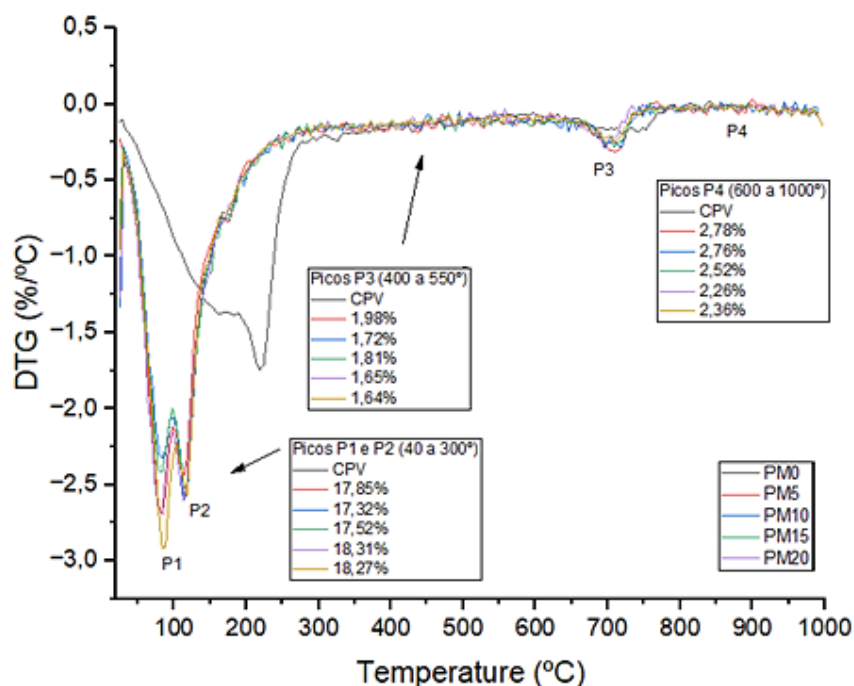


Figure 10. TG analysis of mixtures studied.

The analysis of the TG curves demonstrates a progressive increase in the levels of CSH formed (measured by the mass loss of CSH combined water, which occurs at temperatures between 40 and 300°C) as the replacement of cement by QF and nSiO₂ increased, a factor that has a direct influence on maintaining mechanical strength even with cement reduction (discussed before). On the other hand, the

portlandite contents (measured by the mass loss of portlandite combined water, which occurs at temperatures from 400 to 550°C) remained practically unchanged regardless of the value of cement replacement by QF and nSiO₂. As is widely known, portlandite forms an important alkaline reserve for maintaining a high pH in the matrix in the long term, which is especially important for reinforced cementitious materials. This demonstrates that the replacement of cement by QF and nSiO₂ proposed can maintain conditions that guarantee the long-term durability of reinforced cementitious materials – an extremely important factor since one of the obstacles encountered with the replacement of cement by fillers is precisely the decrease of alkaline reserve to ensure durability for reinforced components.

If this is considered concomitantly with the increase in environmental benefits (due to the progressive decrease in cement content) and maintenance of the rheological and mechanical properties already discussed, it can be concluded that the strategy has a promising future in the search for compositions with reduced cement content and adequate – or equivalent – performance in terms of application, resistance, and durability.

IV. CONCLUSION

Since cement is one of the world's largest emitters of CO₂, the search for construction components with lower content of this material is a natural and one-way path in the search for a more sustainable world. In this sense, research on the replacement of cement by fines, especially inert (filler) has been widely carried out, since these fines do not use processes of high energy consumption in their production and, therefore, release much lower CO₂ content.

The present work sought to replace cement with quartz filler (inert) to contribute to this line of research. To compensate for the losses in rheological, mechanical, and durability performance caused by the inclusion of the fillers, which are inert and therefore do not chemically react, small amounts of nano-silica (nSiO₂) were concomitantly added. It was possible to verify that:

- 1) The nano-silica, due to its nanometric dimensions, increased the packing density of the cementitious matrix, reducing the volume of voids between grains and in the transition zone;
- 2) This increased packing allowed obtaining rheological characteristics (fluidity) of the same order of magnitude as the reference composition, even bringing an increase in the surface area of the system (finer materials have a greater surface area). This proved to be valid up to the limit in which the increase in packing was effective in reducing the voids to the point of compensating for the increase in surface area (the decrease in voids leaves more free water to effectively move the grains and give fluidity, while the increase in of surface area removes free water from the system by its adsorption to the surface of the particles). The increase in packing has a limit given by the volume of voids between coarser grains that can be filled by finer grains, while the increase in the surface area always increases proportionally to the increase of fines in the system;
- 3) The mechanical resistance to bending and compression of the compositions with lower cement content was maintained, since, on the one hand, the inert fines did not contribute to the resistance because they do not react, on the other hand, the nano-silica brought great potential for reactivity because it is an amorphous material and also with high surface area available for reactions;
- 4) Water absorption tests and SEM were able to contribute to the presented analyses;
- 5) Thermogravimetry tests showed that, in addition to an increase in CSH levels in the pastes with a decrease in cement content, there was also maintenance of portlandite levels, which is of fundamental importance for the durability of reinforced cementitious materials.

ACKNOWLEDGMENTS

The authors would like to acknowledge National Council for Scientific and Technological Development (CNPq) for the grant 305109/2022-7, National Institute of Science and Technology for Rheology of

Complex Materials Applied to Advanced Technologies (INCT-Rhe9) grant 406765/2022-7, Coordination for the Improvement of Higher Education Personnel (Capes) for the grant 71906878/2023-2, to Instituto Presbiteriano Mackenzie and the Brazilian taxpayer.

REFERENCES

- [1] Varisha, Varisha & Zaheer, Mohd Moonis & Syed Danish Hasan, (2022) “Effect of nanosilica and Carbon Nanotubes Addition on Mortar Mechanical and Durability Properties”, *Journal of Civil Engineering and Construction*, Vol. 11, No. 4, pp210-227. <https://doi.org/10.32732/jcec.2022.11.4.210>
- [2] Barbhuiya, Gulzar H. & Moiz, Maaz Abdul & Hasan, Syed Danish & Mohd Moonis Zaheer (2020) “Effects of the nanosilica addition on cement concrete: a review”, *Materials Today Proceeding Elsevier*. Vol. 32, No. 4, pp 560-566. <https://doi.org/10.1016/j.matpr.2020.02.143>
- [3] Sobolev, K. (2016) “Modern developments related to nanotechnology and nanoengineering of concrete”, *Frontiers of Structural and Civil Engineering*, Vol. 10, No. 2, pp131–141. <https://doi.org/10.1007/s11709-016-0343-0>
- [4] Hegarty, O. R. & Kinnane, O. & J. Newell, & Roger West, (2021) “High performance, low carbon concrete for building cladding applications”, *Journal of Building Engineering*, Vol. 43. <https://doi.org/10.1016/j.jobe.2021.102566>
- [5] Chen, B.C. & Ji, T. & Huang, Q.W. & Wu, H.Z. & Ding, Q.J. & Y.W. Zhan, (2014) “Review of research on ultra-high-performance concrete”, *Journal Architecture Civil Engineering*, Vol. 31, No. 3, pp 1-24.
- [6] Bhuvana, G.L. & Sherikar, B.N. & Honnavar, G.V. & Madhusudhana, R. & Balaram Sahoo, (2021) “Effect of Fly Ash on Setting Mechanism and Strength of Commercial Cement: A Chemical Approach”, PREPRINT (Version 1), Research Square. <https://doi.org/10.21203/rs.3.rs-479429/v1>
- [7] Jie, Shi. & Wang, Jianrong. & Muzenda, Tafadzwa Ronald. & Qu, Yupeng. & Hou, Pengkun. & Cheng, Xin. & Mingle Liu, (2020) “Effects of nanosilica on the hydration and hardening properties of blended cement-based materials under heat curing”, *Journal of Thermal Analysis and Calorimetry*, Vol. 141, pp1317–1330. <https://doi.org/10.1007/s10973-019-09115-6>
- [8] Sobolev, K. & Flores, I. & Martinez, L.M.T. & Valdez, P.L. & Zarazua, E. & E.L. Cuellar, (2009) “Engineering of SiO₂ nanoparticles for optimal performance in nano cement-based materials”, *Nanotechnology Construction*, Vol. 3, pp139-48. https://doi.org/10.1007/978-3-642-00980-8_18
- [9] Hou, P. & Kawashima, S. & Kong, D. & Corr, D.J. & Qian, J. & Surendra P. Shah, (2013) “Modification effects of colloidal nano SiO₂ on cement hydration and its gel property”, *Composites Part B: Engineering*, Vol. 45, No. 1, pp 440–448. <https://doi.org/10.1016/j.compositesb.2012.05.056>
- [10] Jalal, M. & Mansouri, E. & Sharifipour, M. & Ali Reza Pouladkhan, (2012) “Mechanical, rheological, durability and microstructural properties of high performance self-compacting concrete containing SiO₂ micro and nanoparticles”, *Materials & Design*, Vol. 34, pp. 389–400. <https://doi.org/10.1016/j.matdes.2011.08.037>
- [11] Li, L.G. & Huang, Z.H. & Zhu, J. & Kwan, A.K.H. & H.Y. Chen, (2017) “Synergistic effects of micro-silica and nano-silica on strength and microstructure of mortar”, *Construction and Building Materials*, Vol. 140, pp229–238. <https://doi.org/10.1016/j.conbuildmat.2017.02.115>
- [12] Cardoso, Juliana. (2020) “Influência da adição de nanosilica e nano-metacaulim na formação de etringita tardia: estudos de dispersão das adições e caracterização microestrutural de pastas submetidas à cura térmica”. Ph.D. dissertation, Universidade Federal de Sergipe, Brazil.
- [13] Andrade, S. & Henrique, J. & Cesar, P. & Moisés Frías Rojas, (2018) “Chemical and mechanical characterization of ternary cement pastes containing metakaolin and nanosilica”, *Construction and Building Materials*, Vol. 159, pp18–26. <https://doi.org/10.1016/j.conbuildmat.2017.10.123>
- [14] Andrade, D.S. & Rêgo, J.H.S. & Morais, P.C. & Lopes, A.N.M. & Moisés Frías Rojas, (2019) “Investigation of C-S-H in ternary cement pastes containing nanosilica and highly-reactive supplementary cementitious materials (SCMs): Microstructure and strength”, *Construction and Building Materials*, Vol. 198, pp 445–455. <https://doi.org/10.1016/j.conbuildmat.2018.10.235>
- [15] ABNT NBR 16697: Cimento Portland – Requisitos, Associação Brasileira de Normas Técnicas; Rio de Janeiro, Brasil (2018).

- [16] ABNT NBR 15894-1: Metacaulim para uso com cimento Portland em concreto, argamassa e pasta - Parte 1, Associação Brasileira de Normas Técnicas; Rio de Janeiro, Brasil (2010).
- [17] ABNT NBR 6502: Solos e rochas – Terminologia, Associação Brasileira de Normas Técnicas; Rio de Janeiro, Brasil (1995).
- [18] ABNT. NBR 7215: Cimento Portland - Determinação da resistência à compressão, Associação Brasileira de Normas Técnicas; Rio de Janeiro, Brasil (2019).
- [19] BS EN 196-1: Methods of testing cement Determination of strength. British Standards, UK (2016).
- [20] ABNT NBR 9778: Argamassa e concreto endurecidos - Determinação da absorção de água, índice de vazios e massa específica, Associação Brasileira de Normas Técnicas; Rio de Janeiro, Brasil (2005).
- [21] Chen, X. & Wu, S. & Zhou, J. (2013) “Influence of porosity on compressive and tensile strength of cement mortar”, *Construction and Building Materials*, Vol. 40, pp 869–874. <https://doi.org/10.1016/j.conbuildmat.2012.11.072>
- [22] Papayianni, I. & Stefanidou, Maria. (2013) “Strength–porosity relationships in lime–pozzolan mortars”, *Construction and Building Materials*, Vol. 20, No. 9, pp 700-705. <https://doi.org/10.1016/j.conbuildmat.2005.02.012>
- [23] Zaheer, M.M. (2020) “Mechanical Performance of Cementitious Composites by MWCNTs Addition for Structural Applications”, *Journal of Civil Engineering and Construction*, Vol. 9, pp 51–62. <https://doi.org/10.32732/jcec.2020.9.2.51>.
- [24] Ghafari, E. & Costa, H. & Júlio, E. & Portugal, E. (2013) “Enhanced durability of ultra-high-performance concrete by incorporating supplementary cementitious materials”, In: *The 2nd international conference Microdurability Delft, Amsterdam*, pp1422-1430. https://www.rilem.net/publication/publication/413?id_papier=8333
- [25] Hou, P. & Wang, K. & Qian, J. & Kawashima, S. & Kong, D. & Surendra P. Shah, (2012) “Effects of colloidal nanoSiO₂ on fly ash hydration”, *Cement and Concrete Composites*. Vol. 34, No. 10, pp 1095-1103. <https://doi.org/10.1016/j.cemconcomp.2012.06.013>
- [26] Alireza, N. G. & Suraya, A. R. & Farah, N. A. & Mohamad Amran Mohd Salleh, (2010) “Experimental investigation of the size effects of SiO₂ nanoparticles on the mechanical properties of binary blended concrete”, *Composites Part B: Engineering*, Vol. 41, No. 8, pp 673–677. <https://doi.org/10.1016/j.compositesb.2010.08.003>
- [27] Ghafari, E. & Arezoumandi, M. & Costa, H. & Júlio, E. (2015) “Influence of nano-silica addition on durability of UHPC”, *Construction and Building Materials* Vol. 94, pp181-188. <https://doi.org/10.1016/j.conbuildmat.2015.07.009>
- [28] Berodier, E. & Scrivener, K.L. (2015) “Filler effect at early hydration”. ICCI, International congress on the Chemistry of Cement.
- [29] Durdzinski, P.T. & Snellings, R. & Dunant, C.F. & Ben Haha, M. & K.L. Scrivener, (2015) “Fly Ash an assemblage of model CA-Mg-Na aluminosilicate glasses”, *Cement and Concrete Research*, Vol. 78, pp 263–272. <https://doi.org/10.1016/j.cemconres.2015.08.005>
- [30] Zhang, M.H. & Islam, J. & Peethamparan, S. (2012) “Use of nano-silica to increase early strength and reduce setting time of concretes with high volumes of slag”, *Cement and Concrete Composites* Vol. 34, No. 5, pp 650-662. <https://doi.org/10.1016/j.cemconcomp.2012.02.005>
- [31] Brito, S.B. & Dimas, A.S.R. & Martini, S. & Salvador, R. P. & Freitas, M. F.M. (2021) “Flexural behavior of HPFRCC: Enhancing post-crack strength and toughness by magnetic alignment of the reinforcement”, *Construction and Building Materials* Vol. 269. <https://doi.org/10.1016/j.conbuildmat.2020.121265>
- [32] Kooshafar, M. & Madani, S.H. (2017) “Influential Mechanisms and Potential Applications of Nano-Silicas in Cement Composites”, *Civil Engineering Infrastructures Journal*, Vol. 50, No. 2, pp 375 – 393. <https://doi.org/10.7508/cej.2017.02.010>
- [33] Belkowitz, J. & Armentrout, D. (2010) “An investigation of nano silica in the cement hydration process”, *Faculty of Engineering and Computer Science, University of Denver*, Vol. 267, pp. 87-100.
- [34] Khaloo, A. & Mobini, M.H. & Hosseini, P. (2016) “Influence of different types of nano-SiO₂ particles on properties of high-performance concrete”, *Construction and Building Materials*, Vol. 113, pp. 188-201. <https://doi.org/10.1016/j.conbuildmat.2016.03.041>

[35] Rojas, C. M. & Cincotto, M. A. (2013) “Influência da estrutura molecular dos policarboxilatos na hidratação do cimento Portland”, *Ambiente Construído*, Vol. 13, No. 3, pp 267–283. <https://doi.org/10.1590/S1678-86212013000300016>

[36] Hoppe, J. & Gobbi, A. & Pereira, E. & Tanaka, R.S & Medeiros, M. (2017) “Atividade pozolânica de adições minerais para cimento Portland (Parte II): Índice de atividade pozolânica com cimento Portland (IAP), difração de raios-X (DRX) e termogravimetria (TG/DtG)”. *Materia*, Vol. 22, No. 3. <https://doi.org/10.1590/S1517-707620170003.0207>

AUTHORS

Igor da Silva Brito is Civil Engineer from University São Judas Tadeu (2016), Master in materials engineering, from the Postgraduate program in Civil Engineering at USJT (2019). He is currently a member of the technical team responsible for the Engineering Laboratory at that university. Researcher in the field of cementitious materials with an emphasis on Composite Materials with fibers, concretes and high-performance cementitious nanocomposites. (2019) PhD candidate in the postgraduate program in Materials Engineering and Nanotechnology, at the Nanomaterials Research Institute (MackGraphe) in the field of synthesis and application of carbon nanostructures in Composite Materials.



Sandro Martini holds a degree in Electrical Engineering (1994) from São Judas Tadeu University (USJT). In 1995, he joined the master's program at the Institute of Physics of the University of São Paulo (IFUSP). During this period, he worked on the optical characterization of semiconductor nanostructures grown by molecular beam epitaxy. In 1997, he entered the doctoral program at IFUSP. During his PhD, he worked on the investigation of indium segregation, using diffraction and optical techniques, in epitaxial layers of InGaAs. In 1999, he went to Friedrich-Schiller-Universität Jena (Germany) to work with AlGaAs/GaAs quantum well lasers. He obtained his Doctor of Science degree in 2002. That same year, he began his postdoctoral work on the growth and characterization of InAs nanostructures. In 2003, he joined USJT, where he teaches Theoretical and Experimental Physics, Electromagnetism, Materials, and Electric Circuits, and is also a researcher and instructor in the Professional Master's Program in Civil Engineering, specializing in nanotechnology and electrical measurements applied to cement composites. He is currently a member of the Institutional Committee of PIBIC-USJT-CNPq and a member of the Technical and Scientific Committee of the Journal of Urban Technology and Sustainability (e-ISSN: 2675-780X). In 2023, he joined the Mauá Institute of Technology (IMT) as a guest professor, where he teaches Physics and Computational Modeling in the Computer Science program.



Ricardo Jorge Espanhol Andrade was born in Barreiro, Portugal. He obtained his B.S. degree in Polymer Engineering from University of Minho, Portugal, in 2005, and his M.S. in Formulation and Technology of Product from University of Huelva in Spain, in 2008. Furthermore, he was awarded a Fellowship from Portuguese Science and Education Ministry to pursue his PhD at Case Western Reserve University in Macromolecular Science and Engineering in Cleveland, USA, and finished in 2014. During his Ph.D. he worked on Polymer Rheology and Processing. Upon completion his Ph.D. work, he moved to a post-doctoral research position Institute of Electronic Structure and Laser of the Foundation for Research and Technology-Hellas (IESL-FORTH), Crete, Greece, where he worked until October 2015 on Colloids Rheology, more specifically on Shear Thickening Systems. He is currently Assistant Professor at School of Engineering, Mackenzie Presbyterian University, and Principal Researcher at 4MackGraphe - Mackenzie Institute for Research in Graphene and Nanotechnologies, Mackenzie Presbyterian Institute, both in São Paulo, Brazil. His current research cover topics such as understanding the complex relationship between thermo-mechanical history and the structure and morphology of polymer nanocomposites based on 2D materials (graphene, MoS₂, hBN, phosphorene, etc.). It is also part of his research the study of dispersions of 2D nanomaterials under shear and extensional flows. His research intends to understand



the fundamental mechanisms involved in the morphology and structure development of nanomaterials, with the aim to improve their properties for broad range applications, such as textiles, aeronautics, automobiles, oil recovery, printing inks, packaging and smart materials.

Bruno Luís Damineli is a Full Professor of Building Materials and Technologies at the Institute of Architecture and Urbanism (IAU), University of Sao Paulo (USP), and the main coordinator of the Building Construction Lab at IAU. He holds his Master's degree from Polytechnic School-USP focused on recycled aggregates to use in concrete. He earned his PhD from Polytechnic School-USP with a stage at Royal Institute of Technology (KTH), Sweden, focused on low-cement content in concrete. He won the Starkast Betong international contest (Sweden-2012), developing the highest efficient concrete, and won the USP Thesis Prize 2015 (best 2013-2014 thesis of USP Engineering programs). His main research themes are design of cementitious materials with low-cement content, recycled aggregates and inert fillers, packing and dispersion of particles, development of sustainable building materials and innovative construction systems.

