1 **Characterization of C-S-H in ternary cement pastes containing**
2 **nanosilica and highly-reactive mineral additions: Microstructure**
3 **and strength**

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35 **Abstract**

36 This paper, for the first time, focuses on the characterization of C-S-H of ternary
37 cement pastes with highly reactive mineral additions (silica fume and metakaolin)
38 and colloidal nanosilica. The pastes with ternary mixtures showed increased C-S-
39 H production, as well as a decrease in the Ca/Si ratio and an increase in the size of
40 the chain. The metakaolin pastes also showed an increase in the Al/Ca ratio,
41 which indicates the incorporation of Al in the C-S-H chain. All these changes in
42 the C-S-H nanostructure have led to an increase in compressive strength and
43 refinement of the pore structure of these pastes.

44
45 Keywords: nanosilica; silica fume; metakaolin; ternary cement; C-S-H;
46 microstructure.

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61 **1. Introduction**

62 The main compound formed in all Portland-based cement (PBC) systems is
63 calcium silicate hydrate (C-S-H), which is responsible for bonding and strength
64 properties of the PBC systems. However, incorporation of mineral additions into
65 the PBC leads to composition changes of the C-S-H formed that can deeply
66 interfere in the microstructure, mechanical properties and durability of the
67 cementitious systems [1-3]. As far as cementitious materials are concerned one of
68 the current trends in nanotechnology is the understanding of modifications in the
69 C-S-H caused by incorporation of nanosized additions combined or not with
70 highly-reactive mineral additions [4].

71 Silica fume (SF) is a highly-reactive mineral addition with high content of
72 amorphous silica in its composition, which reacts with calcium hydroxide
73 originating from the cement hydration reaction, thus generating secondary C-S-H
74 gels [5, 6]. Moreover, addition of SF reduces the overall Ca/Si ratio while
75 increasing the mean C-S-H chain size and also altering the C-S-H morphology
76 [7]. The high fineness of these particles also contributes to the physical action
77 (filler effect) by refining the pores and decreasing the total porosity of the
78 cementitious materials [8, 9]. Metakaolin (MK) is also a highly-reactive mineral
79 addition characterized by its high alumina content, which differentiates it from
80 other mineral additions with high amorphous silica content such as SF [10, 11].

81 Partial substitution of silicon by aluminum in the C-S-H chains via the pozzolanic
82 reaction of MK leads to C-A-S-H formation [11, 12]. Compared to the C-S-H
83 formed in the pozzolanic reaction, addition of MK provides more polymerized C-
84 A-S-H gels with altered morphology, presenting lower Ca/Si and higher Al/Ca
85 ratios [13, 14]. On the other hand, while compared with SF, introduction of

86 nanosilica (NS) into the PBC paste enhances the pozzolanic reaction, resulting in
87 new materials with higher performance [15 – 20]. Actually, NS accelerates
88 cement hydration reactions and the as-formed C-S-H is more polymerized, thus
89 presenting longer chains [21 – 26]. Despite this, there is no consensus yet
90 regarding the best percentage of NS addition and under which mixing conditions
91 the best performance can be obtained [27 – 31].

92 Up to now, only a few published papers have reported on the microstructure and
93 mechanical properties of ternary mixtures comprising PBC, colloidal NS, and SF
94 [32 – 36]. Emphasis had been given to beneficial effects on the mechanical
95 properties and microstructure of the end cementitious materials. However, there is
96 only one report evaluating the synergic effect of NS combined with other highly-
97 reactive mineral additions such as MK [37]. Thus, it is of high practical interest to
98 explore this direction of research, aiming at a better understanding of the aspects
99 related to the microstructure and properties of cementitious materials while
100 incorporating NS plus different types of highly-reactive mineral additions.

101 This paper pioneers in focusing on the characterization of the C-S-H in ternary
102 cement pastes incorporating NS plus highly-reactive mineral additions (HRMA)
103 such as SF and MK. Different blended cement pastes incorporating 3% of NS and
104 10% of HRMA were produced and characterized using a wide pallet of
105 experimental techniques in order to explore the evolution of the C-S-H gels and
106 their influence upon both the microstructure and mechanical properties of the end
107 cementitious material.

108 **2. Experimental details**

109 **2.1. Materials and methods**

110 The following materials have been used in the materials' preparation: cement type
111 I (CPI), without incorporation of mineral additions, specific surface area of 467
112 kg/m² (Blaine fineness), meeting the Brazilian standard [38] and supplied by
113 Votorantim Cimentos (Brasília, Brazil); aqueous suspension of NS at 30 wt.%
114 supplied by Akzonobel (São Paulo, Brazil); commercial non-densified SF
115 supplied by Dow Corning Silicon (São Paulo, Brazil); MK supplied by
116 Metacaulim do Brasil (São Paulo, Brazil); superplasticizer (SP) based on
117 polycarboxylate aqueous solution (40 wt.%) supplied by Sika (São Paulo, Brazil);
118 and potable water.

119 Table 1 shows the chemical composition of the cement, SF, MK and NS,
120 determined by x-ray fluorescence spectrometry (XRF). The MK contains 57 wt.%
121 silica and 32 wt.% alumina, whereas both the SF and NS show silica content
122 higher than 89 wt.%. This difference in silica content does influence the hydration
123 process of the cement pastes with the SF or MK. Worth mentioning that the loss
124 on ignition of the NS was determined with the solid residue previously dried at
125 100 °C. The specific surface area values (BET) of the SF, MK and NS are 23.540,
126 18.540 and 80.000 m²/kg, respectively. The BET value of the NS was supplied by
127 the manufacturer (Akzonobel).

128 Figure 1 presents the x-ray diffraction (XRD) patterns obtained for the three
129 pozzolans analyzed. The XRD pattern of the SF presents an amorphous halo
130 corresponding to the baseline deviation between $2\theta = 15^\circ$ and $2\theta = 30^\circ$, indicating
131 the amorphicity of this pozzolan (see Figure 1a). Trace of quartz was identified as
132 a crystalline content in the SF composition. The XRD features observed in the

133 MK's diffractogram indicate that kaolinite, quartz, goethite and illite are present
134 as crystalline phases (see Figure 1b). In Figure 1b the amorphous halo observed
135 between $2\theta = 15^\circ$ and $2\theta = 30^\circ$ indicates the presence of an amorphous phase
136 corresponding to the MK, which is well known for its non-crystalline nature [39].
137 The XRD pattern of the NS is very similar to the XRD observed in the SF, though
138 without the presence of crystalline phases, confirming its amorphous
139 characteristic (see Figure 1c). The data shown in Figure 1 were recorded in a
140 RIGAKU XRD system model ULTMA IV (Osaka, Japan).

141 Granulometric profile analysis of the SF reveals a mean diameter of 15.45 μm ,
142 with $D_{10} = 2.45 \mu\text{m}$ and $D_{90} = 31.80 \mu\text{m}$. However, the granulometric analysis of
143 the MK indicates a mean diameter of 29.07 μm , with D_{10} and D_{90} equal to 2.72 μm
144 and 59.01 μm , respectively. The data presented were collected in a CILAS laser
145 granulometry system, Model Microcurve (Saarbrücken, Germany).

146 According to the TEM image of the NS shown in [37], spherically-shaped SiO_2
147 nanoparticles are dominating the sample's morphology, with mean diameter
148 around 27 nm. Due to high surface energy and short inter-particle distance the
149 nanoparticles suspended within the colloidal NS sample tend to form clusters [40].

150 Figure 2 shows typical scanning electron microscopy (SEM) images of the MK
151 and SF samples. Worth mentioning that while increasing magnification up to
152 7,000 $\times$, as shown in Figure 3d, formation of SF clusters from smaller particles
153 was observed. The analyzes were performed in a Tescan - Vega3 SEM system
154 (Jena, Germany).

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2.2. Composition of cement pastes

Table 2 presents composition of six pastes produced with the PBC, colloidal NS and/or SF or MK. All pastes were produced with a fixed water/cementitious materials ratio equals to 0.35. This means that the water content from colloidal NS and SP were deducted from the total amount of water used to prepare the pastes. Colloidal NS was dosed considering its solid content (30 wt.%) whereas the dosage of the SP varied according to the composition of each paste in order to maintain a fixed consistency equals to 260 ± 10 mm, which was considered the most favorable for the molding process. Consistency was measured in a flow table according to [41].

Pastes were produced in a climatic room kept at 23 ± 1 °C, using universal mortar mixing machine following the guidelines in [41]. The procedure to prepare the pastes consisted in adding the water/SP/NS mix to the SF or MK blended cement and homogenizing the resulting paste for 60 s at 140 rpm and then for 90 s at 280 rpm. The pastes obtained were used to mold cylindrical specimens, measuring 50 mm in diameter and 100 mm in height. After preparation, the molds were kept in a 100% humid chamber for 24 h. Next, specimens were demolded and kept at the same chamber until testing.

2.3. Test methods of cement pastes

Compressive strength was obtained from direct compression tests of the above-described cylindrical paste specimens (50×100 mm). Tests were performed using universal test machine at a pressure application rate equals to 0.25 ± 0.05 MPa/s according to [42]. Thermogravimetric analysis (TGA) was performed from 30 °C to 1000 °C at a heating rate of 10 °C/min under N₂-flow of 100 mL/min using a SDT Q-600 thermal balance (Saarbrücken, Germany). In each TGA analysis,

181 approximately 10 mg of paste was tested in 90 μ L alumina crucibles. Fourier
182 transform infrared (FTIR) spectroscopy was conducted from 4000 to 400 cm^{-1}
183 using KBr pellets at a cement paste/KBr ratio equals to 1/3. The FTIR equipment
184 used was a Mattson Genesis II spectrometer (Saarbrücken, Germany). ^{29}Si solid-
185 state magic angle spinning (MAS) nuclear magnetic resonance (NMR)
186 spectroscopy was performed using a Bruker model Ascend 600 and Console
187 Avance III HD spectrophotometer (Karlshure, Germany) with a field strength of
188 14.1 T (600 MHz) and equipped with a CP/MAS H/X probe of 4.0 mm. The ^{29}Si
189 NMR spectra were obtained at a spinning frequency of 10 kHz, pulse duration of
190 4.25 μ s, pulse interval of 10 s and with a minimum of 1,024 acquisition points for
191 each spectrum. Tetramethylsilane (TMS) was used as reference. The
192 deconvolution of the NMR spectra in its elementary components was performed
193 using the OMNICTm Spectra software and considering the fitting of the spectral
194 profile. In general, NMR spectra are described in the literature by
195 Gaussian/Lorentzian functions or by Voight functions with partial contributions of
196 both. For the samples in the present study, the Gaussian/Lorentzian profiles were
197 used, which presented good agreement with the references studied [43, 44]. The
198 SEM secondary electron detector (SED) allowed to evaluate in detail the
199 characteristics of the pastes' surface by means of three-dimensional images. In the
200 produced six pastes, semi-quantitative microanalysis of Ca/Si, Al/Si and Al/Ca
201 ratios of the C-S-H was carried out by using energy dispersive x-ray (EDX)
202 spectrometry. The microanalyses were performed in $8,000\times$ magnification, being
203 conducted 30 microanalyses per sample (acquisition time set at 120 s) in points
204 with probable presence of C-S-H. Total porosity and pore-size distribution were
205 assessed in the as-produced cement pastes using a Micromeritics Autopore IV
206 9500 (Saarbrücken, Germany) mercury intrusion porosimetry (MIP) system

operating at 227.5 MPa. The mercury contact angle used in this study was 141.3°, with a mercury surface tension of 485 dyne/cm². Compressive strength and TGA were performed in samples aged for 3, 7, 28 and 91 days whereas FT-IR, NMR, SEM and MIP were conducted in samples aged for 91 days. Samples employed for the TGA, FT-IR and NMR tests were obtained from the center of the specimen used in the compression strength test. Samples' hydration was stopped by immersion in acetone during 60 min and drying at 60 °C for 24 h. Next, samples were crushed and grounded in agate mortar to a maximum particle size of 75 µm. Two cubes (1 cm³ edge) were extracted from the center of an intact paste cylinder employing diamond cutter and further used to perform MIP and SEM tests. Samples' hydration was stopped as previously described.

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219 **3. Results and discussion**

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221 **3.1. Fresh state - superplasticizer consumption**

The SP content used in each paste to afford the 260 ± 10 mm consistence in flow table is collected in Table 3. Worth mentioning that due to the higher specific surface area of the NS, the 3NS-containing pastes required higher SP content than the 10SF and 10MK pastes in order to reach the same consistency [18]. In ternary cement pastes, the required content of the SP is higher than in binary ones, due to the combined effect of higher specific surface area of the two pozzolans.

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3.2. Compressive strength data

Figure 3 shows the compressive strength (f_c) of all pastes aged for 3, 7, 28, and 91 days. Note the systematic increase of the compressive strength as the pastes' age increase from 3 to 91 days.

The pastes produced with the NS (3NS, 10SF-3NS, and 10MK-3NS) present a higher compressive strength than the reference paste at all ages. This fact may be explained by the combined effect of both pozzolanic activity and filler effect. In this regard, the NS is significantly beneficial up to 28 days, likely because it increases the reaction rate and the amount of the C-S-H formed during hydration [45]. With respect to the reference paste the 3NS paste presents the highest compressive strength increase at 3 days aging (73.7 MPa), with about 40% increase in mechanical resistance. This relative gain in mechanical resistance tends to decrease with increasing hydration age, presenting only 20% increase at 91 days aging. A reduction in the strength gain rate in late-aged cement pastes containing NS has been already reported in the literature [22, 34]. It is well-known that the cement hydration at longer aging is controlled by diffusion of ions through the hydrates. Thus, the compact C-S-H structure formed by the pozzolanic reaction in the presence of the NS may block diffusion, retarding cement hydration and reducing the rate of strength gain [22].

After 3 days of hydration, the 10SF and 10MK pastes present similar compressive strength as compared to the reference paste (relative compressive strength). As the hydration age increases, there is an increase in the relative compressive strength gain in both pastes, reaching about 10% gain in relative compressive strength after 91 days aging. Pozzolanic additions, such as the SF and MK, induce portlandite to generate secondary C-S-H. Therefore, depending upon the cement hydration progression, the effect of these additions can be reduced during early aging [46].

Both 10SF-3NS and 10MK-3NS pastes present about 20% increase in the compressive strength value in comparison with the 10SF and 10MK pastes after 3 days of hydration. The accelerating effect of NS on the hydration of cement pastes has been already reported in the literature [23, 47, 48]. The highest compressive strengths at 7, 28 and 91 days aging were reached by the 10SF-3NS (84.3 MPa), 10MK-3NS (103.8 MPa) and 10SF-3NS (104.8 MPa) pastes, respectively. After 91 days of hydration, both 10SF-3NS and 10MK-3NS pastes showed around 30% gain in the relative compressive strength.

3.3. TGA data

The portlandite amount (T.CH) of pastes were obtained from the TGA curves. The beginning and end of each step in the TGA curves are used to measure the percentage of mass loss of a given component. The mass loss corresponding to the pitch between approximately 420 °C and 520 °C in a PBC paste is due to decomposition of Ca(OH)_2 . In this temperature range, Ca(OH)_2 decomposes into CaO and H_2O . The mass loss reported by TGA is a result of volatilization of water. Thus, it is possible to determine the portlandite amount (T.CH) of one particular paste of hydrated PBC using the values extracted from the TGA curves and stoichiometric calculations. The portlandite amount (T.CH) of the as-produced pastes aged for 3, 7, 28 and 91 days are collected in Figure 4.

Note from Figure 4 that the T.CH of the reference paste increases monotonically during the whole aging analyzed period. As for the 3NS paste, a significant relative reduction in T.CH content (of about 35% with respect to the reference paste) is observed after 3 days of hydration, indicating the portlandite consumption by the NS at early stage. Nevertheless, from 3 days onward, the

280 T.CH content of the 3NS past increases monotonically and tends to stabilize after
281 28 days of hydration. Actually, all the as-produced pastes show similar trend after
282 3 days of hydration, i.e. relative reduction of T.CH content, with the 10SF-3NS
283 and 10MK pastes revealing the highest (about 61%) and the lowest (about 25%)
284 relative reduction of the T.CH content, respectively (see Figure 4). Except for the
285 MK paste all the as-produced pastes show monotonically increasing T.CH content
286 from 3 days of hydration onward, stabilizing earlier (10SF-3NS after 7 days) or
287 later on (10SF after 91 days), as shown in Figure 4. In contrast, the 10MK paste
288 reaches its highest T.CH content at early stage of hydration (7 days), reducing
289 monotonically afterwards up to 91 days of hydration.

290 Worth mentioning that the inflection observed in the T.CH content of the 10MK
291 paste at early stage of hydration (7 days) is expected, once this paste shows lower
292 cement content than the reference paste, due to the use of mineral addition.
293 However, the main reason of such an early reduction in the T.CH content (after 7
294 days of hydration) is the pozzolanic activity, which was also reported in other
295 studies [49, 50]. Importantly, the 10SF-3NS and 10MK-3NS pastes show two
296 stages of pozzolanic activity credited to additions of the SF and NS in the former
297 and the MK and NS in the latter. While the NS reacts mainly up to 3 days of
298 hydration due to its high surface area, the pozzolanic activity of the SF or MK
299 predominates from 7 days onward. Moreover, the HRMA, such as the SF or MK,
300 present a slower pozzolanic activity, showing its maximum activity between 7 and
301 28 days of hydration [46]. Actually, the difference between the reactivity of the
302 NS and SF or the MK is credited to the higher degree of amorphousness plus the
303 smaller particle size found in the NS. Furthermore, the NS may present a
304 difference in chemical structure: unsaturated Si-O bonds present on the surface of
305 the NS particles is expected to increase the pozzolanic reaction rate [51].

306 Regardless the difference in T.CH contents the 10SF-3NS and 10MK-3NS pastes
307 reveal similar trend upon aging up to 91 days (see Figure 4).

308

309 **3.4. FT-IR data**

310 Figure 5 collects the infrared spectra of the 91 days-aged pastes in the 1350 cm^{-1} -
311 750 cm^{-1} range. Typical vibrations of Si-O bonds in the hydrated C-S-H are
312 observed in the broad band around 975 cm^{-1} [52]. The highest infrared band
313 intensity is observed in the 10SF-3NS and 10MK-3NS pastes, which indicates that
314 these two samples present the highest C-S-H content.

315 The FT-IR spectra collected in Figure 6 show increased amplitude of the C-S-H
316 broad band of the 10MK-3NS paste with respect to the 10SF-3NS paste.
317 Substitution of Si by Al in the C-S-H chain occurs with the use of the MK, which
318 shifts the infrared band to lower frequencies [13, 53, 54].

319

320 **3.5. SEM-EDX data**

321 SEM-EDX semi-quantitative analyses of the as-produced pastes after 91 days of
322 hydration allowed to assess the surface morphology and the Ca/Si, Al/Si and
323 Al/Ca ratios, the later collected in Table 4. The reference paste (first row in Table
324 4) reveals the highest average Ca/Si ratio (2.5). Figure 7 shows a typical
325 backscattered SEM image of the reference paste, indicating one of the thirty spots
326 where the microanalysis was carried out.

327 With respect to the reference paste the 3NS paste shows a reduced Ca/Si ratio
328 (2.1) credited to a higher supply of reactive silica provided by the NS. Singh et al.
329 [25] also observed a reduction of the Ca/Si ratio while replacing cement with the
330 NS. In the 10SF paste the Ca/Si ratio reduces even further (1.7), which is

331 explained by the higher availability of reactive silica in the C-S-H formation.
332 Actually, agglomerates of unreacted silica are observed in the SEM micrographs
333 of the 10SF paste (see Figure 8); the SF acting only as filler in all as-produced
334 pastes containing this addition. Both 10SF and 10MK pastes show the same Ca/Si
335 ratio (1.7), although the SF presents higher silica content than the MK. However,
336 the 10SF paste shows unreacted silica (see Figure 8), thus explaining the
337 similarity with the 10MK paste as far as the Ca/Si ratio (1.7) is concerned. Among
338 the as-produced pastes the lowest Ca/Si ratio (1.6) is found in the 10SF-3NS and
339 10MK-3NS pastes, credited to the higher supply of reactive silica provided by the
340 NS in the C-S-H formation while combining with the SF and MK, respectively.
341 The literature already reported the reduced value of the Ca/Si ratio achieved in
342 pastes containing SF or NS, while the combination of both enhanced even further
343 the reduction of the Ca/Si ratio [36]. Moreover, in pastes containing SF or NS
344 high values of Ca/Si ratio are observed at the initial stage of hydration while
345 decreasing remarkably during aging [17].

346 Regarding the Al/Si ratio the reference paste shows the second highest value
347 (0.24) among all as-prepared samples (see Table 4). As for the 3NS paste, there is
348 a higher supply of reactive silica and a lower supply of aluminum, due to the
349 replacement of CPI by the NS, leading to a relative decrease of the average Al/Si
350 ratio down to 0.18. However, the lowest Al/Si ratio value (0.12) is observed in the
351 10SF and 10SF-3NS pastes, which is due to the higher supply of silica compared
352 to all other pastes (see Table 4). On the other hand, the 10MK paste presents the
353 highest Al/Si ratio value (0.25), credited to addition of the MK (high aluminum
354 content), resulting in the highest incorporation of Al compared to the other pastes.
355 Indeed, the 10MK-3NS paste presents an average Al/Si ratio value (0.23) slightly
356 lower than the 10MK paste (0.25).

357 As for the Al/Ca ratio value the reference paste shows a moderate value of 0.10
358 (see Table 4). Relative to the reference paste, the 3NS paste shows a slight
359 decrease in the average Al/Ca ratio (0.09). Interestingly, relative to the reference
360 paste, the 10SF and 10SF-3NS pastes show the highest reduction in the average
361 Al/Ca ratio values down to 0.07 and 0.08, respectively. On the other hand, the
362 10MK and 10MK-3NS pastes present the highest values of the average Al/Ca
363 ratio among all as-produced pastes, equal to 0.16 and 0.14, respectively. This
364 finding, as well as the Al/Si ratio values, reflects incorporation of Al into the C-S-
365 H chains.

366

367 **3.6. ²⁹Si-NMR data**

368 Figure 9 shows the ²⁹Si-NMR spectra of the as-prepared pastes whereas Table 5
369 collects different parameters, namely the mean chain length (MCL) and the ²⁹Si-
370 NMR component areas extracted from the deconvolution of the ²⁹Si-NMR spectra
371 into different components (Q_n). The Q_n NMR features are typical while
372 evaluating cement pastes under hydration, where Q is the silica tetrahedron and n
373 indicates the number of oxygens that bind to adjacent tetrahedra. The Q0 (-71.3
374 ppm) component is related to the silicate content not yet hydrated and the Q1 (-79
375 ppm) and Q2 (-85 ppm) components are assigned to the C-S-H formation. A weak
376 ²⁹Si-NMR feature at around -95 ppm is also assigned to the C-S-H formation and
377 labeled Q3. It is also observed a feature in the ²⁹Si MAS NMR around 82 ppm,
378 characteristic of the bond Q2 (1Al), due to substitution of Si by Al in the C-S-H
379 chain. This peak is enhanced with incorporation of mineral additions with high
380 percentage of aluminum, as in the case of metacaulim, as can be observed in the
381 lowest panel in Figure 9. According to [55] and [56], the mean chain length

382 (MCL) of the C-S-H or C-A-S-H is calculated using: $MCL = 2/(Q1/Q1 + Q2(0Al)$
383 $+ 3/2Q2(1Al))$.

384 Due to addition of the NS the MCL are improved in the 3NS pastes (6.77) while
385 compared to the reference paste (4.59) (see data in Table 5), as has been pointed
386 out in the literature [24, 44]. The 10SF paste presented increased MCL (9.33)
387 while the 10SF-3NS paste decreased MCL (3.62). However, the 10 MK paste
388 presented an increase in the MCL of C-S-H (8.43) with respect to the reference
389 paste, probably due to substitution of Si by Al in the C-S-H chain, leading to C-A-
390 S-H formation. Worth mentioning that substitution of Si by Al in the MK-
391 containing pastes occurs especially in the bonding tetrahedral position of
392 “dreierkette” chains, leading to an increase in both polymerization degree and C-
393 S-H chain length [1, 55, 56]. The increase of the C-S-H chain is potentiated in the
394 10MK-3NS paste reaching the highest MCL (11.12). According to (44), the use of
395 NS promotes incorporation of Al within the structure of the C-S-H. Moreover,
396 enhancement of the Q1 and Q2 ^{29}Si -NMR features has been correlated with
397 improvement of the pastes in regard to both the modulus of elasticity and
398 mechanical strength [57].

399

400 **3.7. MIP data**

401 Table 6 collects the data obtained by using mercury intrusion porosimetry (MIP)
402 to assess information regarding the total porosity, mean pore size, reduction in
403 mean pore size with respect to the reference paste, and porosity of pore sizes in
404 the range of 50 to 100 nm, in all as-prepared pastes after aging for 91 days.

405 In comparison with the reference paste all as-prepared pastes present a reduction
406 in the mean pore size (see Table 6). The reduction in the mean pore size is higher

407 in the 10MK and 10MK-3NS pastes while it is lower in the 10SF and 10SF-3NS
408 pastes. This effect is probably due to clusters of the SF that are still observed in
409 the pastes after aging for 91 days. Moreover, with respect to the reference paste
410 and except for the 10SF paste, all other pastes present reduced total porosity and
411 reduced porosity with pore size in the range of 50-100 nm. The impressive
412 relative reduction in mean pore diameter observed in the 10MK and 10MK-3NS
413 pastes, respectively equals to 55% and 56%, is accompanied by the lowest
414 porosity with pore sizes in the range of 50-100 nm (see last column in Table 6).
415 Importantly, reduction in the macropore volume influences durability of
416 cementitious materials, once they respond for the matrix permeability and
417 absorption of aggressive agents [6]. Worth mentioning that with respect to the
418 reference paste the 10SF paste presents a slightly lower mean pore diameter,
419 although the total porosity is slightly higher than the reference paste (see Table 6).
420 Note that in the 3NS paste a refinement of the microstructure of the matrix with a
421 reduction of 18% in the mean pore diameter is observed. The pozzolanic reaction
422 of the NS contributes to the refinement of the pore structure [23, 58].
423 Finally, while comparing the data collected in Tables 5 and 6 one finds that the
424 decrease of the Ca/Si ratio occurring in the pastes containing HRMA (SF and/or
425 NS) or the increase in the Al/Ca ratio in the pastes containing MK, lead to
426 changes in the morphology of the C-S-H formed. Actually, upon addition of the
427 HRMA (SF, NS, MK) the morphology evolves from a fiber-like to a foil-like one,
428 which probably leads to porosity refinement and durability improvement of the
429 pastes [7, 55].
430

431 **4. Conclusions**

432 Based on the results obtained in the present study, the following conclusions can
433 be drawn:

- 434 • Once the NS has larger surface area than the SF or MK, pastes produced
435 with the NS require larger amount of the SP to maintain the same
436 workability and consistency. Nevertheless, the use of ternary cement
437 pastes increased the SP demand.

- 438 • Based on the TGA data, the pozzolanic reaction of the NS consumes more
439 portlandite until 3 days of hydration, while the effect of the pozzolanic
440 activity of the SF or MK is mainly observed from 7 days onwards. When
441 the SF and MK are added simultaneously with the NS, a combined effect
442 on portlandite consumption until 3 days and after 7 days was observed.

- 443 • Pastes produced with both NS and SF or MK presented higher content of
444 C-S-H while aged to 91 days than pastes produced with the NS, SF or MK.
445 This fact is supported by the increase in the FTIR band around 975 cm^{-1} .

- 446 • Among all as-produced pastes the 10MK-3NS paste showed the C-S-H
447 with longer LCM, indicating that the NS potentiates the incorporation of
448 Al, present in the MK, in the C-S-H structure.

- 449 • Compared to all as-produced pastes the 10MK and 10MK-3NS ones
450 showed the highest Al/Si and Al/Ca ratios. This indicates highest Al
451 incorporation in the C-S-H chains.

- 452 • The 3NS paste presented the highest compressive strength at 3 days of
453 hydration, whereas the 10SF-3NS and 10MK-3NS pastes revealed the
454 highest compressive strength at 7, 28 and 91 days of hydration,
455 corroborating the results obtained with TGA and FTIR.

- 456 • The 10MK-3NS paste presented highest pore refinement than the other
457 pastes, which is justified by the higher MCL value.

458 The HRMA (SF or MK) and NS shows a synergistic effect on the hydration of the
459 cement pastes. The results herein obtained emphasize the promising of the ternary
460 cement mixes for production of high performance cementitious materials.

461

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624
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Figure Captions

626

627 Figure 1 - X-ray diffraction patterns of (a) SF, (b) MK, and (c) NS.

628

629 Figure 2 - SEM images of (a) MK (2,000×), (b) MK (7,000×), (c) SF (2,000×),
 630 and (d) SF (7,000×).

631

632 Figure 3 - Compressive strength (f_c) of the pastes at 3, 7, 28 and 91 days of
 633 hydration.

634

635 Figure 4 - Portlandite content (T.CH) in the pastes.

636

637 Figure 5 - Infrared spectra of the reference paste and 3NS, 10MK, 10MK-3NS,
638 10SF and 10SF-3NS pastes at 91 days of hydration.

639

640 Figure 6 - Detail of infrared spectra of the pastes at 91 days of hydration in the
641 1050 - 900 cm⁻¹ region.

642 Figure 7 - Scanning electron microscopy of the reference paste (left panel).

643 Figure 8 - Agglomerated of unreacted silica in the 10SF paste.

644

645 Figure 9 - ²⁹Si-NMR spectra of the reference paste and for the 3NS, 10SF, 10SF-3NS,
646 10MK, and 10MK-3NS pastes.

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Table 1 - Chemical composition of the materials

Compounds		Cement (wt.%)	Silica fume (wt.%)	Metakaolin (wt.%)	Nanosilica (wt.%)
Loss on ignition		1.86	3.90	2.89	7.55
Insoluble residue		0.43	-	-	-
Calcium oxide (CaO)		62.5	0.98	0.07	0.02
Silicon dioxide (SiO ₂)		19.72	92.54	57.43	89.08
Aluminum oxide (Al ₂ O ₃)		4.54	0.12	32.58	-
Iron oxide (Fe ₂ O ₃)		3.04	0.14	2.08	-
Magnesium oxide (MgO)		5.26	1.19	1.51	0.79
Sulfur trioxide (SO ₃)		2.82	-	-	-
Total alkali	Sodium oxide (Na ₂ O)	0.08	0.41	1.81	0.08
	Potassium oxide (K ₂ O)	0.59	0.46	-	0.59
	Na ₂ O equivalent	0.47	0.71	1.81	0.47

Table 2 - Composition of Portland cement pastes with SF or MK and colloidal NS

Pastes	Abbreviation	CPI (g)	Water (g)	SF (g)	MK (g)	NS (g)	SP (%)	Consistency (mm)
100% CPI	Reference	1500	523.65	-	-	-	0.15	260
97% cement CPI + 3% NS	3NS	1455	410.83	-	-	150	1.05	262
90% cement CPI + 10% SF	10SF	1350	524.58	150	-	-	0.42	262
87% cement CPI + 10% SF + 3% NS	10SF-3NS	1305	418.45	150	-	150	1.55	260
90% cement CPI + 10% MK	10MK	1350	521.36	-	150	-	0.45	260
87% cement CPI + 10% MK + 3% NS	10MK-3NS	1305	404.97	-	150	150	1.92	259

Table 3 - Superplasticizer content of the pastes required to reach the normalized consistency

Pastes	Referenc e	3NS	10SF	10SF-3NS	10M K	10MK-3NS
SP content (%)	0.15	1.05	0.42	1.45	0.45	1.95

Table 4 - Average Ca/Si, Al/Si and Si/Ca ratios of the pastes aged for 91 days.

Pastes	Ca/Si	Al/Si	Al/Ca
Reference	2.5	0.24	0.10
3NS	2.1	0.18	0.09
10SF	1.7	0.12	0.07
10SF-3NS	1.6	0.12	0.08
10MK	1.7	0.25	0.16
10MK-3NS	1.6	0.23	0.14

Table 5 – Areas of the Qn components and mean chain length (MCL) of C-S-H.

Paste	-	Q0	Q0	Q0	Q1	Q2(1Al)	Q2	Q3	MCL (Å)
REFERENCE	Peak (ppm)	-	-71.1	-73.0	-78.8	-81.7	-84.5	-	4.59
	Area (%)	0.00	7.82	13.74	36.44	10.49	31.51	0.00	
3NS	Peak (ppm)	-	-71.1	-74.5	-78.8	-81.7	-84.5	-	6.77
	Area (%)	0.00	18.87	4.87	25.68	21.24	29.34	0.00	
10SF	Peak (ppm)	-	-71.1	-73.8	-78.8	-81.0	-84.7	-91.7	9.33
	Area (%)	0.00	11.78	7.29	20.32	27.79	27.88	4.94	
10SF-3NS	Peak (ppm)	-69.8	-70.8	-74.5	-78.8	-81.7	-84.2	-	3.62
	Area (%)	26.62	381	8.27	37.74	14.03	9.53	0.00	
10MK	Peak (ppm)	-	-70.8	-74.2	-78.5	-81.0	-84.5	-	8.43
	Area (%)	0.00	15.86	4.98	23.22	37.44	18.51	0.00	
10MK-3NS	Peak (ppm)	-	-70.8	-73.0	-78.8	-80.2	-84.7	-	11.12
	Area (%)	0.00	16.83	3.31	18.30	43.84	17.72	0.00	

Table 6 - Results obtained by MIP of all pastes at 91 days of hydration.

Paste	Total porosity (%)	Mean pore size (µm)	Relative reduction in mean pore size (%)	Porosity with pore sizes in the range of 50-100 nm (%)
Reference	19.29	0.0786	--	12.53
3NS	17.41	0.0644	18	11.20
10SF	19.39	0.0717	9	13.26
10SF-3NS	17.50	0.0533	32	9.96
10MK	16.48	0.0357	55	5.27
10MK-3NS	15.06	0.0349	56	4.59

Figure 1
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Figure 2
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Highlights

- The C-S-H formed in cement pastes with SF or MK in conjunction with NS was characterized.
- The SF or MK and NS shows a synergistic effect on the hydration of the cement pastes.
- Pastes with NS and SF or MK presented higher content of C-S-H at 91 days.
- NS potentiates the incorporation of Al, present in the MK, in the C-S-H structure.
- Pastes with SF or MK and NS present the highest compressive strength and pore refinement at 91 days of hydration.

Portland cement pastes containing nanosilica and highly-reactive mineral additions

TEM micrograph of nanosilica

SEM images of silica fume

SEM images of metakaolin

Higher production of C-S-H with decreased of Ca/Si ratio and longer silicate chain size

Higher compressive strength and pore refinement

Compressive Strength (MPa)

Characterization of C-S-H

Infrared spectra pastes

Pastes	Ca/Si	Al/Si	Al/Ca
Reference	2.3	0.24	0.10
3NS	2.1	0.18	0.09
10SF	1.7	0.12	0.07
10SF-3NS	1.6	0.12	0.08
10MK	1.7	0.25	0.16
10MK-3NS	1.6	0.23	0.14

Average Ca/Si, Al/Si and Si/Ca ratios of the pastes