

COMPARATIVE ANALYSIS OF PERFORMANCE OF PORTLAND CEMENT BLENDED WITH NANOSILICA AND SILICA FUME

ANÁLISIS COMPARATIVO DEL DESEMPEÑO DEL CEMENTO PORTLAND ADICIONADO CON NANOSÍLICE Y HUMO DE SÍLICE

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ABSTRACT: In this paper some physical properties of Colombian Portland cement type III replaced with nanosilica in percentages of 1, 3, 5 and 10% were evaluated. Main determined properties were fluidity, normal consistency, setting times, heat of hydration and compressive strength on pastes and mortars. It was made also a comparative analysis with samples substituted with commercial silica fume in percentages of 5, 10 and 15%. Results showed that the nanosilica from 5% beginning to have a major positive influence on the mechanical strength of mortars and with a 10% of substitution improvements in compressive strength up to 120% with respect to the control sample for one day of curing can be achieved. For longer curing time the improvement is decreased slightly, with near 80%, remaining this improvement in strength after 28 days of curing.

KEYWORDS: Nanoparticles, nanosilica, blended cement, physical properties of cement.

RESUMEN: En este artículo se evalúan propiedades físicas como fluidez, consistencia normal, tiempos de fraguado, calor de hidratación y resistencia a la compresión de pastas y morteros de cemento portland tipo III colombiano reemplazado con nanosílice en porcentajes de 1, 3, 5 y 10%. Se hace también un análisis comparativo con muestras sustituidas con humo de sílice comercial en porcentajes de 5, 10 y 15%. Los resultados mostraron que la nanosílice empieza a tener una significativa influencia sobre las propiedades mecánicas de los morteros a partir del 5% de sustitución y que con un 10% de sustitución se alcanzan mejoras en la resistencia a la compresión hasta del 120% con respecto a la muestra control para un día de curado. Para tiempos mayores de curado las mejoras decrecen ligeramente llegando hasta un 80%, este porcentaje de mejora permanece en la resistencia a compresión aún después de los 28 días de curado.

PALABRAS CLAVE: Nanopartículas, nanosílice, cemento adicionado, propiedades físicas del cemento

1. INTRODUCTION

Mostafa and Brown [1] said that the predominant role of Portland cement is becoming less and has gradually given way to blended cement and

composite cements; this is mainly for environmental, economic and technological reasons.

Many researches [1, 2, 3 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14 among others] have studied the most

commonly used active additions such as silica fume (SF), fly ash (FA), blast furnace slag, metakaolin, zeolite and rice husks ashes. Among these deserve a special place the SF by to be perhaps the most reactive of the commonly used active mineral admixtures and the good results obtained with it ([2], Fidjestol & Lewis, 1998 at [15]; [16]). SF is perhaps only surpassed by the addition of silica nanoparticles in some investigations in the quest to develop high performance concretes.

In the case of nanosilica, several authors have studied the physical effects of its incorporation on the cement, but the results of these investigations suggest some inconsistencies that require studying this issue in more detail.

The first difficulty is related to the positive effect of nanosilica, because while than most researchers were able to increase the compressive strength with replacement percentage, authors such as Ji [17] found that to 28 days the compressive strength of normal concrete (NC) was greater than found for concrete blended with NS.

The second topic under discussion is related to the optimum level of substitution. Shih, Chang & Hsiao [18] found that compressive strength increases with the percentage of NS up to 0.6% in gaining maximum value. Authors such as Li, Zhang & Ou [19] concluded in their work that when the nanoparticles are added in small quantities ($\leq 3\%$) compressive strength and bending of concrete are enhanced. While Byung-Wan Jo et al [20], Li et al [21] and Li, Xiao & Ou [22] proposed that the best replacement ratios should be around 10% by weight.

The third important aspect is the reaction rate and curing time. While Qing et al [23] suggested that the use of NS is only important to achieve high strength in the first 3 days of curing and that in long-term compressive strength is matched to the silica fume blended cement, Li et al [21] and Li, Xiao & Ou [22] proposed that strength is still increasing even at 28 days of curing. Others, like Shih, Chang & Hsiao [18] argue that even for the 56 days of cured the NS particles are contributing to the development of strength.

In the case of silica fume (SF), its use by ASTM 1240 is governed, and it suggests use between 5 and 12% but authors as G Appa Rao [13] obtained the best results with substitutions between 15% and 22 %. SF provides high strength (high strength 80 MPa, Very high strength > 120 MPa) and low permeability for the densification of the matrix in the concrete because the pores are filled by chemical-physical effects (Fidjestol & Lewis at [15]). It has a very high pozzolanic reactivity, especially at early ages, however increases the water requirement for a given workability or requires the use of superplasticizers [16, 24]. However, other authors suggest that the activity of SF at early ages is low (Mitchell et al. cited by 23). Researchers like Heikal et al [25] found that the SF extends initial and final setting time at 20° C, while authors such as Mattesen et al [26] attributed to its high pozzolanic activity the diminution of setting times when mineral addition is increased.

Technical literature allows to conclude that both the silica fume as nanosilica are two very good additions to Portland cement by their chemical, physical and mineralogical characteristics but there are still many questions about their performance and method of use.

2. MATERIALS AND METHODS

In this work pastes and mortars of Colombian Ordinary Portland cement type III, produced by Cementos Argos S. A. of Colombia were prepared, replaced in weight percentage, dry basis with 1, 3, 5 and 10% of commercial nanosilica and 5, 10 and 15% of commercial silica fume. The nanosilica is presented as aqueous suspension and silica fume as densified powder.

2.1 Characterizations of materials

The chemical composition of used materials, cement - nanosilica - silica fume are presented in Table 1. These tests were carried out in an equipment of X-ray Fluorescence ARL 8680s Total Cement Analyzer by the method of wave dispersion under standard ASTM C114-03 [27].

When the SiO₂ content is corrected by the losses on ignition, SiO₂ in NS goes of 93.56% to 98% and in SF goes of 92.84% to 95.6%. This allows conclude that the two materials are very pure.

Table 1. Chemical composition of materials

PARAMETER (%)	CEMENT	NANOSILICA	SILICA FUME
SiO ₂	20,13	93,56	92,84
Al ₂ O ₃	4,37	0,00	0,22
Fe ₂ O ₃	3,71	0,39	1,00
CaO	64,30	0,22	0,46
MgO	2,27	0,13	0,75
Na ₂ O	0,10	0,62	0,26
K ₂ O	0,31	0,02	0,44
SO ₃	1,99	0,30	0,31
Cr ₂ O ₅	0,00	0,04	0,00
MnO	0,05	0,01	0,03
P ₂ O ₅	0,33	0,13	0,16
TiO ₂	0,10	0,02	0,01
Fire losses	2,44	4,46	3,01
Free lime	0,33	-	-

Specific Surface Area values of raw materials in a Micromeritics Gemini 2380 were determined (Table 2).

Table 2. Characteristics of raw materials

Samples	Specific Surface Area (m ² /g)
Cement (C)	1,14
Nanosilica (NS)	51,4
Silica Fume (SF)	28,0

The specific surface area of nanosilica is almost double that of the silica fume used.

Coulter LS 230 was used for determining the size distribution of mineral additions (Figure 1 and Table 3).

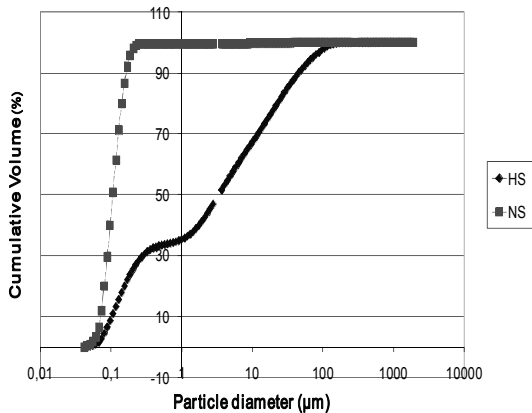


Figure 1. Particle size distributions for silica additions

Table 3. Parameters of particle size distribution for silica additions

Sample	Mode µm	S.D. µm	d10 µm	d50 µm	d90 µm
SF	0,106	27,75	0,0978	3,203	43,31
NS	0,097	1,815	0,0677	0,101	0,157

The NS is much finer and it has more uniform particle size distribution than the SF. The D₉₀ values (Table 3) are 0.16 µm and 43.3 microns for the two silica materials respectively.

The X-ray diffraction (XRD) of the mineral additions (Figure 2) were performed in a PANalytical X'Pert PRO MPD, a 2θ range of 2° to 70° with a step of 0.02° and an accumulation time of 30s.

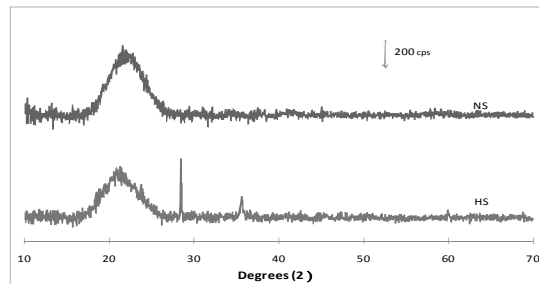


Figure 2. X-ray diffractograms of mineral additions

From the diffractograms it can be established that the two materials have very low mineral crystallinity and high purity. The vitreous silica in SF is accompanied by small amounts of silicon carbide (SiC) and silicon metal (Si) by the method of production.

In a calorimeter TA Instruments at 25 ° C the calorimetric studies on hydration of pastes were performed.

2.2 Water demand for mortars and cement pastes

2.2.1 Mortars

They were prepared in accordance with the procedure laid down in ASTM C 305 [28]. The control mortar with a cement/Ottawa-sand ratio: 1:2.75 and a water/cement ratio of 0.485, according to ASTM C109 [29] was made.

In the case of mortars with replacement were prepared with a cement + addition (NS or SF) / sand ratio: 1:2.75, but the water-cement ratio was enough to get a flow between 105 and 115% agree with ASTM C 109 [29].

Mortars were prepared for testing of compressive strength with a constant water/cementitious-material (w/cm, being cm the sum of cement plus mineral addition) ratio of 0.55 and the corresponding amount of superplasticizer required to achieve a fluidity of 105 - 115%, according to ASTM C109 [29]. Fluidity according with ASTM C 1437 [30] was determined. The superplasticizer (460 Pozzolith BASF Chemical) was homogenized with the mixing water in order to achieve the optimum dispersion into the mixes.

In the replaced mortars with nanosilica, firstly the concentration of suspended solids is determined and the amount of suspension required for each replacement rate was calculated. The homogenization was done previously with the mixing water corrected for the amount of water incorporated by the suspension. For silica fume tests, cementitious mix homogenization was performed by ball milling in dry state during 25 minutes for each 1 kg of sample. The balls have 2 cm in diameter.

2.2.2 Pastes

In pastes, normal consistency (ASTM C 187 [31]) and setting time (ASTM C 191[32]) were determined.

2.3 Compressive and flexural strength measurements

The specimens were prepared and failed in accordance with ASTM C 348-02 [33] and ASTM C 349-02 [34], to 1, 3, 7 and 28 days of normal curing.

3. RESULTS AND DISCUSSION

3.1 Water demand

Figure 3 shows the results of water demand in mortars recommended for fluency between

105% and 115%, Figure 4 shows the water demand (w/cm ratio) on pastes to achieve normal consistency, in both cases without the use of superplasticizers.

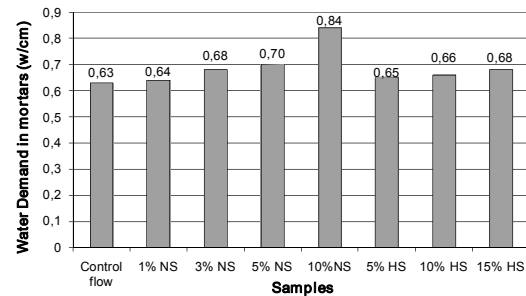


Figure 3. Water demand in mortars

It can be seen as the two mineral additions increase water demand. This behavior is more emphasized in the case of nanosilica which with 10% of replacement its demand can reach up to 33% more water than the control sample, while the silica fume with 15% substitution causes an increase in the water demand of just 7%. This increase in water demand is in agreement with those found by authors such as Qing et al [23], Bjornstrom [35] and Li [36] who explained it as a consequence of the acceleration of hydration process under fineness and surface energy of the additions. According to the observation made by these authors should expect a significantly higher pozzolanic activity for the nanosilica.

In the case of the two additions would require a relationship w/cm above 0.6 for the manufacture of mortars and it is well known in the technical literature that this value is set as the top where the fall of mechanical strength is very important. The excess mixing water becomes in porosity after evaporation [37]. This is why it was decided to make mortars with w/cm = 0.55 constant and adding superplasticizers to achieve appropriate workability performance in the samples. In the case of the mortars the water is high for the evaluation of mechanical strength, but it was to avoid having to add excessive amounts of superplasticizers that as is well known that has a positive effect (increase) on the mechanical properties [38].

Figure 4 shows similarly that nanosilica has increased water demand more than silica fume.

Cement replaced with 3% of NS demand the same amount of water that cement replaced with 15% of SF.

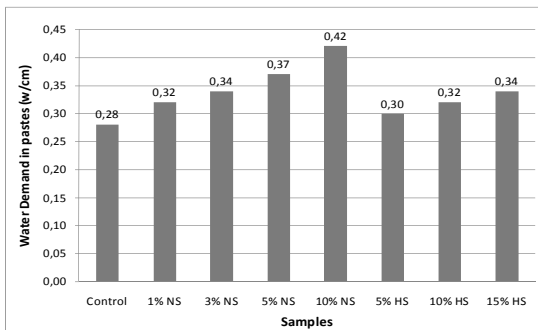


Figure 4. Water demand in pastes

The nanosilica has a minimal effect on setting times compared to the control sample; it is retarded despite the high water demand. In the case of silica fume the retardant effect is much greater even increasing the difference between the final set and the initial set (Figure 5).

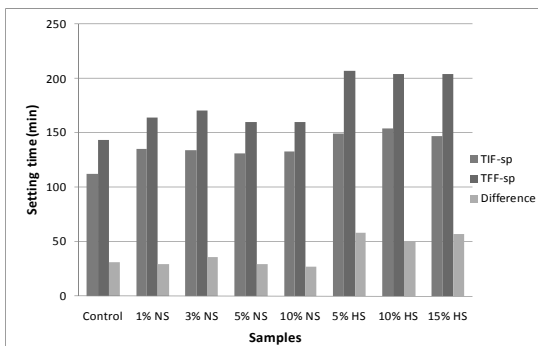


Figure 5. Setting times for pastes with normal consistency without superplasticizer

The cement setting time depends on factors such as fineness of cement, mineral composition of cement, amount of mixing water, mineral admixtures and additives used, curing temperature, relative humidity, etc. In this research, most of these parameters are maintained constant. For understanding the setting times obtained it is necessary to do a balance between the activities of the additions and the w/cm ratio used in the preparation of the pastes.

According to several authors, the NS has a higher pozzolanic activity than the SF [23, 20, 18, 21, 22 and 36], thereby it forms much C-S-H

and Portlandite, whereby with the addition of NS the setting time and workability should decrease [26]. In this work it did not happen, indeed, the opposite occurs and it is because the activity of the additions is partly compensated by the greater amount of mixing water incorporated into the mixture, i.e., although the NS may have higher pozzolanic activity it delay slightly setting time because it demands up to 50% more water than the control sample.

To verify these results, the setting times in samples with a constant ratio w/cm = 0.32 were measured; for all samples superplasticizer was blended with water in the appropriate amount for reaching normal consistency (Figure 6).

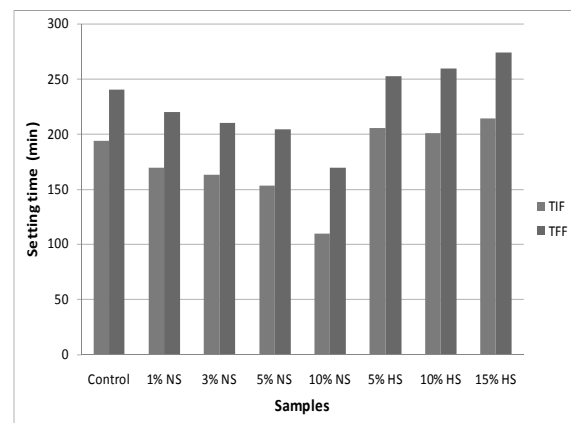


Figure 6. Setting times for pastes with constant water/cementitious-material ratio (0.32)

With the w/cm ratio constant (0.32), the initial and final setting times decreased with the increase in the percentage of replacement of cement by nanosilica (Figure 6). For the 10% NS replaced sample (which had 50% more water demand relative to the control sample), when the test was conducted with constant w/cm ratio, the setting time was diminished over 40%. In the case of SF, it is still producing a delay in the setting times, but not so significant, which would suggest that this material has low pozzolanic activity in the setting period.

3.2 Mechanical strength development

In the case of silica fume (Figure 7), when the samples in which portland cement were replaced with different percentages of this product, it was

found that the mechanical strength was always lower than values found for control sample at different test ages. This behavior found for this silica fume is attributed to that it was used as a densified product and requires a disintegration process that allows separate the particles to perform a good role as pozzolan; in its current state SF is working as a filler, confirming the results obtained with tests of fluency, normal consistence and setting times which showed the SF as a material with very little or no pozzolanic activity. This problem with the densified state of silica fume had been reported by authors such as Martinez-Velandia et al [39, 40, 41].

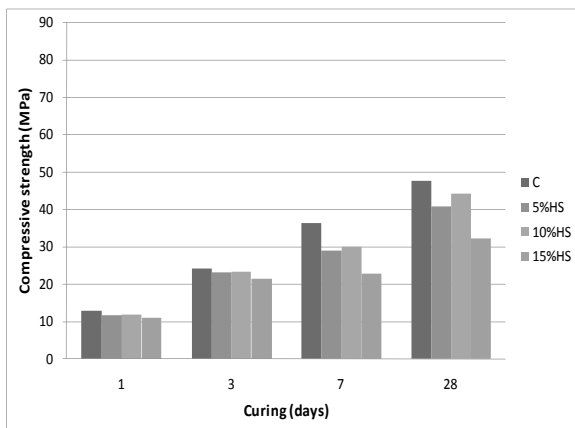


Figure 7. Compressive strength values for control and silica fume blended mortars

In the case of nanosilica blended mortars (Figures 8 and 9) only with replacement percentages equal or greater than 5% significant improvements were reached. It is noteworthy the results obtained for mortars with 10% substitution for which a noticeable improvement in the development of mechanical strength at all curing ages, reaching after 28 days of curing a compressive strength of 80 MPa.

With 10% substitution of cement by NS and to 7 days of curing time, the sample already has more than 10 MPa of compressive strength compared with the strength of the control sample at 28 days, this is showing the great activity that this material has at an early age.

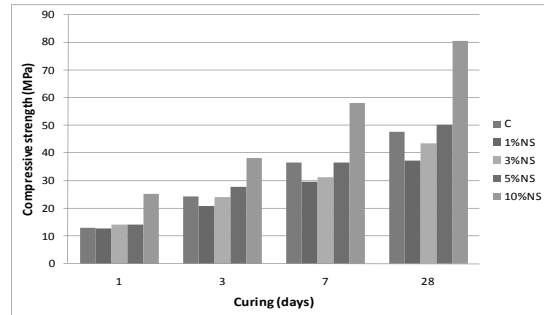


Figure 8. Compressive strength values for nanosilica blended mortars

With 5% NS the improvements are always below 25% compared with the control sample (Figure 9). With 10% is achieved for a day of curing an improvement close to 120% and the rest of the ages of curing the improvement was around 80% (Figure 9).

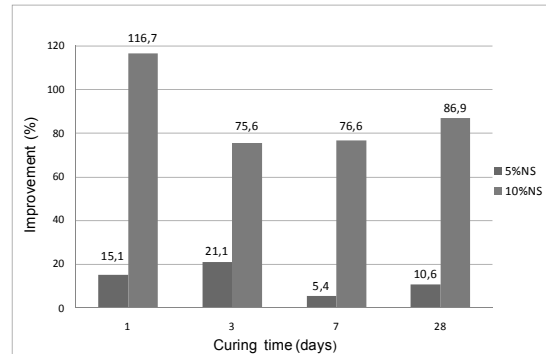


Figure 9. Percentage of improvement in compressive strength with the addition of the nanosilica

From these results trends in mechanical development for the samples blended with nanosilica were calculated by regression analysis (Figure 10).

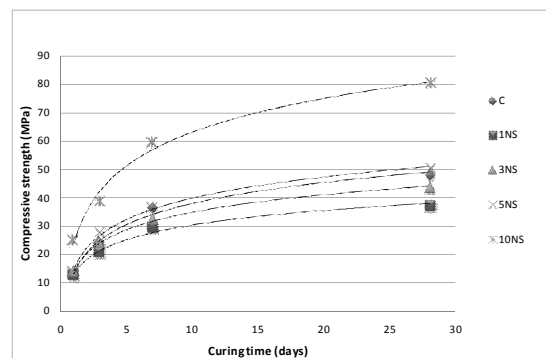


Figure 10. Trends for the compressive strength development in NS blended mortars

For all the samples, adjustment factors (R^2) greater than 0.98 are obtained with logarithmic fit (Table 4).

Table 4. Adjustment equations for the development of strength with curing time for NS blended mortars

Samples	Proposed equation	Correlation coefficient
		(R^2)
Control	$f'_c = 10,704\ln(t) + 13,259$	0,9887
1% NS	$f'_{1\%NS} = 7,4463\ln(t) + 13,183$	0,9859
3% NS	$f'_{3\%NS} = 8,9174\ln(t) + 14,293$	0,9981
5% NS	$f'_{5\%NS} = 10,795\ln(t) + 14,939$	0,9964
10% NS	$f'_{10\%NS} = 17,128\ln(t) + 23,643$	0,9873

3.3 Calorimetry

According to technical references, four peaks are identified [37] in the calorimetric curves for hydration of Portland cement. For pastes prepared in this work (Figures 11 and 12) only the first two peaks were identified, which are also the largest since the other two usually appear as shoulders on the second peak.

The first peak, from left to right in the graph, is a high energy release and it has been associated with early-stage reaction and the formation of the phases AFt from the hydration of C3A and rehydration of calcium sulphate hemihydrate [37, 42]. The second peak is really the principal for the middle-stage reaction which form the tobermorite and portlandite from calcium silicates [37].

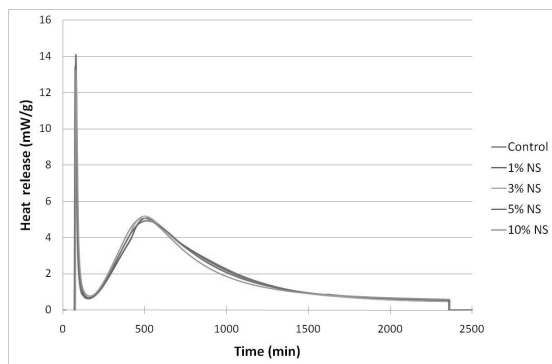


Figure 11. Heat hydration curves for blended pastes with NS

Nanosilica additions released about the same amount of heat that the control sample in the two peaks identified (Figure 11).

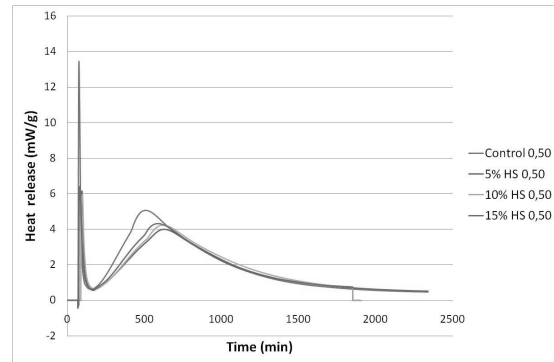


Figure 12. Heat hydration curves for blended pastes with SF

The samples substituted with SF have a lower heat release during hydration and even on the second peak a delayed shift rightward of approximately 100 minutes is evidenced, this is showing a slower rate of hydration and a smaller amount in the formation of C-S-H. This confirms again the low pozzolanic activity of SF as used in this investigation.

Pozzolanic activity of these two mineral admixtures is evident in the cumulative total energy graph against time (Figures 13 y 14), where it can see that the samples with NS accumulate energy per gram very similar to the control sample even for a 10% replacement. While that, samples with SF show cumulative energy curves below the corresponding to control sample.

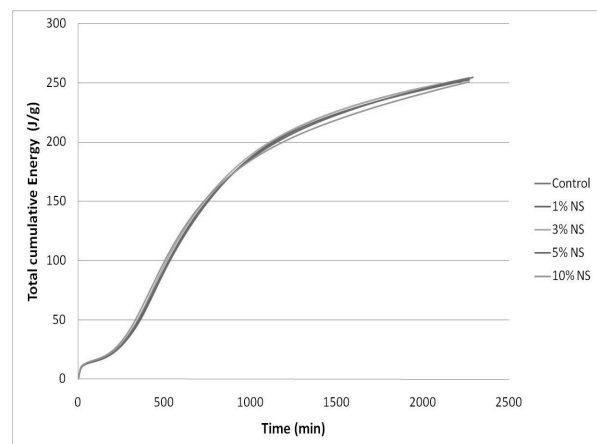


Figure 13. Cumulative total energy for blended pastes with NS

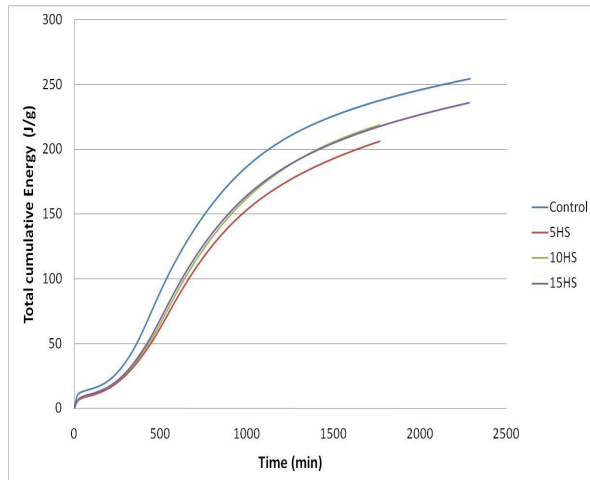


Figure 14. Cumulative total energy for blended pastes with SF

4. CONCLUSIONS

The nanosilica proved to be an effective mineral addition for blending with Portland cement to improve their mechanical performance without affecting the release of heat of hydration.

Nanosilica significantly increases the water demand in mortars and pastes depending to percentage of substitution. This seems to be controlled by the particle size distribution and the high specific surface area of the material.

Still very active pozzolanic additions can retard setting times because of the excess of mixing water they need, but when these blended samples are working with constant w/cm, significantly decrease setting times compared to the control sample.

Only from 5% substitution of cement by nanosilica is beginning to have significant improvements in compressive strength of the mortars, the highest improvements in compressive strength are obtained with 10% nanosilica and three days of curing.

The blended cement with 5 and 10% nanosilica show higher compressive strength than the control sample even after 28 days of curing, with improvements of over 10% and 80% respectively.

The silica fume, in a densified state, acts mainly as filler in the mix, which is evidenced by its low demand for mixing water, delayed setting times; drop in mechanical strength and a decrease in the amount of heat of hydration generated.

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