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Effects of the addition of nanosilica on the rheology, hydration and development of the compressive strength of cement mortars

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ABSTRACT

This paper examines the rheology, hydration kinetics and development of the compressive strength of cement mortars including nanosilica and fly ash. The contents of these materials and the superplasticizer dosage are related to different rheological and strength parameters. Effects on rheology were analyzed through yield stress and viscosity. Calorimetry tests were carried out to assess the variations in cement hydration kinetics, and the maximum and minimum heat release rates were analyzed. Compressive strength was evaluated at different ages up to 56 days. The equations presented in this paper make it possible to optimize mortar proportionings that fulfil required performance levels in both fresh and hardened states.

KEYWORDS:

A. Ceramic-matrix composites (CMCs) ; B. Rheological properties ; B. Strength ; C. Analytical modelling.

1. INTRODUCTION

The terms ‘cement replacement materials’ and ‘supplementary cementitious materials’ refer to raw materials that are generated mostly as by-products of other industries and added to cement-based materials as powders, such as: silica fume, fly ash (FA), ground granulated blast-furnace slag (GGBS), or limestone powder. They have attracted much interest from researchers and industry due to an increasing interest in high performance concretes that typically include important amounts of powders other than cement [1-4].

FA has long been used as a supplementary cementitious material. FA particles are round in shape, and as a result their addition to cement-based materials increases their workability and cohesion [5,6]. Furthermore, due to high vitreous silica and alumina contents, FA reacts with portlandite or calcium hydroxyde, although this pozzolanic effect is not noticeable until two or three months after mixing [5].

Nanosilica (nano-SiO₂ or simply nS) is a nanomaterial which can also be considered a supplementary cementitious material [7]. Most research published so far concerning nanotechnology and construction materials has dealt with nS [8] and it is reportedly the most widely used variety of nanoparticles [9], although its market price is still higher than that of FA or silica fume [7]. Nanosilica consists of ultra-fine particles of amorphous silica, usually distributed in aqueous solution, in the form of a slurry or hydrosol [10]. It can be produced using several methods, and the production method affects its properties as it determines the degree of dispersion in the slurry or gel [11].

Nanosilica has been extensively reported to be a material that potentially enhances density, strength development and mechanical properties of cement-based materials [9,12-15]. Its reactivity is attributed to its high purity in terms of SiO₂ content and its high specific surface area [16,17]. Different simultaneous mechanisms are involved in the enhancement of fresh and hardened properties of cement-based materials by nS particles:

- Filler effect or pore-filling effect. As a result of the extremely small size of nS particles, they function as a filler in the cementitious matrix, improving its microstructure [16] and potentially increase the packing density when correctly dosed and dispersed [9].
- Acceleration of cement hydration through nucleation effect. During cement hydration, nS particles act as nucleation sites for the silica units released from cement particles [18] and also for the first C-S-H seeds [8,16]. This way, the hydration products accumulate not only on the surface of cement grains but also around these additional nucleation sites dispersed in the pore solution, creating a potentially more compact matrix [9].
- Pozzolanic effect. Calcium hydroxide in the pore solution is the result of the hydration of C₃S and C₂S. It reacts very quickly with nS particles to form additional C-S-H is formed. The maximum concentration of calcium hydroxide in the liquid phase is reached during the dormant period of cement hydration [19]. As hydration is accelerated by nS particles due to the nucleation effect, the rate of C₃S consumption is also accelerated [16,18] and, as a result, so is the rate of calcium hydroxide release. This means that the nucleation effect and the consequent acceleration of cement hydration caused by nS particles make the calcium hydroxide more

readily available, thus favoring the pozzolanic effect of nS. In consequence, when nS is present, the induction period of cement hydration is shortened as a result of this accelerated release of calcium ions and their rapid consumption by nS [11]. The pozzolanic activity of nS has been found to be higher than that of other active additions, especially at early ages [20].

The literature shows contradictory results around two key aspects: whether the use of nS offers substantial improvement of the mechanical properties of cement-based materials, and the recommended range for nS contents. There are two main sources that contribute to these discrepancies. First, the nanosilicas used in different studies are of different types, different particle size, different specific surface, or produced by different methods [11]. And second, the difficulty of dispersing nS particles in the fresh cement grout, paste, mortar or concrete [7], which is an issue that cannot be completely explained on mechanistic grounds. Even if they are well dispersed in their original slurry or hydrosol form, once in contact with the pore solution of a cement-based material they tend to aggregate due to the presence of ions such as Ca^{2+} , Na^+ and K^+ released by cement upon contact with water. These ions have a bridging effect, agglomerating silica units according to the pattern $(\text{SiO}^-)-(\text{Ca}^{2+})-(\text{SiO}^-)$ [11,21], which tends to destabilize the distribution of nS particles in the pore fluid and prevents their homogeneous dispersion.

The introduction of nS potentially affects compatibility between the cement, superplasticizers and any other chemical admixture or mineral additions [7,22], and as a consequence the rheology of cement pastes and mortars is affected. In these systems, increasing nS contents tend to significantly increase yield stress values [22].

With respect to the effect of nS on the compressive strength of mortars, different conclusions have been reported. Some studies have found that it has a limited or negligible impact on compressive strength [10], while some others have reported different trends finding an intermediate optimum nS content [14,23]. Some authors have reported higher gains in compressive strength by achieving a better dispersion of the nanoparticles using a defoamer in addition to the water reducing agent [24]. However, there are also studies that have reported a moderate decrease in compressive strength when nS is used at dosages up to 5% [25]. Therefore, there is no consensus regarding the most appropriate range for nS contents, as the values found in current literature are not congruent. It appears that a rule-of-thumb maximum nS content would be 5% over cement weight [7], but other authors have reported that this maximum is 2% over cement weight when the particle size is between 15 nm and 80 nm [26].

2. RESEARCH OBJECTIVES

The aim of this study was to evaluate the effects of different nS and FA contents and different superplasticizer (SP) dosages on the rheology, cement hydration and development of compressive strength of cement mortars. A series of mortars were produced and tested, and the experimental results were analyzed and modelled by means of multiple linear regression. The key parameters and synergies with a statistically significant impact on the rheology, cement hydration kinetics and compressive strength of mortars were identified, and their effect quantified.

Different equations modelling the relationships detected were obtained. They constitute a useful tool to evaluate the influence of the different mortar components, which makes it possible to adjust their dosages

in order to ensure the stability of mortars that include nS and FA. Furthermore, these equations have been used in a multiobjective optimization to find the most effective nS, FA, and SP contents that fulfil certain performance criteria. Such a multiobjective approach can provide a basis to reconcile discrepancies in literature as to the definition of optimum nS contents.

3. EXPERIMENTAL INVESTIGATION

3.1 Factors and levels considered

The factors considered in this research as well as their levels are summarized in Table 1:

- nS added to the mortar. Its solid weight, expressed as percentage of the cement weight in the mortar, was varied between 0.5% and 3.0%.
- FA, as partial replacement of cement. It was used in amounts between 5% and 20% over the weight of cement.
- SP dosage was varied between 0.3% and 0.9% over total binder weight, that is over total weight of cement and FA.

3.2 Materials

The materials used to produce the mortars were tap water, cement, FA, nS, SP, and sand. Table 2 presents the equivalent oxides composition of cement and FA as well as the composition of the solid fraction of the colloidal nS, with all values expressed as percentage relative to total mass.

The cement was Portland cement type CEM I 42.5N, as specified by the standard EN 197-1:2000 [27], FA conformed with the standard EN 450-1:2005 [28], and nS was a commercially available colloidal form, being an aqueous solution with an SiO₂ content of 50% by mass. The SP used was a commercially available modified polycarboxylate, with a solid content of 42% and a specific gravity of 1.10. The same well graded siliceous sand was used for all mortars, with a density of 2.7 Mg/m³, a water absorption capacity of 1%, and a maximum particle size of 1.18 mm.

3.3 Design of the experimental programme

Eleven mortar proportionings were considered, as summarized in Table 4. A water-to-binder ratio (*w/b*) of 0.35 was kept constant throughout the experiment, and the sand content was 30% in volume for all mortars.

Mortars 1 to 8 corresponded to all possible combinations of the maximum and minimum values of the factors considered as shown in Table 1. Mortars 9 to 11 were selected as center points for this experiment and were all proportioned identically, the value for each factor being the central or average value of that listed in Table 1. The introduction of the so-called center points in the experimental programme made it possible to detect possible quadratic trends.

3.4 Experimental methods

All mortars were prepared in seven minutes using a planar-action high-shear mixer with a maximum capacity of 4.5 litres.

The sequence and timing of operations were exactly the same in all cases, as differences in this matter are known to introduce uncontrolled variations in the experimental results obtained with cement-based materials [29,30]. Water, nS and SP were first poured into the mixer and mixed for one minute at low speed (140 rpm). After that, cement and FA were added to the mixer and mixing went on for two more minutes. Then, the mixer was stopped and any lumps that may have formed were crushed and any solids that had adhered to the surfaces of the mixer were rehomogenized (the time for these operations was less than one minute). The mortar was then mixed for two more minutes at high speed (285 rpm) and for one minute at low speed (140 rpm).

Two batches of each mortar were prepared. First, one batch of 2 litres of mortar was produced to be tested with the viscometer, and after that the mortar was used to cast the cubes for determining the compressive strength at ages up to 28 days. A second batch of 2 litres of mortar was produced to cast the cubes for determining the compressive strength at the age of 56 days. Small batches of only 50 g of mortar were prepared for the heat of hydration tests.

Heat of hydration was evaluated by means of isothermal calorimetry [31] using a Thermometric TAM/air calorimeter maintained at 22°C. This equipment measured the heat released by comparing the temperature of the sample to an inert reference held under isothermal conditions. The released heat results were recorded as a function of time. Polyethylene ampoules were filled with approximately 6 g of mortar and the test was conducted for at least 72 hours.

The compressive strength of mortars was determined by crushing three 50 mm cubes [32] per mix at different ages, using a Denison Mayer servo-hydraulic 2000kN compression machine and applying the load at a constant rate of 55 kN/min. The cubes were stored in water at 20±1 °C until the testing age (1, 3, 7, 28, or 56 days).

4. RESULTS AND DISCUSSION

4.1 Rheology: yield stress and viscosity

The rheology of fresh mortars was evaluated with a vane viscometer, resulting in a series of measurements relating shear rate ($\dot{\gamma}$, in 1/sec) to shear stress (τ , in Pa). A Binghamian model was assumed, where shear rate and shear stress are related as follows [33]:

$$\tau = \tau_y + \eta \dot{\gamma} \quad (1)$$

The values of the two Binghamian parameters in equation (1), yield stress τ_y (in Pa) and viscosity η (in Pas), were obtained by means of least squares fitting. These values are given in Table 5. Both parameters were related to the nS, FA, and SP contents by means of Multiple Linear Regression (MLR), and the threshold p-value for selecting statistically significant effects was 0.05.

In terms of yield stress, nS and FA contents were not statistically significant. Only variations in SP dosage were found to have a significant influence on yield stress. The following relationship between these two parameters was obtained (R-squared = 0.95), where SP is the SP dosage expressed as percentage over the total binder weight, and τ_y is expressed in Pa:

$$\tau_y = 139.44 - 165.62 SP^2 \quad (2)$$

Figure 1 plots equation (2) with the experimental values obtained for yield stress. It was observed that yield stress values followed a reverse parabolic trend with respect to increasing SP dosages, and at the same time these values tended to be less scattered for higher SP dosages. The direct relationship between yield stress and SP dosage is attributable to the enhanced adsorption mechanisms of SP when nS particles are present in the mix. The lubrication and deflocculation effects of SP are more efficient, as the steric and electrostatic repulsion between cement particles and between cement and nS particles are enhanced, resulting in better deflocculation of the particles in the mortar [34,35]. The trend observed for yield stress with respect to SP dosage is consistent with the findings of the mini-slump test [36].

With respect to the viscosity (η), all three factors considered (nS and FA contents, and SP dosage) were found to be statistically significant. The following relationship was obtained (R-squared = 0.97), where nS , FA , and SP are expressed as percentage, and η is expressed in Pas:

$$\sqrt{\eta} = -2.66 + 8.63 nS - 2.26 nS^2 + 0.11 nS SP FA \quad (3)$$

Two aspects of equation (3) are particularly notable: first, the effect of varying the nS content on viscosity was not linear, and second, there was an interaction among the latter, the FA content and the SP dosage. In consequence, variations in viscosity due to variations in nS contents were dependent on FA content and SP dosage. Figures 2 and 3 show equation (3) in different scenarios to illustrate these synergies.

Figure 2 shows the response surface of viscosity related to the SP dosage and nS content assuming an FA content of 5%. It can be seen that viscosity follows a non-linear trend with respect to nS content and that maximum viscosity values correspond to an intermediate nS content of about 2%, regardless of SP dosage. This result is consistent with the findings of other authors, who reported significant loss of workability in concretes with nS contents of up to 2% [37].

The effect of variations in SP dosage on viscosity is more noticeable with higher FA contents, as shown in Figure 3, where an FA content of 12.5% is assumed. In this case, the maximum viscosity values corresponded to the same intermediate nS content of about 2%, but in addition it was observed that increasing SP dosage significantly increased viscosity. This trend is most pronounced for an nS content of about 2%.

In comparing Figures 2 and 3, it is evident that increasing FA content in the presence of nS leads to increasing viscosity values, which is remarkable for an nS content of approximately 2%. This loss of compatibility between SP, FA and cement when nS is introduced is attributed to the competitive adsorption of SP molecules on the different particles, affecting its fluidifying efficiency.

The trends observed for viscosity are consistent with those observed in the Marsh cone[38], as the Marsh cone test results are informative of the mix viscosity while the mini-slump test results inform about their yield stress [33,39,40].

4.2 Cement hydration kinetics

Cement hydration in the presence of nS, FA and SP in different proportions was analysed for each of the mortars in Table 4. In each case, a curve was obtained relating the heat rate (q , expressed in mW/g) to the time since the addition of water. Two of these curves are shown in Figure 4 for illustration purposes, corresponding to the mixes referenced as 3 and 4 in Table 4, with an FA content of 5% and SP dosage of 0.9%; the only difference between them was the nS content.

A quantitative analysis was carried out on the following parameters (Figure 5):

- The minimum heat release rate, q_{min} , and the time at which it was detected, $t(q_{min})$, were considered as representative of the duration and end of the dormant period.
- The maximum heat release rate, q_{max} , and the corresponding time, $t(q_{max})$, were retained as representative of the intensity and timing of the peak of hydration.

All the experimental values obtained for the aforementioned parameters are shown in Table 6. Multiple Linear Regression was used to relate these parameters to nS and FA contents and SP dosage.

The end of the dormant period was analysed through the parameters q_{min} and $t(q_{min})$. An inverse relationship between these two parameters was observed, as shown in Figure 6: when one increased, the other decreased, and vice versa. They can therefore be discussed simultaneously.

It was found that FA did not significantly modify the cement hydration kinetics during the dormant period, as variations in FA content did not affect either q_{min} or $t(q_{min})$. This is due to the very low, almost negligible pozzolanic activity of FA during the first hours of the hydration process, in contrast with other pozzolanic materials such as silica fume, which has been reported as responsible for the fixation of a significant amount of lime after two hours [41].

The following relationships were obtained for q_{min} , expressed in mW/g, and for the corresponding time $t(q_{min})$, expressed in minutes (R-squared = 0.85 and 0.80 respectively):

$$q_{min} = 207.74 + 15.42 nS - 106.25 SP \quad (4)$$

$$t(q_{min}) = 127.87 - 6.69 nS + 30.50 SP^2 \quad (5)$$

Figure 7 represents equation (4), and Figure 8 represents equation (5). It was observed that increasing the SP dosage led to a decrease in the heat release rate during the dormant period while extending its duration. This is attributable to the slightly retarding effect that is commonly observed with superplasticizers [42]. With respect to the effect of nS, increasing nS content was observed to increase heat release rates during the dormant period while reducing its duration. This is consistent with the fact that nS has an accelerating effect, which turns out to be noticeable even during the dormant period. In particular, the experimental results showed that the addition of 3.5% of nS increased q_{min} between 26% (with an SP dosage of 0.3%) and 41% (with an SP dosage of 0.9%) on average. The maximum variation of q_{min} and $t(q_{min})$ was observed when nS content was increased from 0.5% to 3.5% and SP dosage was reduced from 0.9% to 0.3%, with q_{min} being increased 85% and $t(q_{min})$ being reduced 26%.

In terms of the peak of hydration, the relationships obtained for q_{max} , expressed in mW/g, and for the corresponding time $t(q_{max})$, expressed in minutes, are as follows (R-squared = 0.86 and 0.92 respectively):

$$q_{max} = 1801.19 + 60.83 nS + 136.67 SP - 6.77 FA \quad (6)$$

$$t(q_{max}) = 603.55 - 27.83 nS + 129 SP^2 + 0.186 FA^2 \quad (7)$$

Figures 9 and 10 represent q_{max} and $t(q_{max})$ as modelled by equations (6) and (7) respectively, related to nS content and SP dosage, for two different FA contents of 5% and 20%. Increasing the SP dosage from 0.3% to 0.9% had a moderate effect on q_{max} (average increase of 5%), as can be seen in Figure 9, but it had a more noticeable effect on $t(q_{max})$ (average increase of 16%), as shown in Figure 10. Therefore, increasing SP dosage had a retarding effect on the peak of hydration, which was consistent with the effect of this component on $t(q_{min})$. As for the effect of nS on the peak of hydration, it is very clearly observed from Figures 9 and 10 that increasing nS content increased the heat release rate q_{max} and reduced $t(q_{max})$: the intensity of the peak of hydration was increased and took place earlier in the hydration process. On average, increasing the nS content from 0.5% to 3.5% led to a 10% increase in q_{max} and a reduction of 16% in $t(q_{max})$.

The effect of variations in FA content from 5% to 20% on the peak of hydration were the opposite of nS: the peak of hydration was retarded and its intensity was decreased. On average, q_{max} was reduced by 5% and $t(q_{max})$ was increased by 12% when FA content was increased from 5% to 20%. This was attributed to the low pozzolanic activity of FA in the short and medium terms [41].

4.3 Development of compressive strength up to 56 days

Experimental results for the compressive strength of mortars at different ages up to 56 days are shown in Table 7. They are plotted versus age in Figure 11, along with the line connecting average values.

For the compressive strength of mortars, f_c , expressed in MPa, the following relationship was obtained, where t is the age of mortar expressed in days (R-squared = 0.98):

$$f_c = 36.34 + 12.82 \ln(t) + 4.82 SP \ln(t) + 10.12 SP - 0.55 FA + 3.72 nS - 1.14 nS^2 \quad (8)$$

Equation (8) is plotted assuming different scenarios in Figures 12 and 13. The effect of nS content on mortar compressive strength followed a quadratic trend, which is consistent with the trend observed for the density of the fresh mortar[38]. The nS content that maximized compressive strength was 1.63%, and was obtained from equation (8) as follows:

$$\frac{\partial f_c}{\partial (nS)} = 0 \rightarrow 3.72 - 1.14 \times 2 \times nS = 0 \rightarrow nS = 1.63\% o/c \quad (9)$$

This value is very close to the nS content that maximizes the density of fresh mortar (1.7%), as reported in a previous paper[38], and is consistent with the findings of other authors [14,23,26].

The average difference in compressive strength with nS contents between 0.5% and 3.5% was 2.5 MPa. The highest difference was 4 MPa, observed when the cases compared corresponded to nS contents of 1.63% and 3.5%. Considering that the average compressive strength values, as predicted by equation (8), were 79 MPa and 90 MPa at 28 days and 56 days respectively, these differences were: $2.5/79=3.2\%$ and $2.5/90=4.4\%$, respectively. Therefore, this study concluded that nS contents between 0.5% and 3.5% moderately increased compressive strength by no more than 5% at any age, which is evident in Figures 12 and 13. With respect to the effect of mortar age, Figure 12 compares the development of compressive strength for SP dosages of 0.3% and 0.9%. Increasing the SP content was observed to increase compressive strength, and this effect became more pronounced with age, as a result of the synergy detected between SP dosage and age (interaction between SP and $\ln(t)$ in equation (8)). Finally, Figure 13 shows that compressive strength at any age was also affected by FA content: its increase reduced compressive strength. This observation is consistent with the negative effect of FA on the hydration peak, and also with the negative effect of increased FA content on density, shrinkage, and cohesion[38].

5. MULTI-OBJECTIVE OPTIMIZATION

The definition of the most favourable nS contents is an issue that has attracted considerable attention, especially on compressive strength, as discussed in the Introduction. In this study, the compressive strength of mortars was observed to be maximized when the nS content was 1.63%, following equation (9). However, this value cannot be regarded as a final optimum for two reasons: a) it is optimal only in terms of compressive strength, considering neither yield stress nor viscosity as part of the problem, and b) it does not take into account the contributions of FA and SP to those parameters. In consequence, a different approach was needed to account for other aspects besides compressive strength.

This can be addressed by reformulating the search for optimum mortar proportionings as a multiobjective optimization problem. In this study, the search was aimed at finding optimal nS, FA, and SP dosages that simultaneously satisfy a number of objectives, namely: yield stress, viscosity and the peak heat rate are to be minimized while minimum target values for compressive strength at different ages are satisfied. This can be mathematically expressed as an objective function, z , that is to be minimized. The objective function was defined according to the weighted sum method [43], as follows:

$$z = \tau_y + \eta + 0.05 q_{max} + 0.1 \sum_i f_c(t_i) \quad (10)$$

where τ_y is the yield stress as modelled by equation (2), η is the viscosity as modelled by equation (3), q_{max} is the maximum heat rate as modelled by equation (6), and $f_c(t_i)$ are the compressive strength values at the ages of $t_i=1, 3, 7, 28,$ and 56 days as given by equation (8). As these parameters are expressed in different units and have different orders of magnitude, coefficients of 0.05 and 0.1 were applied to q_{max} and the sum of all compressive strength values respectively. The introduction of these coefficients, or weights, prevents any one term from being more prominent than the others, as this would introduce undesired biases into the optimization process.

A second, very important aspect in the optimization process is the definition of the feasible region, that is: the objective function z must satisfy a number of constraints. In this case:

- All parameters (nS , FA , and SP) were set as non-negative, and their ranges of variation were constrained to be consistent with the experimental program equation (10) is based upon (less than 3.5%, 20% and 0.9% for nS , FA , and SP respectively).
- Yield stress τ_y not higher than 50 Pa.
- Viscosity η not higher than 50 Pas.
- Compressive strength at the ages of 1 and 56 days $f_c(1d)$ and $f_c(56d)$ not less than their specified values $f_c'(1)$ or $f_c'(56)$ respectively. As different requirements can be considered, different subproblems were optimized depending on these specified values.

The formulation of this optimization problem allows considerable flexibility: the weights of 0.05 and 0.1 in equation (10) can be set to different values, or alternatively all terms can be typified by their average values; and the limits imposed on the yield strength and viscosity can be modified as well. Once the objective function and the set of constraints have been defined, the optimization problem thus formulated was solved by means of the Generalized Reduced Gradient algorithm with multistart search [44].

In this study, different cases (or subproblems) were subjected to optimization, defined by different requirements for the compressive strength of mortars. Table 8 shows a summary of all the subproblems optimized, each one of them defined by different specified values for $f_c'(1)$ or $f_c'(56)$. Values between 25 MPa and 45 MPa were considered for $f_c'(1)$, and between 60 MPa and 110 for $f_c'(56)$.

It was detected that the optimum SP dosage was 0.9% in all cases, as a result of the constraints imposed on yield stress and viscosity to ensure adequate levels of workability. Optimum nS levels were remarkably low in all cases, ranging from 0.24% to 0.3%: higher nS contents had a negative impact on viscosity and increased the heat rate q_{max} without significantly benefiting compressive strength. With respect to the optimum FA contents, it can be seen in Table 8 that they were very closely linked to the strength requirements. For $f_c'(1)$ values not higher than 35 MPa and $f_c'(56)$ values not higher than 100 MPa, the best situation was replacing 20% of cement with FA. When the required $f_c'(1)$ was higher than 35 MPa, then the optimum FA content decreased to 10-12%, as higher replacement levels would have had a negative impact on early age strength. For $f_c'(1)$ values of 45 MPa or higher, the optimum FA content was less than 3%, for the same reason.

For the purposes of comparison, the absolute maximum and minimum values for q_{max} and compressive strength that limit the space defined by the constraints imposed on the optimization problem and verify the aforementioned restraints for τ_y and η were also determined:

- The absolute minimum values for compressive strength were: 32 MPa and 98 MPa at 1 and 56 days respectively, corresponding to nS=3.5%, FA=20%, SP=0.7%.
- The absolute maximum values for compressive strength were: 49 MPa and 118 MPa at 1 and 56 days respectively, corresponding to nS=1.63%, FA=0%, SP=0.9%.

- The absolute minimum for q_{max} was 1766 mW/g, corresponding to nS=0%, FA=20%, SP=0.74%.
- The absolute maximum for q_{max} was 2134 mW/g, corresponding to nS=3.5%, FA=0%, SP=0.9%.

It is especially notable that, even in the context of a multiobjective optimization, the information regarding the absolute maxima and minima for compressive strength and q_{max} was consistent with the results of analyzing each of these variables separately. For example, the absolute maximum values for compressive strength corresponded to an nS content of 1.63%, which was the same value obtained in equation (9). However, when rheological parameters are taken into account, this value is very different to the multiobjective optimum (0.24%-0.3%), which clearly illustrates the convenience of analyzing the effect of nS on cement-based materials from a multiobjective point of view, taking different parameters into account, and not just compressive strength at a certain age.

6. CONCLUSIONS

- In terms of the rheology of fresh mortars, only variations in SP dosage affected yield stress, while viscosity was affected by SP dosage as well as nS and FA contents. Viscosity was maximized when nS content was at 2%, and increasing FA content when nS was also used led to increasing viscosity values. Therefore, in order to ensure a good workability, nS contents should be less than 2%.
- The dormant period of cement hydration was unaffected by FA content. Increasing SP dosage extended the duration of the dormant period, while the addition of nS tended to shorten this phase of cement hydration and increase the heat release rate.
- The maximum heat rate during cement hydration was decreased by increasing FA contents, while adding nS increased this parameter and accelerated its occurrence. Increasing SP dosage tended to intensify this peak of hydration, which was attributed to the enhanced dispersion of nS and cement particles.
- The compressive strength of mortars increased with SP dosage and was slightly reduced with higher FA contents. The addition of nS increased compressive strength and density of the mortar, and a quadratic trend was observed in these relationships. Maximum compressive strength values were observed at an nS content of 1.63%.
- Multiobjective optimization was a convenient tool for optimizing mortar proportionings to ensure good workability while meeting compressive strength requirements. In this context, it was obtained that the optimum SP dosage was 0.9% and that nS contents higher than 0.3% are not justified. The optimum FA content is decreased when higher compressive strength values are required.

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FIGURES

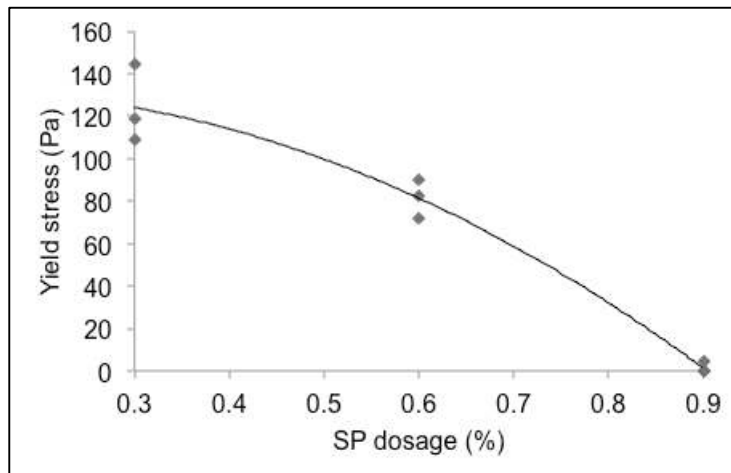


Figure 1. Yield stress (Pa) vs SP dosage (%).

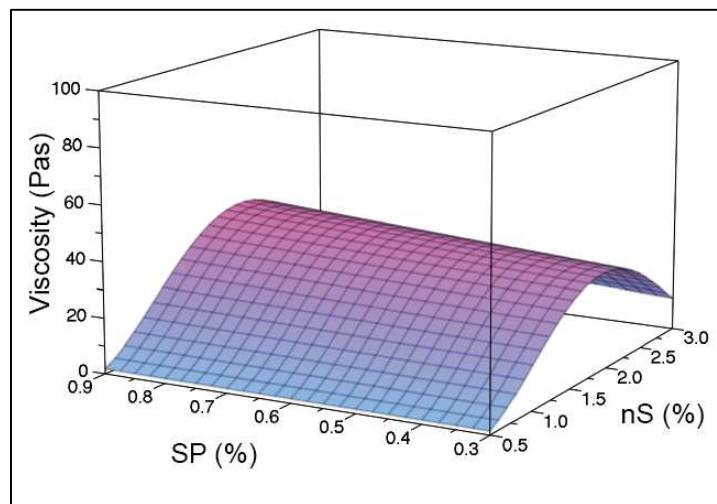


Figure 2. Viscosity vs nS content and SP dosage, assuming FA=5.0%.

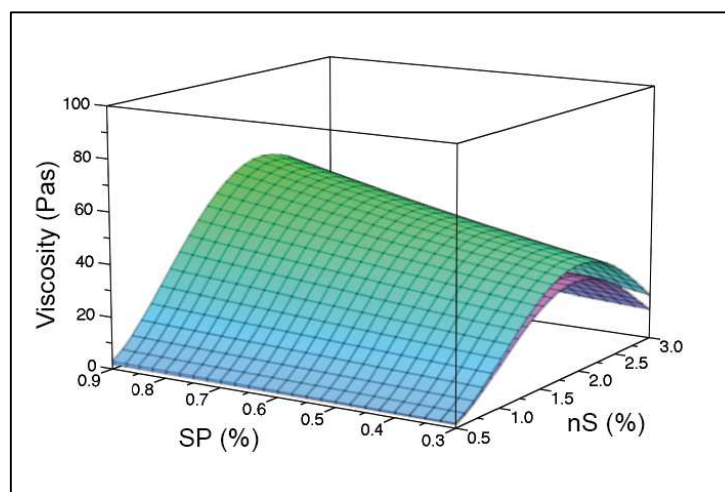


Figure 3. Response surface for viscosity assuming FA=12.5% above the surface corresponding to FA=5%.

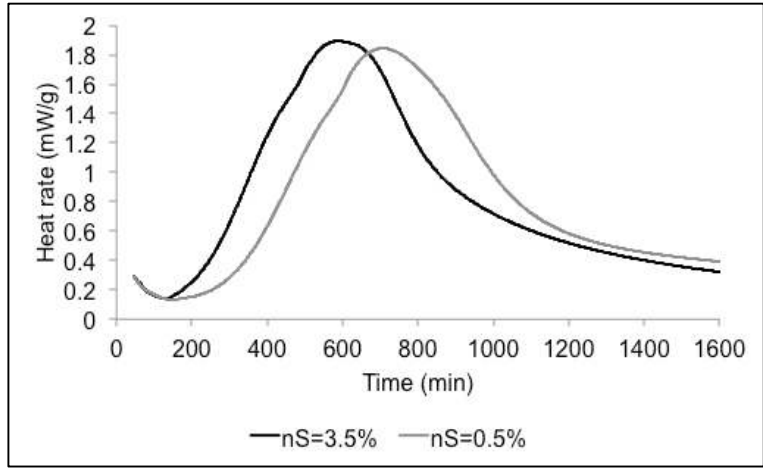


Figure 4. Heat of hydration with FA=5.0% and SP=0.9%.

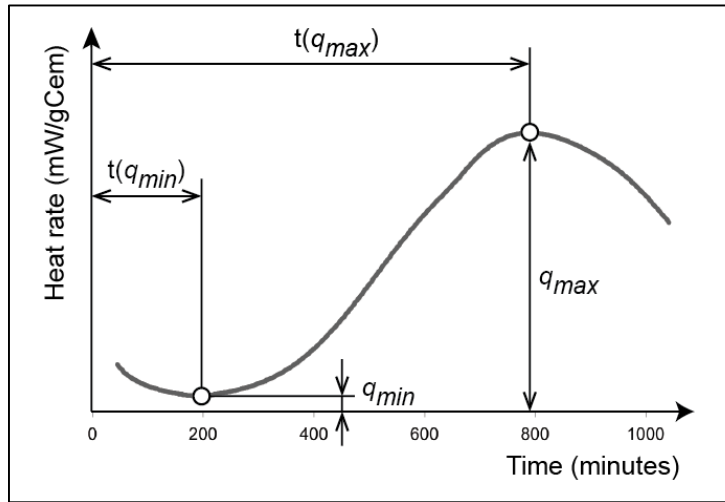


Figure 5. Heat of hydration: definition of parameters analyzed.

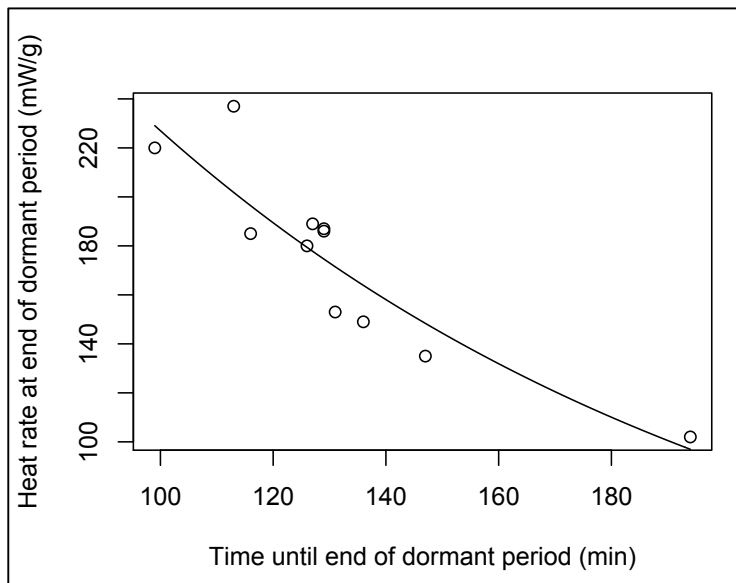


Figure 6. Relationship between the heat rate and time at the end of the dormant period.

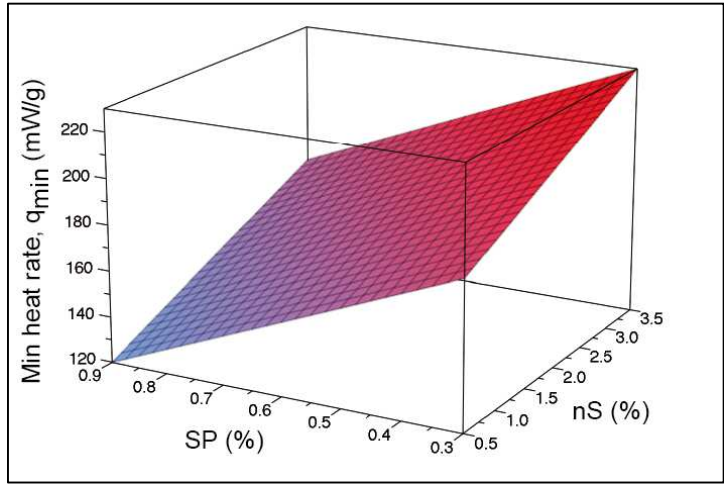


Figure 7. Heat rate q_{min} vs nS content and SP dosage.

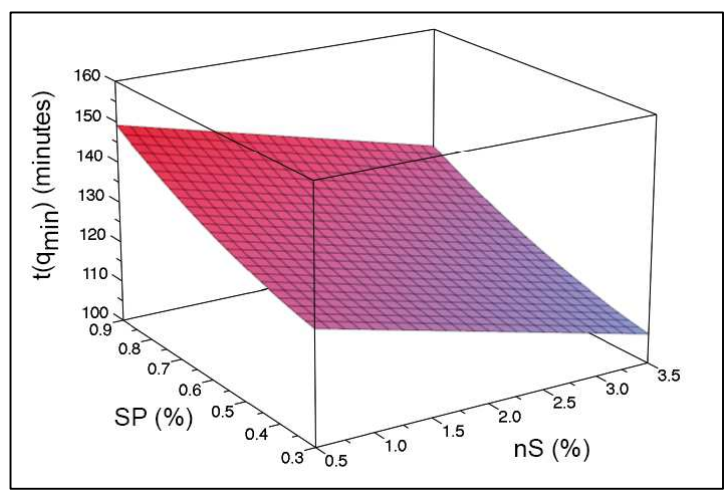


Figure 8. Time until the end of the dormant period, $t(q_{min})$, vs nS content and SP dosage.

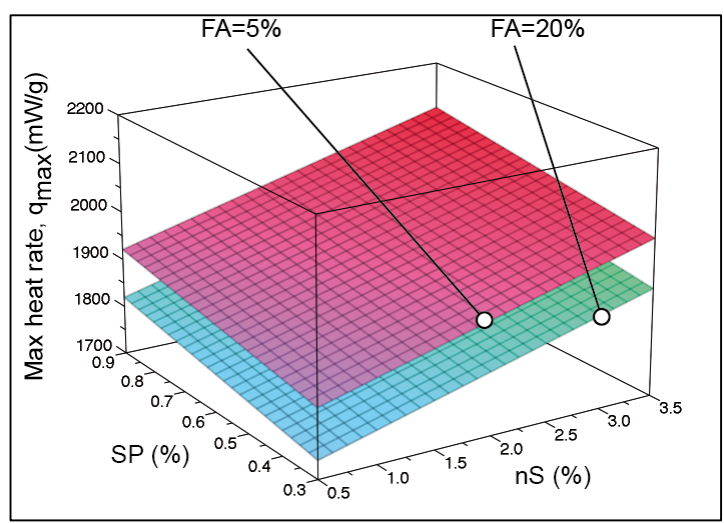


Figure 9. Peak heat rate q_{max} vs nS content and SP dosage, for FA=5.0% (upper surface) and 20.0% (lower surface).

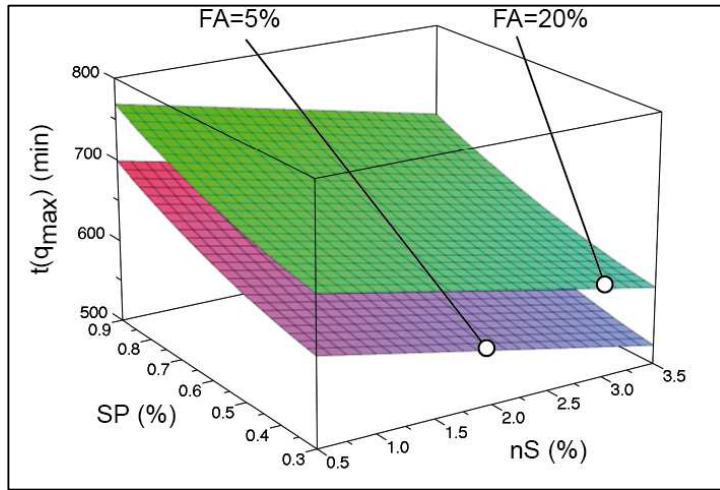


Figure 10. Time until the peak of hydration, $t(q_{max})$, vs nS content and SP dosage, for FA=5.0% (lower surface) and 20.0% (upper surface).

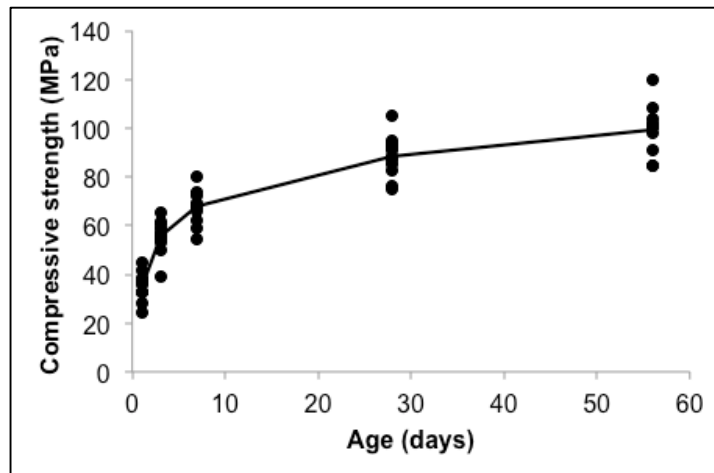


Figure 11. Compressive strength results.

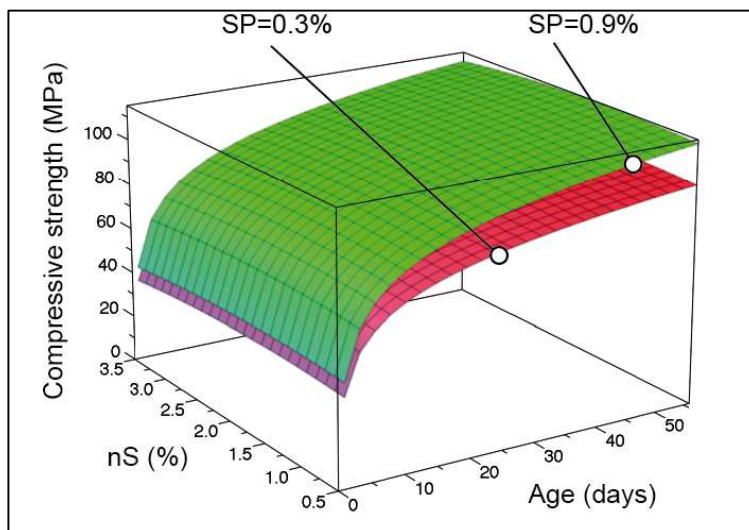


Figure 12. Effect of varying nS content and SP dosage on compressive strength (assuming FA=20%, lower surface corresponds to SP=0.3%; upper surface corresponds to SP=0.9%).

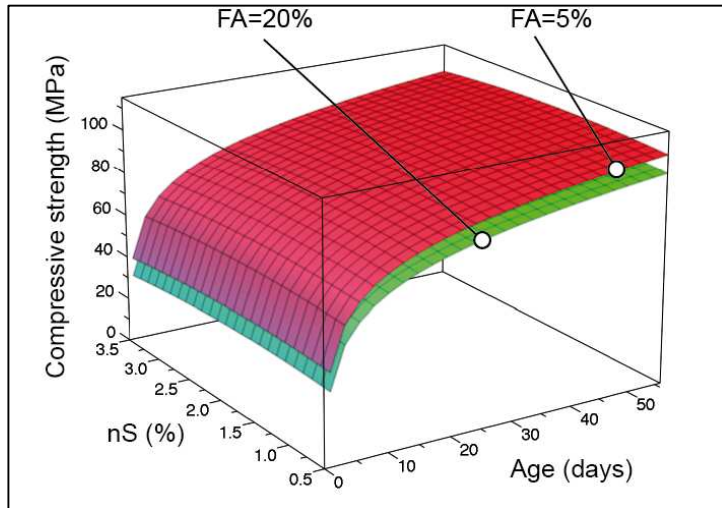


Figure 13. Compressive strength: effect of varying FA content (assuming SP=0.6%, lower surface corresponds to FA=20%, upper surface corresponds to FA=5%).

TABLES

Table 1. Factors and levels considered.

Factor	Levels (*)
Nanosilica addition, nS (solid content)	0.5% o/c
	2.0% o/c
	3.5% o/c
Fly ash, FA (cement replacement)	5.0% o/c
	12.5% o/c
	20.0% o/c
Superplasticiser dosage, SP	0.3% o/b
	0.6% o/b
	0.9% o/b
(*) o/c: over cement weight	
(*) o/b: over binder weight (cement+FA)	

Table 2. Equivalent oxides composition of cement, fly ash and the nanosilica solid fraction.

	Cement	Fly ash	Nanosilica
SiO ₂ (%)	21.01	55.95	99.40
Al ₂ O ₃ (%)	4.92	23.3	0.08
Fe ₂ O ₃ (%)	2.84	4.84	--
MgO (%)	2.20	1.85	--
CaO (%)	64.52	4.76	--
Na ₂ O (%)	0.20	0.91	0.45
K ₂ O (%)	0.71	1.82	--
SO ₃ (%)	2.53	0.65	--
P ₂ O ₅ (%)	0.11	0.73	--
LOI (%)	1.26	3.47	0.10

Table 3. Physical properties of nS, FA and cement.

	Cement	Fly ash	Nanosilica
Specific gravity	3.08	2.21	1.40
% passing 45 µm sieve	85%	85%	--
Mean particle size	22 µm	--	50-60 nm
Specific surface area [m ² /kg]	360	--	--
Specific surface area (BET)	--	--	80 m ² /g

Table 4. Proportionings of the mortars tested.

	Ref.	w/b	Nanosilica (%)	Fly ash (%)	SP (%)
Selected mixes	1	0.35	0.5	5.0	0.3
	2	0.35	3.5	5.0	0.3
	3	0.35	0.5	5.0	0.9
	4	0.35	3.5	5.0	0.9
	5	0.35	0.5	20.0	0.3
	6	0.35	3.5	20.0	0.3
	7	0.35	0.5	20.0	0.9
	8	0.35	3.5	20.0	0.9
Center points	9	0.35	2.0	12.5	0.6
	10	0.35	2.0	12.5	0.6
	11	0.35	2.0	12.5	0.6

Table 5. Rheology.

	Ref.	Yield stress (Pa)	Viscosity (Pas)
Selected mixes	1	118.5	3.43
	2	110	1.19
	3	0.05	0.96
	4	0.04	3.39
	5	144.85	4.19
	6	108.8	3.40
	7	0.05	1.28
	8	4.45	48.79
Center points	9	82.3	54.4
	10	90.3	48.62
	11	71.6	55.86

Table 6. Heat of hydration results.

	Ref.	End of dormant period		Peak of hydration	
		q_{min} (mW/g)	$t(q_{min})$ (min)	q_{max} (mW/g)	$t(q_{max})$ (min)
Selected mixes	1	0.186	129	1.890	605
	2	0.220	99	1.981	536
	3	0.135	147	1.952	707
	4	0.153	131	2.069	588
	5	0.189	127	1.668	643
	6	0.237	113	1.986	606
	7	0.102	194	1.814	789
	8	0.187	129	2.018	680
Center points	9	0.149	136	1.926	609
	10	0.185	116	1.925	622
	11	0.180	126	1.894	649

Table 7. Compressive strength results.

Ref.	Compressive strength* (MPa)					
	1 day	3 days	7 days	28 days	56 days	
Selected mixes	1	35.7 (2.5)	54.3 (0.4)	62.2 (3.7)	82.8 (2.9)	100.6 (4.9)
	2	36.3 (0.6)	56.0 (4.6)	65.9 (2.5)	85.0 (1.8)	91.0 (2.1)
	3	41.8 (2.4)	61.2 (1.9)	73.3 (4.4)	90.9 (10.5)	119.9 (6.6)
	4	44.7 (2.9)	65.6 (5.0)	79.9 (4.7)	105.2 (6.3)	100.9 (9.9)
	5	32.9 (3.0)	49.8 (4.2)	58.8 (1.2)	76.0 (1.5)	84.3 (3.0)
	6	24.3 (3.1)	39.2 (3.8)	54.6 (0.5)	75.0 (0.1)	84.6 (0.2)
	7	32.8 (3.2)	61.0 (6.2)	73.4 (4.1)	95.1 (1.9)	108.6 (3.6)
	8	28.3 (5.1)	52.9 (0.6)	67.9 (1.1)	87.4 (3.2)	100.3 (2.2)
Center points	9	32.8 (5.6)	54.6 (1.0)	68.9 (0.1)	88.2 (2.6)	104.0 (2.4)
	10	38.2 (0.2)	57.2 (1.6)	67.5 (1.5)	93.7 (2.9)	102.1 (0.5)
	11	37.9 (0.5)	58.7 (3.1)	72.1 (3.2)	92.1 (1.4)	98.1 (3.6)

* Each value is the average of 3 specimens; standard deviation values are given in brackets.

Table 8. Summary of the optimization.

Input: minimum compressive strength requirements, in MPa							
$f_c'(1)$	25	30	35	30-35	40	40	45
$f_c'(56)$	60-100	70-90	70-100	110	80-100	110	90-110
Optimal solution of the nonlinear problem							
z (*)	131		137	136	137	141	
τ_y	5.3		5.3	5.3	5.3	5.3	
η	0.06		0.05	0.05	0.05	0.05	
q_{max}	1803		1870	1862	1873	1924	
$f_c(1d)$	35		41	40	41	45	
$f_c(3d)$	54		59	59	60	64	
$f_c(7d)$	69		74	73	74	78	
$f_c(28d)$	92		98	97	98	102	
$f_c(56d)$	104		110	109	110	114	
Output: dosage parameters corresponding to the optimal solution							
NS (%)	0.24		0.27	0.27	0.27	0.3	
FA (%)	20		10.5	11.6	10	2.6	
SP (%)	0.9		0.9	0.9	0.9	0.9	

(*) z is the objective function as defined by equation (10).

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