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Influence of nano silica on the fresh, hardened and durability properties of self-cleaning white Portland cement mortars

Atta-ur-Rehman[a], Jeong Bae Lee[b], Abdul Qudoos[a], Sadam Hussain Jakhrani[a], Hong Gi Kim[a] and Jae-Suk Ryou[a],*
[a]*Department of Civil & Environmental Engineering, Hanyang University, 222 Wangsimni-ro, Seongdong Gu, Seoul, Korea*
[b]*GFC R&D CO., Ltd., 155 Jajak-ro, Pocheon-si, Gyeonggi-do, Korea*

In this study, nano titanium dioxide and nano silica have been added in white Portland cement mortars. The dosage of nano-TiO_2 was fixed to 3% while the dosage of nano-SiO_2 was varied from 0%-3%. Water/binder ratio was 0.45% and binder/sand ratio was 1:3. The workability, water absorption, compressive and flexural strengths of mortars was measured. The permeability of mortars was measured using Nordest test and the carbonation resistance was measured in a carbonation chamber. The degradation of rhodamine B dye on the surface of mortars was measured after exposure of the white mortars to the ultraviolet light. Addition of nano-SiO_2 increased the compressive and flexural strengths of mortars, reduced the water absorption of mortars and resisted the penetration of chloride ions. The self-cleaning of the white mortars was unaffected by the addition of nano-SiO_2 particles.

Key words: Nano silica, Nano titanium dioxide, White Portland cement mortars, Mechanical properties, Self-cleaning, Photocatalysis, durability, Chloride penetration, Carbonation.

Introduction

The application of nanomaterials in the concrete technology is a hot research topic. A variety of concrete products with novel applications and properties are being made with nanomaterials [1]. Concrete products can be tailored to be strong, light, ductile, durable, self-heating, self-cleaning, antifogging, energy-saving, air-purifying by adding nanomaterials in the concrete [2, 3]. For example, the addition of carbon nanotubes enhances the strength of concrete. Nano iron oxide can reinforce concrete products and prevents crack extension. Use of polypropylene nanofibers can enhance the fire resistance performance of mortars. Nano silica can fill the voids between cement particles and reduce the capillary porosity. It can accelerate the hydration of cement particles. It acts as a pozzolanic materials as it reacts with portlandite and produces calcium silicate hydrate gel which is a contributor to the strength of concrete [4]. The use of nano silica can reduce the consumption of ordinary Portland cement which is environmentally beneficial because ordinary Portland cement is one of the contributors of carbon dioxide in atmosphere. Anatase, a crystalline form of TiO_2 can make concrete photocatalytic, such a concrete can clean its surface and can purify air [5]. TiO_2 creates reactive oxygen ions on the surface of concrete which can destroy volatile organic compounds, dirt and even bacteria and algae from the concrete surface [6]. Nano titanium dioxide can make the concrete hydrophilic after exposure to the sunlight [7]. Such a concrete maintains its appearance and therefore, it is called self-cleaning concrete. This beneficial application of TiO_2 is gaining a wide attention in research and construction industry. A number of nanomaterials and cementitious materials like white Portland cement are available in the market. White Portland cement is used for architectural purposes. Its use in facing panels, curtain walls, cement paints, terrazzo surfaces, and tiles increases their aesthetic look [8]. Research is needed to explore the effects of their combined use on the fresh, hardened, microstructure, and durability properties of the product. Such extensive studies can create confidence of constructors for the combined use of nanomaterials with market products. Furthermore, the combined use of nanomaterials in cementitious materials may hinder their target applications, should be studied. In this study, the combined use of nano TiO_2 and nano silica with white Portland cement was investigated. The fresh and hardened properties were measured. Durability parameters like resistance to the penetration of chloride ions, and carbonation attack were also performed. Self-cleaning of the mortars was evaluated by dying mortars with a RhB and then exposing mortars to the ultraviolet light. The degradation of dye on the surface of mortars was evaluated.

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*Corresponding author:
Tel : +82-2-2220-4323
E-mail: jsryou@hanyang.ac.kr

Materials and Experiments

Materials

Anatase (Nano-TiO_2, CristalACTiV™ PC105) and nano-SiO_2 (VK-SP30) were produced by Cristal Corporates, (France) and Hangzhou Wanjing New Material Company, Ltd (China) respectively. Quantity of anatase phase in TiO_2 product was above 99%. Similarly, quantity of nano amorphous silica in the product was more than 99. The size of the nanoparticles of TiO_2 and their specific surface were 10-60 nm and 90 m^2/g, respectively. The size of the nanoparticles of nano-SiO_2 and their specific surface area were 20-40 nm and 150 m^2/g, respectively.

Mix design and experiment method

In this study, the nanomaterials were used as replacement of the white Portland cement. The amount of nano-TiO_2 was 3% in all mix proportions, while the amount of nano-silica was gradually varied among mortars (0%, 0.75%, 1.5%, 2.25%, and 3%). The mix proportions were designated as W1, W2, W3, W4, and W5, respectively. Water/binder ratio was 0.45% and binder/sand ratio was 1:3. A superplasticizer was used to adjust the workability of mortars. Superplasticizer was added in water and water was agitated. Then nanomaterials were dispersed in water using ultra sonification and soon mixed to white Portland cement and sand in mortar mixer. The mix proportions are summarized in Table 1.

Flow table test is a commonly used method to measure the spread of mortars in laboratory. It was used to measure the workability of mortars. Mortars were cast in cubes (5 × 5 × 5 mm), prisms (4 × 4 × 16 mm) and cylinders (ϕ 100 × 200 mm), compacted using vibrating table and then cured in saturated limewater at 25 °C. Cubes and prisms specimens were used for measuring the compressive and flexural strengths according to ASTM C109 [9] and ASTM C348 [10], respectively. Cylinders were sliced with water cooled diamond saw to get specimens of thickness 50 mm for chloride penetration test and carbonation. Nordest test method [11] was used to determine the non-steady state chloride diffusion coefficient of white cement mortars. The sliced specimens of diameter 100 mm and 50 mm thickness were saturated with limewater and then coated with epoxy from sides but top and bottom were left. Then an electrical potential of 30 V was applied across the specimens using an external source for 24 hours according to the guidance of Nordest test method. One side of the specimen was exposed to 10% sodium chloride (NaCl) solution and other side was exposed to 0.3 M sodium hydroxide (NaOH). Fig. 1 shows the accelerated test setup of rapid chloride penetration test which is in accordance to the Nordest test setup. After the testing period, white Portland mortars were axially split and sprayed with a solution of silver nitrate ($AgNO_3$). The chloride penetration depth was measured by calculating the depth of white part which was produced due to precipitation of silver chloride on the surface of mortars after spraying with $AgNO_3$. This depth was measured at intervals of 10 mm. Then chloride diffusion coefficient was measured [12].

For the carbonation depth, sliced mortar specimens having depth 100 mm were used. These specimens were coated with an epoxy resin so that carbon dioxide

Table 1. Summary of mix proportions.

Mix Proportion designation	TiO_2 (% of binder)	SiO_2 (% of binder)	w/c ratio	Superplasticizer (% of binder)
W1	3	0	0.45	0.40
W2		0.75		0.45
W3		1.5		0.45
W4		2.25		0.50
W5		3		0.60

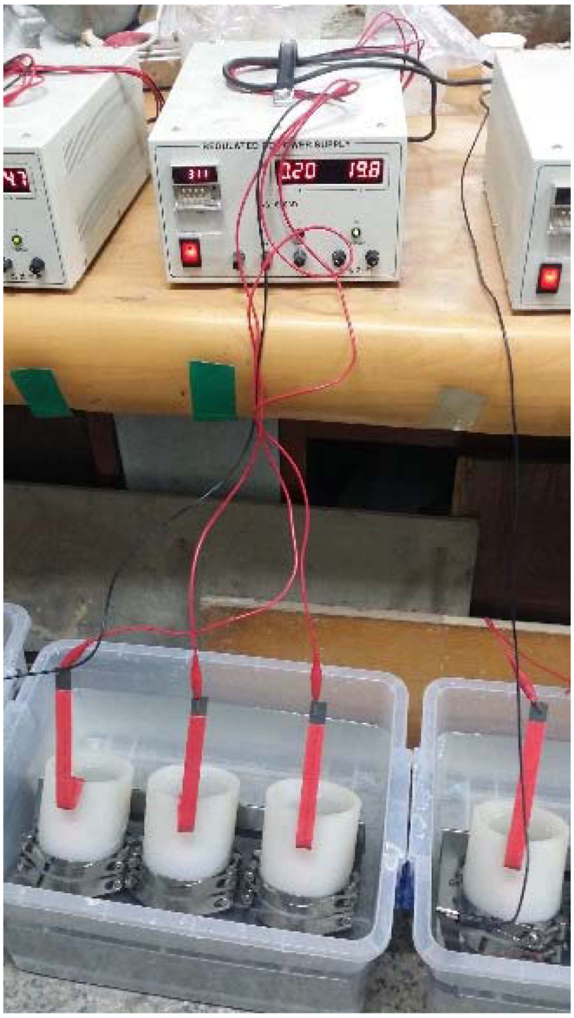

Fig. 1. Test setup of rapid chloride penetration test.

Fig. 2. Accelerated carbonation test setup.

can only attack in a two-dimension mode on mortars. These specimens were put in a sealed carbonation chamber at 5% CO_2, 20 ± 2 ºC, and 70 ± 5 relative humidity. Fig. 2 shows the test setup of carbonation attack. The sliced specimens were broken out using universal testing machine after 4, 8, 12, 16, and 20 weeks. A phenolphthalein indicator solution was sprayed on the surface of freshly split mortars. The carbonated parts, where pH had reduced did not change color, but noncarbonated parts turned their color into red-purple. The carbonated depth was measured at intervals of 10 mm and then averaged to get a representative value for each mix proportion.

The self-cleaning performance of mortars is usually measured by the degradation of a dye on the surface of photocatalyst substrate [13]. In this study, for measuring the self-cleaning efficiency, mortars were immersed in 0.05 g/l solution of rhodamine B (RhB) for 2 hours. After drying, mortars were exposed to UV light [14]. The intensity of UV radiation on the surface of white cement mortars was 1 mW/cm^2. The variation of color on the surface of mortars was measured with the help of a handheld color spectrophotometer [15, 16]. On average, ten measurements were taken on the surface of each specimen. The readings were taken before and after applying RhB and then after mortars exposing to UV light. Self-cleaning (ΔE) after exposure to UV light was calculated as;

$$\Delta E = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1) + (b^*_2 - b^*_1)^2} \tag{1}$$

Whereas L*, a*, and b* represent black-white, green-red, and blue yellow color values of CIELAB model [17]. The percent variation of a* was also calculated as it is one of main color components of RhB solution.

Results and Discussion

Fig. 3 shows the variation of workability of mortars measured using flow table test method. Addition of 0.75%, 1.5%, 2.25%, and 3% nano silica reduced the spread of mortars by 2.17%, 6.52%, 8.67%, and 10.57%, respectively. Although additional superplasticizer was added with the addition of nano silica, but still reduction in workability with the addition of nano silica can be observed in Fig. 3. The mortar became cohesive with the addition of nano silica. The reduction in workability was due to high surface area of nano silica. With the addition of nano silica, the demand of superplasticizers to adjust flow was increased. In this study, a strong water reducing admixture was used to adjust the workability of mortars.

Fig. 4 shows the variation of water absorption (%) of mortars with the addition of nano silica. W1 mix proportion, which contained 0% nano silica, has 9.71% water absorption, while W5 which contained 3% nano silica, has 7.95% water absorption. The linear reduction in water absorption of white mortars can be observed with the addition of nano silica. The reduction in water absorption with the addition of nano silica indicates that porosity reduced with the addition of nano silica.

Fig. 5 shows the changes in the compressive strength of mortars with the addition of nano silica. The effects of nano silica are prominent at later ages (56 days). Addition of 0.75%, 1.5%, 2.25%, and 3% nano silica increased compressive strength by 8.50%, 19.81%, 27.45%, and 32.70%, respectively.

Fig. 6 shows that the addition of nano silica led to an increase in flexural strength of mortars. Addition of 0.75%, 1.5%, 2.25%, and 3% nano silica increased flexural strength by 6.18%, 9.27%, 12.52%, and 22.17%, respectively. The increase in mechanical properties with the addition of nano silica is due to; (a) the filler effect of nano silica (b) pozzolanic effect of nano silica. Nano silica created more calcium silicate hydrate gels by reacting with portlandite and therefore increased the strength [4, 18].

$$\text{Nano silica} + \text{water} \rightarrow H_2SiO_4^{2-} \tag{2}$$

$$\text{Portlandite} + \text{water} \rightarrow Ca^{2+} + OH^- \tag{3}$$

$$Ca^{2+} + H_2SiO_4^{2-} \rightarrow \text{Calcium silicate hydrate} \tag{4}$$

Steel structural members can be embedded or coated with photocatalytic white Portland cement mortars, in such a scenario, the resistance of white Portland cement mortars to chloride penetration is important.

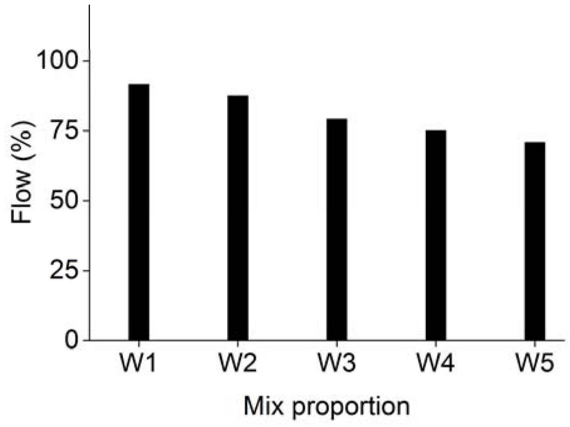

Fig. 3. Variation of flow in mix proportions.

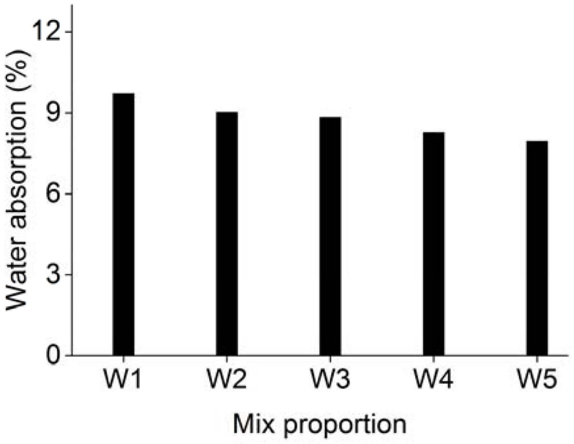

Fig. 4. Variation of water absorption (%) in mortars.

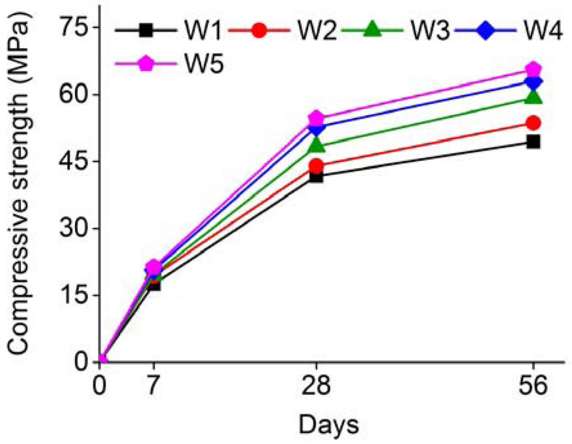

Fig. 5. Variation of compressive strength in mortars.

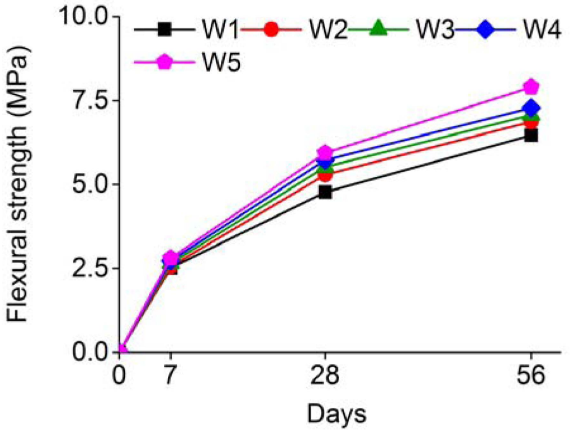

Fig. 6. Variation of flexural strength in mortars.

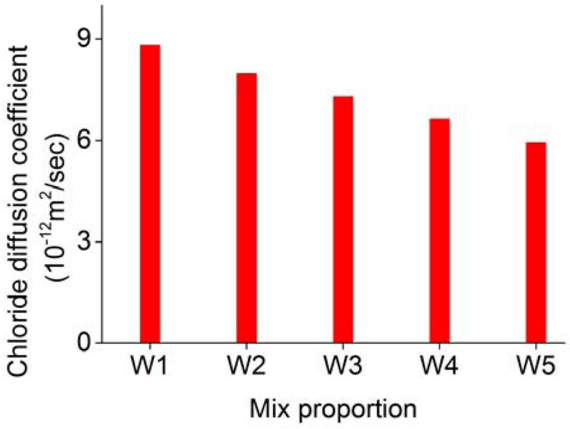

Fig. 7. Variation of chloride diffusion coefficient in mortars**.**

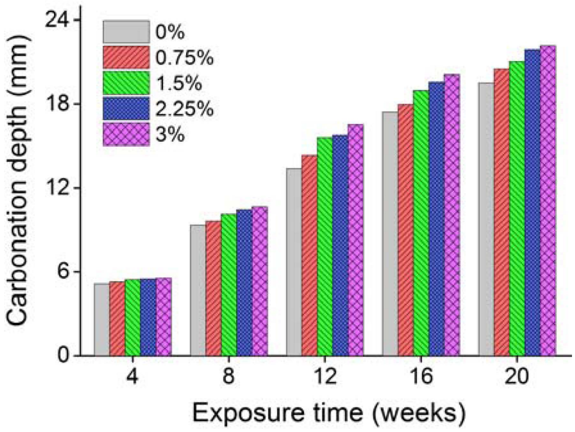

Fig. 8. Variation of carbonation depth in mortars.

The assessment of white Portland cements resistance to chloride penetration resistance will be required for designing of durable structures. Therefore, the variation of the resistance to the penetration of chloride ions in white mortars was studied. Non steady state chloride migration coefficient was evaluated. Fig. 7 shows the variation of chloride diffusion coefficient with the addition of nano-SiO_2 in the mortars. It shows that the resistance to chloride penetration is increased with the addition of nano $SiO_{2.}$ Addition of 0.75%, 1.5%, 2.25%, and 3% nano silica increased chloride diffusion coefficient in W2, W3, W4, and W5 by 9.47%, 17.20%,24.76%, and 31.47%, respectively. A linear reduction in chloride diffusion coefficient can be

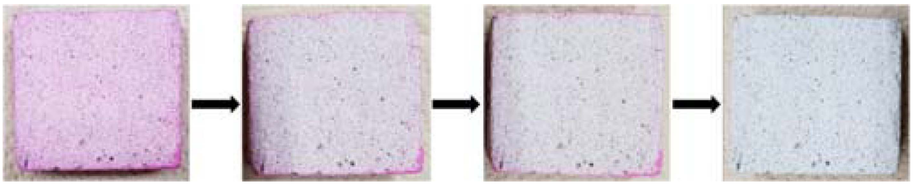

Fig. 9. Discoloration of RhB dye on the surface of mortar light. (Readers are referred to the web version of this article for interpretation of mortar color).

observed with the addition of SiO_2 in the white mortars. The results of rapid chloride penetration test are consistent with the results of water absorption by mortars. Nano silica acted as a nanofiller, filled the spaces between calcium silicate hydrate gels [4]. Additionally, it acted as a pozzolanic material and filled the voids by creating additional calcium silicate hydrate gels in voids [19]. Both these effects reduced the permeability of white photocatalytic mortars and thus reduced the diffusion of chloride ions in white mortars.

In this study, CO_2 diffused into the pores of white Portland cement mortars and reacted with hydrated products like portlandite ($Ca(OH)_2$) and calcium silicate hydrates (CSH) and produced calcium carbonates and silica. In this way, it reduced the pH of white mortars. Carbonation depth showed the depth of penetration of CO_2 into white mortars, the mix proportion with lower carbonation depth will be more resistant to the carbonation attack compared to a mix proportion with higher carbonation depth. Fig. 8 shows the variation of carbonation depth among mix proportions which were measured at different times. W2, W3, W4, and W5 which contained 0.75%, 1.5%, 2.25%, and 3% nano silica, respectively showed carbonation depths of 14.31 mm, 15.6 mm, 15,78 mm, and 16.51 mm, respectively after 12 weeks of exposure to accelerated carbonation chamber. Similarly, W2, W3, W4, and W5 showed carbonation depths of 20.48 mm, 21.03 mm, 21.9 mm, and 22.14 mm, respectively after 20 weeks of exposure to carbonation environment. Results show an increase in carbonation depth with the addition of nano silica. It suggests that nano silica had negatively affected the resistance of the mortars to the carbonation attack.

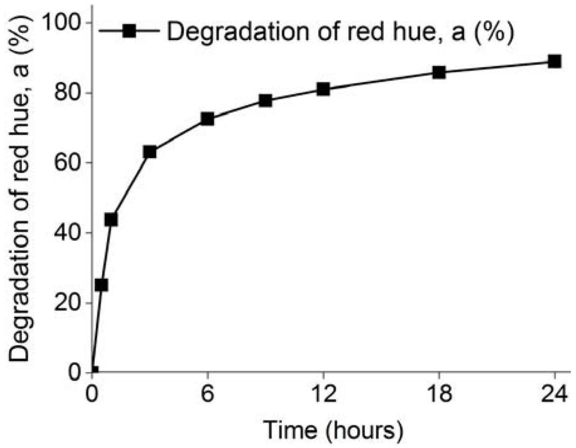

Fig. 10. Variation of ΔE after exposure to UV light.

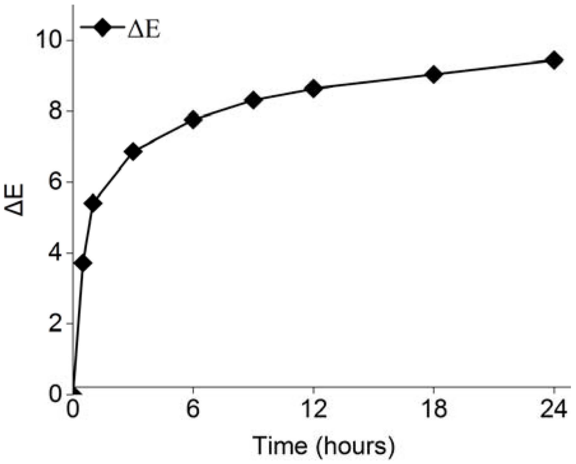

Fig. 11. Variation of ΔE after exposure to UV light.

Self-cleaning of mortars was measured by the degradation of rhodamine B dye on the surface of white mortars. For this purpose, mortars were exposed to UV light. Under UV light, nano titania degraded RhB dye through photocatalysis [20]. Fig. 9 shows the variation of red color on the surface of white mortars with the passage of time and irradiation with UV light. This Figure shows that with the passage of time, RhB dye was degraded and it was invisible after exposing mortars to UV light for 24 hrs. The self-cleaning was quantified using CILEAB system. As in the degradation of RhB dye, a^* component of color is important, so it was also evaluated. The results showed that self-cleaning was independent of addition of nano silica. The effects of adding nano silica on the self-cleaning performance could not noticed. All mortars showed a similar trend of degradation of RhB as all mix proportions contained equal amount of nano titania (3%).

Figs. 10 and 11 are representative results of the degradation of red hue a^*, and self-cleaning of mortars (ΔE), respectively. Approximately 75% of the degradation of a^* was observed within first 6 hours. The variation of a^* after 9 hrs is insignificant as the dye had degraded earlier. The pattern of variation of ΔE is almost similar to the pattern of a^*. It shows that most of self-cleaning occurred within first 6 hours. The degradation of RhB dye on the white mortars surface was due to photoinduced activation of nano titania present inside white substrate. The results of this study suggest that the combined use of nano silica and nano titania will give a pleasant perspective of maintenance and quality of construction of buildings because due to nano titania, self-cleaning of dirt and certain pollutants will occur [21]. The use of nano silica in white photocatalytic mortars can give strong and durable substrate which can be used in the construction of outdoor infrastructure and exterior parts of building. Such photocatalytic materials will have early strength gain due to the addition of nano silica which will facilitate the speedy construction at the site [22]. Improvement in porosity and increase in impermeability due to the addition of nanosilica will give a durable and sustainable structure [23]. Its addition will enhance the service life of white Portland cementitious materials and will decrease repair expenses [24].

Conclusions

Nanosilica reduces the workability and water absorption of mortars. It enhances the compressive and flexural strengths. The increase in mechanical properties is due to the pozzolanic effects and filler effect of nano silica. It can be added in photocatalytic white Portland cement mortars to produce strong and durable products.

Nano silica increases the resistance of white photocatalytic mortars to the chloride penetration. With the addition of nano silica, chloride penetration depth is reduced. The reduction in chloride migration coefficient is due to the increase in impermeability of mortars due to the addition of nano silica.

The addition of nano silica negatively effects the carbonation resistance of mortars. The addition of nano silica increased carbonation depth.

Architects can take advantage of nanomaterials like nano-silica and nano-TiO_2 by combining them with white Portland cement to make envelop of buildings. Such a material will be self-cleaning and depolluting, it will maintain the beauty of buildings.

Researchers should discuss the durability properties of nano silica and nano titania containing white Portland cement mortars as this aspect of white cements is not extensively studied. Additionally, the effect of adding nano silica on the interfacial transition zone and nanomechanical properties of white Portland cement mortars should be studied.

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