Rheological and Physic-mechanical study of metallurgical cements based on Nano-silica combined with blast furnace slag

Studiul reologic și fizico-mecanic al cimenturilor metalurgice pe bază de nano-silice combinate cu zgură de furnal

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DOI:10.37789/rjce.2020.11.2.2

Rezumat. *Această lucrare tratează comportamentul reologic și mecanic al cimenturilor metalurgice bazate pe nano-silice (NS) combinate cu zgură de furnal (GBFS). Un studiu experimental a fost realizat cu un raport constant de apă / liant (A / L) de 0,5 utilizat pentru toate mortarele studiate. Pentru a utiliza maximul GBFS și a scădea consumul de ciment, diferitele conținuturi (36% și 66% .wt) GBFS și 3% .wt de NS au fost alese și adăugate la Portland Cement (PC). Au fost efectuate teste reologice pe paste cimentate și au fost efectuate teste mecanice pe mortare elaborate cu ciment metalurgic studiat. Rezultatele obținute arată că pastele de ciment cu 3% NS fără GBFS au fost cele mai puțin vâscoase și au un efort de forfecare mai scăzut, cu o workabilitate acceptabilă în comparație cu alte paste de ciment. Cu toate acestea, în prezența GBFS, pastele de ciment devin mai vâscoase, ceea ce face ca debitul să fie mai dificil, cu o forță de forfecare mai mare la debit. De asemenea, rezultatele au arătat, în comparație cu mortarele de control GBFS, că încorporarea unei mici cantități de NS în ciment în prezența GBFS crește în mod remarcabil rezistența la compresiune la 28 și 90 de zile. Incorporarea a 3% în greutate NS în pastele de ciment cu un conținut de GBFS de 36% și 66% în greutate a dat valori ale rezistenței la compresie de foarte mare 90 zile (71,70 și 56,30 MPa). NS și LHF pot reduce în mod remarcabil porozitatea matricei de ciment și cresc densitatea acestuia, ceea ce explică de asemenea rezistența ridicată la rezistența la compresiune.*

Cuvinte cheie: mortar de ciment, nano-silice, zgura de furnal, fluiditate, reologie și rezistență mecanică

Abstract. *this work deals the rheological and mechanical behavior of metallurgical cements based on nano-silica (NS) combined with blast furnace slag (GBFS). An experimental study was conducted with constant water-to-binder ratio (W / B) of 0.5 used* *for all studied mortars. In order to use the max of GBFS and decrease the consumption of cement, the different contents (36% and 66%.wt) of GBFS and 3%.wt of NS were chosen and added to Portland Cement (PC). Rheological tests were conducted on cementitious pastes and mechanical tests were carried on mortars elaborated with metallurgical cement studied. Obtained results show that that cementitious pastes with 3% NS without GBFS were the least viscous and have a lower shear stress with acceptable workability compared to other cement pastes. However, in the presence GBFS the cement pastes become more viscous which makes the flow more difficult with higher shear stress at the flow. Also, the results showed in comparison with the GBFS control mortars that the incorporation of a small amount of NS in the cement in the presence of GBFS remarkably increases the compressive strength at 28 and 90 days. Incorporation of 3% wt NS in cement pastes with a 36% and 66% wt GBFS content gave respectively very high 90 day compressive strength values (71.70 and 56.30 MPa). NS and LHF can remarkably reduce the porosity of the cement matrix, and increase the density of the latter, which also explains the high resistance of the compressive strength.*

Key words: Materii prime locale, nisip de dune, fibre de înaltă performanță (UHPFC), performanță mecanică și rezistență la compresiune

1. Introduction

The Granulated Blast Furnace Slag (GBFS) is often used as cement additives in concrete construction seen the cost benefit and environmental protection. In addition, the pozzolanic effect and physical effect of the GBFS grains can also improve the workability, strength and durability of concrete [1-4]. In recent years, several studies have shown that the use of Nano-Silica (NS) in cement based materials can remarkably improve the properties in the solid state. Research by Land et al. [5] has shown that when the NS combines with C3S, CSH nuclei described by Thomas et al. [6] are formed on the silica surface by premature pozzolanic reaction to accelerate the process of hydration of the C_3S. Jo et al. [7] found that the adding of 3%wt NS may develop resistance mortar. The research Nazari et al. [8-10] showed that NS can reduce the porosity of the concrete block by filling the gaps, improving the pore structure of hardened concrete. Results of Ji et al. [11] confirms that NS may promote the impermeability and resistance to freeze-thaw cycle of the concrete by improving the internal structure of pores. Thus, the role of NS can be summarized below [11]: confirms that NS may promote the impermeability and resistance to freeze-thaw cycle of the concrete by improving the internal structure of pores. Thus, the role of NS can be summarized below: [11] confirms that NS may promote the impermeability and resistance to freeze-thaw cycle of the concrete by improving the internal structure of pores. Thus, the role of NS can be summarized below:

- NS does not play the role of fillers, but also catalyst pozzolanic reaction [12].
- NS act as a nucleation site for the germs of CSH which accelerates the hydration of cement [5].
- The NS accelerate the hydration of C3S and crystal formation portlandite and homogeneous groups of HSCs. [5]

Zhang et al. [13, 14] found that the use of NS reduces the gel time and increases the concrete strength early age in the presence of large amounts of GBFS. But regarding the interaction between NS and the latter, they have not given a clear explanation. Recently, the effect of adding nano-particles SiO_2 and Al_2O_3 on the mechanical, physical and structural properties of cement pastes was studied by E. Tsampali et al. [15]. using CEMI 52,5, nano-particles of SiO_2 and Al_2O_3 were added in 1.5% and 3%wt of cement and the produced samples were tested after 7, 28, 90 and 120 days of curing. Authors have observed a positive effect, in terms of structural properties, of nano-particle admixture in cementitious systems. They also found that the addition of nano-particles influence the workability of the composites and contributes to the formation of crystallization nuclei, which in turn enhance the durability of the material. It was noted that high concentration of nano Al_2O_3 in the admixure, results in improvement of mechanical properties. It was also found that combined effect of NS with other mineral additions can have a positive effect on properties of cement mortars or concretes. Indeed, a recent study has been conducted on effect of NS on the properties of cement when in conjugation with other supplementary cementitious materials. In this work, authors have deals with the changes in characteristic properties of cement and cement-based materials upon incorporation of NS [16]. According to the literature report [5,12,17], we can deduce that NS and GBFS can regularize the microstructure and properties of cement materials by maximizing the synergistic effect of filling, nucleating and activity effect between them, therefore, a considerable increase in performance of cementitious materials.

This paper presents an experimental study on the physical and mechanical behavior of metallurgical cements based on GBFS in the presence of NS. Rheological tests were carried out cementitious pastes elaborated with GBFS combined with NS. After, cement mortars were elaborated with adequate binder based on GBFS and NS from which we have selected well-defined percentages of GBFS (36% and 66%wt) to be in CEMIII/A and CEMIII/B respectively, in order to evaluate mechanical strength at 3, 28 and 90 days. All variants have been studied in several curing ages to allow a better comparison.

2. Experimental Program

2.1. Raw materials

An artificial Portland cement (CEMI) prepared based on the clinker used for cement production (Algerian Cement). A Ground-Granulated Blast Furnace Slag (GBFS) obtained from El-Hadjar complex with a fineness of 500 m2/kg, was used in this study. A Nano-Silica dioxide (NS) with a very high fineness of 200 000 m2/kg has been used at this work. The chemical compositions and physical properties of cementitious materials are given in the table 1. Microscopic structure of GBFS and NS by Scanning Electron Microscopy (SEM) is also shown in Fig. 1 and Fig. 2, respectively. Standardized sand (CEN EN 196-1) was used to make the mixtures mortars. In order to facilitate the work, it was opted a high superplasticizer (SIKA type), as a water reducer usually used for mix concrete.

Table 1: chemical compositions and physical properties of cementitious materials

Component/Property	CEMI	GBFS	NS
CaO	64.77	38.95	----
SiO_2	21.24	36.52	>99.8*
Al_2O_3	4.84	9.09	----
Fe_2O_3	3.73	3.37	----
MgO	1.90	3.90	----
SO_3	2.11	0.33	----
K_2O	0.84	0.29	----
Na_2O	0.22	0.80	----
P_2O_5	----	0.03	----
TiO_2	----	0.31	----
PAF	0.91	6.40	----
SSB (m^2/kg)	400	500	200 000*
R_{C28j}	56.95	----	----

* Values mentioned on the technical data sheet.

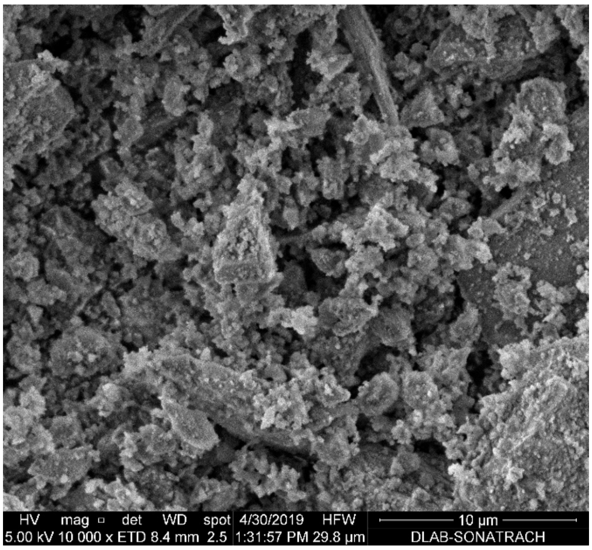

Figure 1. SEM Image of GBFS

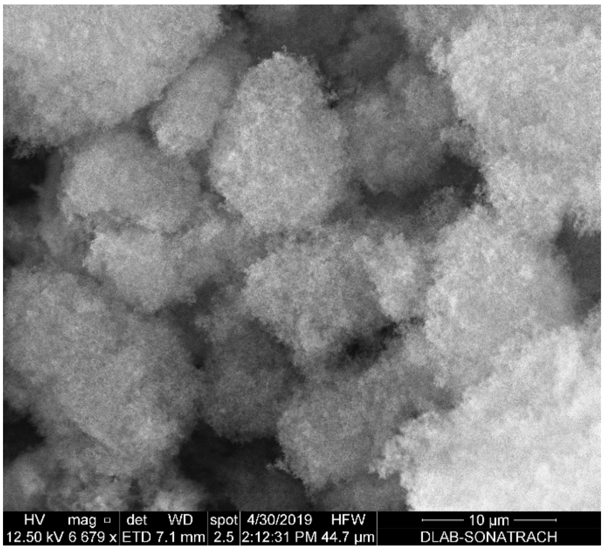

Figure 2. SEM Image of NS

2.2. Mixtures of cement pastes and mortars

The study was divided into two parts. The experimental study was conducted on two parts. In first, the work involves studying the effect of NS on the rheological behavior of GFBS based cement pastes. For this, the work was done on two series of pastes (with and without NS adding) in GFBS presence. These are identified in Table 2 by detailing the different mixing ratios for each sample. Water to binder ratio (w/b= 0.5) was chosen and kept constant in this work. In second work part, study was conducted on the cement mortars while studying the effect of NS in presence of GFBS on the development of the mechanical strength of cement mortars; namely compressive and flexural strength. The Control Mortar (CM) was prepared according to the European standard EN 196-1 [18]. After, other mortars were made by varying the dosages of GBFS and NS. NS is fixed at 3%wt with different amounts (36% and 66%wt) of GBFS were added to cement in order to promote synergistic effect between NS and GBFS. In this part also w/b was kept constant. Table 3 give all mortar mixtures studied.

Table 2: Mortars identification made from GBFS and NS.

IDF	CEMI/g	GFBS/g	NS/g	Sand/g	Superplasticizer/%
M	450	0	0	1350	0
L36	288	162	0	1350	0
L66	153	297	0	1350	0
MNS	436.5	0	13.5	1350	2
L36NS	274.5	162	13.5	1350	2
L66NS	139.5	297	13.5	1350	2

M: Control mortar; MNS: Control mortar with NS
L36 and L66: Mortar with 36 and 66%wt of GFBS, respectively.
L36NS and L66NS: Mortar with 36 and 66%wt of GFBS, respectively combined with NS.

2.3. Test methods

Rheological study: In order to establish a rheological study, an AR2000-rheometer from TA Instruments with the rotor valve geometry, was used Fig. 3. All rheological measurements were performed according to the chosen protocol which is applied on series of cementitious pastes samples for two studies cases (with and without NS). The tests were carried out at t0 (pre-shear with 350 S-1 for all samples during the 60 seconds after mixing) and under laboratory conditions (T= 20 ± 1 °C). The test was carried out at an imposed shear rate (the imposed shear rate is approximately 500 S-1). The rheological test protocol adopted has been chosen according to the bibliographic resource which is recommended to apply a pre-shear on the cement paste to obtain reproducible rheological measurements. Some authors have also confirmed the dependence between the shear stress and the fluidity of cementitious pastes.

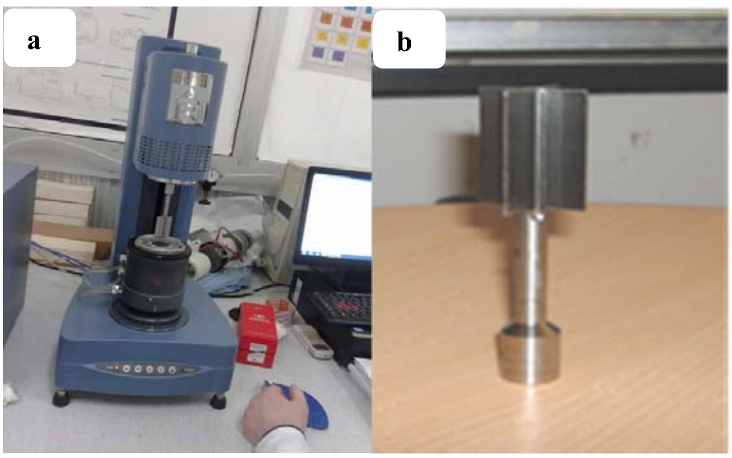

Figure 3. Rheological tests; (a) AR2000-Rheometer (b) Geometry valve rotor

Mechanical Strength: After mixing, for each mixture, specimens of 4×4×16 cm were prepared for in accordance with ASTM specification. The test specimens were unmolded after 24 h and then cured in water. The compressive strengths of cement mortar specimens were tested at 3 and 28 days of curing times by using a uniaxial hydraulic compression machine under a load control rate of 0.20 MPa/s. Three-point bending tests were carried out on prismatic samples according to ASTM C348 [19]. Half samples were subjected to compressive stress by using a hydraulic press with a capacity of 3000 KN according to ASTM C349 [19].

3. Results and Discussion

3.1. Rheological study of cement pastes

a) GBFS effect on rheology of pastes

The rheograms of Fig. 4 and Fig. 5, respectively represent the shear stress evolution and plastic viscosity of the cement pastes based on GBFS (0, 36 and 66%wt). Clearly, from these results, the presence of the GBFS has significantly increased shear stress and plastic viscosity of cement pastes compared to the control dough without GBFS, a 38% increase of the shear stress was recorded. This increase also followed by an increase in viscosity making them any more viscous cement pastes. This is explained by the nature and activity of the GBFS which often increase the viscosity pastes.

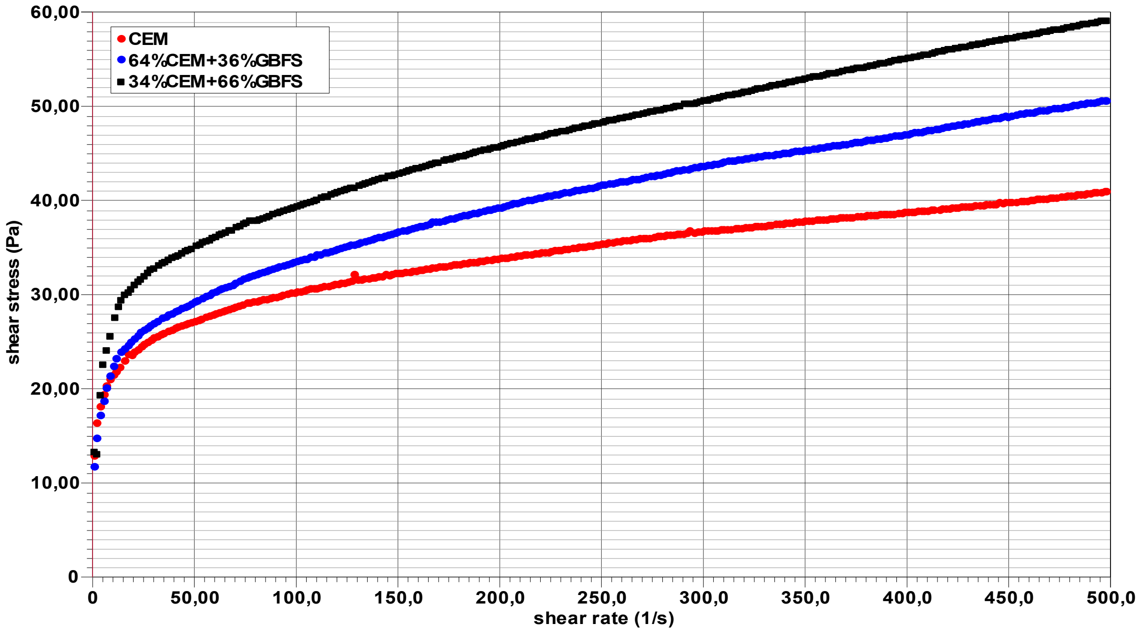

Figure 4 Shear stress evolutions of cement pastes based on GBFS

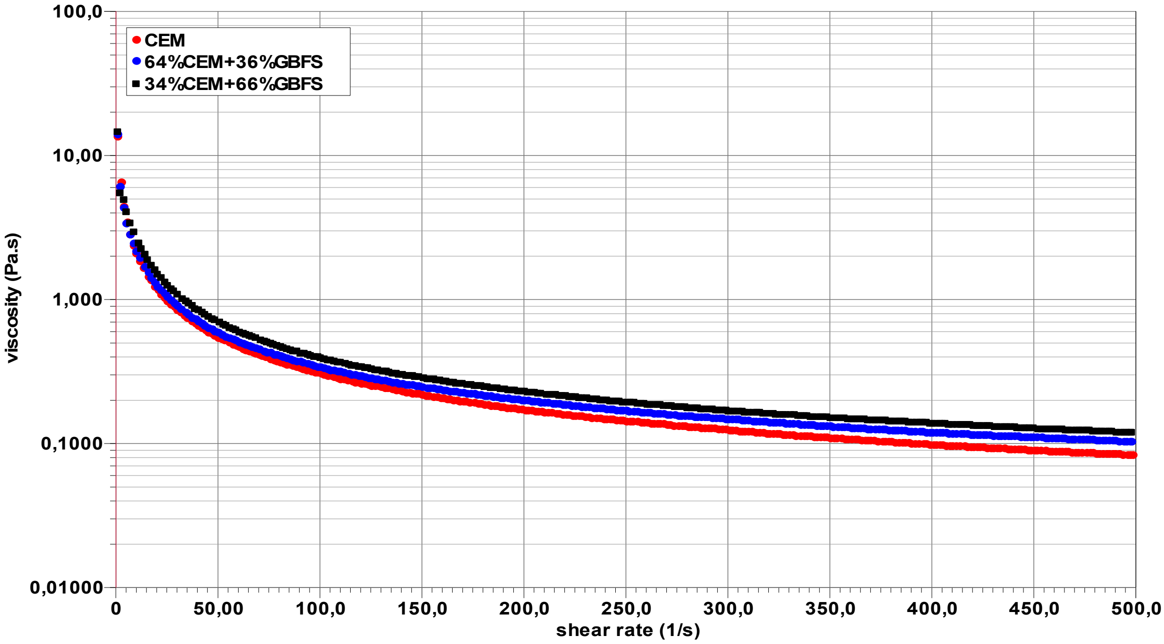

Figure 5 viscosity variations of cement pastes based on GBFS

b) Combined effect of GBFS and NS on the rheology of pastes

The Fig.6 and Fig. 7 represent the shear stress evolution and plastic viscosity of the cement pastes based on 0, 36 and 66%wt of GBFS in presence of 3%wt of NS. It is noteworthy that the cement pastes with 3%wt without GBFS NS are less viscous and have a lower shear stress with acceptable maneuverability compared to other pastes. However, in the presence of GBFS pastes become more viscous making it difficult to flow with a shear stress to flow more important. Note that these pastes contain 1 to 2% superplasticizer. Based on these results, clearly we can see the effect provided by GBFS combined with NS and in particular the presence of NS to significant GBFS test.

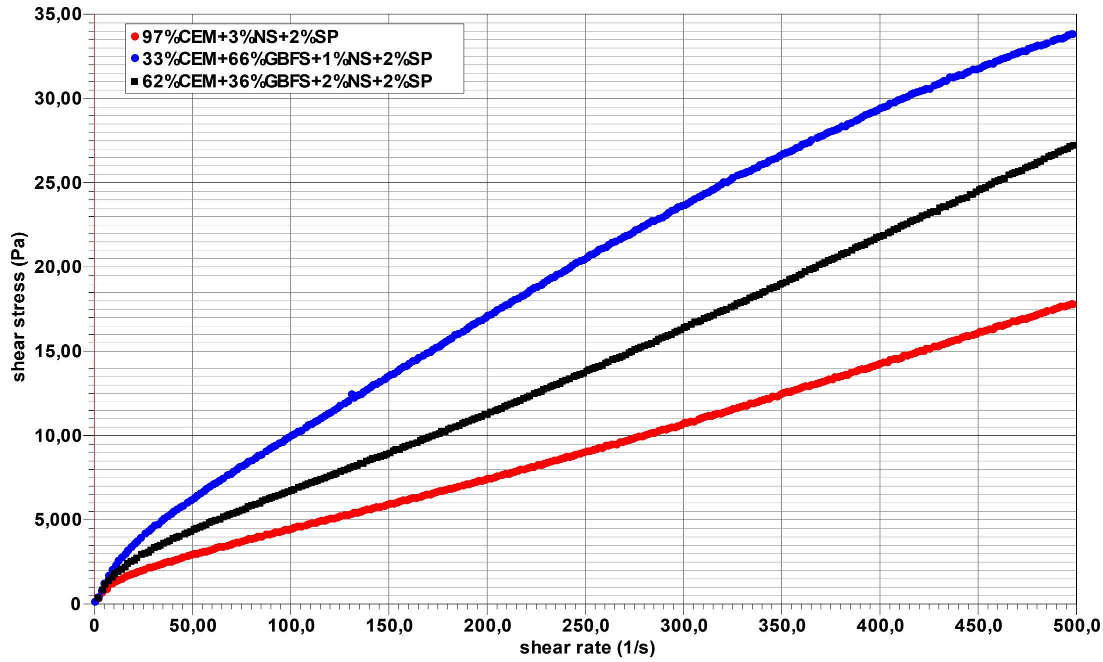

Figure 6 Shear stress evolutions of Cement pastes based on GBFS combined with NS

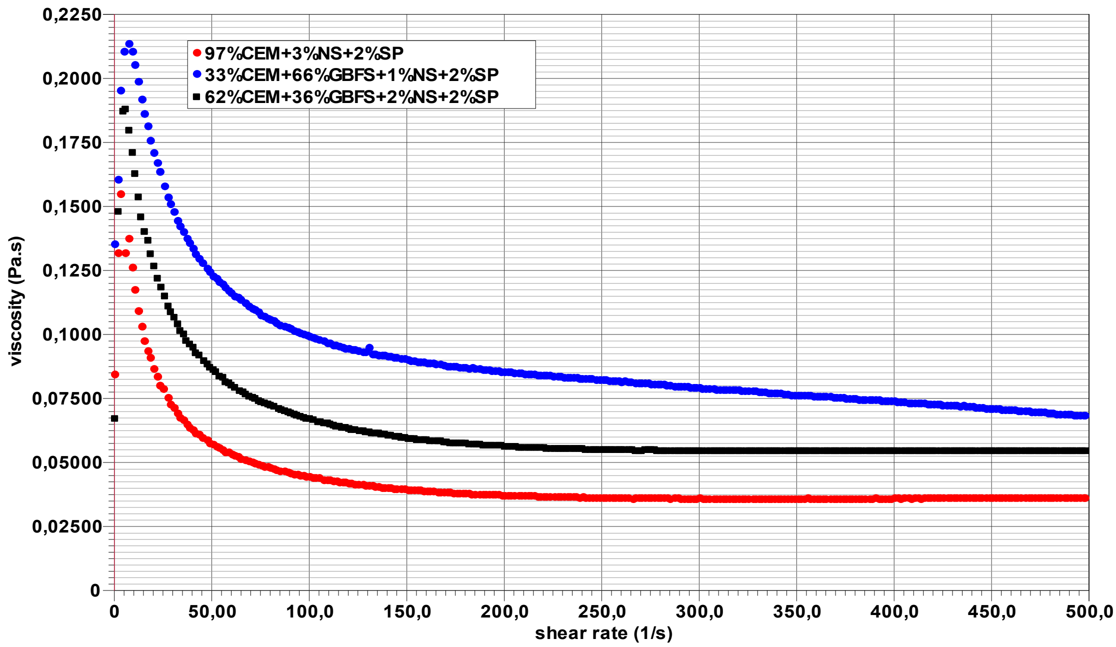

Figure 7 Viscosity variations of Cement pastes viscosity based on GBFS combined with NS

c) Rheological behavior of cement pastes

Using rheometer software, we could identify the rheological behavior of cement pastes calibration of existing models in the software as shown in Fig. 8 and Fig. 9. Based on the results, all the pastes has a similar behavior with Herschel-Bulkley model described by equation (1), which is shaped in bibliographic resources [21, 22 and 23]. The rheograms of cement pastes show the evolution of the shear stress versus shear rate. It is clear from these figures that the rheological behavior of pastes follows the Herschel-Bulkley model described by the following equation (1):

$$\tau = \tau_0 + K.\dot{\gamma}^n \quad (1)$$

τ_0: Yield stress;
K: Consistency;
n: Flow index.

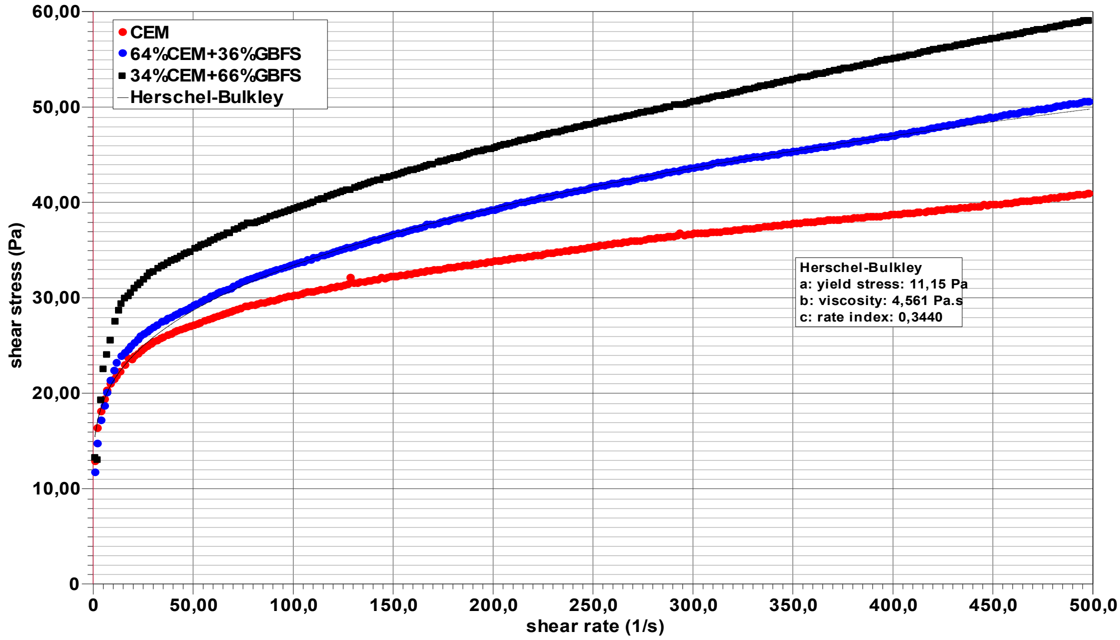

Figure 8 Rheological behavior of cementitious pastes based on GBFS

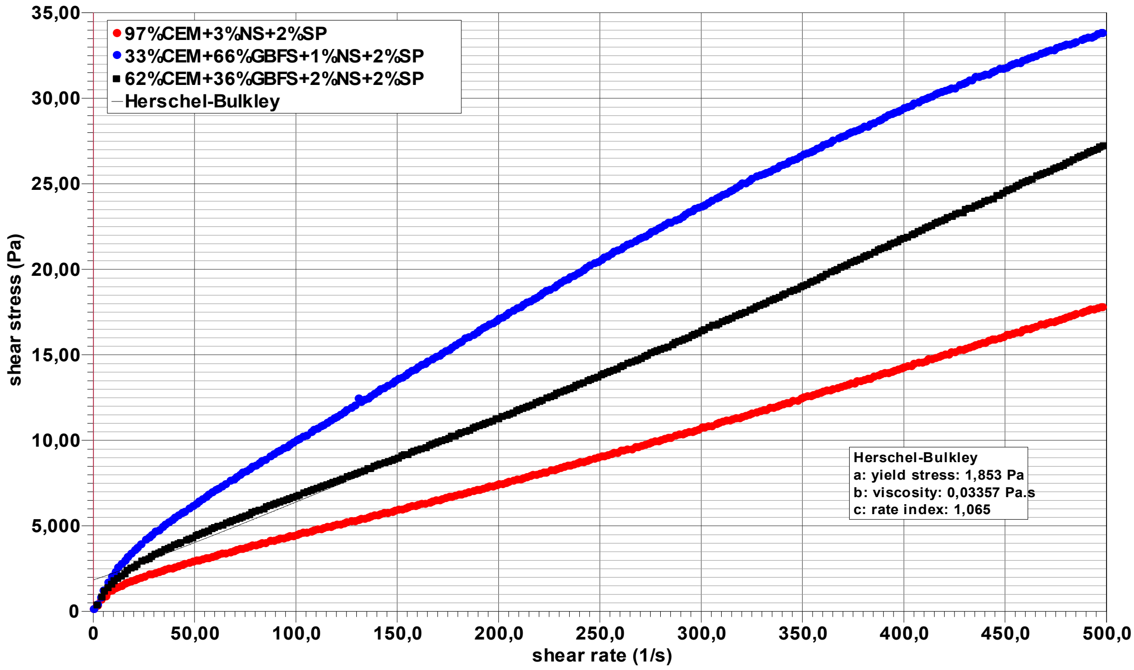

Figure 9 Rheological behavior of cementitious pastes based on GBFS combined with NS

3.2. Development of flexural and compression strength

The development of mechanical bending resistance and compression of different mortars at 3, 28 and 90 days is presented in Fig. 10 and Fig. 11, respectively These results are detailed in Table 3 and Table 4.

Table 3: Résults of mechanical flexural strengths of various mortars (MPa)

IDF	3d	28d	90d
M	6.10	7.47	7.81
L36	5.43	8.37	8.86
L66	1.69	8.70	8.42
MNS	5.98	7.92	7.95
L36NS	5.28	7.92	8.46
L66NS	1.89	4.40	6.27

Table 4: Résults of mechanical compressive strengths of various mortars (MPa)

IDF	3d	28d	90d
M	30.08	56.95	66.65
L36	18.32	52.33	64.43
L66	4.86	41.33	59.35
MNS	38.59	70.05	75.95
L36NS	24.12	62.45	71.70
L66NS	6.50	44.88	56.30

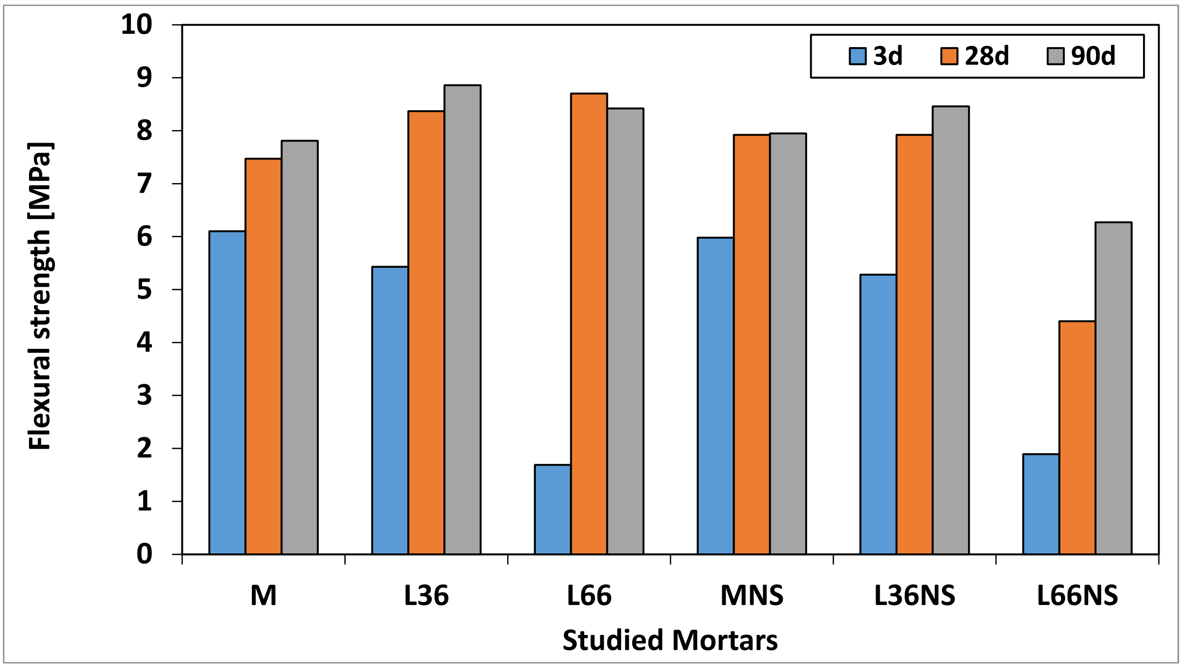

Figure 10 Flexural strengths development of studied mortars

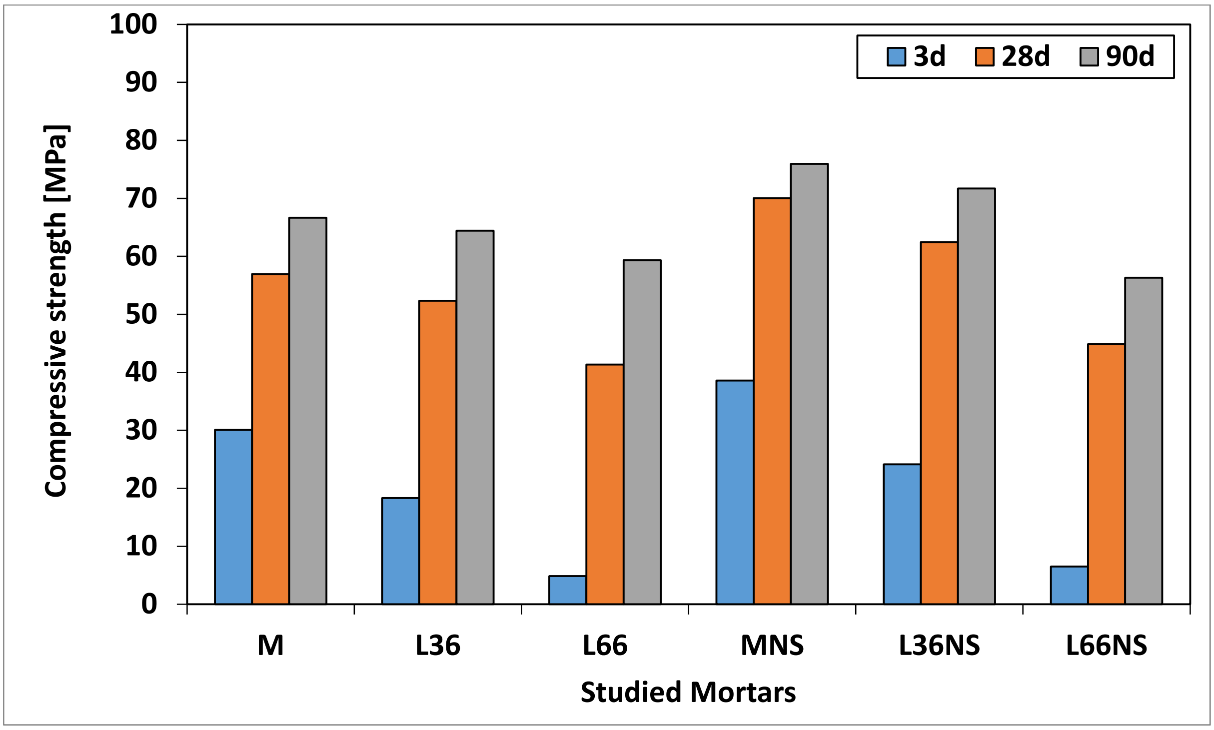

Figure 11 Compressive strengths development of studied mortars

Based on the research of Liu et al. [17, 24] it is able to choose the percentages (36 and 66%wt) when it gave valuate results with 30% and 40%wt of GBFS in that study.

Table 4 shows the different results obtained in the crash of the different pieces, it is clearly see the development of mechanical strength over time. The value obtained by adding 66%wt of GBFS in presence of NS gave an acceptable value of 44.88 MPa at 28 days. The latter can qualify the cement to be used as CEMIII/B 42.5 R.

It is apparent in Table 5 that the gradual addition of GBFS (36% and 66%wt) penalizes mortars in terms of mechanical resistance to compression especially young age, on the other hand, the incorporation of the latter with same dosages in the presence of 3%wt of NS gave better result translated into a gain in mechanical compressive strength of 9.66% and 7.58% respectively at 28 and 90 days for the L36NS mortar.

Table 6 gives the contributions of NS in the presence of GBFS in various mortars. Increased values of compressive strengths were recorded particularly those in 3 days with high percentages 28.29%, 31.66% and 33.74%, respectively for mortars TMNS, L36NS and L66NS nevertheless one of 5.14% regression was observed in 90 days mortar L66NS hence dysfunctional behavior between NS and GBFS.

The figure 12 gives the strength gains provided by the combinet effect of NS and GFBS. It is clear that the effect of NS is significant in the short-term especially its effect in the presence of GFBS. Indeed, there has been a marked improvement in the compressive strength of nanosilica-based mortars in GFBS presence compared to those without GFBS. This improvement in the compressive strength is in order of 30%. However at long-term, the NS has reduced the strength of mortars especially those with a higher dosage of GFBS [5, 12, 16]. This may be due to the large surface area of the nanosilica that causes the need for water and also the competition of nanosilica and GFBS to consume Ca $(OH)_2$ [12, 16].

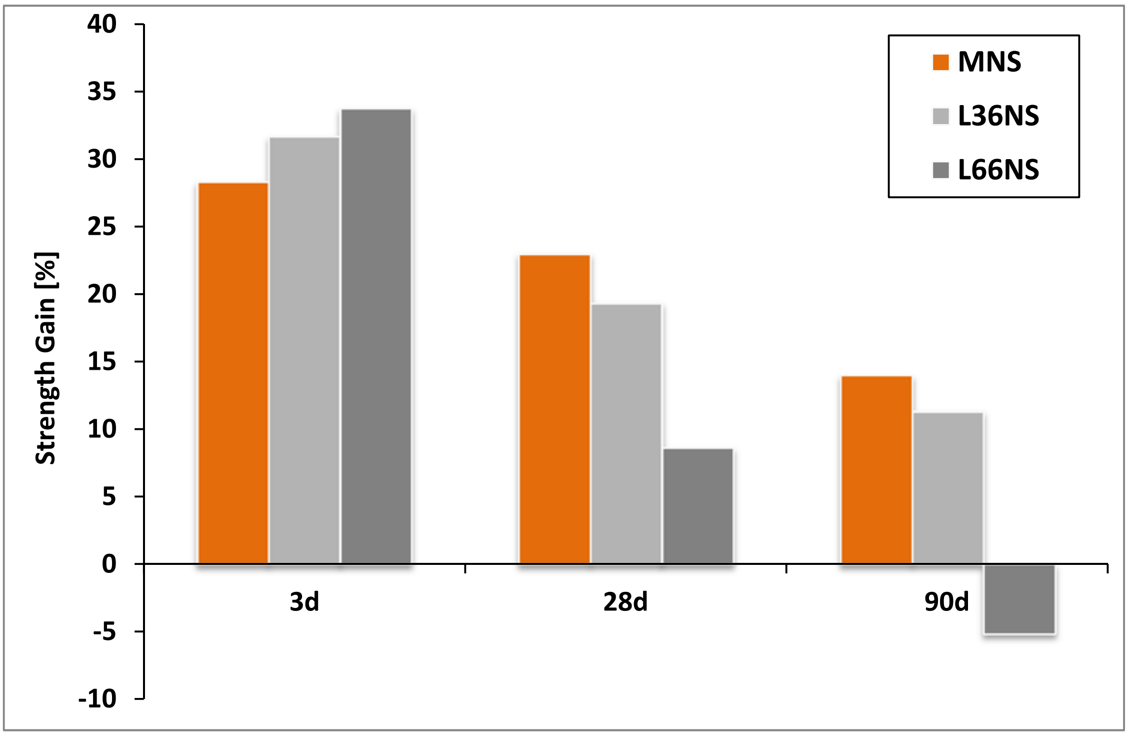

Figure 12 Strength gains of GGBS-NS based mortar relative to control mortar

In order to estimate well the combined effect of GGBS and NS, Figure 13 presents the normalized compressive strength of mortars reported compared to mortars with only NS. It should be noted that GFBS and NS-based mortars have the same appearance of developing strength to NS-based mortars. However, higher content of GFBS and NS have caused significant reductions in mortar strength. Beyond 90 days of curing, the reduction is greater for higher grade cement mortars from GFBS and NS.

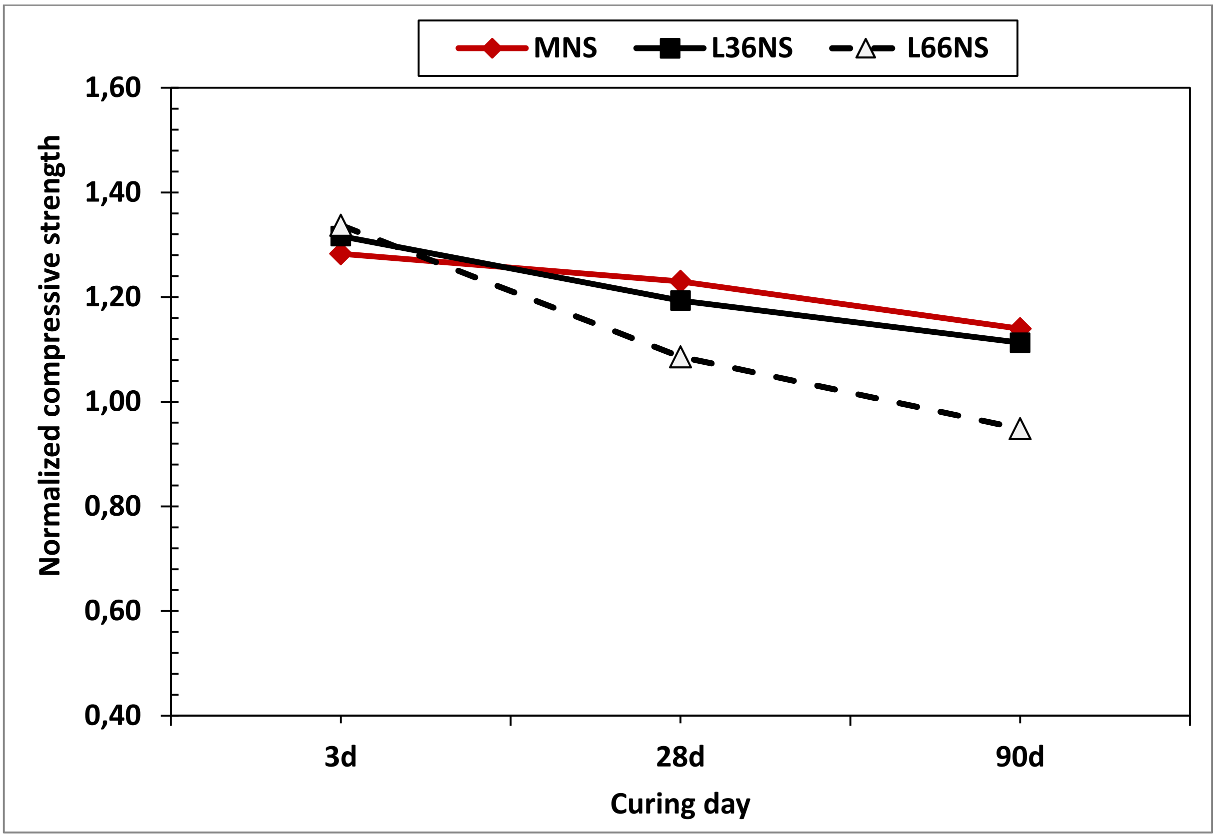

Figure 13 Combined effects of GFBS and NS on the development of mortar strength

4. Conclusion

In this review, the rheological and mechanical behavior of metallurgical cements based on nano-silica (NS) combined with blast furnace slag (GBFS) was investigated under the main objective is to produce a higher performance cement with lower clinker content. The conclusions of this investigation are summarized below:

- Results obtained of rheological tests on cement pastes, have shown that GBFS-based cement has significantly increased shear stress and plastic viscosity of cement pastes compared to the control dough without GBFS. This has allowed us to conclude that the nature and activity of GBFS have an important effect. However GBFS presence, the NS-based cement pastes (2% NS) become more fluid favouring flow with a lower shear stress. Concerning rheological behavior of studied cement pastes, the results have given, all the pastes has a behavior Binghamian plastic fluid identical to that of the Herschel-Bulkley rheological model, this has been proven by several researchers;
- The results of the mechanical tests, revealed that effect of NS was significant in the short-term especially its effect in the presence of GFBS. Indeed, there has been a marked improvement in the compressive strength of nanosilica-based mortars in GFBS presence compared to those without GFBS. This improvement in the

compressive strength is in order of 30%. The incorporation of 36%wt GBFS combined with 3% NSwt gave a significant value of compressive strength (62.45 MPa) at 28 days (71.70 MPa) at 90 days. The incorporation of 66%wt GBFS combined with 3%wt NS pt gave a sufficient value that allows us to develop this study by obtaining a value of 44.88 MPa at 28 days may assign this cement being a CEMIII/B 42.5 R.

- At long-term, the NS has reduced the strength of mortars especially those with a higher dosage of GFBS. This is due to the large surface area of the nanosilica that causes the need for water and also the competition of nanosilica and GFBS to consume Ca $(OH)_2$.

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