Research Article

Effect of Nano-CaCO₃ on the Mechanical Properties and Durability of Concrete Incorporating Fly Ash

Yanqun Sun, Peng Zhang, Weina Guo, Jiuwen Bao, and Chengping Qu

School of Civil Engineering, Qingdao University of Technology, Qingdao 266033, China

Correspondence should be addressed to Peng Zhang; peng.zhang@qut.edu.cn

Received 18 January 2020; Accepted 23 March 2020; Published 9 April 2020

Copyright © 2020 Yanqun Sun et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Concrete mixtures consisting of nanomaterials and fly ash have been shown to be effective for improving the performance of concrete. This study investigates the combined effects of nano-CaCO₃ and fly ash on the mechanical properties and durability of concrete; the mix proportion is optimized through orthogonal experiments. In the first phase, nine concrete mixtures were prepared with three water-to-binder ratios (0.4, 0.5, and 0.6), three fly ash contents (15%, 20%, and 25% replacement of the cement weight), and three nano-CaCO₃ contents (1%, 2%, and 3% replacement of the cement weight). Based on the orthogonal analysis, the optimal concrete mix proportion was determined as a water-to-binder ratio of 0.4, 20% fly ash, and 1% nano-CaCO₃. In the second phase, further investigations were carried out to examine the superiority of the optimal concrete and evaluate the synergistic effect of nano-CaCO₃ and fly ash. The results showed that nano-CaCO₃ contributed to increasing the compressive strength of fly ash concrete at the early ages, but its effect was quite limited at later ages. Furthermore, the scanning electron microscopy analysis revealed that the seeding effect, filling effect, and pozzolanic effect were the primary mechanisms for the improvement of concrete performance.

1. Introduction

In recent years, concrete has been used extensively for the construction of high-rise buildings and marine structures as well as for long-span bridges under harsh environmental conditions [1]. To satisfy the demands of these applications, modern concrete materials must possess high strength, toughness, and durability. However, concrete has some intrinsic defects, such as low tensile strength, poor toughness, and high brittleness, which makes it susceptible to deterioration under adverse conditions [2]. As a by-product of industrial processes, the addition of fly ash to concrete not only benefits the environment but also confers economic benefits [3]. Moreover, fly ash possesses pozzolanic activity that reacts with calcium hydroxide (CH) during cement hydration, forming additional hydration products such as calcium silicate hydrate (C-S-H) and calcium aluminate hydrate (C-A-H) [4]. Most previous studies [5–10] have shown that these hydration products of the pozzolanic reaction can effectively improve the density of concrete, leading to higher strength and better durability. For instance, the resulting reduced permeability of concrete can inhibit damage to the concrete through the alkali–aggregate reaction. However, the pozzolanic reaction of fly ash is slow, with lower strength at early ages, which remains a concern.

Recently, valuable research has been conducted to investigate the influence of nanomaterials on the properties of concrete. Jo et al. [11] reported that nano-SiO₂ can improve the compressive and flexural strength of cement mortars. Nazari et al. [12] showed that the hydration degree of cement was also improved with the addition of nano-Al₂O₃. Meanwhile, Senff et al. [13] and Nazari et al. [14] found that the setting time of fresh cement paste could be shortened by nano-SiO₂ and nano-Al₂O₃, and the initial setting time and the final setting time became shorter with the increase of the nanoparticles content. Thus, combining nanomaterials with fly ash could provide a more practical and reliable method for enhancing the properties of concrete. However, it is undeniable that their high cost restricts the application and development of nanomaterials [15]. Moreover, it must be
taken into consideration that nanomaterials may be difficult
to disperse in the cement paste owing to their huge specific
surface area and strong surface activity [16].

Owing to its high efficacy and inexpensive price, nano-
CaCO₃ has been widely used in the plastics industry as an
additive [17]. If nano-CaCO₃ has a positive effect when
added to concrete, it could be a feasible prospect for the
application of nanomodified concrete. Chemically, nano-
CaCO₃ can improve the rate of reaction of tricalcium alu-
minate (C₃A) to form a carboaluminate complex, increasing
the total hydration products and thus the strength [18]. In
addition, it also reacts with tricalcium silicate (C₃S) and
promotes setting, producing a higher volume of hydrates,
which are effective for filling the microstructure [19]. As a
consequence, nano-CaCO₃ concrete possesses a higher
initial strength [20, 21]. Sato and Diallo [22] studied the
influence of nano-CaCO₃ on cement hydration, and the
results revealed that the rapid growth of C-S-H was sig-
nificantly improved by adding nano-CaCO₃ owing to the
seeding effect of the nanoparticles. Supit and Shaikh [23]
evaluated four different contents of nano-CaCO₃ added to
fly ash concrete, and the results showed that the addition of
1% nano-CaCO₃ provided an optimal improvement in the
compressive strength of concrete. Xu et al. [24] reported that
the addition of 1%-2% nano-CaCO₃ could improve the
compressive strength of high-performance concrete by
13%-18%.

While most studies have investigated the effects of nano-
CaCO₃ and fly ash on the hydration, compressive strength,
and microstructure of concrete, only a few have performed
detailed investigations of the comprehensive performance
of concrete containing nano-CaCO₃ and fly ash. Therefore, the
objectives of this study were to investigate the synergistic
mechanism for the effect of nano-CaCO₃ and fly ash not
only on strength development but also on the durability of
concrete, including its chloride penetrability, carbonation
resistance, and frost resistance. In addition, the optimal
concrete mix proportion was determined. The results of this
study may serve to facilitate the proper use of nano-CaCO₃
and fly ash in concrete to achieve the increasing demands of
practical applications.

## 2. Materials and Methods

### 2.1. Materials

Ordinary Portland cement with a 28-d compressive strength of 42.5 MPa and class I fly ash with a
surface area of approximately 380 m²/kg were used as
cement paste materials. The chemical compositions of the
ordinary Portland cement and fly ash are listed in Table 1.
River sand with a maximum particle size of 5 mm and
granite gravel with a particle size range of 5 mm to 20 mm,
both from the Qingdao area, were used as the fine ag-
gregate and coarse aggregate, respectively. Nano-CaCO₃
was used in this study owing to its lower price, and the
physical properties of nano-CaCO₃ are summarized in
Table 2. One type of polycarboxylate superplasticizer was
used as an additive to the concrete to obtain the desired
slump and fluidity as well as to act as a dispersant for the
nano-CaCO₃.

### 2.2. Test Specimens

In the first phase, a total of 90 concrete
blocks with a size of 100 mm were produced for compressive
strength tests, and 30 prism specimens with dimensions of
100 mm × 100 mm × 400 mm were produced for flexural
strength tests. In the second phase, the 100 mm concrete
blocks and 100 mm × 100 mm × 400 mm prism speci-
mens, and cylindrical specimens with dimensions of
100 mm × 50 mm were cast for tests of mechanical properties
and durability. All of the specimens were demolded after one
day and placed under a standard condition (T = 20 ± 2°C and
RH ≥ 95%) to cure until the testing ages. A set of three
specimens were tested for each concrete mix, and the
average value was reported as the final value. The reference
cement concrete contained 190 kg/m³ water, 380 kg/m³ cement,
622 kg/m³ fine aggregate, and 1208 kg/m³ coarse aggregate;
the weight of water reducer was adjusted according to the
nano-CaCO₃ content. For all mixes, the weights of water and
aggregate were kept constant. It should be noted that nano-
CaCO₃ is insoluble in water. However, polycarboxylate
superplasticizer has a strong dispersing effect; and therefore
nano-CaCO₃ could be dispersed in water and form a sub-
stantially uniform mixed solution with a high-speed mixing.
Half of the solution was then mixed with cement and ag-
gregates for 30 s. After that, another half of the solution was
added to the mixtures, followed by further stirring for 90 s.

### 2.3. Orthogonal Experiments

The orthogonal experiments
were designed based on statistics; the test data was analyzed
using mathematical methods, and the factors and levels were
simplified to obtain the optimal mix proportion [25]. Three
factors affecting the properties of concrete were studied: (A)
the water-to-binder ratio (W/C), (B) the fly ash content, and
(C) the nano-CaCO₃ content. Each factor was designed with
three different levels (https://www.sciencedirect.com/
science/article/pii/S095006181932478X?via
one reference concrete (https://www.sciencedirect.com/
science/article/pii/S095006181932478X?via
Table 3).

According to the L9 (3⁴) orthogonal experiment design
table, a total of ten concrete mixtures were tested, including
one reference concrete (https://www.sciencedirect.com/
science/article/pii/S095006181932478X?via
Table 4).

The tests of mechanical properties were conducted based on
standard GB/T50081-2002 [26]. At ages of 3, 7, and 28 d, the
cubic specimens were removed from the curing room for
compressive strength tests. After 28 d of aging, the flexural
strength of the prism specimens was measured using the
third-point loading method. The test levels and composi-
tions of the concrete specimens were selected based on
previous studies [27, 28].

A range analysis was conducted to determine the order
of influence and select the optimal level of each factor. Based
on the range analysis, the values of K and R were first
calculated. The K value for each level of a parameter is the
sum of three values of samples with the same level, and the
highest K value represents the optimal level. The R value is an
indicator that reflects the order of influence of each factor,
which is calculated as the difference between the maximum
and minimum values of the three levels. The most significant
factor has the highest R value. In this manner, the optimal
concrete mix could be determined. A variance analysis was
conducted to test the significance of the factors. Based on the variance analysis theory, the sum of squares (SS), degree of freedom (DF), mean square (MS), and F values were computed. The F value is a major pointer reflecting the significance of factors. For a certain factor, the significance can be evaluated by comparing the F value with predetermined significance criteria: $F_{0.01}(2, 8)$ and $F_{0.05}(2, 8)$. A factor F value $> F_{0.01}(2, 8)$ indicates a major impact; $F_{0.05}(2, 8) < F$ value $< F_{0.01}(2, 8)$ indicates a moderate impact; $F$ value $< F_{0.05}(2, 8)$ indicates a minor impact. Thus, the optimal concrete mix can be confirmed.

### Table 1: Chemical composition of ordinary Portland cement and fly ash (%).

| Type   | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO  | MgO  | SO$_3$ | K$_2$O | Na$_2$O | TiO$_2$ | P$_2$O$_5$ |
|--------|---------|-------------|-------------|------|------|--------|--------|---------|---------|-----------|
| OPC    | 22.13   | 7.35        | 3.93        | 61.22| 4.07 | 1.52   | 0.47   | 0.99    | 0.35    | 0.05      |
| FA     | 53.30   | 29.68       | 5.60        | 8.07 | 1.45 | 1.14   | 1.54   | —       | —       | —         |

Note: OPC: ordinary Portland cement; FA: fly ash.

### Table 2: Physical properties of nano-CaCO$_3$.

| Factor/level | Average particle size (nm) | Specific surface area (m$^2$/g) | CaCO$_3$ content (%) | pH value | Apparent density (g/L) |
|--------------|---------------------------|---------------------------------|----------------------|----------|------------------------|
| A (W/C)      | 15--40                    | 180                             | 98.9                 | 8.5--10.5| 300                    |
| B (fly ash content/%) | 15 | 0.5 | 0.6 |
| C (nano-CaCO$_3$ content/%) | 1 | 2 | 3 |

### Table 3: Factors and levels.

| No. | A (W/C) | B (%)       | C (%)       |
|-----|---------|-------------|-------------|
| A0  | 0.5     | 0           | 0           |
| A1  | 0.4 (1) | 15 (1)      | 1 (1)       |
| A2  | 0.4 (1) | 20 (2)      | 2 (2)       |
| A3  | 0.4 (1) | 25 (3)      | 3 (3)       |
| A4  | 0.5 (1) | 15 (1)      | 2 (2)       |
| A5  | 0.5 (2) | 20 (2)      | 3 (3)       |
| A6  | 0.5 (2) | 25 (3)      | 1 (1)       |
| A7  | 0.6 (3) | 15 (1)      | 3 (3)       |
| A8  | 0.6 (3) | 20 (2)      | 1 (1)       |
| A9  | 0.6 (3) | 25 (3)      | 2 (2)       |

Then, the chloride ion diffusion coefficient of the concrete was calculated. The carbonation tests were carried out at 3, 7, 14, and 28 d, and the carbonation depths were tested by spraying a 1% phenolphthalein alcohol solution on the surface of the reserved side, which was not sealed with paraffin wax. The freeze-thaw tests utilized the rapid freezing and thawing method. One freeze-thaw cycle lasted for 3.5 h, with the highest temperature in the center of $(5 ± 2) ^\circ C$ and lowest temperature of $(−18 ± 2) ^\circ C$. In total, 175 freeze-thaw cycles were conducted.

### Table 4: Design table for the orthogonal experiments.

### 2.5. Microstructure Analysis.

After the strength tests at the age of 7 and 28 d, small size of 3 to 5 mm pieces was taken from the specimens. The hydration reaction was stopped by putting them into pure alcohol. When their microstructures were observed by SEM method. Before observation, the samples were sprayed with gold to improve the conductivity and then placed in the sample chamber. The sample microstructures were observed with a JSM-7610F field emission scanning electron microscope.

### 3. Results and Discussion

#### 3.1. Optimal Mix Proportion.

The results of the mechanical properties tests are presented in Figure 1. Figures 1(a), 1(b), and 1(c) show that A1 had the highest compressive strengths at 3, 7, and 28 d: 30.65 MPa, 41.43 MPa, and 53.30 MPa, respectively. Based on the compressive strength results, the optimal concrete mix is A1B1C1, which corresponds to level 1 for the W/C, fly ash, and nano-CaCO$_3$ contents. This is followed by A2, which has W/C at level 1, fly ash at level 2, and nano-CaCO$_3$ at level 2. For the flexural strength, as shown in Figure 1(d), the optimal concrete mixture is A2, with mix proportions of A1B2C2.
A variance analysis was also conducted based on the compressive strength, and the significance of factors was obtained; the results are listed in Table 6. The effect of W/C on the compressive strength is always significant. At 3 and 7 d, the influence of nano-CaCO$_3$ is greater than that of fly ash. The order of significance is A, C, B. At 28 d, nano-CaCO$_3$ does not have a significant effect on the compressive strength. The order of the factor importance is A, B, C. Thus, the range and variance analysis results are consistent.

Table 7 lists the results obtained from the range and variance analyses based on the flexural strength at 28 d. According to the $K$ value, the optimal mix proportion is A$_1$B$_2$C$_1$. W/C has a significant effect on the concrete strength, while the other factors are not important. Thus, the range and variance analysis results are consistent, and the order of factor importance is A, C, B.

The optimal levels and the significance of factors obtained in the orthogonal analysis are summarized in Table 8; Figure 2 shows the effect of different levels on the mechanical properties. Thus, using the compressive strength and flexural strength as indices, the optimal levels for the concrete mixture could be determined.

As shown in Figure 2, curve A has the largest fluctuations, illustrating that W/C is the most significant factor affecting the performance of concrete. Therefore, the optimal level of W/C is determined as A$_1$ (0.4). For fly ash, the optimal level is B$_1$ at 3 and 7 d; however, Figure 2(c) indicates that the fly ash content is increased from B$_1$ to B$_2$ and the compressive strength at 28 d increased by 7.74%. With further increase in the fly ash content, curve B exhibits a downward trend. Considering that adding fly ash not only improves the concrete strength at later ages but also reduces the cost of concrete [30], the optimal level of fly ash was determined to be B$_2$ (20%). For nano-CaCO$_3$, the optimal level of C$_1$ is better than C$_2$ based on the visual analysis and range analysis. When the amount of nano-CaCO$_3$ increased...
from C₁ to C₂, the compressive strength at 3d increased by 1.6%. However, it should be noted that when a high amount of nano-CaCO₃ is added to the concrete, the agglomeration of nano-CaCO₃, increase in viscosity, and reduction in flowability of the mixture can result in more cracks and air voids. Such cracks and air voids are triggers for the failure of concrete as they can have detrimental effects on the mechanical properties of concrete. The results indicate that, with an increase in the nano-CaCO₃ content from C₂ to C₃, the compressive strength at 28d decreased by 16.65%. Moreover, the flexural strength exhibited the same trend at 28d. In addition, considering the economic effect, C₁ is the optimal level for improving the concrete strength. Based on the above discussion, the optimal mix proportion is A₁B₂C₁, which represents a W/C of 0.4, 20% fly ash, and 1% nano-CaCO₃.

3.2. Effects of Nano-CaCO₃ and Fly Ash on the Mechanical Properties of Concrete. The mechanical properties of different concrete compositions are presented in Figure 3. The results show the effects of nano-CaCO₃ and fly ash on the strength of concrete. It is clear that sample NC (concrete with 20% fly ash and 1% nano-CaCO₃) had a higher strength than samples JZ (concrete without fly ash or nano-CaCO₃) and FA (concrete with 20% fly ash only) at all ages. As expected, on comparing JZ and FA, it can be observed that the compressive strength of the concrete with fly ash slowly increased at early ages but significantly improved at 28d.

Compared with FA, the compressive strength of NC was increased by approximately 10.98% and 12.98% at 3 and 7 d, respectively. However, this improvement ceased at 28d, indicating that the addition of nano-CaCO₃ can compensate for the low compressive strength of concrete with fly ash at early ages but is quite limited at later ages; compared with JZ, NC exhibited higher compressive strengths at 3, 7, and 28d, representing improvements of approximately 8.25%, 11.01%, and 13.67%, respectively. The results reveal that the combination of nano-CaCO₃ and fly ash in concrete is beneficial for improving the compressive strength.

As shown in Figure 3(b), the flexural strength of NC was increased by 19.00% and 8.22%, compared to JZ and FA, respectively, indicating that the addition of nano-CaCO₃ could increase the flexural strength of concrete, while the synergistic effect is much better than single-doped nano-CaCO₃.

3.3. Effects of Nano-CaCO₃ and Fly Ash on the Durability of Concrete. In Figure 4(a), it can be seen that the chloride diffusion coefficient of concrete JZ was the highest, representing the worst chloride resistance of the concrete samples. Compared with JZ, the chloride diffusion coefficients of FA and NC were decreased by 27.42% and 40.12%, respectively, indicating that fly ash can effectively limit the diffusion of chloride ions in concrete; the chloride resistance was further enhanced by the addition of 1% nano-CaCO₃. Previous studies [31, 32] have shown that the continuous evaporation...
of free water in the concrete during the hydration process caused a large number of pores to be left in the interior. These pores intersect with each other to form an open capillary bleeding channel, which increases the permeability. Only pore sizes larger than 50 nm will affect the permeability of concrete [33]. The filling effects of the fly ash can fill the

![Figure 2: Impact of different levels: compressive strength at (a) 3 d, (b) 7 d, and (c) 28 d; (d) flexural strength at 28 d.](image)

![Figure 3: Mechanical properties of different concretes: (a) compressive strength at 3, 7, and 28 d; (b) flexural strength at 28 d.](image)
tiny pores, and adding nano-CaCO3 can further refine the pore structure, transform the harmful pores into harmless or less pores, and reduce porosity. Therefore, nano-CaCO3 and fly ash can significantly improve the permeability of concrete.

As shown in Figure 4(b), the concrete carbonation depth exhibited roughly the same trend of gradually deepening with age; the carbonation depth increased faster in the early stage than the later stage. This may be because CaCO3 and other solid substances generated during the early carbonation of concrete blocked the internal micropores, thus reducing the diffusion rate of CO2 [34]. The carbonation depth of FA is the largest, indicating that FA is more susceptible to carbonization. The reason is that fly ash can cause a “secondary reaction” with the cement hydration product Ca(OH)2, which reduces the alkalinity of the pore solution and carbonizable substances, leading to a decreased resistance to carbonation [35, 36]. Comparing NC and FA shows that the addition of nano-CaCO3 can not only make up for the adverse effect of fly ash but also greatly enhance the carbonation resistance.

As shown in Figures 4(c) and 4(d), before 50 freeze-thaw cycles, the relative dynamic elastic modulus of decay was slow, and the mass loss rate increased gradually. It is speculated that the loss process of concrete depends on the pore structure during the freeze-thaw process [37]. During the initial freezing and thawing of concrete, the degree of internal pore expansion is small. With an increasing number of freeze-thaw cycles, the tensile and compressive stresses generated in the concrete constantly change during the freezing and thawing processes, causing the internal pores to continuously expand, eventually forming cracks [38]. As a result, the rate of decrease in the relative dynamic elastic modulus of concrete accelerated continuously. Moreover, JZ exhibited a sharp mass loss when the number of freeze-thaw cycles reached 25, which represents the initiation of damage to the concrete; NC exhibited a much slower weight loss than JC. When the number of freeze-thaw cycles reached 175, the relative dynamic elastic modulus of NC was 65.79%, representing a decrease of 49.48%, and the mass loss rate was within 5%; JZ and FA were damaged after 125 and 150 freeze-thaw cycles, respectively. Compared to JZ, it can be

### Figure 4: The results of durability tests:

| (a) Chloride diffusion coefficient | (b) Carbonation depth |
|-----------------------------------|----------------------|
| [JZ, FA, NC]                      | [3d, 7d, 14d, 28d]   |

| (c) Relative dynamic modulus (%) |
|----------------------------------|
| [JZ, FA, NC]                     |

| (d) Mass loss rate (%)           |
|---------------------------------|
| [JZ, FA, NC]                    |
seen that the frost resistance of NC has been greatly improved, indicating that the effect of combining nano-CaCO$_3$ and fly ash is beneficial for the frost resistance.

3.4. Effects of Nano-CaCO$_3$ and Fly Ash on the Microstructure of Concrete. Figure 5 shows SEM images of selected concrete samples JZ and NC at 7 and 28 d, respectively. Comparing Figures 5(a) and 5(b) shows that the microstructure of sample JZ was relatively loose, confirming that the degree of hydration of JZ was lower than that of NC. As shown in Figure 5(a), many hydration products were formed on the surface of the fly ash particles, and it appears that a network-type structure was formed by these hydrates as a result of the accelerated hydration of cement and fly ash by nano-CaCO$_3$. Furthermore, some small piles, which may be composed of nano-CaCO$_3$, hydrates, and fly ash, can be observed in the network. This may also indicate nano-CaCO$_3$ was helpful for accelerating the hydration process as a result of its high hydration activity and ability to provide nucleation sites. In addition, researchers have found [39] that nano-CaCO$_3$ can increase the content of C-S-H gel at the interface and improve the orientation of Ca (OH)$_2$ crystals, resulting in a transition in the hydration structure at the interface position from a planar arrangement to a spatial structure. Moreover, nano-CaCO$_3$ filled up the pores of loose net structure around the cement particles, thereby decreasing the porosity of concrete and increasing the density degree [40]. Thus, it can be concluded that nano-CaCO$_3$ was helpful for increasing the hydration degree and enhancing the strength of concrete at early ages.

With continued progress of the hydration, the microstructure became more compact at 28 d, as shown in Figures 5(c) and 5(d). A comparison of (c) and (d) reveals that, with the generation of new C-S-H gels and the growth of ettringite crystals, the internal pores in the cement became more completely filled. After 28 d, the C-S-H gels and ettringites attached to each other and needle-like ettringites were wrapped by the C-S-H gels, which also contributed to increasing the density. This may be a result of the pozzolanic effect of the fly ash, which plays an important role in the improvement of strength at later ages.

Based on the above analysis, it can be concluded that concrete containing nano-CaCO$_3$ and fly ash can accelerate the hydration process and lead to a denser microstructure, consequently enhancing the mechanical properties and
durability of the concrete. This may be the result of a few mechanisms: the seeding effect, filling effect, and pozzolanic effect.

4. Conclusions

Based on the results of this study, the following conclusions can be drawn:

(1) An evaluation revealed that the concrete with a W/C ratio of 0.4, 20% fly ash, and 1% nano-CaCO₃ exhibited the best mechanical properties.

(2) Under the synergistic effect of nano-CaCO₃ and fly ash, the durability of the concrete was significantly enhanced owing to the filling effect. In particular, with the addition of nano-CaCO₃, the adverse effects of fly ash on the carbonation resistance could be balanced out.

(3) SEM analysis reveals that nano-CaCO₃ was helpful for increasing the compressive strength of the concrete at early ages due to the acceleration of cement hydration by the seeding effect and the tighter pore structure of cement as a result of nanofilling. On the other hand, the pozzolanic effect of the fly ash at later ages can further enhance the mechanical strength of concrete, making up for the limited effect of the nano-CaCO₃.

For practical applications, reasonable guidance on the optimal concrete mix proportion can be provided. However, detailed researches on the production and preparation technology of nanomaterials are required to facilitate the application of nanomodified concrete.

Data Availability

All the data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgments

Financial support for ongoing projects from the National Natural Science Foundation of China (51922052, U1706222, and 51778309) and the Natural Science Foundation of Shandong Province (ZR2018JL018) is gratefully acknowledged.

References

[1] F. Pacheco-Torgal and S. Jalali, “Nanotechnology: advantages and drawbacks in the field of construction and building materials,” Construction and Building Materials, vol. 25, no. 2, pp. 582–590, 2011.

[2] M. F. Najjar, M. L. Nehdi, A. M. Soliman, and T. M. Azabi, “Damage mechanisms of two-stage concrete exposed to chemical and physical sulfate attack,” Construction and Building Materials, vol. 137, no. 4, pp. 141–152, 2017.

[3] D. Wang, X. Zhou, Y. Meng, and Z. Chen, “Durability of concrete containing fly ash and silica fume against combined freezing-thawing and sulfate attack,” Construction and Building Materials, vol. 147, no. 8, pp. 398–406, 2017.

[4] M. S. Kirgiz, “Advance treatment by nanographite for Portland pulvred fly ash cement (the class F) systems,” Composites Part B: Engineering, vol. 82, no. 12, pp. 59–71, 2015.

[5] P. Zhang, D. Li, Y. Qiao, S. Zhang, C. Sun, and T. J. Zhao, “The effect of air entrainment on the mechanical properties, chloride migration and microstructure of ordinary concrete and fly ash concrete,” Journal of Materials in Civil Engineering, vol. 30, no. 10, Article ID 04018265, 2018.

[6] S. B. Xue, P. Zhang, J. W. Bao, L. F. He, Y. Hu, and S. D. Yang, “Comparison of mercury intrusion porosimetry and multiscale X-ray CT on characterizing the microstructure of heat-treated cement mortar,” Materials Characterization, vol. 160, no. 2, Article ID 110085, 2020.

[7] J. W. Bao, S. G. Li, P. Zhang et al., “Influence of the incorporation of recycled coarse aggregate on water absorption and chloride penetration into concrete,” Construction and Building Materials, vol. 239, no. 4, Article ID 117845, 2020.

[8] Y. Su, J. Li, C. Wu, P. Wu, and Z.-X. Li, “Influences of nanoparticles on dynamic strength of ultra-high performance concrete,” Composites Part B: Engineering, vol. 91, no. 4, pp. 595–609, 2016.

[9] M.-H. Zhang and J. Islam, “Use of nano-silica to reduce setting time and increase early strength of concretes with high volumes of fly ash or slag,” Construction and Building Materials, vol. 29, no. 4, pp. 573–580, 2012.

[10] A. Nazari and S. Riahi, “The effects of SiO₂ nanoparticles on physical and mechanical properties of high strength compacting concrete,” Composites Part B: Engineering, vol. 42, no. 3, pp. 570–578, 2011.

[11] B.-W. Jo, C.-H. Kim, G.-H. Tae, and J.-B. Park, “Characteristics of cement mortar with nano-SiO₂ particles,” Construction and Building Materials, vol. 21, no. 6, pp. 1351–1355, 2007.

[12] A. Nazari, R. Shadi, R. Shirin, S. F. Shamekhi, and A. Khademno, “Mechanical properties of cement mortar with Al₂O₃ nanoparticles,” Journal of American Science, vol. 6, no. 4, pp. 94–97, 2010.

[13] L. Senff, J. A. Labrincha, V. M. Ferreira, D. Hotza, and W. L. Repette, “Effect of nano-silica on rheology and fresh properties of cement pastes and mortars,” Construction and Building Materials, vol. 23, no. 7, pp. 2487–2491, 2009.

[14] A. Nazari, R. Shadi, R. Shirin, S. F. Shamekhi, and A. Khademno, “Influence of Al₂O₃ nanoparticles on the compressive strength and workability of blended concrete,” Journal of American Science, vol. 6, no. 5, pp. 6–9, 2010.

[15] E. Garcia-Taengua, M. Sonebi, K. M. A. Hossain, M. Lachemi, and J. Khatib, “Effects of the addition of nanosilica on the rheology, hydration and development of the compressive strength of cement mortars,” Composites Part B: Engineering, vol. 81, no. 11, pp. 120–129, 2015.

[16] T. Sato and J. J. Beaudoin, “Effect of nano-CaCO₃ on hydration of cement containing supplementary cementitious materials,” Advances in Cement Research, vol. 23, no. 1, pp. 1–29, 2010.

[17] P. Hou, K. Wang, J. Qian, S. Kawashima, D. Kong, and S. P. Shah, “Effects of colloidal nano SiO₂ on fly ash hydration,” Cement and Concrete Composites, vol. 34, no. 10, pp. 1095–1103, 2012.

[18] F. Sanchez and K. Sobolev, “Nanotechnology in concrete—a review,” Construction and Building Materials, vol. 24, no. 11, pp. 2060–2071, 2010.
[19] G. Kakali, S. Tsivilis, E. Aggeli, and M. Bati, “Hydration products of C₃A, C₃S and Portland cement in the presence of CaCO₃,” *Cement and Concrete Research*, vol. 30, no. 7, pp. 1073–1077, 2000.

[20] T. Meng, Y. Yu, and Z. Wang, “Effect of nano-CaCO₃ slurry on the mechanical properties and micro-structure of concrete with and without fly ash,” *Composites Part B: Engineering*, vol. 117, no. 5, pp. 124–129, 2017.

[21] T. Meng, K. Qian, X. Qian, and S. Zhan, “Effect of the nano-CaCO₃ on hydrated properties and interface of cement paste,” *Rare Metal Materials and Engineering*, vol. 37, no. 5, pp. 667–669, 2008.

[22] T. Sato and F. Diallo, “Seeding effect of nano-CaCO₃ on the hydration of tricalcium silicate,” *Transportation Research Record: Journal of the Transportation Research Board*, vol. 2141, no. 1, pp. 61–67, 2010.

[23] S. W. M. Supit and F. U. A. Shaikh, “Effect of nano-CaCO₃ on compressive strength development of high volume fly ash mortars and concretes,” *Journal of Advanced Concrete Technology*, vol. 12, no. 6, pp. 178–186, 2014.

[24] Q. L. Xu, T. Meng, and M. Z. Huang, “Effects of nano-CaCO₃ on the compressive strength and microstructure of high strength concrete in different curing temperature,” *Applied Mechanics and Materials*, vol. 121–126, no. 1, pp. 126–131, 2011.

[25] Z. Ge, Z. Gao, R. Sun, and L. Zheng, “Mix design of concrete with recycled clay-brick-powder using the orthogonal design method,” *Construction and Building Materials*, vol. 31, no. 7, pp. 289–293, 2012.

[26] C. Standard, GB/T50081-2002.

[27] M. Stefanidou and I. Papayianni, “Influence of nano-SiO₂ on the Portland cement pastes,” *Composites Part B: Engineering*, vol. 43, no. 6, pp. 2706–2710, 2012.

[28] S. C. K. Bendapudi and P. Saha, “Contribution of fly ash to the properties of mortar and concrete,” *International Journal of Earth Sciences and Engineering*, vol. 4, no. 6, pp. 1017–1023, 2011.

[29] C. Standard, GB/T50082-2009.

[30] G. Land and D. Stephan, “The influence of nano-silica on the hydration of ordinary Portland cement,” *Journal of Materials Science*, vol. 47, no. 2, pp. 1011–1017, 2012.

[31] Y. Wang, T. Cao, P. Zhang et al., “Water absorption and chloride diffusivity of concrete under the coupling effect of uniaxial compressive load and freeze-thaw cycles,” *Construction and Building Materials*, vol. 209, no. 6, pp. 566–576, 2019.

[32] F. U. A. Shaikh and S. W. M. Supit, “Chloride induced corrosion durability of high volume fly ash concretes containing nano particles,” *Construction and Building Materials*, vol. 99, no. 11, pp. 208–225, 2015.

[33] T. Gonen and S. Yazicioglu, “The influence of compaction pores on sorptivity and carbonation of concrete,” *Construction and Building Materials*, vol. 21, no. 5, pp. 1040–1045, 2007.

[34] S. Kawashima, P. Hou, D. J. Corr, and S. P. Shah, “Modification of cement-based materials with nanoparticles,” *Cement and Concrete Composites*, vol. 36, no. 5, pp. 8–15, 2013.

[35] J. Camiletti, A. M. Soliman, and M. L. Nehdi, “Effects of nano- and micro-limestone addition on early-age properties of ultra-high-performance concrete,” *Materials and Structures*, vol. 46, no. 6, pp. 881–898, 2013.

[36] S. A. Barbhuiya, J. K. Ghagbo, M. I. Russell, and P. A. M. Basheer, “Properties of fly ash concrete modified with hydrated lime and silica fume,” *Construction and Building Materials*, vol. 20, no. 3, pp. 3233–3239, 2009.

[37] P. Zhang, F. H. Wittmann, M. Vogel, H. S. Müller, and T. Zhao, “Influence of freeze-thaw cycles on capillary absorption and chloride penetration into concrete,” *Cement and Concrete Research*, vol. 100, no. 10, pp. 60–67, 2017.

[38] J. Bao, S. Xue, P. Zhang, Z. Dai, and Y. Cui, “Coupled effects of sustained compressive loading and freeze-thaw cycles on water penetration into concrete,” *Structural Concrete*, vol. 1–11, 2020.

[39] A. Chaipanich, T. Nochaya, W. Wongkeo, and P. Torkittikul, “Compressive strength and microstructure of carbon nanotubes-fly ash cement composites,” *Materials Science and Engineering: A*, vol. 527, no. 1, pp. 1063–1076, 2010.

[40] H. Li, H.-G. Xiao, J. Yuan, and J. Ou, “Microstructure of cement mortar with nano-particles,” *Composites Part B: Engineering*, vol. 35, no. 2, pp. 185–189, 2004.