



Research article

Investigation of cementitious composites reinforced with metallic nanomaterials, boric acid, and lime for infrastructure enhancement

Ahmed Al-Ramthan¹ and Ruaa Al Mezrakchi^{2,*}

¹ Construction Management, School of Human Sciences, Stephen F. Austin State University, 1936 North St, Nacogdoches, TX 75965, USA

² Department of Engineering, College of Science and Engineering, University of Houston-Clear Lake, 2700 Bay Area Boulevard, Houston, TX 77058, USA

* **Correspondence:** Email: almezrakchi@uhcl.edu; Tel: +1-281-283-3828.

Abstract: Nanomaterials integration within construction materials could promote the generation of more sophisticated structural materials, as it imbues reinforcement at the nanoscale. This research adopted experimental approaches to assess the influence of metallic nanomaterials on the performance of cementitious composites with various ratios of boric acid (1%, 3%, and 5% by sand's weight) and lime (0.5%, 1.5%, and 2.5% by sand's weight), respectively, for use in construction infrastructure facilities. This research provides valuable insight into the potential of using boric acid and lime as well as metallic nanomaterials to strengthen cement-based composites. Initial curing stages revealed a notable decrease in compressive strength attributed to the inhibitory effects of boric acid and lime on cement hydration. However, the introduction of TiO₂ nanoparticles demonstrated significant enhancements in compressive strength and durability. Statistical analysis emphasized the significance of nanomaterials in augmenting compressive strength, with implications for long-term performance. This study has shown that the addition of nano-titanium dioxide TiO₂ can significantly enhance the compressive strength of Portland cement mortars, particularly when used in conjunction with appropriate ratios of boric acid and lime. The results of the 7 days test indicated that the inclusion of boric acid and lime in the cement mortars significantly decreased the compressive strength. However, the addition of nano-TiO₂ to cement mortars containing 1% boric acid and 0.5% lime resulted in a 31-fold increase in compressive strength compared to cementitious composites without nano-TiO₂. In contrast, the compressive strength significantly increased by 1.2 times, 85.3 times, and 65.1 times, respectively, after 56 days for the addition of boric acid (1%, 3%, and 5%) with lime (0.5%, 1.5%, and 2.5%), respectively, in the presence of nano-TiO₂, compared to the 7 days strength. The results

also illustrated that, in general, the incorporation of various types of nano-TiO₂ into cementitious composites containing boric acid and lime increases their compressive strength as the ratios of boric acid and lime increase, as long as sufficient curing time is allowed.

Keywords: cementitious composites; nanomaterials; metallic nanomaterials; nano-TiO₂; boric acid; lime; compressive strength; cement mortar; experimental study; infrastructure

1. Introduction

Cementitious materials are widely used for infrastructures such as building, transport networks, geotechnical structures, nuclear and radiation buildings, and grouting applications. The resilience of infrastructure is typically associated with the design of individual elements such that they have sufficient capacity or potential to react in an appropriate manner to adverse events; however, frequent inspections and repairs are often needed. Construction materials are designed to meet a prescribed specification, while degradation of these materials is viewed as inevitable, which necessitates the mitigation of expensive maintenance systems. Since cementitious composites are nanostructure in nature and feature obvious nano-behavior, the developments in nano-science have great impacts on the field of construction materials. Nanoscience has the great potential to engineer cementitious composites with superior mechanical performance and durability. Small changes at the nanoscale make performances differ significantly at larger scales [1,2]. Innovative design and production of materials and infrastructures lead to large accumulated benefits, such as lower use of raw materials, improved properties, and higher construction/industry efficiency that make materials stronger and more durable throughout their life cycles [3,4]. Additionally, the incorporation of macromolecules, such as boric acid, is challenging due to the inherent costs associated with the initial construction process, as well as the negative impact on physical properties. The use of boric acid significantly deteriorates the mechanical properties of Portland cement [5]. One of the other key challenges in the use of boric acid is its costly nature, which makes it economically unviable. Besides, the addition of lime powder to the cement mortars may lead to a reduction in compressive strength of mortars [6]. Additionally, an array of materials has emerged as potent reinforcements for cement composites, such as fly ash, silica fume, and nano-silica [7]. In addition, investigating the long-term durability and performance of these composites under various environmental conditions, such as exposure to aggressive chemicals or cyclic loading [8], could be a valuable avenue for future research that can contribute to the development of sustainable and resilient infrastructure materials.

Nanotechnology has now become a widely accepted technology to improve the performance and functionality of materials. Recently, the use of reinforcements has led to significant improvement in the mechanical properties of cement-based materials by delaying the transformation of microcracks into macroforms; however, they could not stop the crack growth [9–11]. Opportunities for using nano-sized reinforcement were also explored [12,13] mainly in the form of carbon nano-fibers and nano-tubes [14], as well as of various nano-fibers [15,16]. Besides working out their reinforcement effect at the size of crystalline structure of the material, they have also proved effective in providing additional functionalities, including enhanced corrosion resistance [17], self-curing, and self-sensing abilities [18,19], while also being able to upgrade durability in a cracked state [18], e.g., fostering and enhancing the autogenous self-healing capacity [19]. The latest developments in this field include the

use of graphene nano-platelets and graphene oxide which were able to provide enhancement due to both nano-filling and nano-reinforcing effects but at even much lower loading than other “conventional” nano-constituents [20], provided, like for all other nanoparticles, tailored methods are adopted to adequately disperse and stabilize it into alkaline cementitious solutions [21]. Moreover, the coating materials for fiber treatment, exploiting their interaction with cement hydrates in enhancing the overall performance of the composites have been recently explored [22,23]. Early investigations showed that nanomaterials have a strong influence on the hydration process and hardness of cementitious composites [24].

Nano-titania (NT) is titanium dioxide (TiO_2) nanoparticles that can be found as three crystalline polymorphs: anatase, rutile, and brookite. NT is one of the most used nanoparticles in human life, being found in biomedical applications, sunscreen, and photovoltaic devices [25], among others. In cement-based composites, titanium dioxide has been considered a potential additive for building materials such as cement pastes, mortars, and concretes. The primary focus of using TiO_2 in the construction industry has been implemented to generate environmental coating of pavements and protection of building facades, as well as to impart self-cleaning, air-purifying, and antimicrobial properties to cement-based materials. These enumerated benefits stem from the photocatalytic efficiency exhibited by titania. Since the inception of photocatalysis development in the 1970s, the majority of research and applications in this field have been centered on titanium dioxide as a photocatalyst of particular interest [26–35]. Despite the extraordinary properties of nano-titania, a very limited number of studies have been conducted to investigate its effects on the mechanical characteristics of cement-based materials. In the fresh state, nano-titania has been observed to decrease the setting time [36,37] and workability [38] of cement-based matrices. Studies involving the incorporation of various nanomaterials into cement-based materials have been conducted extensively. However, the investigation of the influence exerted by NT on cementitious materials containing boric acid and lime has not been undertaken until now.

The aim of this research is to enhance the properties of the cementitious materials via embedding nanoparticles and forming interconnected nanocomposites. An optimal processing procedure for adding TiO_2 nanomaterials to the cement-lime-boric acid mixtures are developed. The mechanical characteristics of the produced nanocomposite cement-based mixtures with various ratios of boric acid (1%, 3%, and 5% by sand's weight) and lime (0.5%, 1.5%, and 2.5% by sand's weight) are investigated.

2. Materials and methods

2.1. Materials

Ordinary Portland cement type I/II was utilized in this work, supplemented with standard sand that had been graded between the 600 μm (No. 30) sieve and the 150 μm (No. 100) sieve, according to the specification of ASTM C778 [39]. The sand was added with 200% by weight of cement, alongside a water/cement (w/c) ratio of 35%. Additionally, commercially available contents of boric acid and lime powders were incorporated into the mixtures in a manner relative to the weight of sand in the mixtures.

Generally, NT is titanium dioxide (TiO_2) nanoparticles that can be found in different crystalline polymorph forms such as anatase and rutile. Various nano- TiO_2 types were employed in the mixtures

with different ratios according to the cement's weight in the mixtures, due to its enhanced decomposition capability when incorporated in nanometer-size particles. The NT types were: type (A) nanoparticles, anatase, purity 99+%, size 10 nm; type (B) nanotubes, anatase, purity 99%, 10–15 nm; type (C) silica- and alumina-coated nanoparticles, anatase/rutile, size 20 nm. For transmission electron microscopy (TEM), 10 mL of ethanol was measured and added to 0.5 g of metallic nanomaterials followed by ultrasonication for 10 min. A carbon film was used to place a drop of the mixture then dried for 72 h in a vacuum desiccator. In addition, a polycarboxylate superplasticizer, namely ADVA 140M, was incorporated to disperse the NT by acquiring an adequate workability and flowable mortar with the presence of NT. The ADVA ratio was 0.4% by weight of cement for mixtures without NT and 0.6% by weight of cement for mixtures with NT.

2.2. Methods

2.2.1. Transmission electron microscopy (TEM)

TEM was utilized to unveil the structure of the metal particles and evaluate their dimensions along with their size distributions via dark field contrast. JEOL TEM equipment with 80–200 kV acceleration voltages along with a cold field emission gun (CFEG) and an energy dispersive X-ray analyzer (EDX) was used to examine the samples. 1 μg of nanomaterial was dissolved in 1 mL isopropanol then sonicated for 15 min to acquire a good dispersion of the nanomaterial. A drop of this produced solution was placed on a carbon film and left for 24 h to dry for further analysis.

2.2.2. Composite samples preparation

The cement composite samples were prepared by controlling the ratios of cement, sand, metallic nanomaterials, boric acid, and lime. Various proportions of boric acid and lime contents were considered including (1%, 3%, and 5%) and (0.5%, 1.5%, and 2.5%) by sand's weight, respectively. Types A, B, and C of metallic nanomaterials NT with and without nanocoating were incorporated within the samples. Prior to mixing with cement, nano-titania was dispersed in aqueous solution with added superplasticizer at 0.6% by the weight of the cement mixtures. Ultrasonic dispersion treatment for 5 min was used to disperse the nanomaterials [40]. Then, cement, sand, lime, and boric acid were added to the NT solution. The mixture was placed in the cement mixer and mixed for 15 min, then casted into a cube mold of 2 in. size according to the test method of ASTM C109 [41]. The process of the sample preparation is shown in Figure 1.

The mixing proportions of the test specimens are depicted in Table 1. The specimens utilized to test the compressive strength of the composite cement mortars were molded using $2 \times 2 \times 2$ in. molds. The samples were cured under controlled conditions for a period of 24 h, demolded, and then immersed in a curing box filled with saturated lime water in accordance with the test method of ASTM C109 [41] until they reached their designated test ages of 7 and 56 days. Subsequently, the samples were tested using a compression test machine to determine their compressive strength.

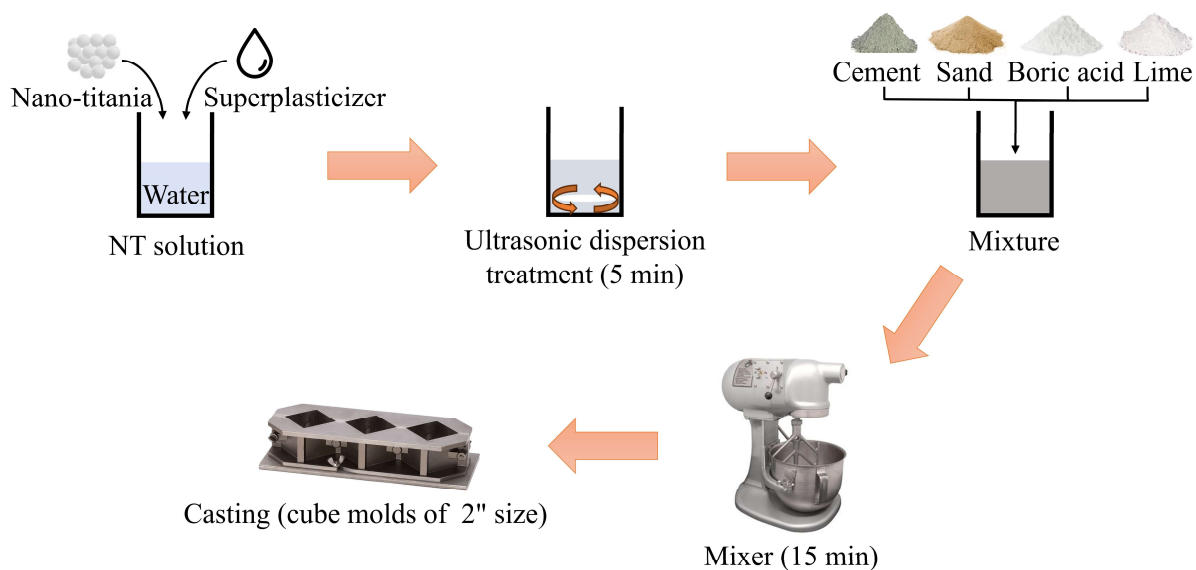


Figure 1. The process of sample preparation.

Table 1. Mixing proportions of test samples (wt.%).

Mix #	Nano type	Cement	TiO ₂ (by cement's weight)	Boric acid (by sand's weight)	Lime (by sand's weight)
1	—	100	—	—	—
2	—	100	—	1	0.5
3	—	100	—	3	1.5
4	—	100	—	5	2.5
2-A	A	95	5	1	0.5
3-A	A	95	5	3	1.5
4-A	A	95	5	5	2.5
2-B	B	95	5	1	0.5
3-B	B	95	5	3	1.5
4-B	B	95	5	5	2.5
2-C	C	95	5	1	0.5
3-C	C	95	5	3	1.5
4-C	C	95	5	5	2.5

2.2.3. Compressive strength testing

The compressive strength tests were conducted using a Test Mark Industries machine with a maximum capacity of 300,000 lb. The tests were carried out using a 2 in. cube test set according to the test method of ASTM C109 [41]. Three samples were tested per batch, and the average strength value was reported to ensure the accuracy and reproducibility of the test results.

3. Results and discussion

3.1. Nano-titania morphology observation

TEM images of nano-titania are shown in Figure 2. Three different types of metallic nanomaterials are presented in this figure including type A anatase nanoparticles in Figure 2a, type B anatase nanotubes in Figure 2b, and type C anatase/rutile nanoparticles coated with silica and alumina nanocoating in Figure 2c. The nanoparticles' sizes in Figure 2 were measured manually. The average measurements were found to be: 10 ± 4 nm for type A nanoparticles, 20 ± 2 nm for type C nanoparticles with nanocoating, and for type B nanotubes, the dimensions were 4 ± 1 nm inner diameter and 12 ± 3 nm outer diameter with over $1 \mu\text{m}$ length.

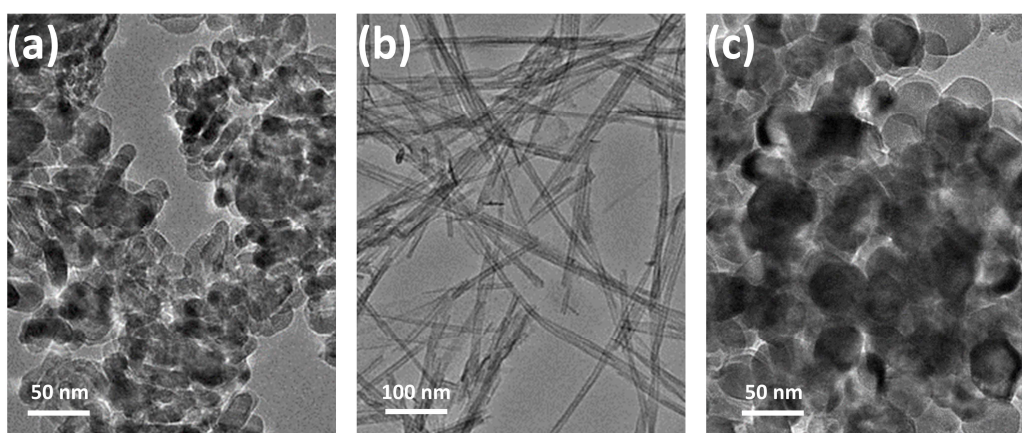


Figure 2. TEM images of various TiO_2 metallic nanomaterials (a) anatase nanoparticles, (b) anatase nanotubes, (c) anatase/rutile nanoparticles with nanocoating.

3.2. The effect of adding boric acid and lime

An investigation into the effects of boric acid and lime additions to cement mortars at various curing periods has been undertaken. It has been noted that no significant changes in strength at the 28 days curing period were observed, aligning with earlier research findings [42]. As a result, emphasis was placed on determining the compressive strength of the specimens at 7 and 56 days of curing to ensure the emergence of conclusive results. Thus, the results of adding boric acid (1%, 3%, and 5% by sand's weight) and lime powder (0.5%, 1.5%, and 2.5% by sand's weight), respectively, to cement mortars and curing for 7 and 56 days are presented in Figures 3–5. It can be noticed that the addition of the boric acid and lime to the cement mortars leads to a decrease in the compressive strength significantly at the 7 days test, as presented in Figure 3. This decrease might be attributed to a weakening of the hardening strength of cement mortar with increasing boric acid and lime contents, in addition to the effect of the boric acid and lime on the hydration of the cementitious material at the early ages [43–46]. However, at the later testing age of 56 days (Figure 4), the compressive strength of the cement mortars augmented in proportion to the percentage increase of boric acid and lime. As depicted in Figure 5, it can be observed that the compressive strength of the control mix (mix #1) increased by 28% at the 56 days test in comparison to its strength at the 7 days test. Additionally, the

compressive strength significantly increased by 30.5 times, 36.3 times, and 46.7 times for adding boric acid (1%, 3%, and 5%) and lime (0.5%, 1.5%, and 2.5%), respectively.

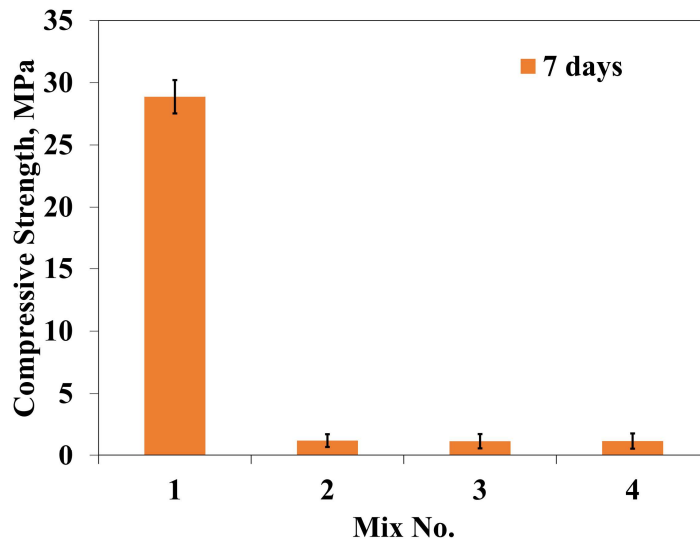


Figure 3. Compressive strength of cementitious composites at the 7 days test with different ratios of boric acid and lime.

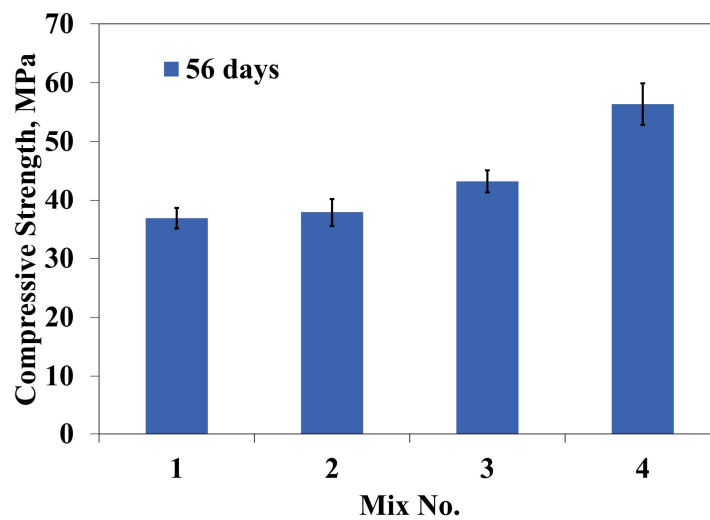


Figure 4. Compressive strength of cementitious composites at the 56 days test with different ratios of boric acid and lime.

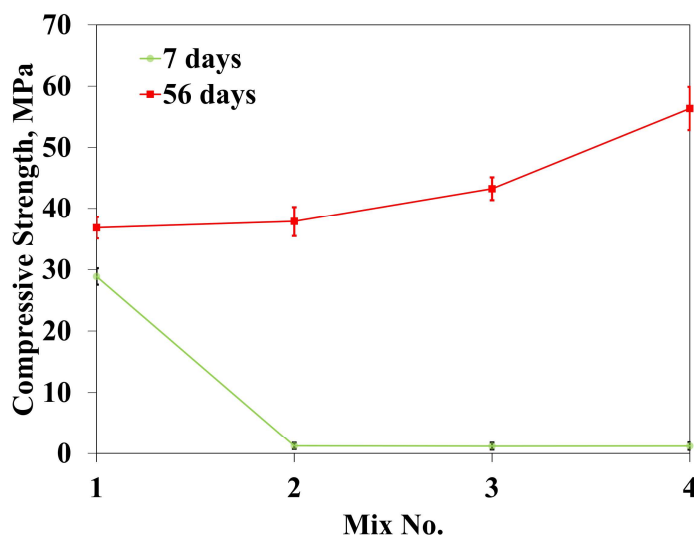


Figure 5. Compressive strength of cementitious composites with different ratios of boric acid and lime.

3.3. The effect of adding nano-titania with boric acid and lime

The influence of embedding nano-metallics into cementitious composites with boric acid and lime additives are presented in Figures 6–8. Adding 5% nano-TiO₂, type A, by cement's weight with different boric acid and lime ratios improves the mechanical properties of these cementitious composites regarding the compressive strength of the samples for the early testing age (7 days) with 1% boric acid and 0.5% lime, as shown in Figure 6. The reason could be attributed to the hydration of cement and the formation of calcium silicate hydrate (CSH) which are greatly accelerated due to the presence of the TiO₂ particles. The titanium dioxide can scavenge reactive oxygen species (ROS) and significantly improve the durability of the cement matrix. From the results of the early age (7 days) test shown in Figure 6, it can be noticed that the addition of 5% nano-TiO₂ to cement mortars containing 1% boric acid and 0.5% lime markedly improves the compressive strength by 31 times compared to the cementitious composites without nano-TiO₂ and containing the same ratios of boric acid and lime. However, further increases in the percentages of the boric acid and lime tended to dominate and therefore compromised any improvements in the properties due to the nano-titania additives at early ages. The results of the 56 days tests presented in Figure 7 show an overall increase in the compressive strength of the samples with the integration of nano-TiO₂ (type A) compared to the samples without nano-TiO₂. Additionally, it can be observed that the compressive strength of the composites with nano-TiO₂ (type A) noticeably increases at 56 days by 26%, 17%, and 2% for the cases of boric acid ratios of 1%, 3%, and 5% in combination with lime ratios of 0.5%, 1.5%, and 2.5%, respectively, compared to the samples without nano-TiO₂. The results at highest percentages of boric acid and lime show their dominant effect over the nano-titania. Consequently, from the results of 56 days strength compared with the results of 7 days strength with nano-TiO₂ additives shown in Figure 8, it can be depicted that the compressive strength at the 56 days test significantly increases by 1.2 times, 85.3 times, and 65.1 times for the addition of boric acid (1%, 3%, and 5%) with lime (0.5%, 1.5%, and 2.5%), respectively, in the presence of nano-titania. Thus, these findings suggest

that the nanometallic particles assist in enhancing the cementitious composites with higher ratios of boric acid and lime. These outcomes are consistent with prior studies that have proposed the acceleration of the hydration rate of cement-based materials by the addition of nano-TiO₂ particles, except in their composites devoid of boric acid and lime. It has been claimed that nano-TiO₂ particles expedite the hydration rate, with hydration products forming on the surfaces of the TiO₂ nanoparticles and the C₃S [37,47].

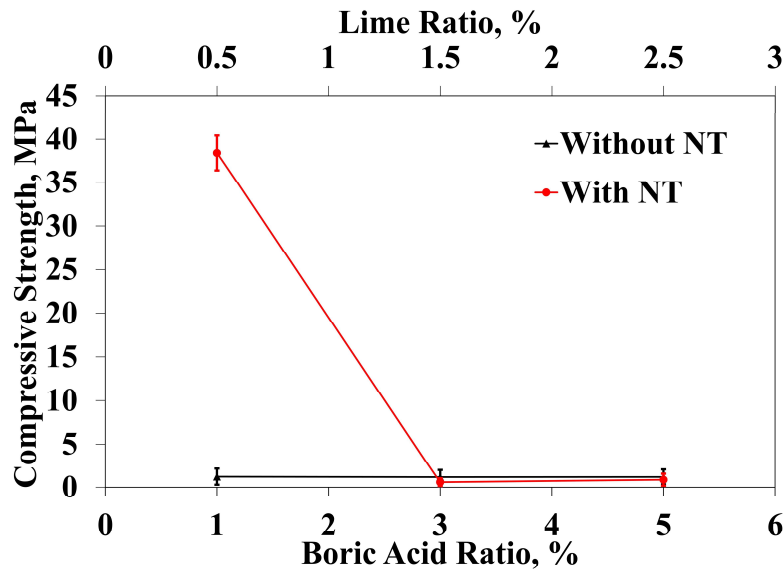


Figure 6. Compressive strength of cementitious composites at the 7 days test with and without nano-TiO₂ (type A) and different ratios of boric acid and lime.

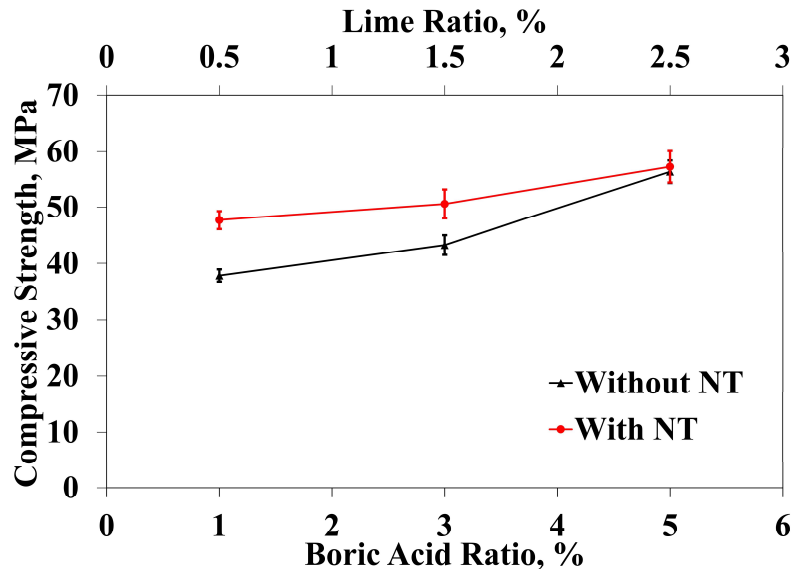


Figure 7. Compressive strength of cementitious composites at the 56 days test with and without nano-TiO₂ (type A) and different ratios of boric acid and lime.

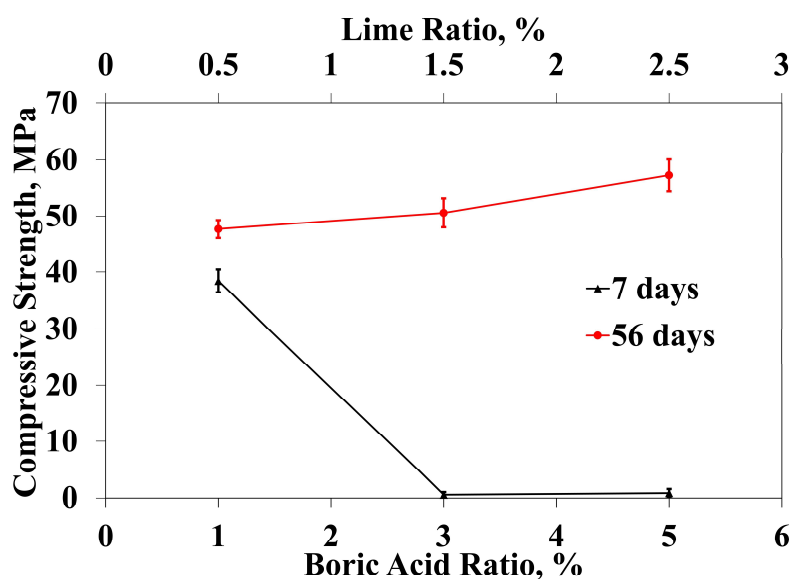


Figure 8. Compressive strength of cementitious composites with nano-TiO₂ (type A) additives and different ratios of boric acid and lime.

3.4. Influence of changing nano-titania types with boric acid and lime presence

The addition of three different types (types A, B, and C) of nano-TiO₂ at a concentration of 5% by weight of cement into the cementitious composites with different ratios of boric acid and lime has been shown to improve the 7 days compressive strength of the cementitious composites by 31 times, 18.3 times, and 13.4 times for the inclusion of nano-TiO₂ type A (mix #2-A), type B (mix #2-B), and type C (mix #2-C), respectively, compared to the cementitious composite with 1% boric acid and 0.5% lime (mix #2) only, as depicted in Figure 9. This improvement was only seen in samples with 1% boric acid and 0.5% lime, while other percentages did not show improvements, indicating a potential decrease in the overall durability of the composites. Thus, all nano-TiO₂ types contribute, at different levels, to the strength of the cement composites with lower ratios of boric acid and lime at the early age.

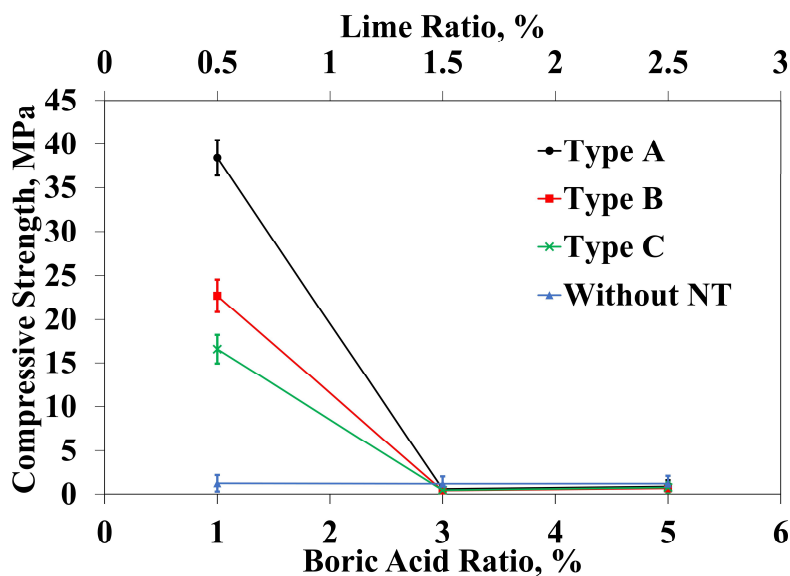


Figure 9. Compressive strength of cementitious composites at the 7 days test with three different types of nano-TiO₂ and different ratios of boric acid and lime.

Additionally, the improvement in the 56 days compressive strength of the cementitious composites for mix #2-A, 2-B, and 2-C compared to the control composite (mix #1) can be shown in Figure 10. Although mixes #2-B and #2-C exhibited lower values than mix #2-A, they still demonstrated an enhancement in mechanical properties compared to the control mix #1, likely due to the influence of metallic nanotubes and nano-coated metallic nanoparticles in comparison to uncoated nanoparticles. The presence of TiO₂ nanotubes with lengths exceeding 1 micron compromised the microstructure of the mixture, leading to a reduction in the overall compressive strength. These observations with metallic nanotubes are consistent with the trend previously observed in the use of long carbon nanotubes as additives [48]. On the other hand, experiencing lower properties of the coated nanoparticles compared with the uncoated ones could be attributed to the surface roughness. Typically, a certain level of roughness on the surface of nanoparticles is desirable to introduce a better mechanism for transferring and distributing the load within the matrix. The nano-coating of nanoparticles adds a thin layer to the surface of the nanoparticles, which may have reduced their surface roughness by sealing the pores and thus weakened the interface locking forces or adhesion between the nanoparticles and the mixture. All mixes #3-A, 3-B, and 3-C had a similar trend to mixes #2-A, 2-B, and 2-C with higher property rates due to the influence of increasing boric acid and lime and allowing enough curing time of 56 days, as shown in Figure 11. Moreover, the compressive strength of mix #3-A at the 56 days test with 3% boric acid and 1.5% lime had higher values compared to the control composite (mix #1). However, the other mixtures of #3-B and #3-C had lower values compared to mix #3-A, although they were still higher than mix #1.

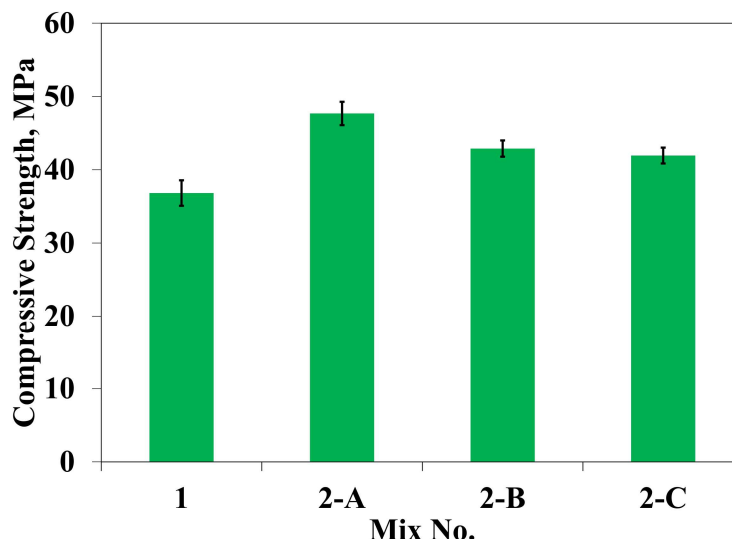


Figure 10. Compressive strength of cementitious composites at the 56 days test with three different types of nano-TiO₂ (2-A, 2-B, and 2-C) compared to the control composite.

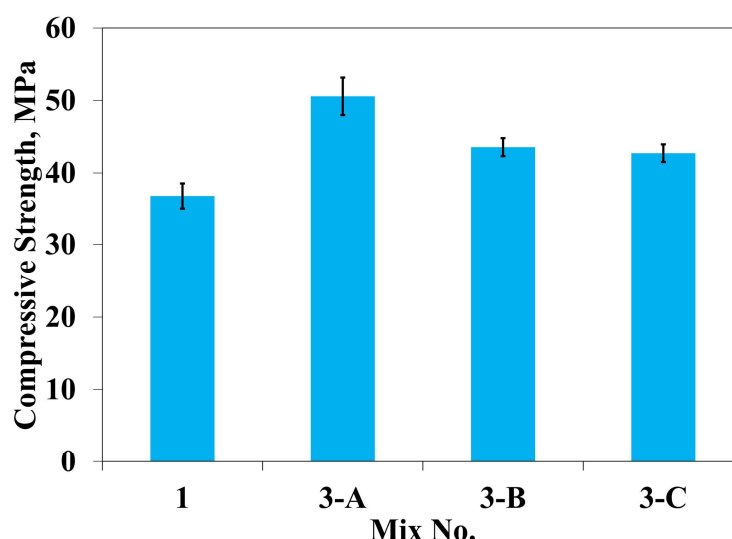


Figure 11. Compressive strength of cementitious composites at the 56 days test with three different types of nano-TiO₂ (3-A, 3-B, and 3-C) compared to the control composite.

Furthermore, Figure 12 illustrates that the addition of three types of nano-TiO₂ into the cementitious composites (mix #4-A, mix #4-B, and mix #4-C) containing 5% boric acid and 2.5% lime led to an increase in the compressive strength of these composites. Among the three, mix #4-A exhibited the highest value compared to the others. Generally, the data suggested that the incorporation of nano-titania with nanosized particles into cementitious composites can improve their durability and overall performance. However, the degree of improvement is influenced by the ratios of boric acid and lime. Additionally, the results of the 56 days tests (depicted in Figure 13) for the mixtures with varying ratios of boric acid and lime that incorporated three different types of nano-TiO₂ demonstrated a trend of increasing compressive strength in the cementitious composites with the inclusion of nano-TiO₂ and

increasing ratios of boric acid and lime. These enhancements are related to the increase in the ratios of boric acid and lime with the presence of different nanomaterials added to the cementitious composites, as well as sufficient curing time.

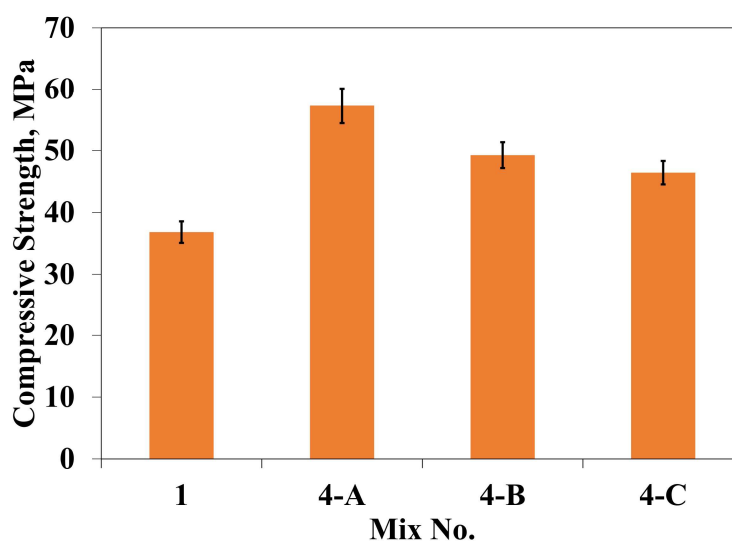


Figure 12. Compressive strength of cementitious composites at the 56 days test with three different types of nano-TiO₂ (4-A, 4-B, and 4-C) compared to the control composite.

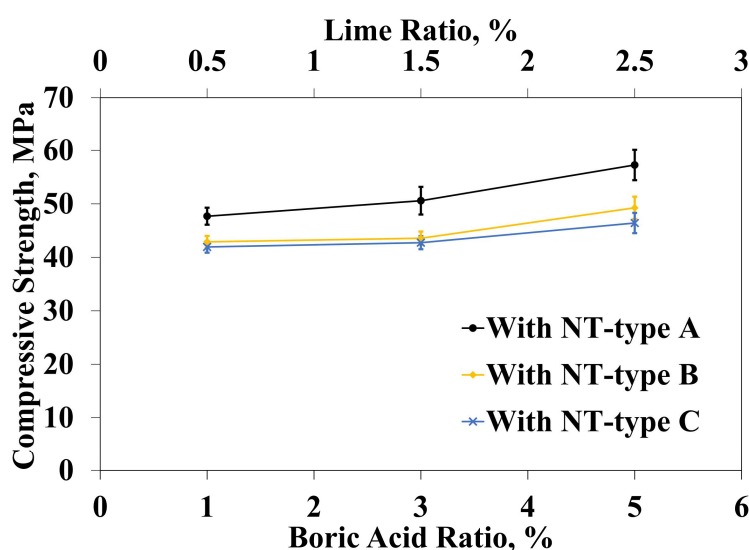


Figure 13. Compressive strength of cementitious composites at the 56 days test with three different types of nano-TiO₂ and different ratios of boric acid and lime.

3.5. Statistical evaluation of the compressive strength measurements

In this study, analysis of the variance method (abbreviated as ANOVA) was used to evaluate statistically significant process parameters. Furthermore, the percent contribution of the experimental parameters on the compressive strength were investigated. The ANOVA method gives the variance

and reliability of any experimental data with particular relations. Here, the ANOVA test was applied to determine whether the effects of adding the nano-TiO₂ on cement mortar compressive strength are statistically significant based on a significance level of 5% ($p = 0.05$). Furthermore, a large F-value can show that the variation of the process parameter made a big change in the performance characteristics of the cement mortar.

The results of average compressive strengths for cementitious composites at 7 and 56 days tests with three different types of nano-TiO₂ (A, B, and C) compared to control composites without nanomaterials are shown in Tables 2 and 3, respectively.

Table 2. Compressive strength at the 7 days test for cementitious composites with 1% boric acid and 0.5% lime (mix #2) without/with three different types of nano-TiO₂ (A, B, and C).

Mix #	Compressive Strength, MPa (without NT)
2	1.24
2	1.24
2	1.24
Compressive Strength, MPa (with NT)	
2-A	38.41
2-B	22.70
2-C	16.57

Table 3. Compressive strength at the 56 days test for cementitious composites with 1% boric acid and 0.5% lime (mix #2) without/with three different types of nano-TiO₂ (A, B, and C).

Mix #	Compressive Strength, MPa (without NT)
2	37.85
2	37.85
2	37.85
Compressive Strength, MPa (with NT)	
2-A	47.68
2-B	42.89
2-C	41.94

The results of ANOVA for these compressive strengths at the 7 and 56 days tests are shown in Tables 4 and 5, respectively. The calculated p-value of around 0.02, in the mentioned tables, highlighted that the effects of adding three different types of nano-TiO₂ (A, B, and C) on the compressive strength of cementitious composites is less than the significance level of $p = 0.05$. When the p-value is less than 0.05, it suggests that there is strong statistical evidence to reject the null hypothesis. In other words, you have sufficient statistical evidence to conclude that there are significant differences among the groups. In addition, the calculated F-value (approximately 12 to 14) is larger than the critical F-value for the chosen significance level. This indicates that the variation between groups is large enough to be considered statistically significant. In practical terms, when both the p-value is less than 0.05 and the F-value is larger than the critical F-value, it can typically be concluded

that there are statistically significant differences among the groups being compared. In such cases, the null hypothesis is rejected and it can be drawn that the observed variation in the data is unlikely to be due to random chance, but rather, it is due to meaningful differences between the groups.

Table 4. Results of ANOVA for compressive strength at the 7 days test for cementitious composites with 1% boric acid and 0.5% lime (mix #2) without/with three different types of nano-TiO₂ (A, B, and C).

Summary						
Groups	Count	Sum	Average	Variance		
Without NT	3	3.72	1.24	0		
With NT	3	77.68729	25.89576205	126.8068374		
ANOVA						
Source of variation	Sum of squares (SS)	Degree of freedom (df)	Mean squares (MS)	F-value	p-value	F _{crit} -value
Between groups	911.8599	1	911.859904	14.38187281	0.01923	7.708647
Within groups	253.6137	4	63.4034187			
Total	1165.474	5				

Table 5. Results of ANOVA for compressive strength at the 56 days test for cementitious composites with 1% boric acid and 0.5% lime (mix #2) without/with three different types of nano-TiO₂ (A, B, and C).

Summary						
Groups	Count	Sum	Average	Variance		
Without NT	3	113.55	37.85	0		
With NT	3	132.51	44.17	9.4657		
ANOVA						
Source of variation	Sum of squares (SS)	Degree of freedom (df)	Mean squares (MS)	F-value	p-value	F _{crit} -value
Between groups	59.9136	1	59.9136	12.659095	0.0236292	7.708647422
Within groups	18.9314	4	4.73285			
Total	1165.474	5				

4. Conclusions

The potential for enhancing structural materials through the incorporation of nanomaterials in construction has been investigated in this study. Experimental methods were employed to assess the impact of metallic nanomaterials on cementitious composites with varying proportions of boric acid (1%, 3%, and 5% by sand's weight) and lime powder (0.5%, 1.5%, and 2.5% by sand's weight), essential components in infrastructure construction. Based on the outcomes of the conducted research, it becomes feasible to draw conclusions regarding the effects of incorporating metallic nanomaterials into construction materials, particularly cementitious composites with boric acid and lime:

- At the early stages of curing, the addition of boric acid and lime to cement mortar may lead to a significant decrease in compressive strength, which may be attributed to the inhibiting effect of the substances of the boric acid and lime on the hydration of the cementitious material. The results of

the 7 days test (Figures 3, 5, 6, and 9) indicated that the implication of boric acid and lime in the cement mortars significantly decreased the compressive strength.

- The incorporation of TiO₂ nanoparticles into cementitious composites with boric acid and lime can improve the mechanical properties of these composites, particularly in terms of compressive strength and durability.

- The ANOVA analysis (Tables 4 and 5) demonstrates that the nanomaterials effect on the compressive strength of cementitious composites with boric acid and lime contents is statistically significant for a significance level of $p = 0.05$ and can never be neglected.

- At 56 days, the compressive strength significantly increased by 1.2 times, 85.3 times, and 65.1 times, respectively, for the addition of boric acid (1%, 3%, and 5%) with lime (0.5%, 1.5%, and 2.5%) in the presence of nano-TiO₂ (Figures 10–13), compared to the 7 days strength.

- The results indicated that, in general, the compressive strength of cementitious composites with the integration of various types of nano-TiO₂ (types A, B, and C) and containing boric acid and lime increases with increasing ratios of boric acid and lime at a sufficient curing time of 56 days (Figure 13).

- The nano-TiO₂ enhances the bonding and filling between the cement and aggregate particles, leading to a more homogenous mortar. As such, nano-TiO₂ is an effective solution for improving the compressive strength and durability of cement mortars.

Overall, the nano-TiO₂ can significantly improve the compressive strength of Portland cement mortars, particularly with the development of hydration of cement mortar when used with suitable ratios of boric acid and lime.

The findings presented here highlight the transformative potential of nanomaterial integration in advancing the structural performance of construction materials. Future research endeavors could open avenues for further exploration and refinement in the realm of advanced construction materials. Future investigations could delve into exploring the long-term durability and performance of these composite materials under various environmental conditions, such as exposure to aggressive chemicals or cyclic loading, which would provide valuable insights for real-world applications. Moreover, considering the potential synergistic effects of incorporating diverse types of metallic nanomaterials alongside boric acid and lime could unlock further improvements in mechanical properties and durability. By addressing these avenues of inquiry, future research endeavors can contribute to the continued advancement of sustainable and resilient infrastructure materials, thereby fostering innovation and addressing the evolving needs of the construction industry.

Use of AI tools declaration

The authors declare that they have not used artificial intelligence (AI) tools in the creation of this article.

Acknowledgments

The authors would like to thank GCP company for providing the ADVA materials required for this research.

Conflict of interest

The authors declare no conflict of interest.

References

1. Pacheco-Torgal F, Diamanti MV, Nazari A, et al. (2019) *Nanotechnology in Eco-Efficient Construction: Materials, Processes and Applications*, 2 Eds., Amsterdam: Woodhead Publishing. <https://doi.org/10.1016/B978-0-08-102641-0.01001-X>
2. Bartos P, Hughes J, Trtik P, et al. (2004) *Nanotechnology in Construction*, London: Royal Society of Chemistry. <https://doi.org/10.1039/9781847551528>
3. Al-Mezrakchi R, Al-Ramthan A, Alam S (2020) Designing and modeling new generation of advanced hybrid composite sandwich structure armors for ballistic threats in defense applications. *AIMS Mater Sci* 7: 608–631. <https://doi.org/10.3934/matersci.2020.5.608>
4. Al-Mezrakchi R (2018) An investigation into scalability production of ultra-fine nanofiber using electrospinning systems. *Fibers Polym* 19: 105–115. <https://doi.org/10.1007/s12221-018-7506-z>
5. Lee B, Woo BH, Ryou JS (2021) Basic mechanical and neutron shielding performance of mortar mixed with boron compounds with various alkalinity. *Sustainability* 13: 6252. <https://doi.org/10.3390/su13116252>
6. Qadir W, Ghafor K, Mohammed A (2019) Evaluation the effect of lime on the plastic and hardened properties of cement mortar and quantified using Vipulanandan model. *Open Eng* 9: 468–480. <https://doi.org/10.1515/eng-2019-0055>
7. Golewski GL (2023) Mechanical properties and brittleness of concrete made by combined fly ash, silica fume and nanosilica with ordinary Portland cement. *AIMS Mater Sci* 10: 390–404. <https://doi.org/10.3934/matersci.2023021>
8. Al-Ramthan A (2019) Behavior of walls and piles in cohesive soils under cyclic loads. Texas A&M University. Available from: <https://hdl.handle.net/1969.1/185013>.
9. Akkaya Y, Shah S, Ghandehari M (2003) Influence of fiber dispersion on the performance of microfiber reinforced cement composites. *ACI* 216: 1–18. <https://doi.org/10.14359/12888>
10. Yang H, Cui H, Tang W, et al. (2017) A critical review on research progress of graphene/cement based composites. *Compos Part A Appl Sci Manuf* 102: 273–296. <https://doi.org/10.1016/j.compositesa.2017.07.019>
11. Józwiak-Niedźwiedzka D, Lessing PA (2019) High-density and radiation shielding concrete, In: Mindess S, *Developments in the Formulation and Reinforcement of Concrete*, 2Eds., Amsterdam: Elsevier, 193–228. <https://doi.org/10.1016/B978-0-08-102616-8.00009-5>
12. Vera-Agullo J, Chozas-Ligero V, Portillo-Rico D, et al. (2009) Mortar and concrete reinforced with nanomaterials. *Nanotechnology in Construction* 3, Springer, Berlin, Heidelberg, 383–388. https://doi.org/10.1007/978-3-642-00980-8_52
13. Zhao Z, Qi T, Zhou W, et al. (2020) A review on the properties, reinforcing effects, and commercialization of nanomaterials for cement-based materials. *Nanotechnol Rev* 9: 303–322. <https://doi.org/10.1515/ntrev-2020-0023>
14. Konsta-Gdoutos MS, Metaxa ZS, Shah SP (2010) Highly dispersed carbon nanotube reinforced cement based materials. *Cement Concrete Res* 40: 1052–1059. <https://doi.org/10.1016/j.cemconres.2010.02.015>

15. Chu SH, Yang EH, Unluer C (2023) Development of nanofiber reinforced reactive magnesia-based composites for 3D printing. *Constr Build Mater* 366: 130270. <https://doi.org/https://doi.org/10.1016/j.conbuildmat.2022.130270>
16. Chu SH, Li LG, Kwan AKH (2021) Development of extrudable high strength fiber reinforced concrete incorporating nano calcium carbonate. *Addit Manuf* 37: 101617. <https://doi.org/https://doi.org/10.1016/j.addma.2020.101617>
17. Konsta-Gdoutos MS, Batis G, Danoglidis PA, et al. (2017) Effect of CNT and CNF loading and count on the corrosion resistance, conductivity and mechanical properties of nanomodified OPC mortars. *Constr Build Mater* 147: 48–57. <https://doi.org/10.1016/j.conbuildmat.2017.04.112>
18. Cuenca E, Rigamonti S, Gastaldo Brac E, et al. (2021) Crystalline admixture as healing promoter in concrete exposed to chloride-rich environments: Experimental study. *J Mater Civil Eng* 33: 04020491. [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0003604](https://doi.org/10.1061/(ASCE)MT.1943-5533.0003604)
19. Cuenca E, Mezzena A, Ferrara L (2021) Synergy between crystalline admixtures and nano-constituents in enhancing autogenous healing capacity of cementitious composites under cracking and healing cycles in aggressive waters. *Constr Build Mater* 266: 121447. <https://doi.org/10.1016/j.conbuildmat.2020.121447>
20. Alatawna A, Birenboim M, Nadiv R, et al. (2020) The effect of compatibility and dimensionality of carbon nanofillers on cement composites. *Constr Build Mater* 232: 117141. <https://doi.org/10.1016/j.conbuildmat.2019.117141>
21. Qureshi TS, Panesar DK (2019) Impact of graphene oxide and highly reduced graphene oxide on cement based composites. *Constr Build Mater* 206: 71–83. <https://doi.org/10.1016/j.conbuildmat.2019.01.176>
22. Lu L, Zhao P, Lu Z (2018) A short discussion on how to effectively use graphene oxide to reinforce cementitious composites. *Constr Build Mater* 189: 33–41. <https://doi.org/10.1016/j.conbuildmat.2018.08.170>
23. Lu Z, Li X, Hanif A, et al. (2017) Early-age interaction mechanism between the graphene oxide and cement hydrates. *Constr Build Mater* 152: 232–239. <https://doi.org/10.1016/j.conbuildmat.2017.06.176>
24. Sanchez F, Sobolev K (2010) Nanotechnology in concrete—A review. *Constr Build Mater* 24: 2060–2071. <https://doi.org/10.1016/j.conbuildmat.2010.03.014>
25. Rehman F, Zhao C, Jiang H, et al. (2016) Biomedical applications of nano-titania in theranostics and photodynamic therapy. *Biomater Sci* 4: 40–54. <https://doi.org/10.1039/C5BM00332F>
26. Hassan MM, Dylla H, Mohammad LN, et al. (2010) Evaluation of the durability of titanium dioxide photocatalyst coating for concrete pavement. *Constr Build Mater* 24: 1456–1461. <https://doi.org/10.1016/j.conbuildmat.2010.01.009>
27. Loh K, Gaylarde CC, Shirakawa MA (2018) Photocatalytic activity of ZnO and TiO₂ ‘nanoparticles’ for use in cement mixes. *Constr Build Mater* 167: 853–859. <https://doi.org/10.1016/j.conbuildmat.2018.02.103>
28. Carp O, Huisman CL, Reller A (2004) Photoinduced reactivity of titanium dioxide. *Prog Solid State Ch* 32: 33–177. <https://doi.org/10.1016/j.progsolidstchem.2004.08.001>
29. Cassar L (2004) Photocatalysis of cementitious materials: clean buildings and clean air. *MRS Bull* 29: 328–331. <https://doi.org/10.1557/mrs2004.99>

30. Folli A, Pade C, Hansen TB, et al. (2012) TiO₂ photocatalysis in cementitious systems: Insights into self-cleaning and depollution chemistry. *Cement Concrete Res* 42: 539–548. <https://doi.org/10.1016/j.cemconres.2011.12.001>
31. Gopalan AI, Lee JC, Saianand G, et al. (2020) Recent progress in the abatement of hazardous pollutants using photocatalytic TiO₂-based building materials. *Nanomaterials* 10: 1854. <https://doi.org/10.3390/nano10091854>
32. Chen J, Poon CS (2009) Photocatalytic construction and building materials: From fundamentals to applications. *Build Environ* 44: 1899–1906. <https://doi.org/10.1016/j.buildenv.2009.01.002>
33. Chen F, Yang X, Mak HKC, et al. (2010) Photocatalytic oxidation for antimicrobial control in built environment: A brief literature overview. *Build Environ* 45: 1747–1754. <https://doi.org/https://doi.org/10.1016/j.buildenv.2010.01.024>
34. Macphee DE, Folli A (2016) Photocatalytic concretes—The interface between photocatalysis and cement chemistry. *Cement Concrete Res* 85: 48–54. <https://doi.org/https://doi.org/10.1016/j.cemconres.2016.03.007>
35. Hamidi F, Aslani F (2019) TiO₂-based photocatalytic cementitious composites: Materials, properties, influential parameters, and assessment techniques. *Nanomaterials* 9: 1444. <https://doi.org/10.3390/nano9101444>
36. Essawy AA, Abd El.Aleem S (2014) Physico-mechanical properties, potent adsorptive and photocatalytic efficacies of sulfate resisting cement blends containing micro silica and nano-TiO₂. *Constr Build Mater* 52: 1–8. <https://doi.org/10.1016/j.conbuildmat.2013.11.026>
37. Chen J, Kou SC, Poon CS (2012) Hydration and properties of nano-TiO₂ blended cement composites. *Cement Concrete Comp* 34: 642–649. <https://doi.org/10.1016/j.cemconcomp.2012.02.009>
38. Zhang R, Cheng X, Hou P, et al. (2015) Influences of nano-TiO₂ on the properties of cement-based materials: Hydration and drying shrinkage. *Constr Build Mater* 81: 35–41. <https://doi.org/10.1016/j.conbuildmat.2015.02.003>
39. ASTM International (2021) Standard specification for standard sand. ASTM C778, West Conshohocken, PA. <https://doi.org/10.1520/C0778-21>
40. Yousefi A, Allahverdi A, Hejazi P (2013) Effective dispersion of nano-TiO₂ powder for enhancement of photocatalytic properties in cement mixes. *Constr Build Mater* 41: 224–230. <https://doi.org/10.1016/j.conbuildmat.2012.11.057>
41. ASTM International (2021) Standard test method for compressive strength of hydraulic cement mortars (using 2-in. or 50 mm cube specimens). ASTM C109/C109M, West Conshohocken, PA. https://doi.org/10.1520/C0109_C0109M-21
42. Rajadesingu S, Arunachalam KD (2020) Hydration effect of boric acid on the strength of high-performance concrete (HPC). *IOP Conf Ser Mater Sci Eng* 912: 062073. <https://doi.org/10.1088/1757-899X/912/6/062073>
43. Davraz M (2015) The effect of boron compound to cement hydration and controllability of this effect. *Acta Phys Pol A* 128. <https://doi.org/10.12693/APhysPolA.128.B-26>
44. Volkman D, Bussolini P (1992) Comparison of fine particle colemanite and boron frit in concrete for time-strength relationship. *J Test Eval* 20: 92–96. <https://doi.org/10.1520/JTE11903J>
45. Olgun A, Kavas T, Erdogan Y, et al. (2007) Physico-chemical characteristics of chemically activated cement containing boron. *Build Environ* 42: 2384–2395. <https://doi.org/10.1016/j.buildenv.2006.06.003>

46. Targan Ş, Olgun A, Erdogan Y, et al. (2002) Effects of supplementary cementing materials on the properties of cement and concrete. *Cement Concrete Res* 32: 1551–1558. [https://doi.org/10.1016/S0008-8846\(02\)00831-1](https://doi.org/10.1016/S0008-8846(02)00831-1)
47. Jayapalan A, Lee B, Kurtis K (2009) Effect of nano-sized titanium dioxide on early age hydration of Portland cement. *Nanotechnology in Construction* 3, Springer, Berlin, Heidelberg, 267–273. https://doi.org/10.1007/978-3-642-00980-8_35
48. Parveen S (2016) Microstructure and mechanical properties of nanomaterial reinforced cementitious composites. Universidade do Minho (Portugal). Available from: <https://hdl.handle.net/1822/45268>.



AIMS Press

© 2024 the Author(s), licensee AIMS Press. This is an open access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>)