



Effect of Nano-SiO₂ on Strength and Hydration Characteristics of Ternary Cementitious Systems

Hediye Yorulmaz¹ · Burak Uzal¹ · Okan Karahan² · Uğur Durak² · Serhan İlkentapar² · Cengiz Duran Atış²

Received: 22 April 2022 / Accepted: 17 May 2023 / Published online: 31 May 2023
© King Fahd University of Petroleum & Minerals 2023

Abstract

This paper shows results of laboratory study on the effects of nano-SiO₂ on Portland cement-fly ash systems. It is aimed to improve performance of fly ash–cement systems, particularly at early age, with the inclusion of nano-SiO₂. In order to observe the effects of nano-SiO₂ particles on the strength and hydration kinetics of fly ash blended cementitious systems, binary and ternary systems were prepared by adding 0.25–1.5% nano-SiO₂ by weight of blended cements. Workability, setting time, water absorption capacity, fire resistance, compressive strength and isothermal calorimeter tests were conducted on the cementitious systems. The results indicate that increasing quantity of fly ash increased workability, setting time, water absorption capacity of cementitious systems, whereas the increasing quantity of nano-SiO₂ reduced these values. Significant increment in compressive strength were observed, especially at early ages of fly ash–cement systems with nano-SiO₂ addition, compared to fly ash added systems, which may compensate for the decrease in compressive strength caused by fly ash. Nano-SiO₂ addition accelerated hydration reactions at early age. By partially eliminating the negative effects of fly ash with nano-SiO₂, high rates of fly ash can be used in cementitious systems, thus forming more sustainable systems.

Keywords Cementitious systems · Fly ash · Nano-SiO₂ · Ternary

1 Introduction

Nanotechnology is a promising technology that can be used in a variety of scientific fields [1]. As a result of the development of nanotechnology, various nanomaterials have been produced recently [2]. The addition of nanoscale particle has both an environmentally advantages and can enhance the durability and strength of the cementitious system [3]. Besides, the nanoparticles acting as filler, if the nanoparticles are properly dispersed, it can promote hydration, thereby improving the microstructure of the cementitious paste [4].

The most commonly used nanoparticles in cementitious systems were nano-SiO₂, nano-TiO₂, nano-Al₂O₃ and nano-clay [4–14]. Among various nanomaterials, nano-SiO₂ (NS) has been one of the nanoparticles that has attracted a great attention in research of the cementitious materials. There

were many studies in the literature on use of NS in the cementitious systems [9, 10, 15–26]. The beneficial impact of NS on the characteristics of cementitious systems may be explained in a variety of ways. Firstly, NS is very active due to its large surface area. Therefore, it can improve the durability of cementitious materials by forming a denser microstructure [27]. Secondly, fine particles of NS can fill ultrafine voids in the microstructure and they illustrate the filling effect [27]. Besides, NS can produce extra C–S–H gel by reacting with Portlandite [5]. Liu et. al noted that the inclusion of NS can accelerates the cement and fly ash hydration at early stage, and the fly ash pozzolanic reaction can increases [28]. Land and Stephan reported that the ordinary Portland cement containing NS considerably increased the heat of hydration in the main period as the NS's surface area increased, and C₃S hydration is accelerated by the addition of NS [29]. Cement used as the main binder of its concrete is known as “Portland cement”. During the production of cement, energy consumption is quite high since high temperatures such as 1400–1500 °C were required. Cement is used extensively in construction operations all over the world, resulting in CO₂ emissions into the atmosphere, which is regarded one of the most serious environmental issues [30]. Portland cement

✉ Hediye Yorulmaz
hediye.yorulmaz@agu.edu.tr

¹ Civil Engineering Department, Abdullah Gül University, 38080 Kayseri, Turkey

² Civil Engineering Department, Erciyes University, 38280 Kayseri, Turkey



clinker (PCC) production in worldwide is responsible for nearly 8% of the total CO₂ emissions released into nature [31–33]. The usage of mineral additives such as FA and natural pozzolan in cementitious systems is an effective way to reduce PCC consumption and consequently reducing CO₂ emission released to nature [9]. FA is an industrial waste from coal consuming thermal power plants. The global generation of coal ash is expected to be approximately 600 million tons per year; FA accounting for 75–80% of the total amount of ash generated. Thus, quantity of FA released to nature is increasing all around the world and it will become a serious environmental problem if not used [34]. It is known that the FA is a by-product material, therefore it is economical compared to Portland cement. Additionally, the usage FA in cementitious systems is economical and more sustainable, when FA replaced with cement, it can increase the durability of the cementitious system. However, with the increase of mineral additives, technical properties such as low early compressive strength and low strength development rates, which are weaker than Portland cement, have limited the use of mineral additives at high rates.

The objective of this research is to overcome the disadvantages of FA such as low early compressive strength in cementitious systems by using NS. For this purpose, 0.25, 0.5, 1.0 and 1.5% NS was added to Portland cement-fly ash systems. The workability, setting time, high temperature resistance, and water absorption capacity of the prepared systems were also examined. NS's effect on hydration of cementitious systems containing FA was investigated using isothermal calorimetry. Limited research has been conducted on cementitious systems containing both high volume and low volume FA modified by the inclusion of NS for enhanced properties. With this study, it is aimed to contribute to the literature. In the future, the negative properties of waste materials can be suppressed with the use of nanoparticles and more sustainable systems can be used.

2 Materials and Methods

2.1 Materials

Normal Portland cement (PC) CEM I 42,5R was used in this research. FA was supplied from Çatalağzı Thermal Power Plant. The total SiO₂ + Al₂O₃ + Fe₂O₃ of chemical compositions of fly ash is more than 70% by mass, and CaO content is lower than 10%, therefore it is classified as low calcium F class FA confirming to ASTM C618 [35]. The pozzolanic activity index of FA used was 66.6% for 3 d, 75.5% for 7 d and 76.6% for 28 d. The density of FA was determined as 2.13 g/cm³. Chemical compositions of FA and NS were presented in Table 1. It is seen that the table that NS has purity more than 99%. Figure 1 presented the XRD pattern of NS.

Based on the Fig. 1, the crystallinity of NS is low and it mainly consists of amorphous phase. Clean and potable tap water from the city water supply system is used in the preparation of cementitious systems. In this study, 0–3 mm natural river sand is used to make the system more economical.

2.2 Mix Proportion

A total of 30 mortar mixes were prepared with the same sand/binder ratio of 3 and the water/binder ratio of 0.55 constant for all samples. Mortar mixtures were prepared with 0, 15, 30, 45, 60 and 75% of cement replacement by FA and 0, 0.25, 0.5, 1.0 and 1.5% of cement replacement by NS particles. Details of the mortar mixture proportions for the binary and ternary systems were presented in Table 2. The control sample (PC) was poured just using Portland cement, while other mixtures were casted by replacing the Portland cement with FA and NS on a mass-for-mass basis.

2.3 Mix Procedure

Nano particles difficult to disperse uniformly since their large surface area. In order to obtain well-disperse of NS, water and NS were mixed together for 3 min in the mixer. Hobart type mixer was used to mix the materials according to TS EN 196-1 [36]. To ensure good compaction, it was cast in 2 layers and a vibrating table was used. The fresh mortars were cast in 50 × 50 × 50 mm of cubic molds. All samples were demolded after 1 day, all specimens were placed into water tank at 21 ± 1 °C until the testing day. Three samples of each mortar type were prepared for each tests. The average values of test were used as the result.

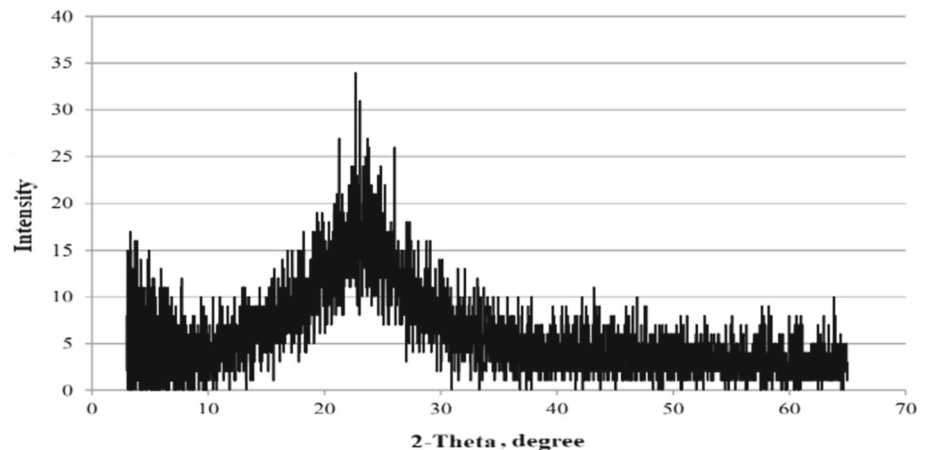
2.4 Testing

2.4.1 Tests Performed on Mortars

The workability of the mortars on a mini flow table was tested for fresh properties in accordance with TS EN 1015-3 [37]. Flow diameter in two directions was measured for each mortar mixture and workability results were determined as the average of these values. Determination of water absorption test were performed on the prepared mortar samples on the 3rd, 28th and 90th days. For each mixture, the water absorption capacity was determined using average of three specimens. In order to observe the strength development, compressive strengths of all mortar mixtures were determined at 1, 3, 7, 28 and 90 days according to TS EN 1015-11 [38]. Samples were heated to very high temperatures of 300 °C and 600 °C, at a rate of 5 °C/min and kept at these temperatures for 60 min in a laboratory furnace to determine the fire resistance of systems. Compressive strength test was

Table 1 Chemical composition of cement, fly ash and NS (%)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	Na ₂ O	K ₂ O	MgO	P ₂ O ₅	TiO ₂	LOI
Cement	17.33	4.82	3.21	60.93	3.28	0.26	0.54	3.80			4.44
Fly ash	55.60	24.04	7.29	2.72	0.57	1.11	2.42	1.55	0.70	1.29	2.50
Nano-SiO ₂	99.49	0.09	0.02	0.12	–	0.03	0.01	–	0.02	0.06	0.10

Fig. 1 XRD of nano-SiO₂

performed after the mortar specimens were cooled to ambient temperature.

2.4.2 Tests Performed on Pastes

Using an automatic Vicat apparatus, setting time of the cementitious pastes were determined. Hydration kinetics of binary and ternary systems were investigated by isothermal calorimetry (TAM Air, TA Instruments). Reaction kinetics studies were performed on selected pastes. For example, 0.5%, 1% and 1.5% NS additions were investigated in samples with FA content less than 50%, 1% and 1.5% NS additions were investigated in samples with FA content of more than 50%. Pastes prepared with water/binder ratio of 0.4. In order to determine the hydration kinetics of the cementitious pastes, cementitious systems were observed at 25 °C degrees for 72 h.

3 Results and Discussion

3.1 Workability

Figure 2 demonstrates the results of flow workability testing. According to Fig. 2, it could be observed that workability of the mortars increases as the increasing percentage of FA replacement with the cement. Compared to the control mixture (PC), 2%, 17%, 19%, 31% and 39% increment in flow values were observed for FA replacement of 15%, 30%, 45%,

60% and 75% by cement, respectively. Higher FA contents resulted in higher workability. It has been determined that this finding valid for all mortar mixtures prepared regardless of whether they contain NS. The fineness of fly ash and spherical grains have positive effects on workability. Besides, as can be seen from Fig. 2, it could be observed that workability decreased as the increasing percentage of NS replacement with the cement. Compared to the control mixture (PC) 1%, 3%, 5%, 12% reduction in flow values were observed due to NS replacement of 0.25%, 0.5%, 1.0% and 1.5% by cement, respectively. Higher NS ratio resulted with lower workability. These results could be caused by the relatively high surface area of the NS. Besides, it might be because the surface area of the powdered materials increases after nanoparticles are added, which requires more water to wet the binder particles [22]. According to the data found, the same workability value as PC could be obtained by adding 1% NS to the sample containing FA30. Additionally, the workability value found by adding 1.5% NS to the sample containing FA45 is comparable to PC.

3.2 Setting Time

Cement paste is plastic at an early age. After a while, hydration reactions continue and setting occurs with the formation of hydration products [39]. The development of setting and strength was enhanced by C–S–H, a hydration product produced from cement grains [40]. Table 3 showed the effect

Table 2 Mix proportions for blended mixes (%)

Blends	Different combination	Specimen	Materials (%)		
			PC	Fly ash	Nano-SiO ₂
Control		PC	100	–	–
Binary blends	PC + NS	NS0.25	99.75	–	0.25
		NS0.5	99.50	–	0.50
		NS1.0	99	–	1.00
		NS1.5	98.50	–	1.50
		FA15	85	15	–
	PC + FA	FA30	70	30	–
		FA45	55	45	–
		FA60	40	60	–
		FA75	25	75	–
		Ternary blends	PC + NS + FA	NS0.25-FA15	84.75
NS0.25-FA30	69.75			30	0.25
NS0.25-FA45	54.75			45	0.25
NS0.25-FA60	39.75			60	0.25
NS0.25-FA75	24.75			75	0.25
NS0.5-FA15	84.50			15	0.50
NS0.5-FA30	69.50			30	0.50
NS0.5-FA45	54.50			45	0.50
NS0.5-FA60	39.50			60	0.50
NS0.5-FA75	24.50			75	0.50
NS1.0-FA15	84			15	1.00
NS1.0-FA30	69			30	1.00
NS1.0-FA45	54			45	1.00
NS1.0-FA60	39			60	1.00
NS1.0-FA75	24			75	1.00
NS1.5-FA15	83.50	15	1.50		
NS1.5-FA30	68.50	30	1.50		
NS1.5-FA45	53.50	45	1.50		
NS1.5-FA60	38.50	60	1.50		
NS1.5-FA75	23.50	75	1.50		

Fig. 2 Flow of fresh mortars

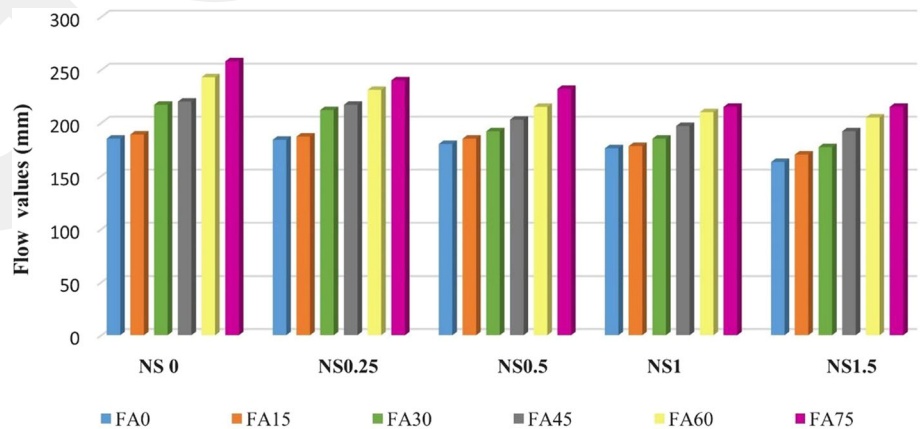


Table 3 Setting time of blended pastes

Mixture notation	Initial setting time (min)	Final setting time (min)
PC	170	290
FA15	180	360
FA30	190	370
FA45	190	380
FA60	190	400
FA75	220	460
NS0.25	160	260
NS0.25-FA15	170	280
NS0.25-FA30	170	300
NS0.25-FA45	170	320
NS0.25-FA60	180	370
NS0.25-FA75	190	420
NS0.5	140	230
NS0.5-FA15	160	250
NS0.5-FA30	160	290
NS0.5-FA45	160	310
NS0.5-FA60	170	360
NS0.5-FA75	180	380
NS1	110	210
NS1-FA15	120	220
NS1-FA30	130	250
NS1-FA45	150	280
NS1-FA60	150	290
NS1-FA75	170	360
NS1.5	100	180
NS1.5-FA15	110	210
NS1.5-FA30	120	220
NS1.5-FA45	140	250
NS1.5-FA60	140	270
NS1.5-FA75	160	330

of NS on the initial and final setting times of the cementitious system containing FA. Generally, results showed that as FA was added to the cementitious system, setting times were increased. The effect of FA on the setting time depends on the properties of the FA and the used amount. In the literature, it has been determined by many researchers that the use of FA can delay setting times. For instance, Huang et al. and Duràn-Herrera et al. noted that the replacement of FA with cement increased the setting time of cementitious materials [41, 42]. The addition of the NS resulted in significant reduction in the initial and final setting periods for all cementitious systems, as shown in Table 3. As 0.25%, 0.5%, 1.0% and 1.5% NS were added to the system, the initial setting time was reduced by 10 min, 30 min, 60 min and 70 min, respectively, when

compared to the control mixture. In terms of final setting time, compared to the control sample 30 min, 60 min, 80 min and 110 min decrement were found for NS replacement of 0.25%, 0.5%, 1.0% and 1.5% by cement, respectively. According to these findings, the inclusion of NS has a greater effect on the final setting time. Moreover, it could be said that as the quantity of NS in the system increases, the initial and final setting times decrease.

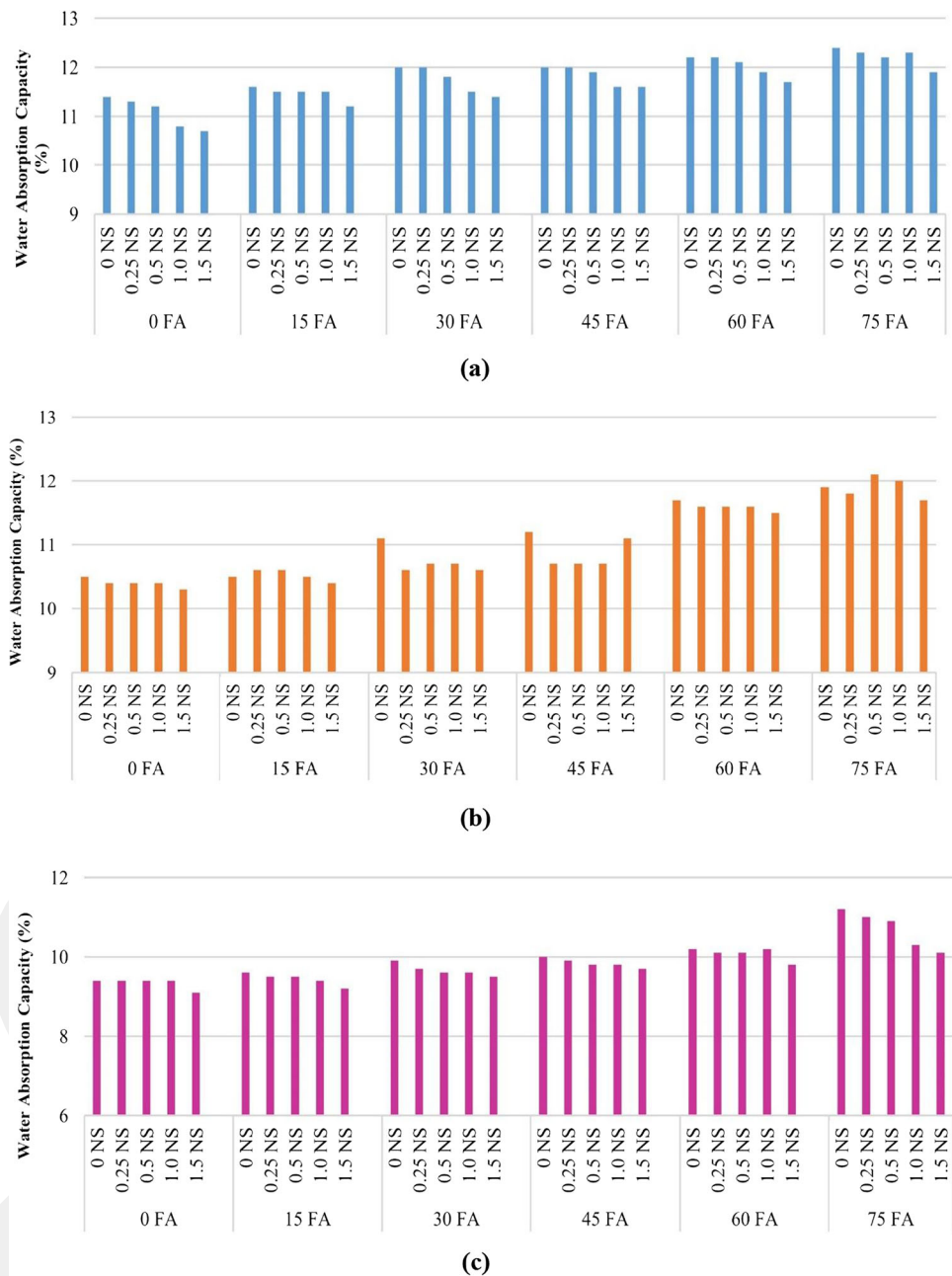
On the one hand, the initial setting time was comparable to PC when 0.25% NS was added to the sample containing FA45, 0.5% NS to the sample containing FA60 and 1% NS to the sample containing FA75. On the other hand, when 0.5% NS was added to the sample containing FA30 and 1% NS was added to the specimen containing FA60, it was observed that the setting time was comparable to PC. Thus, it has been seen that the problem of setting time in systems containing high volumes of FA can be overcome by adding NS in very small amounts. The reason for the reduction in setting time with the use of nanoparticles is the acceleration of the hydration of tricalcium silicate and dicalcium silicate and, consequently, the acceleration of C–S–H gel formation [43].

3.3 Water Absorption Capacity Results

Water absorption of binary and ternary cementitious systems at 3, 28 and 90 days were presented in Fig. 3. It indicates that the water absorption of mortars was slightly increased by adding FA. Karahan and Atiş reported that water absorption values increased with increase of FA content in the system [44].

While the water absorption ratio was found as 11.4% in the control sample cured for 3 days in water, this ratio was found as 9.4% in the samples cured for 90 days. As curing time increases, water absorption capacity was decreased. The addition of 0.25%, 0.5%, 1% and 1.5% NS to without FA samples cured for 3 days, decreased the water absorption ratio by approximately 1%, 2%, 5%, 6% respectively. In general NS amount increased, the water absorption rate decreased slightly. NS is considerably small particle and due to its size, it can fill the voids in the mortar and may have reduced the water absorption. Figure 3 also shows that 0.25%, 0.5%, and 1% NS additives had almost no effect on the water absorption capacity of the 90 days cured Portland cement samples compared to the control sample. Inclusion of 1.5% NS reduced the water absorption capacity of Portland cement by approximately 3% at 90 days. On the other hand, when 0.25, 0.5, 1 and 1.5% NS is added to the samples containing 75% FA, the water absorption rates of the systems at the 90th day are decreased approximately 2, 3, 8 and 10% compared to the sample containing only 75% FA. The reason why NS has a greater effect at later ages in systems containing high volume fly ash may be that NS fills the larger voids in the

Fig. 3 Water absorption capacity of mortars for different days
a 3 d, **b** 28 d, **c** 90 d



system compared to Portland cement, both with its filling effect and with the production of extra C–S–H.

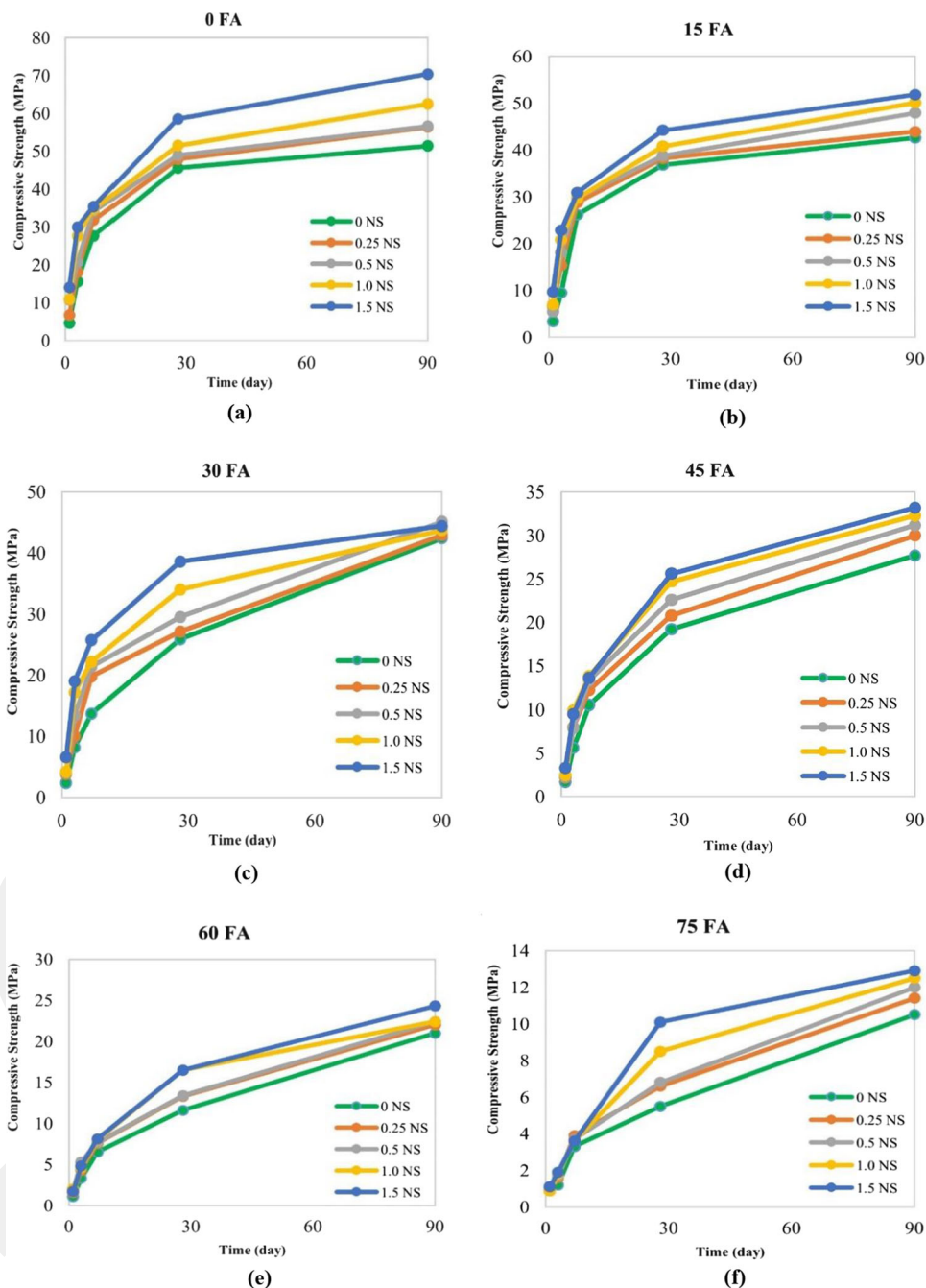
3.4 Development of Compressive Strength

Figure 4 demonstrated the relationship between the addition of NS and the compressive strength of cement systems containing different ratio of FA at 1, 3, 7, 28 and 90 days. Regardless of whether or not the mortar contains FA, the results show that adding NS increases the compressive strength significantly. Generally, it can be said that the compressive strength for all dosages of the addition of NS has

higher strength values than the reference cementitious mortars. It can be stated that the inclusion of NS contributes to the pozzolanic reaction and helps the improvement of compressive strength of the samples. The reason for increment in the strength of the systems formed by the inclusion of NS can be that NS decreases the amount of crystalline $\text{Ca}(\text{OH})_2$ particularly at early ages and accelerates the formation of C–S–H gel [45]. On the basis of the mechanisms underlying the NS addition to increase the compressive strength of the system, there are both the nano-filling effect due to the very small particle size of NS and the pozzolanic reaction [46].



Fig. 4 Effects of NS on the compressive strength development of cementitious mortars. **a** Without FA, **b** With 15% FA, **c** With 30% FA, **d** With 45% FA, **e** With 60% FA, **f** With 75% FA



While one-day compressive strength value of the reference sample produced only with PC was 4.6 MPa, when 1.5% NS was added to the system than corresponding compressive strength increased to 14 MPa. It implies that the mortar containing just 1.5% NS, it greatly contributes to the development of compressive strength, particularly at early age. Specimens cured for 3 days, compressive strength of the sample containing 1.5% NS was 30 MPa while Portland cement mortar developed 15.6 MPa. It indicates that the incorporation of NS is significantly improved the early age strength of the system. The reason for the high increment in

the compressive strength of cementitious mortars may be the rapid consumption of Portlandite, especially at early ages, due to the high reactivity of NS [22]. For 90 days, the mortar made with 1.5%NS showed 70.4 MPa compressive strength while Portland cement mortar had 51.4 MPa. As a result, the addition of NS not only contributes to the early strength but also the long term strength. Inclusion of NS can improve the nucleation of $\text{Ca}(\text{OH})_2$ [25], therefore it can improve development of compressive strength.

On the other hand, with FA replaced with of 15%, 30%, 45%, 60% and 75% by cement and cured for 1 d, the compressive strength values decreased 26%, 48%, 63%, 76% and 78%, respectively. The lowest compressive strength was obtained from the 75% FA mortar at all ages. Generally, it can be stated that the compressive strength of the cementitious samples was reduced by increasing the quantity of FA. Lower compressive strengths were obtained by replacing more cement with FA. When ordinary Portland cement is replaced with a high volume of FA, all FA components cannot be activated by $\text{Ca}(\text{OH})_2$ and many FA particles cannot react to start a pozzolanic reaction. As a result, the matrix becomes more porous overall and its compressive strength decreases [47].

However, the inclusion of NS resulted in improvement in the compressive strength of the samples. Besides, NS increased the early age compressive strength of the samples by accelerating the hydration process. For instance, Portland cement mortar had 4.6 MPa for 1 day, mortar with 30% FA incorporating 0.5% NS had 4.0 MPa. These values were close to each other. For 3 days cured specimens, 1% NS incorporation the 30% FA mortar had 17.2 MPa, while PC had 15.6 MPa. If early strength development was required both NS and by-product FA could be used together. By using fly ash in the system causes lower CO_2 emissions release to the nature and contributes the sustainability. Besides, its contribution to the early strength, NS also has a very positive impact on the long term strength. For example, with the addition of 1.5% NS to Portland cement, 37% increment in strength was observed in the specimens that were cured 90 days compared to the control sample. With the inclusion of 1.5% NS to the samples containing 15% FA, which were cured for 90 d, a 22% increment in compressive strength was observed compared to the specimens without NS addition.

3.5 High Temperature Resistance

The produced samples were exposed to elevated temperature of 300 and 600 °C for certain duration. The average high temperature resistance test results for mortars including FA and NS for 90 days cured in water, exposed to 300 °C and 600 °C high temperature were shown in Fig. 5. The compressive strengths of the specimens on the 90th day were taken as reference. After exposure to 300 °C, samples with FA contents of 15, 45, 60% and containing 1% and 1.5% NS showed increment in compressive strength. For instance, mortars containing 60% FA and adding 1% and 1.5% NS increased compressive strength by 23% and 30%, respectively, after exposure to 300 °C. Besides, the highest fire resistance observed in the 60% FA sample containing 1.5% NS. Exposure of mortar samples to high temperatures, increases the reaction of NS in some mixtures, resulting in the formation of extra C–S–H and consequently increased

strength [48]. Besides, the reason for this increase might be due to the compatibility of the amount of FA and NS added to the system. Pozzolanic effect of FA and NS were also a positive factor.

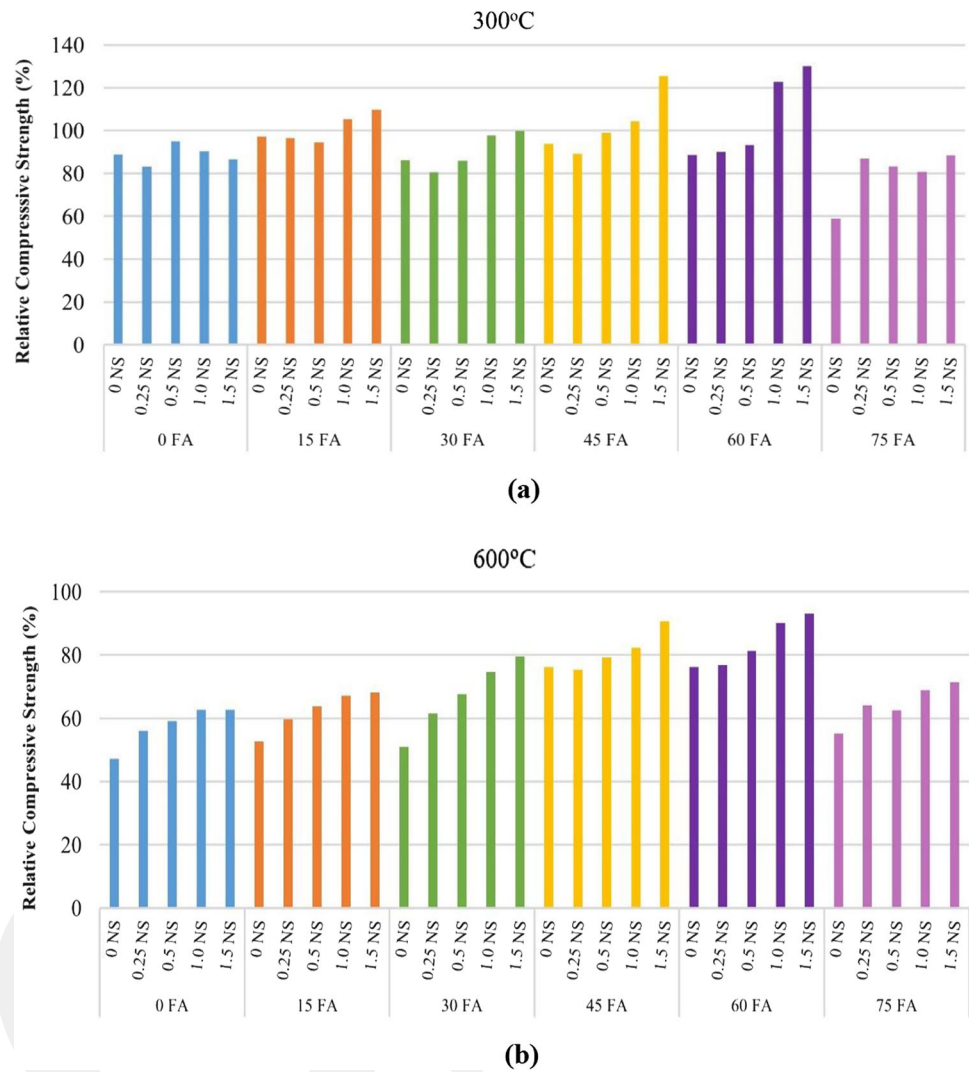
On the other hand, samples exhibited different behavior in high temperature resistance strength at 600 °C. The compressive strength of all samples was dramatically reduced when exposed to 600 °C. With the addition of both 45% and 60% FA, the residual strength after exposing to elevated temperature was more positively affected than others. Generally, the highest decrease occurred in mortar prepared with just PC and FA. It was clearly seen that the use of NS increases the resistance to high temperatures. Furthermore, it has been observed that very high temperatures have detrimental effect on compressive strength. Additionally, when the binder products in the cementitious paste were exposed to such high temperatures, they can dehydrate and cause a decrease in strength [48]. However, samples including NS showed a higher resistance to fire after exposure to 600 °C, the compressive strength of samples containing 1.5% NS and 60% FA is almost comparable to the compressive strength before high temperature application, probably due to the filling effect of NS and the higher C–S–H content of samples containing NS.

3.6 Hydration Kinetics

The quantity of heat generated during setting and hardening is known as hydration heat [21]. Figure 6 showed the effects of various doses of both NS and FA on the reaction rate and corresponding cumulative heat of reaction curves of cementitious pastes within 72 h. The data based on Fig. 6 show that, in general, the height of the rate peaks increased with the addition of NS, i.e. maximum rate of hydration increased. The reason for the increment in maximum hydration rate with increasing NS content is that NS has very high surface area and great activity. As a result of these properties, it can provide many nucleating site, which means that NS can activate both cement and FA [18]. The nucleation effect is one of the common mechanisms for growth the hydration of PC with the fine additives [49]. It was found that the hydration rate increased as the addition dose increased up to 1.5%, indicating that NS can support the hydration process of PC.

According to Fig. 6, maximum hydration heat increased with the increase of NS ratio in the cementitious paste. The 1st peak of the heat of hydration indicates C_3S hydration and formation of C–S–H phase and $\text{Ca}(\text{OH})_2$. With the inclusion of NS, the hydration rate of C_3S also increases [29]. Furthermore, according to the literature, it has been observed that the surfaces of NS are highly reactive and their high surface areas lead to the acceleration of hydration reactions of C_3S [50]. Generally, it is seen that the addition of nanoparticles during the first 17 h accelerates the cement hydration. Besides,

Fig. 5 a Relative compressive strength for samples exposed to 300 °C, **b** Relative compressive strength for samples exposed to 600 °C



1st and 2nd peaks of the binary and ternary pastes shifted to left as a result of the addition of NS. Furthermore, the size of the 2nd peak of the fly ash cement pastes containing NS increased. Consequently, it was observed that the hydration of the cementitious system accelerated with the increase of NS content up to 1.5%. The higher the addition dose, the higher the hydration rate was within testing period of 72 h, indicating that NS can support the hydration process of PC. From cumulative rate of hydration curves, as FA addition increased, cumulative heat of hydration decreases gradually due to dilution of PC content. When NS particles were added to cementitious materials, even in very small dosages, they both consume Ca(OH)₂ and act as nucleation sites, thus it can improve the hydration process [51].

4 Conclusions

The following conclusion can be made from the results:

1. Workability of mortar increased by increasing replacement of FA with cement. However, the inclusion of nano-SiO₂ has reduced the workability of the system due to their high surface area.
2. As the amount of FA increased in mixture, setting time of the system was increased, and as the amount of NS increased; setting time of the system was decreased. This was attributed to the NS’s high surface area.
3. In general, as the amount of FA increases, the water absorption rate increases slightly, while as the amount of NS increases, the water absorption rate decreases slightly.
4. The compressive strength decreased with increment amount of FA and while the compressive strength increased with increasing amount of NS. This situation was clearly observed from the samples cured at 1 d and 3 d. From these results, it was seen that the low early strength of FA, could be compensated by the using NS.
5. As the NS content of the cement paste increases, the reaction rate reaches its maximum speed earlier. From the

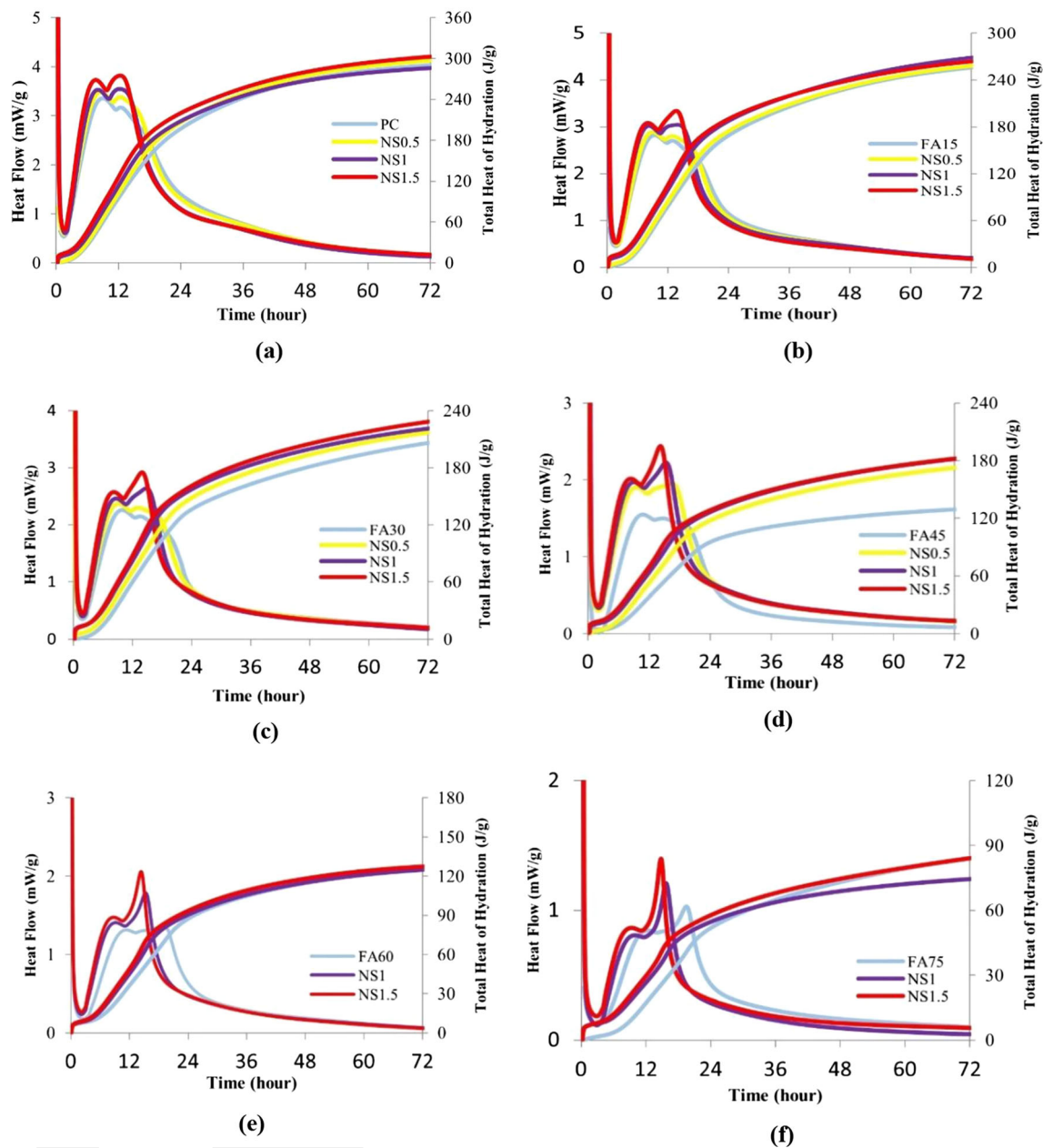


Fig. 6 Effects of NS on the rate of hydration curves of pastes and cumulative heat of hydration of pastes. **a** without FA, **b** containing 15% FA, **c** containing 30% FA, **d** containing 45% FA, **e** containing 60% FA, **f** containing 75% FA

isothermal calorimetry test results, increment in the used dosage of NS provided peak formation earlier than NS-free samples. Addition of NS accelerate rate of hydration in all samples for the first 17 h. After that, it is generally seen that not containing NS samples exhibit a higher rate of hydration than NS-containing samples, and then all samples are continue at approximately the same rate. NS supports the duration of hydration. Rate of hydration decreased as FA ratio increased in all mixtures. In general, as the amount of FA used in cement paste increased, the total heat of hydration decreased.

- From an economic point of view, it has been noted that the cost is much higher to achieve similar compressive strength with PC. However, it is thought that in the coming years, with the increase in the demand for nanotechnology, more nanomaterials will be produced and thus the price of nanomaterials will decrease.
- In our world, where sustainability is gaining more importance every year, it is expected that the use of PC will be restricted due to its high carbon footprint, and thus more

mineral additives will be preferred. The use of nanoparticles can be an effective option to compensate the negative effects of using mineral additives such as fly ash.

Acknowledgements The authors would like to thank H. İlcan for his assistance with the tests and preparing mortars.

Declarations

Conflict of interest The authors declare that there is no conflict of interest.

References

- Patil, M.P.; Do Kim, G.: Marine microorganisms for synthesis of metallic nanoparticles and their biomedical applications. *Colloids Surf. B Biointerfaces* **172**(September), 487–495 (2018). <https://doi.org/10.1016/j.colsurfb.2018.09.007>
- Li, L.G.; Zhu, J.; Huang, Z.H.; Kwan, A.K.H.; Li, L.J.: Combined effects of micro-silica and nano-silica on durability of mortar. *Constr. Build. Mater.* **157**, 337–347 (2017). <https://doi.org/10.1016/j.conbuildmat.2017.09.105>
- Raheem, A.A.; Abdulwahab, R.; Kareem, M.A.: Incorporation of metakaolin and nanosilica in blended cement mortar and concrete—a review. *J. Clean. Prod.* **290**, 125852 (2021). <https://doi.org/10.1016/j.jclepro.2021.125852>
- Oltulu, M.; Şahin, R.: Effect of nano-SiO₂, nano-Al₂O₃ and nano-Fe₂O₃ powders on compressive strengths and capillary water absorption of cement mortar containing fly ash: a comparative study. *Energy Build.* **58**, 292–301 (2013). <https://doi.org/10.1016/j.enbuild.2012.12.014>
- Singh, L.P.; Karade, S.R.; Bhattacharyya, S.K.; Yousuf, M.M.; Ahalawat, S.: Beneficial role of nanosilica in cement based materials—a review. *Constr. Build. Mater.* (2013). <https://doi.org/10.1016/j.conbuildmat.2013.05.052>
- Fu, Q.; Zhao, X.; Zhang, Z.; Xu, W.; Niu, D.: Effects of nanosilica on microstructure and durability of cement-based materials. *Powder Technol.* **404**, 117447 (2022). <https://doi.org/10.1016/j.powtec.2022.117447>
- Lee, B.Y.; Kurtis, K.E.: Influence of TiO₂ nanoparticles on early C₃S hydration. *J. Am. Ceram. Soc.* **93**(10), 3399–3405 (2010). <https://doi.org/10.1111/j.1551-2916.2010.03868.x>
- Stefanidou, M.; Papayianni, I.: Influence of nano-SiO₂ on the Portland cement pastes. *Compos. Part B Eng.* **43**(6), 2706–2710 (2012). <https://doi.org/10.1016/j.compositesb.2011.12.015>
- Berra, M.; Carassiti, F.; Mangialardi, T.; Paolini, A.E.; Sebastiani, M.: Effects of nanosilica addition on workability and compressive strength of Portland cement pastes. *Constr. Build. Mater.* **35**, 666–675 (2012). <https://doi.org/10.1016/j.conbuildmat.2012.04.132>
- Senff, L.; Labrincha, J.A.; Ferreira, V.M.; Hotza, D.; Repette, W.L.: Effect of nano-silica on rheology and fresh properties of cement pastes and mortars. *Constr. Build. Mater.* **23**(7), 2487–2491 (2009). <https://doi.org/10.1016/j.conbuildmat.2009.02.005>
- Lang, L.; Liu, N.; Chen, B.: Strength development of solidified dredged sludge containing humic acid with cement, lime and nano-SiO₂. *Constr. Build. Mater.* **230**, 116971 (2020). <https://doi.org/10.1016/j.conbuildmat.2019.116971>
- Yang, Z., et al.: Improving the chloride binding capacity of cement paste by adding nano-Al₂O₃: the cases of blended cement pastes. *Constr. Build. Mater.* **232**, 117219 (2020). <https://doi.org/10.1016/j.conbuildmat.2019.117219>
- Jia, Z.M.; Zhao, Y.R.; Shi, J.N.: Adsorption kinetics of the photocatalytic reaction of nano-TiO₂ cement-based materials: a review. *Constr. Build. Mater.* **370**(January), 130462 (2023). <https://doi.org/10.1016/j.conbuildmat.2023.130462>
- Gamal, H.A.; El-Feky, M.S.; Alharbi, Y.R.; Abadel, A.A.; Kohail, M.: Enhancement of the concrete durability with hybrid nano materials. *Sustainability* **13**(3), 1–17 (2021). <https://doi.org/10.3390/su13031373>
- Abhilash, P.P.; Nayak, D.K.; Sangoju, B.; Kumar, R.; Kumar, V.: Effect of nano-silica in concrete; a review. *Constr. Build. Mater.* **278**, 122347 (2021). <https://doi.org/10.1016/j.conbuildmat.2021.122347>
- Wang, D.; Li, J.; Zhang, L.; Jiang, C.; Yang, P.; Cheng, X.: Synthesis and effect of highly active nano-SiO₂ on ion/water transmission property of cement-based materials. *J. Build. Eng.* **59**(August), 105054 (2022). <https://doi.org/10.1016/j.job.2022.105054>
- Ji, T.: Preliminary study on the water permeability and microstructure of concrete incorporating nano-SiO₂. *Cem. Concr. Res.* **35**(10), 1943–1947 (2005). <https://doi.org/10.1016/j.cemconres.2005.07.004>
- Li, G.: Properties of high-volume fly ash concrete incorporating nano-SiO₂. *Cem. Concr. Res.* (2004). <https://doi.org/10.1016/j.cemconres.2003.11.013>
- Brzozowski, P.; Strzałkowski, J.; Rychtowski, P.; Wróbel, R.; Tryba, B.; Horszczaruk, E.: Effect of nano-SiO₂ on the microstructure and mechanical properties of concrete under high temperature conditions. *Materials* (2022). <https://doi.org/10.3390/ma15010166>
- Prasad Bhatta, D.; Singla, S.; Garg, R.: Microstructural and strength parameters of Nano-SiO₂ based cement composites. *Mater. Today Proc.* **46**, 6743–6747 (2020). <https://doi.org/10.1016/j.matpr.2021.04.276>
- Jo, B.W.; Kim, C.H.; Tae, G.H.; Bin Park, J.: Characteristics of cement mortar with nano-SiO₂ particles. *Constr. Build. Mater.* **21**(6), 1351–1355 (2007). <https://doi.org/10.1016/j.conbuildmat.2005.12.020>
- Najjigivi, A.; Khaloo, A.; Iraj Zad, A.; Abdul Rashid, S.: Investigating the effects of using different types of SiO₂ nanoparticles on the mechanical properties of binary blended concrete. *Compos. Part B Eng.* **54**(1), 52–58 (2013). <https://doi.org/10.1016/j.compositesb.2013.04.035>
- Gaitero, J.J.; Campillo, I.; Guerrero, A.: Reduction of the calcium leaching rate of cement paste by addition of silica nanoparticles. *Cem. Concr. Res.* **38**(8–9), 1112–1118 (2008). <https://doi.org/10.1016/j.cemconres.2008.03.021>
- Huang, Q., et al.: Long-term performance and microstructural characteristics of cement mortars containing nano-SiO₂ exposed to sodium sulfate attack. *Constr. Build. Mater.* **364**(November 2022), 130011 (2023). <https://doi.org/10.1016/j.conbuildmat.2022.130011>
- Lin, D.F.; Lin, K.L.; Chang, W.C.; Luo, H.L.; Cai, M.Q.: Improvements of nano-SiO₂ on sludge/fly ash mortar. *Waste Manag.* (2008). <https://doi.org/10.1016/j.wasman.2007.03.023>
- Liu, H.; Li, Q.; Ni, S.; Wang, L.; Yue, G.; Guo, Y.: Effect of nano-silica dispersed at different temperatures on the properties of cement-based materials. *J. Build. Eng.* **46**(November 2021), 103750 (2022). <https://doi.org/10.1016/j.job.2021.103750>
- Kooshafar, M.; Madani, H.: An investigation on the influence of nano silica morphology on the characteristics of cement composites. *J. Build. Eng.* **30**(January), 101293 (2020). <https://doi.org/10.1016/j.job.2020.101293>
- Liu, M.; Tan, H.; He, X.: Effects of nano-SiO₂ on early strength and microstructure of steam-cured high volume fly ash cement system. *Constr. Build. Mater.* **194**, 350–359 (2019). <https://doi.org/10.1016/j.conbuildmat.2018.10.214>



29. Land, G.; Stephan, D.: “The influence of nano-silica on the hydration of ordinary Portland cement. *J. Mater. Sci.* **47**(2), 1011–1017 (2012). <https://doi.org/10.1007/s10853-011-5881-1>
30. Karahan, O.: Transport properties of high volume fly ash or slag concrete exposed to high temperature. *Constr. Build. Mater.* **152**, 898–906 (2017). <https://doi.org/10.1016/j.conbuildmat.2017.07.051>
31. Uzal, B.; Turanlı, L.: Studies on blended cements containing a high volume of natural pozzolans. *Cem. Concr. Res.* **33**(11), 1777–1781 (2003). [https://doi.org/10.1016/S0008-8846\(03\)00173-X](https://doi.org/10.1016/S0008-8846(03)00173-X)
32. Durak, U.; Karahan, O.; Uzal, B.; İlkentapar, S.; Atiş, C.D.: Influence of nano SiO₂ and nano CaCO₃ particles on strength, workability, and microstructural properties of fly ash-based geopolymer. *Struct. Concr.* **22**(S1), E352–E367 (2021). <https://doi.org/10.1002/suco.201900479>
33. Atiş, C.D.; Görür, E.B.; Karahan, O.; Bilim, C.; İlkentapar, S.; Luga, E.: Very high strength (120 MPa) class F fly ash geopolymer mortar activated at different NaOH amount, heat curing temperature and heat curing duration. *Constr. Build. Mater.* **96**, 673–678 (2015). <https://doi.org/10.1016/j.conbuildmat.2015.08.089>
34. Ahmaruzzaman, M.: A review on the utilization of fly ash. *Prog. Energy Combust. Sci.* **36**(3), 327–363 (2010). <https://doi.org/10.1016/j.peccs.2009.11.003>
35. ASTM C618: Standard specification for coal fly ash and raw or calcined natural Pozzolan for use in concrete. Merican Society for Testing and Material (2014)
36. TS EN 196-1. Methods of testing cement—part:1 determination of strength. TSE, Ankara, Turkey (2016)
37. TS EN 1015-3. Methods of test for mortar for masonry: Part 3. Determination of consistence of fresh mortar (by flow table). TSE, Ankara (2000)
38. TS EN 1015-11. Methods of test for mortar for masonry- Part 11: Determination of flexural and compressive strength of hardened mortar. TSE, Ankara (2020)
39. Camiletti, J.; Soliman, A.M.; Nehdi, M.L.: Effects of nano- and micro-limestone addition on early-age properties of ultra-high-performance concrete. *Mater. Struct. Constr.* **46**(6), 881–898 (2013). <https://doi.org/10.1617/s11527-012-9940-0>
40. Stark, J.: Recent advances in the field of cement hydration and microstructure analysis. *Cem. Concr. Res.* **41**(7), 666–678 (2011). <https://doi.org/10.1016/j.cemconres.2011.03.028>
41. Huang, C.H.; Lin, S.K.; Chang, C.S.; Chen, H.J.: Mix proportions and mechanical properties of concrete containing very high-volume of Class F fly ash. *Constr. Build. Mater.* **46**, 71–78 (2013). <https://doi.org/10.1016/j.conbuildmat.2013.04.016>
42. Durán-Herrera, A.; Juárez, C.A.; Valdez, P.; Bentz, D.P.: Evaluation of sustainable high-volume fly ash concretes. *Cem. Concr. Compos.* **33**(1), 39–45 (2011). <https://doi.org/10.1016/j.cemconcomp.2010.09.020>
43. Zhuang, C.; Chen, Y.: The effect of nano-SiO₂ on concrete properties: a review. *Nanotechnol. Rev.* **8**(1), 562–572 (2019). <https://doi.org/10.1515/ntrev-2019-0050>
44. Karahan, O.; Atiş, C.D.: The durability properties of polypropylene fiber reinforced fly ash concrete. *Mater. Des.* **32**(2), 1044–1049 (2011). <https://doi.org/10.1016/j.matdes.2010.07.011>
45. Liu, J.; Li, Q.; Xu, S.: Influence of nanoparticles on fluidity and mechanical properties of cement mortar. *Constr. Build. Mater.* **101**, 892–901 (2015). <https://doi.org/10.1016/j.conbuildmat.2015.10.149>
46. Du, H.; Du, S.; Liu, X.: Durability performances of concrete with nano-silica. *Constr. Build. Mater.* **73**, 705–712 (2014). <https://doi.org/10.1016/j.conbuildmat.2014.10.014>
47. Alharbi, Y.R.; Abadel, A.A.: Engineering properties of high-volume fly ash modified cement incorporated with bottle glass waste nanoparticles. *Sustainability* (2022). <https://doi.org/10.3390/su141912459>
48. Ibrahim, R.K.; Hamid, R.; Taha, M.R.: Fire resistance of high-volume fly ash mortars with nanosilica addition. *Constr. Build. Mater.* **36**, 779–786 (2012). <https://doi.org/10.1016/j.conbuildmat.2012.05.028>
49. Argın, G.; Uzal, B.: Enhancement of pozzolanic activity of calcined clays by limestone powder addition. *Constr. Build. Mater.* **284**, 9–14 (2021). <https://doi.org/10.1016/j.conbuildmat.2021.122789>
50. Sanchez, F.; Sobolev, K.: Nanotechnology in concrete—a review. *Constr. Build. Mater.* **24**(11), 2060–2071 (2010). <https://doi.org/10.1016/j.conbuildmat.2010.03.014>
51. Rong, Z.; Sun, W.; Xiao, H.; Jiang, G.: Effects of nano-SiO₂ particles on the mechanical and microstructural properties of ultra-high performance cementitious composites. *Cem. Concr. Compos.* **56**, 25–31 (2015). <https://doi.org/10.1016/j.cemconcomp.2014.11.001>

Springer Nature or its licensor (e.g. a society or other partner) holds exclusive rights to this article under a publishing agreement with the author(s) or other rightsholder(s); author self-archiving of the accepted manuscript version of this article is solely governed by the terms of such publishing agreement and applicable law.

