Influence of functionalized nanosilica with different functional groups in the properties of cementitious composites: A review

Influência da nanossílica funcionalizada com diferentes grupos funcionais nas propriedades de compósitos cimentícios: Uma revisão

Influencia de la nanosílice funcionalizada con diferentes grupos funcionales en las propiedades de los composites cementosos: Una revisión

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Abstract
The use of supplementary nano cementitious material (SNCM) to improve the mechanical properties and durability performances of cementitious composites (cement paste, mortar and concrete) has received remarkable attention in recent studies. The use of nanosilica as SNCM is a consolidated practice in the scientific community. However, recent developments in the synthesis of monodisperse and narrow-size distribution of nanoparticles by functionalization methods provide a significant improvement to the development of silica-group nano composites (among the functional groups: amine, carboxyls and glycol groups), the so-called functionalized nanosilica (FNS). This article aims to raise a literature review on the properties of FNS in cementitious materials and the advanced techniques of nano/micro structural analysis used to characterize cementitious composites containing FNS’s.
Keywords: Cementitious composites; Functional groups; Supplementary nano cementitious material; Functionalized nanosilica.

Resumo
O uso de nanomaterial cimentício suplementar (NMCS) para melhorar as propriedades mecânicas e de durabilidade de compósitos cimentícios (pasta de cimento, argamassa e concreto) tem recebido atenção notável em estudos recentes. O uso da nanossílica como NMCS é uma prática consolidada na comunidade científica. No entanto, desenvolvimentos recentes na síntese de distribuição monodispersa e de tamanho estreito de nanopartículas por métodos de funcionalização fornecem uma melhoria significativa para o desenvolvimento de nano compósitos do grupo de sílica (entre os grupos funcionais: amina, carboxilas e grupos glicol), as chamadas nanossílicas funcionalizadas (NSF). Este artigo tem como objetivo levantar uma revisão da literatura sobre as propriedades de NSF em materiais cimentícios e as técnicas avançadas de análise nano/microestrutural utilizadas para caracterizar compósitos cimentícios contendo NSF.
Palavras-chave: Compósitos cimentícios; Grupos funcionais; Nanomaterial cimentício suplementar; Nanossílica funcionalizada.

Resumen
El uso de material nanocementoso suplementario (SNCM) para mejorar las propiedades mecánicas y la durabilidad de los compuestos cementosos (pasta de cemento, mortero y hormigón) ha recibido una atención notable en estudios recientes. El uso de nanosílice como SNCM es una práctica común en la comunidad científica. Sin embargo, los desarrollos recientes en la síntesis de nanopartículas mono-dispersas y de distribución de tamaño estrecho mediante métodos de funcionalización proporcionan una mejora significativa para el desarrollo de nanocompuestos del grupo de sílice (entre los grupos funcionales: amina, carboxilos y grupos de glicol), las llamadas nanosílice funcionalizada (FNS). Este artículo tiene como objetivo realizar una revisión de la literatura sobre las propiedades de FNS en

materiales cementosos y las técnicas avanzadas de análisis nano/microestructural utilizadas para caracterizar compuestos cementosos que contienen FNS.
Palabras clave: Composites cementosos; Grupos funcionales; Material nanocementoso suplementario; Nanosílice funcionalizada.

1. Introduction

Nanotechnology is the understanding and control of matter from a nanoscale perspective. The nanoparticles are, in terms of size, between 1 and 100 nm, reaching the level of molecules and atoms. In general, there are two main ways of applying nanotechnology to cementitious materials: one is the observation and analysis of the basic phenomena of cementitious materials at the nanoscale; the other is the manipulation of the microstructure to develop and improve the properties of materials at the nanoscale using nanoparticles. The incorporation of nanoparticles as supplementary nano cementitious material (SNCM) provides changes in the micro/nanostructure in cementitious composites. Thus, it modifies the physical, chemical, mechanical, and durability properties. Among the nanoparticles used in cementitious materials, carbon nanotubes, titanium dioxide nanoparticles and, mainly, nanosilica (NS) stand out.

The use of nanosilica as supplementary nano cementitious material is a consolidated practice in the scientific community (Fraga et al., 2020; Kontoleontos et al., 2012; Senff et al., 2010; Varghese et al., 2019; Xu et al., 2003). Due to their size (nanoscale) and their wide composition of silica in the amorphous state, the nanosilica particles have a high specific surface with an abundant presence of reactive siliceous groups (the silanol groups). These groups, in an adequate reaction conditions, provide an intense pozzolanic activity and a pore filling effect (Chithra et al., 2016; Nair et al., 2008; Singh et al., 2016).

The synthesis of silica nanoparticles is a field of enormous scientific interest due to its abundant and varied applications. In general, nanomaterials exhibit unique physical properties that are industrially useful; however, in most cases, the challenge is to adjust the surface for the required application.

Despite the great potential to improve the properties of cementitious composites, NS still has imperfections that can be improved. Among them, the following stand out: nanoparticles have a strong tendency to heap together. In order to obtain a better performance of the composite, the nanoparticles need to be dispersed in the matrix. Therefore, a dispersion procedure is necessary for advancement. The most widely used methods for dispersing nanoparticles are processing techniques direct mixing, ultrasonic mixing, and shear mixing (three-roller mill) (Cai et al., 2017; Gu et al., 2018; Gu, Ran, et al., 2017; Kong et al., 2013; Martins et al., 2020; Reches, 2018; Varghese et al., 2019).

In the literature, other methods of dispersion are also reported, such as centrifugation, sedimentation, filtration, among others (Wang et al., 2006). Autogenous shrinkage in cementitious composites with nanosilica is another challenge that has been widely studied in the scientific environment. Autogenous deformation is greater in high performance concrete (HPC) with nanosilica due to the quick development of a fine and porous network within the cement paste, which generates higher capillary action. As the structures have one or more restriction, the risk of cracking in the HPC is greater, especially in the early ages, which may compromise its strength, durability, and aesthetics (Kong et al., 2013); NS surface compatibility with superplasticizer and the like (Gu et al., 2018; Gu, Ran, et al., 2017; Gu, Wei, et al., 2017).

To answer these challenges, some researchers started to promote changes in the NS surface (or NS functionalization) in order to create adaptations according to the need (Azevedo & Gleize, 2018; Collodetti et al., 2014; Gu et al., 2016, 2018; Gu, Ran, et al., 2017; Huang & Wang, 2017; Monasterio et al., 2015; Perez et al., 2015). The functionalization of nanosilica is a chemical process that consists of adding new chemical functions to the NS surface. In the case of nanosilica, this chemical reaction replaces the silanol groups (OH) on the surface of the nanosilica with another function of greater interest; this process is also called silanization.

The aminosilanes are known to have a polarity that allows them to be dispersed in ionic medium (such as Portland cement pastes) more easily than other organic groups, such as the silanol groups present in NS. Therefore, it is an organic function that is among the most used in functionalization/silanization processes for cementitious medium (Collodetti et al., 2014; Gu, Ran, et al., 2017; Khalil et al., 2007). In addition, studies indicate that the functionalization of NS with aminosilanes increases its affinity to connect to other chemical additives such as shrinkage reducing additive (SRA) and polycarboxylate ether superplasticizers (PCE) (Gu et al., 2016, 2018; Gu, Ran, et al., 2017; Gu, Wei, et al., 2017). Besides aminosilanes, other functional groups also were researched, such as SRA, glycol, carboxyl, graphene, and others.

The incorporation of different functionalizing agents results in different properties in cementitious materials. As an innovative theme, the study of the effect of different functionalizing agents is of great importance for the cementitious materials. From the synthesis of this information, new research fields can be opened. Given the above, this research aims to conduct a study of the state of the art of the effects of NS functionalization by different functional groups on cementitious materials.

2. Methodology

The literature review was carried out in a systematic way using the Meta-Analytical Approach Theory Model (Mariano & Rocha Santos, 2017). The Web of Science, Scopus and Google Scholar databases were used. The following descriptors were used: cement, microstructure, shrinkage, nanosilica, modified, functionalized.

From the papers found in the databases, an analysis of the titles and abstracts was performed in order to restrict the papers to the effect of functionalization of the NS on the properties of cementitious composites. With the selected papers, an analysis of the effect of different functional groups on the properties of cementitious composites with functionalized nanosilica (FNS) was performed.

3. Results and Discussion

In Table 1 are shown the nanosilicas with the respective functionalizing agents used for investigating the properties in cementitious materials.

Table 1 - Functionalized nanosilica used in studies with cementitious materials.

Authors	**Functionalized Nanosilica**
(Collodetti et al., 2014)	3-aminopropyl-trimethoxysilane (ANS) and FNS with glycol groups.
(Monasterio et al., 2015)	ANS
(Gu, Ran, et al., 2017)	NS@PCE
(Gu, Wei, et al., 2017)	NS@SRA
(Huang & Wang, 2017)	NS@PCE
(Sun et al., 2017)	NS@PCE
(Gu et al., 2020)	NS@GO (Nano-silica functionalized with graphene oxide)
(Huang et al., 2020)	NS@DADMAC (Nano-silica functionalized with Dimethyl Dialyl Ammonium Chloride)
(Rong et al., 2020)	FNSA
(Feng et al., 2020)	NS@PCE
(Liu et al., 2020)	NS@PCE
(Vasconcellos et al., 2020)	FNSA
(Guo et al., 2020)	NS@KH-550
(Ren et al., 2020)	NS@PCE

Source: Authors (2021).

The effect of FNS on the cementitious matrix depends on several factors such as the functionalizing agent, the content of the functionalizing material grafted into the NS, and the water/cement (w/c) or water/binder (w/b) ratio and the SNCM addition content in the cementitious composite. Table 2 shows the type of cementitious composite, the water/cement ratio, and the degree of the addition of FNS that were used in recent research that investigated the effect of modifications on the surface of NS by means of functionalization processes in cementitious composites.

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Table 2 - Types of cementitious composites, water/cement ratio, and degree of addition of functionalized materials.

Authors	Type of cementitious composite	Water/binder or water/cement (w/b or w/c)	Degree of addition (weight of cement)
(Collodetti et al., 2014)	Paste	0.3 (w/b)	0.1% and 0.5% of NS or FNS with APTMS and GS.
(Monasterio et al., 2015)	Mixture of pure C_3S, Nanoparticles and distilled water	281.6 - excess water (w/C_3S)	2,5 grams of C_3S to 700g of distilled water with and w/o nanoparticles
(Gu, Ran, et al., 2017)	Paste	0.4 (w/b)	0%, 0.3%,1%, 2%, and 3% de NS or NS@PCE
(Gu, Wei, et al., 2017)	Paste	0.3 (w/c)	2% de NS or NS@SRA
(Huang & Wang, 2017)	Paste	0.35 (w/c)	0,6% of NS or NS@PCE
(Sun et al., 2017)	Paste	0.50 (w/b)	0.3% and 0.6% of NS@PCE
(Gu et al., 2020)	Paste	0.4 (w/b)	1.55% de NS@GO; 1.5% de NS; 1.5% of NS with 0.05% of GO; and 0.05% of GO
(Huang et al., 2020)	Paste	0.35 (w/b)	0,3%, 1%, and 3% of NS or NS@DADMAC
(Rong et al., 2020)	Paste	0.2 (w/b)	0.3%, 0.5% and 1.0% of NS (reference) or of ANS
(Feng et al., 2020)	Paste	0.5 (w/c)	0.5%, 1.0%, and 1.5% of NS (reference) or of Nano@PCE
(Liu et al., 2020)	Paste	0.5 (w/c)	1,5% de NS or Nano@PCE
(Vasconcellos et al., 2020)	Paste	0.4 (w/b)	0.3, 0.9, and 2.7 of NS or ANS
(Guo et al., 2020)	Paste	0,16 (w/b)	0.01%, 0.05% and 0.1% of Nanoparticle
(Ren et al., 2020)	Paste	0.29 (w/c)	0.15% of NS/PCE
	Mortar	0.32; 0.33; 0.34; 0.36 e 0.44 (w/c)	0.30% of NS/PCE

Source: Authors.

From Table 2, it can be seen that most of the researches were carried out on Portland cement pastes with low water/cement or water/binder ratios (generally up to 0.50). In addition, in general, the levels of nanosilica used in the studies ranged from 0.3% to 3%, with most studies between 1% and 2% of different functionalizing agents. It also stands out the research carried out to investigated the effect of NS functionalization on C_3S and C_2S (Monasterio et al., 2015).

As the different functionalizing agents are used to improve a certain property of the studied composites, different techniques were used by the authors to evaluate the effect of NS functionalization on the properties of cementitious composites, as can be seen in Table 3.

Table 3 - Techniques used to evaluate the properties of cementitious composites with FNS.

Authors	**Isothermal conduction calorimetry**	**Compressive strength**	**SEM[1]**	**TEM[2]**	**FTIR[3]**	**XRD[4]**	**TGA[5]**	**MIP[6]**	**NMR[7]**	**XPS[8]**	**Autogenous shrinkage**	**XN-1 Microscopy**	**Fluidity test**	**Flexural strength**	**Nanoindentation**	**Electrical resistivity**
(Collodetti et al., 2014)	X											X				
(Monasterio et al., 2015)					X	X	X		X	X						
(Gu, Ran, et al., 2017)	X	X	X			X										
(Gu, Wei, et al., 2017)		X									X					
(Huang & Wang, 2017)													X			
(Sun et al., 2017)	X	X			X	X	X	X								
(Gu et al., 2020)		X	X											X		
(Huang et al., 2020)	X															
(Rong et al., 2020)	X	X	X			X										
(Feng et al., 2020)	X		X				X	X								
(Liu et al., 2020)	X		X			X	X	X							X	
(Vasconcellos et al., 2020)	X	X		X				X								
(Guo et al., 2020)		x	x				x	x					x	x		x
(Ren et al., 2020)		x	x			x	x						x	x		

[1]SEM: Scanning electron microscopy;
[2]TEM: Transmission electron microscopy
[3]FTIR: Fourier Transform Infrared;
[4]XRD: X-ray diffraction;
[5]TGA: Thermogravimetric analysis;
[6]MIP: Mercury intrusion porosimetry;
[7]NMR: Nuclear Magnetic Resonance;
[8]XPS: X-ray photoelectron spectroscopy.

Source: Authors.

Among the techniques used to evaluate the properties of FNS cement pastes, it is observed that the most performed test was the isothermal conduction calorimeter method. This reveals that the functionalized nanosilica mainly influences the hydration kinetics of cementitious composites. Table 4 shows a summary of the main results of recent studies involving isothermal conduction calorimetry.

Table 4 - Synthesis of the main results of isothermal conduction calorimeter method in cementitious composites.

Authors	**Main comments**
(Collodetti et al., 2014)	The authors noted that the FNS showed a significant change in the inactive period of the Portland cement pastes for the two types of siloxane used. The hydration time of the cement particles, which affects the application time of the concrete made with this paste, was increased by more than 15 h for addition of 0.1% and around 30 h for pastes with 0.5% of FNS with APTMS.
(Gu, Ran, et al., 2017)	The hydration rate of the NS@PCE samples caused an upward shift in the calorimetry curves. In one sample, this impact was slighter, becoming similar to the reference NS.
(Sun et al., 2017)	The heat development of the samples containing NS@PCE was more intense and there was no change in the hydration time. The only difference observed was that the peak of sulfate depletion was greater than the peak of hydration of silicates for samples with NS@PCE.
(Huang et al., 2020)	In the cement paste with 0.3% NS@DADMAC, a delay in the peak of hydration from 9.4 to 9.8 hours was observed. When the NS@DADMAC dosage increased from 0.3% to 1%, NS @ DADMAC accelerated the hydration of the cement instead of slowing it down. However, the effect of NS@DADMAC on accelerating cement hydration did not increase significantly when the content was increased to 3%.
(Rong et al., 2020)	The authors investigated 5 specimens and obtained relatively close hydration heat curves. The period of acceleration of the hydration of the samples without NS was about 15 to 20 hours. Also, the maximum peak value was reached in about 32 h. The addition of NS and FNS increased the rate of heat release and the time to reach the maximum value increased 2 h and 6 h, respectively. The accumulated heat released by the addition of FNS was also greater than that of NS after 3 days of hydration.
(Feng et al., 2020)	The authors reported a significant increase in the heat flow of the cement paste samples with NS@PCE. This increase was more significant in the sample with 1.1% of NS@PCE. It was also observed that there was a delay of the hydration peak of 2.5 hours in relation to the silicate and sulfate peaks.
(Liu et al., 2020)	The NS@PCE sample resulted in increased heat flow at two reference peaks (the peak of hydration of silicates and the peak of sulfate depletion). In terms of time, the NS@PCE sample obtained hydration delay in relation to the unmodified NS, but it did accelerate in relation to the reference paste (without NS).
(Vasconcellos et al., 2020)	The ANS cement pastes had their heat peaks shifted to the right in the hydration heat *x* time graph. Thus, it means there was a delay in the maximum heat peak for the sample containing 2.7% ANS for 60 hours, while for the reference sample was approximately 10 hours. The higher the ANS proportion, the greater the peak shift to the right.

Source: Authors.

The research presented in Table 4 reveals that the hydration kinetics of cement pastes is altered with the incorporation of the FNS when compared to a reference paste containing only cement or with a paste containing NS. The effects vary according to the chemical group used; however, in general, there is a delay in hydration of the studied cementitious composites.

Another prominent property for cementitious composites with FNS was the compressive strength. Table 5 presents a summary of the results of this property in the surveys.

Table 5 - The effect of NS functionalization on the compressive strength of cementitious composites.

Authors	Ages	Main comments
(Gu, Ran, et al., 2017)	12 hours, 1, 2 e 3 days	Samples with NS and NS@PCE resulted in compressive strength superior to the reference sample after 1 day of hydration. The authors highlighted the NS@PCE sample, which obtained the greatest compression strength. This result was attributed to the greater dispersion of this nanomaterial in the cement paste matrix. The authors also attributed this increase to the production of C-S-H with different quantity or qualities.
(Gu, Wei, et al., 2017)	1, 3, 7, 14 e 28 days	The incorporation of NS@SRA improved the compressive strength of the cement paste in the early ages compared to the reference (without addition). However, when compared to the reference sample containing nanosilica (without functionalization), its accelerating effect of resistance gain is slightly weaker up to 7 days. The authors justified this behavior by the fact that the FNS particles are covered with SRA. This "protective effect" of the SRA layer makes NS core less available as sites for the formation of C-S-H, as well as for reacting with CH in the pore solution. So, the resistance gain is relatively slower. After 7 days, the NS@SRA paste resulted in ever greater resistance than the NS@SRA paste over time. This effect was attributed to two main aspects: improved dispersion of the nanoparticles and the protective effect is undone by the alteration of the electrical charge during hydration.
(Sun et al., 2017)	12 hours, 1 and 3 days	The compressive strength of pastes with 0.3% and 0.6% of FNS was higher than the reference paste.
(Gu et al., 2020)	3 and 28 days	In general, the incorporation of nanoparticles improved the compressive strength at the ages of initial and subsequent curing. The authors attributed this behavior to the effects of nucleation and refinement of the microstructure. The compressive strength of cement pastes containing NS@GO was 28.2% greater than that of the reference sample (paste without the addition of NS).
(Rong et al., 2020)	3, 7 and 28 days	The FNS with better dispersibility can accelerate the hydration of the cement and fill the internal voids in the paste. At 7 days of hydration, the compressive strength of the reference sample (only with Portland cement) was 62.2 MPa. On the other hand, the strength of the samples with unmodified and 0.5% modified NS was 65.3 MPa and 69.0 MPa, which increased by 5% and 11%, respectively.
(Vasconcellos et al., 2020)	1, 3, 7 and 28 days	The ANS samples resulted in lower strength than the reference samples up to 3 days of hydration due to the delay in hydration caused by ANS. However, the best result of compressive strength at 28 days was for the sample containing 0.9% ANS.

Source: Authors.

The mechanical performance was evaluated between 12 hours and 28 days of hydration. For all investigated NS functionalizing agents (polycarboxylate-based superplasticizer additive - PCE (Gu, Ran, et al., 2017; Sun et al., 2017), shrinkage-reducing additive – SRA (Gu, Wei, et al., 2017), graphene oxide – GO (Gu et al., 2020), amine groups (Rong et al., 2020; Vasconcellos et al., 2020)), an increase in the mechanical performance of pastes was observed after 7 days of hydration. In contrast, the functionalization of NS with amine groups resulted in a reduction in the compressive strength of the pastes at the initial ages (up to 7 days) due to the delay in hydration reactions caused by this process.

From the systematic literature review, it was observed that only one study investigated the effect of NS functionalization with SRA (Gu, Wei, et al., 2017). In this study, three Portland cement pastes with water/cement ratio equal to 0.3 were investigated; being: one reference only with Portland cement, one containing 2% NS, and one containing 2% NS functionalized with SRA (NS@SRA). It is observed that the addition of NS in the cement paste resulted in an increase in autogenous shrinkage since the initial ages compared to the reference paste. This behavior is expected considering that the addition of NS accelerates the hydration reactions of the cement and, consequently, self-drying occurs. On the other hand, the addition of NS@SRA resulted in a behavior similar to that of the reference paste, especially at ages up to 14 days of hydration. This was attributed to the SRA layer on the NS surface, which limited the effect of the acceleration of NS hydration at early ages.

After 14 days of hydration, the NS@SRA paste resulted in a small reduction in autogenous shrinkage compared to the reference paste, indicating that some NS nuclei existing in the NS@SRA particles were gradually consumed during the pozzolanic reaction to produce the C-S-H, releasing the SRA to mitigate the autogenous shrinkage. Thus, the application of NS@SRA can contribute not only to increase the compressive strength of cementitious materials, but also to reduce the autogenous shrinkage in cement pastes, mitigating the occurrence of cracks in the early ages (Gu, Wei, et al., 2017).

4. Conclusion

The functionalized nanosilica with (3-Aminopropyl) trimethoxysilane (APTMS) delayed the hydration reactions of the cement. The composition with the addition of 0.1% of FNS with APTMS was delayed in 15 hours and the other with the addition of 0.5% was delayed in 30 hours. The functionalization of NS with superplasticizer additive based on polycarboxylate (PCE) increased the heat flow, beyond of the time delay for the occurrence of peak heat flow compared to the paste containing NS. There was an acceleration of the hydration reactions of the paste with the functionalized NS with PCE in relation to the reference paste (without NS). The functionalization of NS with Diallyldimethylammonium chloride (DADMAC) resulted in the delay in peak hydration from 9.4 hours to 9.8 hours when the 0.3% ratio was used. When this quantity was increased to 1%, the functionalized NS with DADMAC contributed to the acceleration of cement hydration reactions. There was a delay in the hydration of the pastes also when NS was functionalized with amine groups (ANS) compared to pastes with NS.

With regard to mechanical performance, the functionalization of NS with PCE resulted in an increase in the compressive strength of pastes after 1 day of hydration compared to the reference paste and the paste containing NS without the functionalization process. The functionalization of NS with SRA resulted in an increase in the compressive strength of the cement paste compared to the reference paste in the early ages; although, its effect in increasing the compressive strength was less compared to the paste containing non-functionalized NS until the 7 days of hydration. After 7 days of hydration, the compressive strength of the paste containing functionalized NS with SRA was greater than the reference paste and containing NS. The NS functionalization process with graphene oxide (GO) resulted in an increase in mechanical performance in the initial ages (3 days) and later (28 days). The functionalization of NS with amine groups (ANS) resulted in a delay in hydration of cement pastes and consequently in a reduction in mechanical performance until 7 days of hydration. However, after that period, the compressive strength of these pastes was greater than that of reference paste and the paste containing NS.

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References

Azevedo, N. H. de, & Gleize, P. J. P. (2018). Effect of silicon carbide nanowhiskers on hydration and mechanical properties of a Portland cement paste. *Construction and Building Materials*, *169*, 388–395. https://doi.org/10.1016/j.conbuildmat.2018.02.185

Cai, Y., Hou, P., Cheng, X., Du, P., & Ye, Z. (2017). The effects of nanoSiO 2 on the properties of fresh and hardened cement-based materials through its dispersion with silica fume. *Construction and Building Materials*, *148*, 770–780. https://doi.org/10.1016/j.conbuildmat.2017.05.091

Chithra, S., Senthil Kumar, S. R. R., & Chinnaraju, K. (2016). The effect of Colloidal Nano-silica on workability, mechanical and durability properties of High Performance Concrete with Copper slag as partial fine aggregate. *Construction and Building Materials*, *113*, 794–804. https://doi.org/10.1016/j.conbuildmat.2016.03.119

Collodetti, G., Gleize, P. J. P., & Monteiro, P. J. M. (2014). Exploring the potential of siloxane surface modified nano-SiO2 to improve the Portland cement pastes hydration properties. *Construction and Building Materials*, *54*, 99–105. https://doi.org/10.1016/j.conbuildmat.2013.12.028

Feng, P., Chang, H., Liu, X., Ye, S., Shu, X., & Ran, Q. (2020). The significance of dispersion of nano-SiO2 on early age hydration of cement pastes. *Materials and Design*, *186*, 108320. https://doi.org/10.1016/j.matdes.2019.108320

Fraga, Y. S. B., Rêgo, J. H. da S., Capuzzo, V. M. S., Andrade, D. da S., & Morais, P. C. (2020). Ultrasonication and synergistic effects of silica fume and colloidal nanosilica on the C–S–H microstructure. *Journal of Building Engineering*, *32*(March), 101702. https://doi.org/10.1016/j.jobe.2020.101702

Gu, Y., Ran, Q., She, W., & Liu, J. (2017). Modifying Cement Hydration with NS@PCE Core-Shell Nanoparticles. *Advances in Materials Science and Engineering*, *2017*(1), 1–13. https://doi.org/10.1155/2017/3823621

Gu, Y., Ran, Q., She, W., Shu, X., & Liu, J. (2018). Effects and mechanisms of surface-treatment of cementitious materials with nanoSiO2@PCE core-shell nanoparticles. *Construction and Building Materials*, *166*, 12–22. https://doi.org/10.1016/j.conbuildmat.2018.01.082

Gu, Y., Ran, Q., Shu, X., Yu, C., Chang, H., & Liu, J. (2016). Synthesis of nanoSiO2@PCE core-shell nanoparticles and its effect on cement hydration at early age. *Construction and Building Materials*, *114*, 673–680. https://doi.org/10.1016/j.conbuildmat.2016.03.093

Gu, Y., Wei, Z., Ran, Q., Shu, X., Lv, K., & Liu, J. (2017). Characterizing cement paste containing SRA modified nanoSiO2 and evaluating its strength development and shrinkage behavior. *Cement and Concrete Composites*, *75*, 30–37. https://doi.org/10.1016/j.cemconcomp.2016.11.001

Gu, Y., Xia, K., Wei, Z., Jiang, L., She, W., & Lyu, K. (2020). Synthesis of nanoSiO2@graphene-oxide core-shell nanoparticles and its influence on mechanical properties of cementitious materials. *Construction and Building Materials*, *236*, 117619. https://doi.org/10.1016/j.conbuildmat.2019.117619

Guo, L., Wu, J., & Wang, H. (2020). Mechanical and perceptual characterization of ultra-high-performance cement-based composites with silane-treated graphene nano-platelets. *Construction and Building Materials*, *240*, 117926. https://doi.org/10.1016/j.conbuildmat.2019.117926

Huang, C., & Wang, D. (2017). Surface Modification of Nano-SiO2 Particles with Polycarboxylate Ether-Based Superplasticizer under Microwave Irradiation. *ChemistrySelect*, *2*(29), 9349–9354. https://doi.org/10.1002/slct.201701493

Huang, C., Wang, Y., Zhao, J., & Wang, D. (2020). Potential Effect of Surface Modified Nano-SiO2 with PDDA on the Cement Paste Early Hydration. *ChemistrySelect*, *5*(11), 3159–3163. https://doi.org/10.1002/slct.201904791

Khalil, M., Saeed, S., & Ahmad, Z. (2007). Mechanical and Thermal Properties of Polyimide/Silica Hybrids with Imide-Modified Silica Network Structures. *Wiley InterScience*. https://doi.org/10.1002/app

Kong, D., Su, Y., Du, X., Yang, Y., Wei, S., & Shah, S. P. (2013). Influence of nano-silica agglomeration on fresh properties of cement pastes. *Construction and Building Materials*, *43*, 557–562. https://doi.org/10.1016/j.conbuildmat.2013.02.066

Kontoleontos, F., Tsakiridis, P. E., Marinos, A., Kaloidas, V., & Katsioti, M. (2012). Influence of colloidal nanosilica on ultrafine cement hydration: Physicochemical and microstructural characterization. *Construction and Building Materials*, *35*, 347–360. https://doi.org/10.1016/j.conbuildmat.2012.04.022

Liu, X., Feng, P., Shu, X., & Ran, Q. (2020). Effects of highly dispersed nano-SiO2 on the microstructure development of cement pastes. *Materials and Structures/Materiaux et Constructions*, *53*(1), 1–12. https://doi.org/10.1617/s11527-019-1431-0

Mariano, A. M., & Rocha Santos, M. (2017). Revisão da Literatura: Apresentação de uma Abordagem Integradora Structural Equations View project Service Quality View project. *XXVI Congreso Internacional de La Academia Europea de Dirección y Economía de La Empresa (AEDEM)*, *September*, v.26. https://www.researchgate.net/publication/319547360

Martins, G. L. O., Fraga, Y. S. B., Vasconcellos, J. S., & da S. Rêgo, J. H. (2020). Synthesis and characterization of functionalized nanosilica for cementitious composites: review. *Journal of Nanoparticle Research*, *22*(11). https://doi.org/10.1007/s11051-020-05063-7

Monasterio, M., Gaitero, J. J., Erkizia, E., Guerrero Bustos, A. M., Miccio, L. A., Dolado, J. S., & Cerveny, S. (2015). Effect of addition of silica- and amine functionalized silica-nanoparticles on the microstructure of calcium silicate hydrate (C-S-H) gel. *Journal of Colloid and Interface Science*, *450*, 109–118. https://doi.org/10.1016/j.jcis.2015.02.066

Nair, D. G., Fraaij, A., Klaassen, A. A. K., & Kentgens, A. P. M. (2008). A structural investigation relating to the pozzolanic activity of rice husk ashes. *Cement and Concrete Research*, *38*(6), 861–869. https://doi.org/10.1016/j.cemconres.2007.10.004

Perez, G., Gaitero, J. J., Erkizia, E., Jimenez, I., & Guerrero, A. (2015). Characterisation of cement pastes with innovative self-healing system based in epoxy-amine adhesive. *Cement and Concrete Composites*, *60*, 55–64. https://doi.org/10.1016/j.cemconcomp.2015.03.010

Reches, Y. (2018). Nanoparticles as concrete additives: Review and perspectives. *Construction and Building Materials*, *175*, 483–495. https://doi.org/10.1016/j.conbuildmat.2018.04.214

Ren, C., Hou, L., Li, J., Lu, Z., & Niu, Y. (2020). Preparation and properties of nanosilica-doped polycarboxylate superplasticizer. *Construction and Building Materials*, *252*, 119037. https://doi.org/10.1016/j.conbuildmat.2020.119037

Rong, Z., Zhao, M., & Wang, Y. (2020). Effects of modified nano-SiO2 particles on properties of high-performance cement-based composites. *Materials*, *13*(3), 1–12. https://doi.org/10.3390/ma13030646

Senff, L., Hotza, D., Repette, W. L., Ferreira, V. M., & Labrincha, J. A. (2010). Mortars with nano-SiO2 and micro-SiO2 investigated by experimental design. *Construction and Building Materials*, *24*(8), 1432–1437. https://doi.org/10.1016/j.conbuildmat.2010.01.012

Singh, L. P., Bhattacharyya, S. K., Shah, S. P., Mishra, G., & Sharma, U. (2016). Studies on early stage hydration of tricalcium silicate incorporating silica nanoparticles: Part II. *Construction and Building Materials*, *102*, 943–949. https://doi.org/10.1016/j.conbuildmat.2015.05.084

Sun, J., Shi, H., Qian, B., Xu, Z., Li, W., & Shen, X. (2017). Effects of synthetic C-S-H/PCE nanocomposites on early cement hydration. *Construction and Building Materials*, *140*, 282–292. https://doi.org/10.1016/j.conbuildmat.2017.02.075

Varghese, L., Kanta Rao, V. V. L., & Parameswaran, L. (2019). Nanosilica-added concrete: Strength and its correlation with time-dependent properties. *Proceedings of Institution of Civil Engineers: Construction Materials*, *172*(2), 85–94. https://doi.org/10.1680/jcoma.17.00031

Vasconcellos, J. S., Martins, G. L. O., de Almeida Ribeiro Oliveira, G., Lião, L. M., da Silva Rêgo, J. H., & Sartoratto, P. P. C. (2020). Effect of amine functionalized nanosilica on the cement hydration and on the physical-mechanical properties of Portland cement pastes. *Journal of Nanoparticle Research*, *22*(8). https://doi.org/10.1007/s11051-020-04940-5

Wang, J., White, W. B., & Adair, J. H. (2006). Evaluation of dispersion methods for silica-based composite nanoparticles. *Journal of the American Ceramic Society*, *89*(7), 2359–2363. https://doi.org/10.1111/j.1551-2916.2006.01064.x

Xu, G., Zhang, J., & Song, G. (2003). Effect of complexation on the zeta potential of silica powder. *Powder Technology*, *134*(3), 218–222. https://doi.org/10.1016/S0032-5910(03)00172-4