



**QUEEN'S
UNIVERSITY
BELFAST**

Rheological and hardened performance of grout containing Nano Silica

Abdalqader, A., Fayyad, T., Nassar, A. I. M., & Sonebi, M. (2024). Rheological and hardened performance of grout containing Nano Silica. In W. Finnegan , & M. Hajdukiewicz (Eds.), *Proceedings of the Civil Engineering Research in Ireland Conference 2024* (pp. 132-137). Civil Engineering Research Association of Ireland. <https://researchrepository.universityofgalway.ie/entities/publication/a20c47af-9b4f-4b30-b534-9d639565d920>

Published in:

Proceedings of the Civil Engineering Research in Ireland Conference 2024

Document Version:

Publisher's PDF, also known as Version of record

Queen's University Belfast - Research Portal:

[Link to publication record in Queen's University Belfast Research Portal](#)

Publisher rights

Copyright 2024 CER12024 Conference.

This is an open access article published under a Creative Commons Attribution-NonCommercial-NoDerivs License

(<https://creativecommons.org/licenses/by-nc-nd/4.0/>), which permits distribution and reproduction for non-commercial purposes, provided the author and source are cited.

General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Open Access

This research has been made openly available by Queen's academics and its Open Research team. We would love to hear how access to this research benefits you. – Share your feedback with us: <http://go.qub.ac.uk/oa-feedback>

Rheological and Hardened Performance of Grout Containing Nano Silica

Ahmed Abdalqader¹, Tahreer Fayyad², Ahmed I. M. Nassar³, Mohammed Sonebi²

¹Tracey Concrete Ltd, Sligo Road, Enniskillen, BT74 7LF, Northern Ireland

²School of Natural and Built Environment Belfast BT7 1NN, Northern Ireland

³Jean Lefebvre (UK) Ltd, 193 Windmill Ln, Cheshunt, Waltham Cross EN8 9AW, United Kingdom

email: abdalqader@cantab.net, t.fayyad@qub.ac.uk, ahmed.nassar@jluuk.co.uk, m.sonebi@qub.ac.uk

ABSTRACT: This study investigates the influence of nano silica and silica fume on the properties of fresh and hardened cement grout. The experimental variables included the content of nano silica and silica fume, as well as the dosage of superplasticiser (SP). A series of tests were conducted to examine the properties of both fresh and hardened grout. The findings suggest that nano silica has a more pronounced effect on reducing grout workability compared to silica fume. Additionally, an increase in cohesion was observed with the rise in nano silica content. Yield stress and viscosity increased with the incorporation of both nano silica and silica fume, while SP dosage exhibited an inverse relationship with these parameters. The compressive strength was found to be highly dependent on the interplay between SP dosage, nano silica content, and silica fume content. For instance, at an SP dosage of 1.6%, nano silica and silica fume mixes exhibited higher compressive strength at 1 day compared to the ordinary Portland cement (OPC) mix, but displayed lower strength at all subsequent ages. Overall, nano silica mixes demonstrated generally superior strength at 1, 3, and 7 days compared to silica fume mixes, although this trend reversed at 28 days. X-ray diffraction (XRD) analysis revealed an increased consumption of $\text{Ca}(\text{OH})_2$ crystals with increasing content of both nano silica and silica fume. This phenomenon can be attributed to the high surface area of these particles, potentially coupled with their pozzolanic activity. Notably, the effect was more pronounced in nano silica mixes.

KEY WORDS: Nano Silica; Silica Fume; Grout; Rheology.

1 INTRODUCTION

Grout, a versatile construction material, consists of cement, water, and often incorporates supplementary cementitious materials (SCMs), and chemical admixtures. Its primary function is to fill voids, anchor objects, and transfer loads in various applications such as foundations, underwater structures, and post-tensioned ducts [1]–[3]. Effective grouting necessitates optimal flow properties (high slump, low viscosity) for successful injection or pumping to minimize segregation during placement [2].

Recent advancements have introduced nano silica as a potential SCM for grout. With its extremely high surface area (in the order of 100-1500 m²/g) and pozzolanic activity, nano silica offers potential benefits like improved packing density, increased strength, and enhanced durability compared to conventional grouts [4]. The high surface area of nano silica particles enables them to effectively fill the voids between cement particles, leading to a denser microstructure and improved mechanical properties [5]–[7]. Furthermore, nano silica reacts with calcium hydroxide (CH), a by-product of cement hydration, to form additional calcium silicate hydrate (C-SH), the main binding phase in cement. This pozzolanic reaction refines the pore structure of the grout, enhancing its strength and durability [8]. However, proper dispersion of these nanoparticles is crucial to fully exploit these advantages and avoid inconsistencies in performance due to agglomeration (30-100 nm) [9]. Agglomeration can hinder the reactivity of nano silica particles and reduce their effectiveness in improving grout properties [6].

This would include the use and optimisation of the chemical admixtures in the mix. Another solution is to use ultrasonic treatment on the nano silica, which breaks up the angular agglomerates to form more rounded agglomerate [10]. Increasing the nano silica content also increases the amount of water

necessary to lubricate the grout, more so than silica fume. As a result, the use of a superplasticiser (SP) in the mix is essential to ensure good pumpability of the grout.

This study investigates the influence of nano silica and silica fume on the rheological (workability, viscosity) and hardened (compressive strength) performance of grout. The properties will be compared to mixes containing similar quantities of silica fume and the impact of SP dosage will be explored. A testing program will be employed to assess these properties. Additionally, X-ray diffraction (XRD) analysis will be conducted to understand the hydration process and resulting microstructure. The findings will contribute to a deeper understanding of incorporating nano silica and silica fume into grout formulations for achieving superior performance.

2 EXPERIMENTAL PROGRAM

The goal of the experimental procedure is to ascertain the effect of nano silica on the fresh rheological properties and the hardened properties of grout. The fresh rheological properties and the hardened properties of both OPC grout and grout containing silica fume were obtained for comparing with the mixes containing nano silica. Comparisons were made between increasing SCM content and increasing SP content.

Each two litre mix contained between 0.5% and 5% by weight of grout of either nano silica or silica fume. The super plasticizer content was either be 1.2% or 1.6% by weight of grout. All other mix proportions and properties are fixed. The properties to be obtained are: flow spread, fresh density, flow time, Lombardi plate thickness, both static and dynamic yield stress and viscosity, heat of hydration using Isothermal Conduction Calorimetry (ICC); 1, 3, 7 and 28 day compressive strength and the mineral composition using XRD.

2.1 Materials

The cement to be used in this experimental programme is Portland cement from Quinn Cement.

The nano silica used was Cembinder 8 from EKA Chemicals. The chemical composition and physical properties of Cembinder 8 are shown in Table 1.

Table 1 Chemical Composition and Physical Properties of the Nano Silica

Surface Area (m ² /g)	80
Average Particle Size (nm)	35
Concentration % of Silica by Weight	50
Density (g/cm ³)	1.4
SiO ₂ Content	>99%
pH	9.5

The silica fume was ELKEM 500 S Micro Silica. The chemical composition and physical properties of ELKEM 500 S is shown in Table 2.

Table 2 Chemical Composition and Physical Properties of ELKEM 500 S

Surface Area (m ² /g)	15-35
Concentration % of Silica by Weight	50
Density (g/cm ³)	1.4
SiO ₂ (% by weight of Dry Mass)	> 90%
SO ₃ (% by weight of Dry Mass)	< 2
Cl (% by weight of Dry Mass)	< 0.3
Free CaO (% by weight of Dry Mass)	< 1
Free Si (% by weight of Dry Mass)	< 0.4
C (% by weight of Dry Mass)	< 2.0
pH	4 - 7

The SIKA Premium SP from SIKA was chosen.

2.2 Mix Design

Fourteen mix designs were used in this study. The variation in mixes were by introducing nano silica in a range of 0.5 to 5 % by weight of grout or adding silica fume in the same range. All mixes have a SP content of either 1.2% or 1.6% by weight of grout. The mixes are summarised in Table 3.

The mixes were prepared in 1.8L batches using a 5L planar-action high-shear mixer. Cement and the nano silica or silica fume were added to the mixer and mixed for one minute at low speed (140 rpm). Tap water (16 ± 0.5 °C) was introduced within 2 min, at the end of which the mixer was stopped and any lumps of solids formed were crushed (1 min). Subsequently, the SP is added and the grout was mixed for 2 min at a higher speed of 285 rpm and for 1 min at the lower speed of 140 rpm.

Table 3 Mix Design

Mix	w/b	OPC %	nS %	SF %	SP %
OPC	0.3	100	0	0	1.6
nS 0.5%	0.3	99.5	0.5	0	1.6
nS 2%	0.3	98	2	0	1.6
nS 3.5%	0.3	96.5	3.5	0	1.6
nS 5%	0.3	95	5	0	1.6
OPC x	0.3	100	0	0	1.2
nSx 2%	0.3	98	2	0	1.2
nSx 5%	0.3	95	5	0	1.2
SF 0.5%	0.3	99.5	0	0.5	1.6
SF 2%	0.3	98	0	2	1.6
SF 3.5%	0.3	96.5	0	3.5	1.6

SF 5%	0.3	95	0	5	1.6
SFx 2%	0.3	98	0	2	1.2
SFx 5%	0.3	95	0	5	1.2

2.3 Testing Methods

After mixing, the temperature of the grout and several tests were performed made to check the workability, cohesion, weight of the fresh grout and compression strength for the hardened concrete. Tests were mini slump (1-2minutes), Lombardi cohesion (7-16 minutes), mud balance and viscometer (21-40 minutes). After all tests were done, grout was then poured into cube mould of dimension 50 x 50 x 50 mm which each mould consists of three cubes and demoulded after 24 hours. Two set of cubes were made to test the strength at 7days and 28 days.

The mini slump test is carried out to test the workability of a grout mix, through measuring the spread of grout from a mould. A cone shaped mould and smooth plate were used to carry out this test. The cone shaped mould has an upper inner diameter of 19mm, a lower inner diameter of 38.1mm and a height of 57.1mm. The mould and plate were initially dampened with water to reduce friction between the fluid and the mould. The mould was placed into the centre of a smooth plate and consequently filled with grout. The cone was lifted vertically and the grout inside was allowed to flow freely. When the grout stops moving, the spread diameter was measured at four right angles using a measuring tape. The average diameter is then calculated from these values.

The Lombardi plate test was used to measure the cohesiveness of a fluid mix. A thin steel plate and electronic scale were necessary for this test. The steel plate is 100 x 100mm with a thickness of 1mm. The steel plate was hung up and the set is then placed on top of an electronic scale and once the weight settles, the scale value set to zero. The clean, dry steel plate was then removed and submerged into the grout mix. Once fully covered, the plate was removed from the suspension and the excess fluid was allowed to drip. When the dripping stopped, the plate was hung back up on top of the scale. The final value on the scale is the amount of grout which has stuck to either side of the plate.

The density of the mix needs to be found, using the mud balance, prior to calculating the cohesion value. To find the relative cohesion of the mix, the weight of the grout remaining on the plate should be divided by the area of both sides of the plate and the density of the suspension. For grouts, relative cohesion is calculated as a thickness and its units are therefore millimetres. A highly cohesive grout may have a relative cohesion between 0.2mm and 0.4mm, while low cohesion grouts may have relative cohesion values around 0.06mm [11].

The mud balance is used to determine the specific gravity of a fresh cementitious suspension. A Fann 140 mud balance was used. The cup, within the mud balance, was filled by pouring grout into it from a measuring cylinder. The cup is full when a small amount of grout escapes from the top of the lid. This excess grout was then removed so it did not skew the results. The cup and beam were then placed on the fulcrum and the weight is adjusted until the system is balanced. The system is completely balanced when the bubble in the spirit level is centred. The density was then read off a scale at the bottom of the beam. In the case of this mud balance, the specific gravity is given in units of g/cm³.

The rheological measurements were carried out with a computer-controlled vane rheometer (Haake VT550). Approximately 800 ml of the sample was put into a plastic container into which the vane was plunged. Using the computer program RheoWIN 3, two test programmes are conducted: a low shear five-minute test and a Log based speed up / speed down test. The low shear test allows the grout to rest for one minute. At this time, the grout is considered to have settled. The shear vane then rotates at low speeds. Using the RheoWIN software, a curve analysis is carried out on the plot of shear stress against shear rate. This produces a line equation which gives the static viscosity and yield stress. Once the test is complete, the grout is hand mixed with a spatula to avoid settlement. For each step, when the equilibrium was reached, the strain rate was increased from an initial value of 0.188 s^{-1} to a top value of 41.6 s^{-1} (ascending curve), and afterward, it is decreased to ending the descending curve. The rheological parameters, yield stress (τ_0) and plastic viscosity (μ_p), were obtained from the descending curve.

A Servo Plus compression testing machine was used to test three grout cubes from each mix at both 7 days and 28 days. Three cubes were tested from each mix, to allow for average values to be calculated. The cubes were removed from the curing tank and dried before testing. They were then placed into the machine and loaded with a rate of 200kN/minute. The testing machine gave a value for both maximum load (kN) and maximum strength (MPa) of each cube.

A set of mixes were selected for heat of hydration analysis using ICC machine. Once the experiment is ready to be started, the water was added to the mixes. five grams of each mix was inserted by syringe into small containers. These containers were then inserted into the Isothermal Conduction Calorimetry machine.

The mixes OPC, nS 2%, nS 5%, SF 2% and SF 5% at 1 and 3 day age were selected for X Ray Diffraction testing to determine the crystalline compounds resulted from the hydration process. After the cubes were crushed, they were broken apart using a hammer to obtain samples from the centre of the cubes. These samples were then ground into small nodules manually using a mortar and pestle. These were then placed in a container filled with acetone, in order to cease the hydration reaction. When the samples are required for testing, the acetone was drained from the container and the sample was put in a desiccator for three days to remove the acetone residue. The sample was then further ground to a size passing a 63 micron sieve manually using a mortar and pestle. This yields a powdered sample which was then mounted onto a sample holder and put in the machine for testing.

3 RESULTS AND DISCUSSIONS

3.1 Mini slump spread

The results of the mini slump are presented in Table 4. The results showed that as the nano silica content increased past 0.5%, the flow spread decreased and as the silica fume increased, the flow spread also decreased, but at a lower rate than that of nano silica.

Between the SP dosage of 1.2% and 1.6%, the spread increased by 9% for OPC due to the increase in the steric and electro static repulsion provided by the SP [12]. For both nS 2% and SF 2% mixes, the flow spread remained unchanged for both super plasticizer dosage of 1.2% and 1.6%. Any greater SCM content decreased the flow spreads, especially the nSx 5% mix where the

flow spread was reduced by 31% when compared to OPCx mix. This could be due to the very high surface area of silica fume and especially nano silica, which reduces the amount of super plasticizer per unit surface area [12].

When the super plasticizer dosage was at 1.6%, which is beyond the normal saturation point, there was still enough SP to counter this surface area effect. The effect may have been in balance at SCM content of 2%, but any greater SCM content caused a reduction in flow spread.

Table 4 Results of Mini Slump Spread and Marsh Cone Flow

Mix	Spread (mm)	% change to OPC	Flow time (sec)	% change to OPC
OPC	205	0.00	53	17.78
nS 0.5%	185	-9.76	50	11.11
nS 2%	180	-12.20	57	26.67
nS 3.5%	170	-17.07	69	53.33
nS 5%	165	-19.51	71	57.78
OPC x	190	0.00	54	0.00
nSx 2%	180	-5.56	68	25.93
nSx 5%	145	-31.03	125	131.48
SF 0.5%	200	-2.44	54	20.00
SF 2%	190	-7.32	51	13.33
SF 3.5%	190	-7.32	57	26.67
SF 5%	190	-7.32	52	15.56
SFx 2%	190	0.00	61	12.96
SFx 5%	175	-8.57	61	12.96

3.2 March Cone-Flow

The results of the Marsh cone are presented in Table 4. The flow time generally increased as nano silica content increased, with the largest increase occurring between nS 3.5% and nS 5%. This may be an indication of agglomeration of the nano silica particles. Nano particles are not easy to disperse due to their high surface energy [13] and so they are prone to form angular agglomerates [10]. The high surface area of nano silica also reduce the amount of water available for the mix, which could also account for the increase in flow time [2].

The flow time for the SF mixes were varied, ranging between a 4% decrease and an 8% increase when compared to the OPC mix. The reduction in flow time maybe due to the small rounded particles of silica fume which can improve the flow characteristics of the grout if used in small dosages [10]. As the SP dosage decreased, the flow time increased. Once again, the nSx 5% mix has an exceedingly high value of 131 seconds. The effect of the SP is reduced by the high surface area of the nano silica.

3.3 Cohesion

The results of the cohesion are presented in Table 5. Both nS and SF mixes show an increase in plate thickness with increasing SCM content. This higher thickness implies a higher cohesion in the grout, which coincides with the decrease of flow spread.

There is a decrease in thickness, and therefore cohesion, with the decrease of SP for all mixes except nS 5% and SF 5%. This is not usual, as it has been reported that cohesion should increase for decreasing SP [12]. There may be errors in the calculation of the fresh density for the mixes with SP dosage of 1.2%. However, the plate weights for all mixes except nS 5% and SF 5% also decreased with decreasing SP content so the data may be valid.

Table 5 Results of Lombardi Plate.

Mix	Weight on Plate (g)	Thickness on Plate (mm)	% Change to OPC
OPC	2.74	0.06523	0.00
nS 0.5%	2.8	0.06676	2.34
nS 2%	3	0.07149	9.60
nS 3.5%	3.2	0.07645	17.20
nS 5%	3.5	0.08284	27.00
OPC x	2.43	0.05780	0.00
nSx 2%	2.88	0.06734	16.51
nSx 5%	4	0.09322	61.27
SF 0.5%	2.75	0.06706	2.81
SF 2%	3	0.07249	11.13
SF 3.5%	3.46	0.08300	27.25
SF 5%	3.21	0.07725	18.42
SFx 2%	3	0.07069	22.29
SFx 5%	3.4	0.08008	38.54

3.4 Vane Viscometer Results

The results of the rheological properties of mixes in Figure 1 and Figure 2. Dynamic yield stress increased with increasing nano silica content, especially for the nS 5% mix. There is a point between nS 3.5% and nS 5% where the workability of the grout is severely reduced. This could be due to high nano silica content causing the packing of particles, which decreases the free water and thus increase the internal friction between the solid particles [14]. The silica fume content had little effect, with a small increase for the SF 5% mix. Decreasing super plasticizer dosage increased the static yield stress. This correlates with the minislump data obtained for the mixes [15].

Dynamic viscosity increased with increasing nano silica and roughly stayed the same with increasing silica fume content. The agglomeration of nano silica and its very high surface area could explain the increase, while the small rounded particles of silica fume could explain the reduction in viscosity. The null readings for both SF 3.5% and SF 5% mixes are most likely due to machine error. The dynamic viscosity also increased with increasing silica fume content, but the effect was not as great as that of nano silica. The dynamic viscosity increased with decreasing SP dosage.

It can be concluded that nano silica and silica fume content of up to 2% has a small effect on the viscosity and yield stress, but beyond that, these parameters begin to be appreciably affected, especially the yield stress parameter.

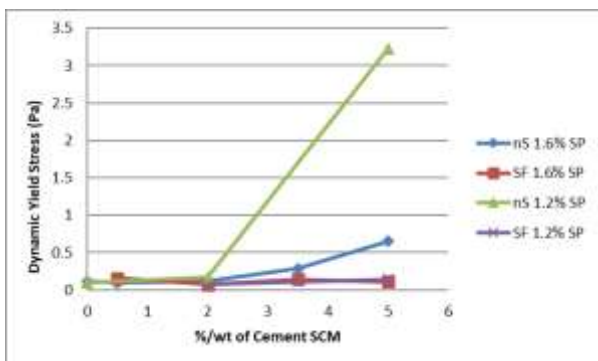


Figure 1 Dynamic Yield Stress for Increasing SCM Content.

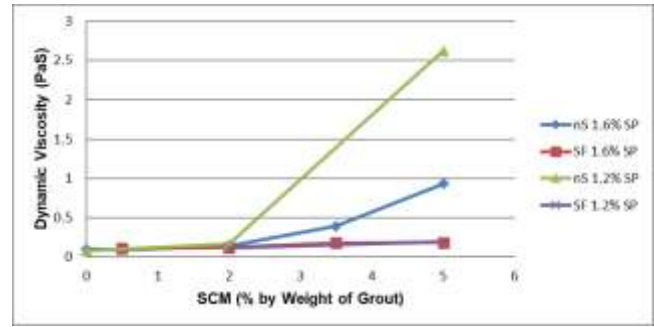


Figure 2 Dynamic Viscosity for Increasing SCM Content.

3.5 Heat of hydration

The isothermal calorimetry results are shown in Figure 3. It can be seen that for increasing nano silica content, the peak of maximum heat flow occurs earlier and is of greater magnitude when compared to OPC. It can also be seen that when compared to silica fume of similar content, the peak of maximum heat flow for nano silica occurs earlier and is of greater magnitude. This is due to the nano silica particles having a higher surface area than the silica fume, increasing its reactivity.

This trend indicates the occurrence of an increased reaction rate for mixes containing nano silica. It corresponds to a quicker setting time of the mix. This was evident visually from the cubes; cubes that had low nS content were not as fully hardened as those with higher nS content. Decreased initial setting times for mixes containing nano silica have been reported by different researchers [14], [16].

Though the mixes had the super plasticizer dosage set at 1.6%, it would be expected that the heat evolved by the nS mixes would increase with reducing super plasticizer content, due to the relieving of the retarding effect of SP [13].

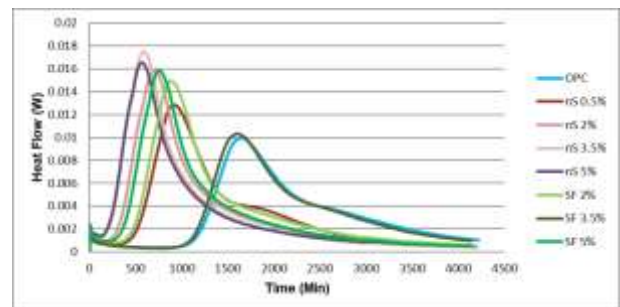


Figure 3 ICC Heat Flow Results.

3.6 Compressive Strength

The summary of the results for the compressive strength tests are shown in Figure 4. The addition of nano silica increased the 1 day compressive strength when compared to OPC. This is attributed to that nano silica reacts faster than OPC, which promotes early age strength. The addition of nano silica decreased the compressive strength at all other ages when compared to the OPC mix, with nS 3.5% 28 day only showing a 116% increase on OPC 1 day strength compared to OPC 28 days increase of 166%. The nS 5% mix showed an increase in compressive strength when compared to the nS 3.5% mix, but was still weaker than the OPC mix, with nS 5% 28 day showing a 131% increase when compared to OPC 1 day.

The addition of silica fume increases the 1 day compressive strength when compared to OPC except for the SF 0.5% mix. This

mix displayed minimum, irregular breakage during crushing, and so its strength data may be erroneous. The increase was not as great as what was observed for nano silica, as silica fume is not as reactive, due to its lower surface area, as nano silica. The nS 5% mix at 1 day had a 17% increase while the SF 5% mix had a 12% increase when compared to the OPC mix at 1 day. At 3 and 7 days, the nS mixes tended to be stronger than SF mixes, except at 28 days, where they were weaker: SF 5% at 28 days had a 135% increase compared to nS 5% having a 131% increase when compared to OPC at 1 day.

It should be noted that the SF 3.5% mix achieved a greater compressive strength at 28 days than the SF 2%, going against the trend of increasing silica fume content decreasing late age strength. The SP dosage of 1.6% may be particularly suited to this silica fume content.

The strength for the OPC mix has decreased for the reduction of super plasticizer content, with a reduction from 150.5 MPa for OPC to 142 MPa for OPCx, a 5.6% decrease. This could be due to a reduction of cement particle surface area available for hydration in the OPCx mix. The nS 2% mix has also reduced in strength for all ages, especially the one day strength, which reduced from 72 MPa to 59 MPa, an 18% decrease. The 1-day strength of the nS 2% mixes is still greater than that of the OPC mixes.

There is an increase in strength for the nS 5% mixes for all ages with a reduction in super plasticizer content. Although it is still not as strong as the OPC mixes, the difference between the 28 day strengths has reduced from 20 MPa to 7 MPa. As the nS 2% mixes had a reduction in strength, this trend may indicate that each specific percentage content of nano silica has a specific SP dosage needed to optimise the compressive strength.

The SF 2% mix has increased in strength with the reduction of super plasticizer content. The SFx 2% mix achieves greater strength, past 3 days, when compared to the OPCx mix, with a 5.2% increase in compressive strength at 7 and 28 day. The SFx 2% mix was the only mix with super plasticizer content of 1.2% that was stronger than the OPCx mix at 28 days.

The SF 5% mixes showed a small increase in compressive strength with the reduced super plasticizer dosage. Except at the 1 day strength, the SFx 5% mixes were still weaker than the OPCx mix. The SFx 2% mix was the strongest mix at 28 days, although it had the weakest strength at 1 day. For both super plasticizer dosages, the SF 2% mixes were stronger than the nS 2% mixes at all other ages, with the largest difference seen at 28 days: the SFx 2% mix was 149.3 MPa to nSx 2% 131.9 MPa, a 13.2% increase.

The nS mixes achieved a greater compressive strength at days 1, 3 and 7 when compared to the SF mixes. At 28 days, the SF mixes are slightly stronger. The greater early age strength of the nS mixes may be due to the increased reactivity of the smaller particles when compared to the larger particles of silica fume. The nSx 5% mix may be better optimised at a super plasticizes dosage of 1.2% than the SFx 5% mix.

It could be inferred from these results that reducing the SP dosage decrease the early age strength of the mixes containing nano silica or silica fume, but increases the later age strengths. The opposite is true for the OPC mix. The early age reduction of strength is greater for the 2% mixes than the 5% mixes.

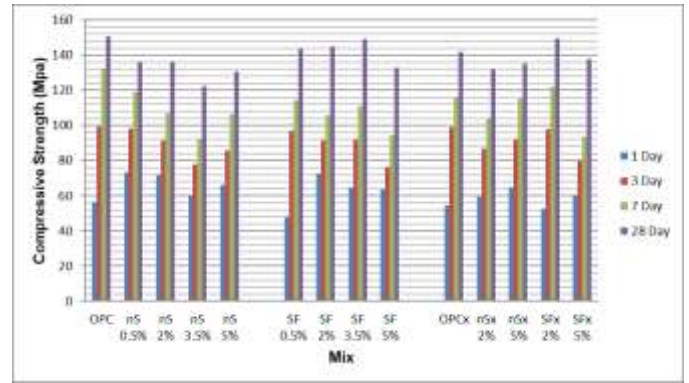


Figure 4 Compressive Strength Results.

3.7 XRD results

The XRD results for the mixes OPC, nS 2%, nS 5%, SF 2% and SF 5% at 1 and 3 days are shown in Figure 5, Figure 6 and Table 6.

For the nS mix and SF mix, silica was located, as they are primarily a silica based material. The C-A-S-H identified is very close chemically to ettringite, and could be counted as such. Both the nS and SF mixes contained calcite, or calcium carbonate. A reaction product from carbon dioxide in the air, the very finely ground powder samples used for XRD analysis are prone to this carbonation unless stored in acetone. This calcite would have formed between the time taken to crush the sample with the mortar and pestle and to put the powdered sample into acetone.

Table 6 Main Crystalline Compounds.

OPC	nS	SF
Ettringite	Ettringite	Ettringite
C-A-S-H	C-A-S-H	C-A-S-H
CS4	CS4	CS4
CS5	CS5	CS5
Portlandite	CS3	CS3
	Portlandite	Portlandite
	Silica	Silica
	Calcite	Calcite
	Alumina	Alumina
	Calcium	Calcium
	Aluminate Oxide	Aluminate Oxide
		Brownmellerite

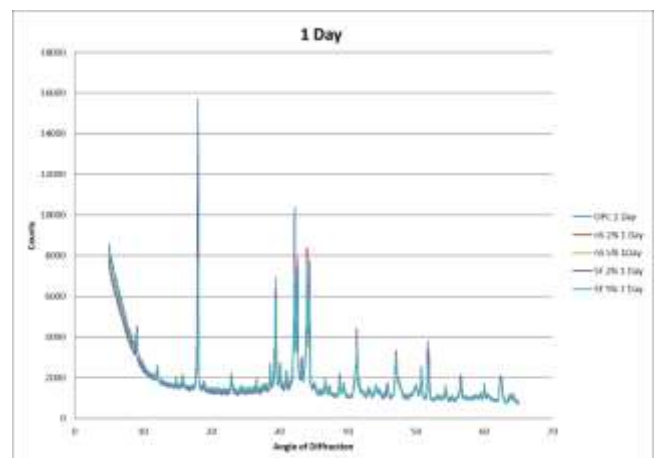


Figure 5 XRD results of some samples at 1 day.

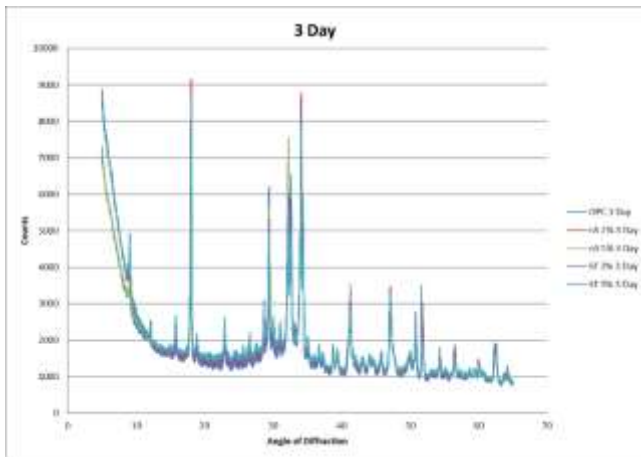


Figure 6 XRD results of some samples at 3 days.

4 CONCLUSION

This study investigated the influence of nano silica and silica fume on the rheological and mechanical properties of grout. Nano silica incorporation generally resulted in lower workability (flow spread, flow time) compared to silica fume at similar replacement levels. However, both SCMs exhibited increased workability with higher superplasticizer dosages. Nano silica displayed a greater dependence on superplasticizer content for maintaining workability. Yield stress and viscosity increased with increasing SCM content and decreased with increasing superplasticizer dosage. The effect was more pronounced for nano silica, particularly at higher replacement levels (3.5% and 5%) with a lower superplasticizer dosage (1.2%). These findings suggest the potential of nano silica as an inorganic viscosity modifying admixture.

Isothermal calorimetry indicated faster setting times and early-age strength development with increasing SCM content, with a more significant effect observed for nano silica. At a superplasticizer dosage of 1.6%, both nano silica and silica fume mixes exhibited higher 1-day compressive strength compared to the control grout, but lower strength at later ages. Interestingly, nano silica mixes generally displayed higher strength than silica fume mixes at early ages (1, 3, and 7 days), but this trend reversed at 28 days. At a lower superplasticizer dosage (1.2%), the interaction between superplasticizer and SCM content became more evident. While silica fume mixes showed a slight overall strength increase, certain nano silica mixes exhibited significant strength reductions (nS 2%) or even strength gains (nS 5%). These observations suggest an optimal superplasticizer dosage for specific SCM replacement levels to ensure adequate workability and strength development.

XRD analysis revealed increased consumption of calcium hydroxide ($\text{Ca}(\text{OH})_2$) with increasing SCM content, attributed to pozzolanic activity and the high surface area of the nanoparticles. This effect was more pronounced for nano silica, indicating its enhanced reactivity. Overall, nano silica appears to promote high early-age strength and faster setting times in grouts, potentially at the expense of workability at later ages and some loss of long-term strength compared to silica fume. However, the pozzolanic activity of nano silica particles may contribute to regaining strength over time beyond the 28-day period investigated in this study. Further research is warranted to explore the long-term performance of nano silica-modified grouts and optimize mix design strategies for achieving a balance between early-age and long-term properties.

ACKNOWLEDGMENTS

The authors would like to thank Patrick Carr for his experimental work.

REFERENCES

- [1] H. Güllü, M. E. Yetim, and E. B. Güllü, "Effect of using nano-silica on the rheological, fresh and strength characteristics of cement-based grout for grouting columns," *J. Build. Eng.*, vol. 76, no. June, p. 107100, 2023, doi: 10.1016/j.jobbe.2023.107100.
- [2] M. Sonebi, M. T. Bassuoni, J. Kwasny, and A. K. Amanuddin, "Effect of Nanosilica on Rheology, Fresh Properties, and Strength of Cement-Based Grouts," *J. Mater. Civ. Eng.*, vol. 27, no. 4, 2015, doi: 10.1061/(asce)mt.1943-5533.0001080.
- [3] R. Vadivel and V. K. Stalin, "Effect of nano silica on the performance of cementitious grout for ground modification," *15th Asian Reg. Conf. Soil Mech. Geotech. Eng. ARC 2015 New Innov. Sustain.*, pp. 2138–2143, 2015, doi: 10.3208/jgssp.OTH-32.
- [4] P. P. Abhilash, D. K. Nayak, B. Sangoju, R. Kumar, and V. Kumar, "Effect of nano-silica in concrete; a review," *Constr. Build. Mater.*, vol. 278, p. 122347, 2021, doi: 10.1016/j.conbuildmat.2021.122347.
- [5] A. M. Said, M. S. Zeidan, M. T. Bassuoni, and Y. Tian, "Properties of concrete incorporating nano-silica," *Constr. Build. Mater.*, vol. 36, pp. 838–844, 2012, doi: 10.1016/j.conbuildmat.2012.06.044.
- [6] S. Zhang, W. G. Qiao, P. C. Chen, and K. Xi, "Rheological and mechanical properties of microfine-cement-based grouts mixed with microfine fly ash, colloidal nanosilica and superplasticizer," *Constr. Build. Mater.*, vol. 212, pp. 10–18, 2019, doi: 10.1016/j.conbuildmat.2019.03.314.
- [7] P. Wang *et al.*, "Experimental research on rheological and mechanical properties of nano silica sol grout," *J. Sol-Gel Sci. Technol.*, vol. 91, no. 1, pp. 178–188, 2019, doi: 10.1007/s10971-019-04994-5.
- [8] H. Du, S. Du, and X. Liu, "Durability performances of concrete with nano-silica," *Constr. Build. Mater.*, vol. 73, pp. 705–712, 2014, doi: 10.1016/j.conbuildmat.2014.10.014.
- [9] K. Khan, W. Ahmad, M. N. Amin, and S. Nazar, "Nano-Silica-Modified Concrete: A Bibliographic Analysis and Comprehensive Review of Material Properties," *Nanomaterials*, vol. 12, no. 12, 2022, doi: 10.3390/nano12121989.
- [10] K. Sobolev, I. Flores, R. Hermosillo, and L. M. Torres-Martínez, "Nanomaterials and nanotechnology for high-performance cement composites," *Proc. ACI Sess. Nanotechnol. Concr. Recent Dev. Futur. Perspect.*, vol. 7, pp. 93–120, 2006.
- [11] James Warner, *Practical Handbook of Grouting: Soil, Rock, and Structures*. 2004.
- [12] M. Sonebi, "Optimization of Cement Grouts Containing Silica Fume and Viscosity Modifying Admixture," *J. Mater. Civ. Eng.*, vol. 22, no. 4, pp. 332–342, 2010, doi: 10.1061/(asce)mt.1943-5533.0000026.
- [13] B. W. Jo, C. H. Kim, G. ho Tae, and J. Bin Park, "Characteristics of cement mortar with nano-SiO₂ particles," *Constr. Build. Mater.*, vol. 21, no. 6, pp. 1351–1355, 2007, doi: 10.1016/j.conbuildmat.2005.12.020.
- [14] L. Senff, J. A. Labrincha, V. M. Ferreira, D. Hotza, and W. L. Repette, "Effect of nano-silica on rheology and fresh properties of cement pastes and mortars," *Constr. Build. Mater.*, vol. 23, no. 7, pp. 2487–2491, 2009, doi: 10.1016/j.conbuildmat.2009.02.005.
- [15] A. Yahia, K. H. Khayat, and B. Benmokrane, "Evaluation of cement grouts for embedding anchors under water," *Mater. Struct. Constr.*, vol. 31, no. 4, pp. 267–274, 1998, doi: 10.1007/bf02480425.
- [16] Y. Qing, Z. Zenan, K. Deyu, and C. Rongshen, "Influence of nano-SiO₂ addition on properties of hardened cement paste as compared with silica fume," *Constr. Build. Mater.*, vol. 21, no. 3, pp. 539–545, 2007, doi: 10.1016/j.conbuildmat.2005.09.001.