Journal of the Korean Society of Agricultural Engineers
DOI : https://doi.org/10.5389/KSAE.2020.62.5.039

Vol. 62, No. 5, pp.39~46, September 2020
ISSN 1738-3692 | eISSN 2093-7709

이산화티타늄을 이용한 대기정화 블록의 질소산화물 제거 성능 평가

Performance Evaluation of Nitrogen Oxide Removal by Air Purification Blocks with Titanium Dioxide

오리온[a] · 김황희[b] · 박성기[c] · 차상선[d] · 박찬기[e, †]
Oh, Ri-On · Kim, Hwang-Hee · Park, Sung-Ki · Cha, Sang-Sun · Park, Chan-Gi

ABSTRACT

This study evaluated the nitrogen oxide (NO_x) removal efficiency by air purification concrete blocks with titanium dioxide (TiO_2). The concrete in the mixtures had a 30% water:cement ratio, to which TiO_2 was added at 0%, 5%, and 10% of cement weight. The compressive strength reduction rate and removal efficiency of NO_x were investigated. The result of the compressive strength test in the study indicated that addition rate of TiO_2 did not lead to signifcant effect. In terms of the average removal efficiency of NO_x, mix No. 1 using a TiO_2 mixing ratio of 0% had a removal efficiency of 0.57% on average; thus, the removal effect was not significant. For the other samples prepared by mixing, the average removal efficiencies for mix No. 2 (5% TiO_2) were 58.86% and 62.05% for normal and washing surface treatments, respectively, and those of sample No. 3 (10% TiO_2) were 59.94% and 67.61%. mixs No. 4 (5%) and No. 5 (10%), in which TiO_2 diluted with distilled water was sprayed onto the block surface, had an average NO_x removal efficiency of 61.72% and 68.48%, respectively. In terms of NOx removal efficiency, Mixs No. 3 and No. 5 with 10% TiO_2 were better than Mixs No. 2 and No. 4 with 5% TiO_2. In addition, analyzing the NO_x removal efficiency results from the fixing method, it was capable to apply mixing (washing) and the diluted spray methods. Therefore, it was found that the diluted spray method applied in this study can be employed in any manufacture of air purification concrete blocks.

Keywords: Air purification blocks; compressive strength; nitrogen oxide; titanium dioxide

Ⅰ. Introduction

Recently, South Korea has recognized the seriousness of environmental problems that transcend national borders as it experiences direct and indirect air pollution exposure caused by yellow dust blowing from China (Kim, 2010). Among the many environmental problems in Korea, the increase in emissions of various air pollutants is unprecedented, as evidenced by the increasing number of people suffering with respiratory diseases, particularly in urban areas. Environmental pollution has been attributed to economic development and industrialization, and a large portion of this pollution is caused by harmful gases, such as those emitted from factories and automobiles (Kim, 2000). Among the many pollutants, nitrogen oxides (NO_x) are responsible for a large portion of air pollution and have been linked to various respiratory issues, as well as photochemical smog and acid rain (Kim et al., 2001). In Europe, photocatalyst materials are mixed with cement and applied to building walls, sidewalk blocks, and plasters to remove NO_x (Youn et al., 2013), and in Japan, photoreactive materials are applied to tile coatings for pollution control (Youn et al., 2013). In Korea, there has been great interest in photocatalyst development as an alternative construction material to the one for creating more environmentally friendly living spaces. Some studies investigated recycling the stone sludge generated during surface polishing processes and mixing them with photocatalysts for sidewalk block production (Jung et al., 2015). And others evaluated the air purification properties of sidewalk blocks with the mixing ratio of concrete and the number of photocatalyst coatings (Jung et al., 2015). For example, concrete sidewalk block to which a photocatalyst was applied exhibited 70% air purification performance initially and 68% air purification performance under accelerated weathering conditions (Jung et

[a] Researcher, Research Center, Contecheng Co., Ltd
[b] Director of Research, Research Center, Contecheng Co., Ltd
[c] Chief Executive Officer, Contecheng Co., Ltd
[d] Research Professor, Institute of Industrial Development Research, Kongju National University
[e] Professor, Department of Rural Construction Engineering, Kongju National University
† **Corresponding author**
Tel.: +82-41-330-1266, Fax: +82-41-330-1260
E-mail: cgpark@kongju.ac.kr
Received: July 28, 2020
Revised: August 21, 2020
Accepted: August 25, 2020

al., 2015). Another study evaluated self-purification and removal of toxic gases by surface- impregnated concrete after spraying a photocatalyst on the concrete surface; the purification performance inherent in the photocatalyst was maintained, even after application to the concrete (Kim et al., 2018). Thus, the application of photocatalysts to building materials, such as concrete, should be effective in the removal of organic pollutants; additionally, this approach can treat high concentrations of air pollutants and does not require a special installation site.

The study examined NO_x removal by air purification concrete blocks treated with titanium dioxide (TiO_2) under the conditions of automobile/agricultural machine, in which NO_x was present in the exhaust gas.

In the previous study, a concrete block was manufactured by adding TiO_2 to the concrete mix to evaluate the NO_x removal effect. However, in this study, the NO_x removal effect was evaluated by applying the method of spraying TiO_2 on the concrete block surface in consideration of maintenance.

Ⅱ. Materials and Methods

1. Materials

This study used type I ordinary Portland cement; Table 1 lists the physical properties. The fine aggregate was silica sand, with a density (g/㎣) of 2.65. The principle of the photocatalytic reaction is that electrons in the photocatalyst material, such as titanium dioxide (TiO_2), are excited to higher energy states under ultraviolet (UV) light exposure (for TiO_2, UV light having a wavelength of about 400 nm or less). This creates electrons (e^-) and holes (h^+, i.e., the absence of an electron) (Kim et al., 2014). The electrons diffuse to the surface and react with oxygen or moisture in the atmosphere to produce reactive oxygen species with strong oxidizing power. Chemicals or superoxide ions generated in this way remove various pollutants and create anti-fouling and antibacterial effects, while removing NO_x from automobile exhaust gas. TiO_2 can be classified into three crystalline forms: (1) anatase, (2) rutile, and (3) brookite types. The rutile type is mostly used as a coating, paint, or pigment, due to its weather resistance, hiding power, and brightness (white) (Kim et al., 2014). The anatase type is often used as a photocatalyst, as it is easy to decompose or crystallize; however, it is not used for products requiring weatherproofing or pure white coatings. Additionally, the anatase type is less expensive than the rutile type (Kim, 2010). In this study, given that white luminance is not required and the unit price is considered in production, we used anatase-type TiO_2 in the development of our air purification block products to reduce costs (Fig. 2). Table 2 and Fig. 2 present the characteristics and form of TiO_2.

Table 1 Properties of cement

Fineness (㎠/g)	Density (g/㎣)	Stability (%)	Setting time (min)	
			Initial	Final
3,200	3.15	0.02	220	400

Table 2 Characteristics of titanium dioxide (TiO_2)

Type	Content (%)	Shape	Melting point (℃)	Molecular weight (g/mol)	Density (g/㎣)
Anatase	98	Solid (white)	1850	79.88	3.8–4.3

Fig. 1 Titanium dioxide (TiO_2, anatase type)

2. Mix proportions

In this study, the effect of the addition rate of TiO_2 was evaluated based on the mix proportion at the surface finish layer of the sidewalk block. TiO_2 was added for cement at weights of 0, 5, and 10% to evaluate the influence of the addition of TiO_2. Table 3 lists the mix proportions applied in this study.

Table 3 Mix design of air purification concrete blocks

<table>
<tr><th rowspan="2">NO.</th><th rowspan="2">Cement (kg)</th><th rowspan="2">Fine aggregate (kg)</th><th rowspan="2">Water (kg)</th><th>Fixing method 1</th><th colspan="2">Fixing method 2</th><th rowspan="2">Surface treatment</th></tr>
<tr><th>TiO_2 (kg)</th><th>TiO_2 (kg)</th><th>Distilled water (kg)</th></tr>
<tr><td>1</td><td rowspan="7">78.75</td><td rowspan="7">350</td><td rowspan="7">31.50</td><td>-</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td rowspan="2">2</td><td rowspan="2">4.00</td><td rowspan="2">-</td><td rowspan="2">-</td><td>Normal</td></tr>
<tr><td>Washing</td></tr>
<tr><td rowspan="2">3</td><td rowspan="2">8.00</td><td rowspan="2">-</td><td rowspan="2">-</td><td>Normal</td></tr>
<tr><td>Washing</td></tr>
<tr><td>4</td><td>-</td><td>4.00</td><td>4.00</td><td></td></tr>
<tr><td>5</td><td>-</td><td>8.00</td><td>8.00</td><td></td></tr>
</table>

The concrete block mix No. 1 had 0% TiO_2. mix No. 2 and No. 3 involved incorporating TiO_2 into the concrete mixture (fixing method 1) at 5% and 10%, respectively, with general/normal surface treatment or washing of the surface. Mix No. 4 and No. 5 involved TiO_2 incorporation through a diluted spray treatment (fixing method 2).

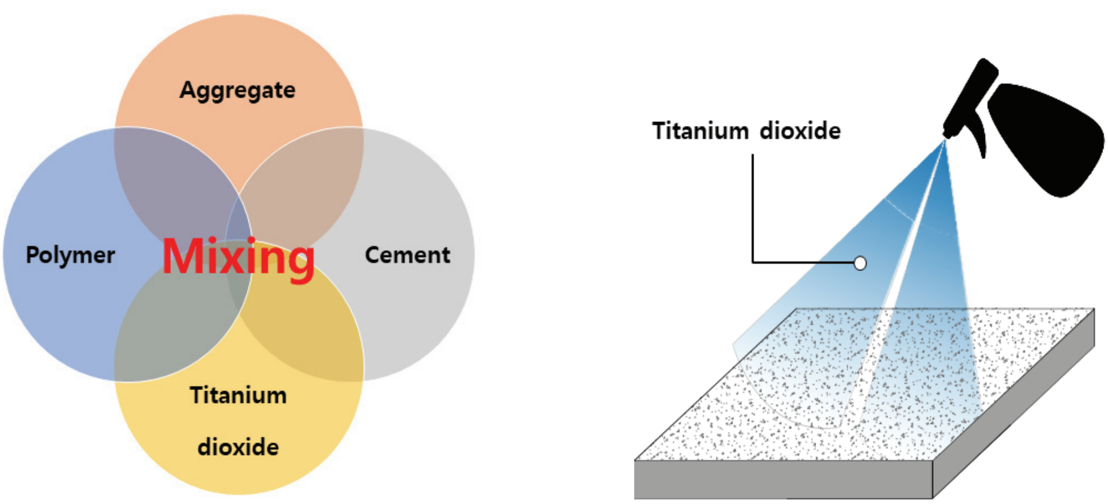
3. Fixation method of titanium dioxide (TiO_2)

Because differences in the TiO_2 mixing rate and fixation technique may lead to differences in the removal of NO_x, we used two methods to produce specimens, as shown in Figure 2. The first (fixing method 1) involved drying the cement and fine aggregate for 1 min and then mixing in the TiO_2 additive. Here, simultaneous mixing of TiO_2 resulted in the removal of exhaust gas through a photoreaction that occurred on the surface of the air purification block. The second (fixing method 2) involved diluting TiO_2 with distilled water or alcohol and then spraying the liquid mixture onto the block surface. Thus, from the two methods, we obtained one specimen type in which the cement mixture incorporated the TiO_2 during mixing and a second type in which the block surface was coated with a diluted TiO_2 solution. Fig. 3 presents the surface treatment method. Fig. 4 presents the as-fabricated specimens.

4. Test methods

(1) Compressive Strength

Compressive strength tests were performed by the KS L 5105. Six specimens were fabricated with a size of 50×50×50 mm. Tests were performed after 28 days of curing.



(a) Fixing method 1: mixing (b) Fixing method 2: diluted spray

Fig. 2 Fixing methods for TiO_2 incorporation into air purification concrete blocks through mixing or using a diluted spray application

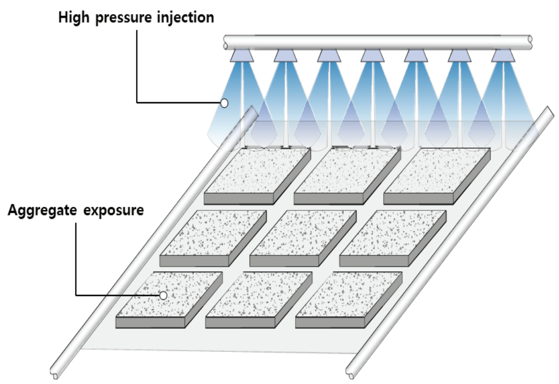


Fig. 3 Image of the air purification concrete blocks washing process

Fig. 4 Air purification concrete blocks specimens

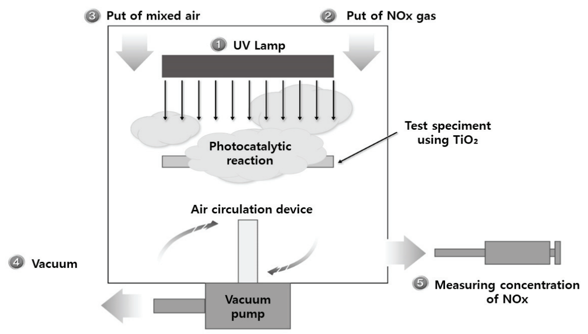


Fig. 5 Schematic diagram of the pollutant reactor

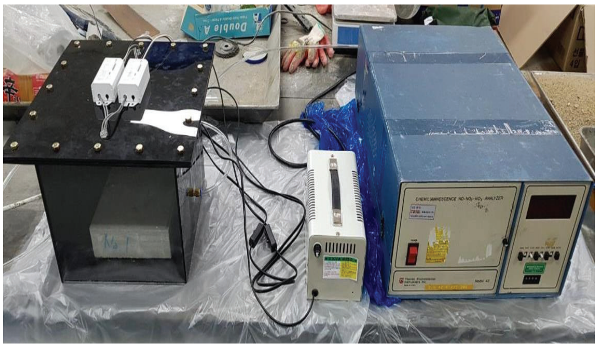


Fig. 6 Photograph of the test set-up for nitrogen oxide (NO_x) removal

(2) Nitrogen oxide removal test

Although NO_x was the main consideration in this study, Korea currently has no standardized procedures for evaluating exhaust gas removal. In domestic studies, performance evaluations of the NO_x elimination effect have mainly been conducted using pollutant reactors. This study carried out our tests according to KS L ISO 22197-1 “Fine ceramics (advanced ceramics, advanced technical ceramics)-Test method for air-purification performance of semiconducting photocatalytic materials-Part 1: Removal of nitric oxide,” which uses a NO_x pollutant reactor. The pollutant reactor in which the specimen was exposed to the test gas was manufactured as a box shape with a size of 310×310×265 mm, to facilitate the attachment of UV-A and blacklight blue lamps for photoreaction. The test gas NO_x was introduced at a concentration of 1.4 ppm. The concentration of NO_x gas discharged through the NO_x meter at the outlet was measured for 60 min. Fig. 5 and Fig. 6 are present schematic diagrams of the pollutant reactor and the NO_x removal test, respectively (Park et al., 2001).

Ⅲ. Test results

1. Compressive Strength

Tests revealed that compressive strength values were 12.37 MPa for sample No. 1 with a 0% TiO_2 mixing ratio, 11.7 MPa for sample No. 2 with a 5% TiO_2 mixing ratio, and 12.24 MPa for sample No. 3 with a 10% TiO_2 mixing ratio (Fig. 7).

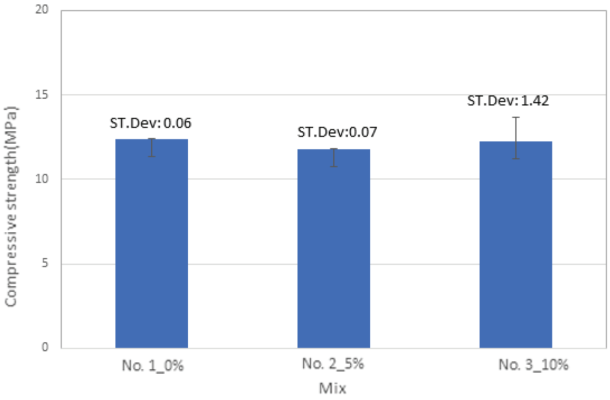


Fig. 7 Compressive strength test results

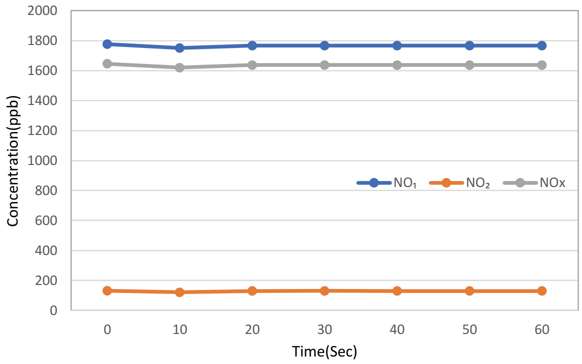


Fig. 8 Results of NO_x removal test for mix No. 1 with 0% TiO_2 addition

Compared to the mix without TiO_2, the mixes with 5% and 10% TiO_2 mixing ratio provided 4.93% and 1.05% reductions in compressive strength, respectively. As a result of the test, the strength decreased slightly, although the change was not significant. Therefore, it was concluded that the addition of TiO_2 did not significantly affect the compressive strength.

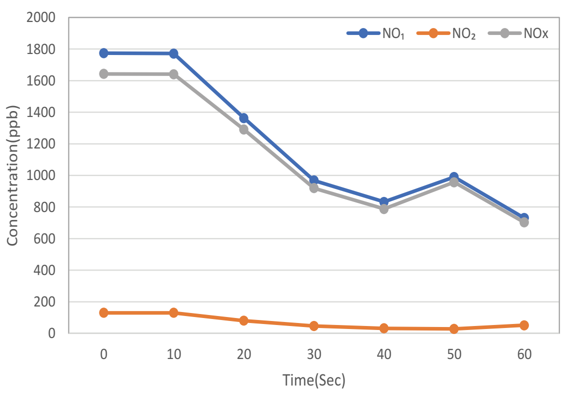
2. Removal efficiency of nitrogen oxides

The test gas was introduced at a concentration of 1.4 ppm, and the concentrations of NO_1, NO_2, and NO_x gases discharged for each mix were measured for 60 min. Figs. 8-10 shows the changes in the NO_1, NO_2, and NO_x concentrations for up to 60 s of elapsed time for 0%, 5%, and 10% TiO_2 under simultaneous mixing with respect to the surface treatment (general/normal versus washing). The NO_1, NO_2, and NO_x removal efficiencies of mix No. 1 with a TiO_2 mixing ratio of 0% were 0.56%, 0.61%, and 0.55%, respectively, and there was no change in the gas concentration after 60 min. Thus, these results show no removal effect, as there was no mixing of TiO_2 in this mix (Fig. 8).

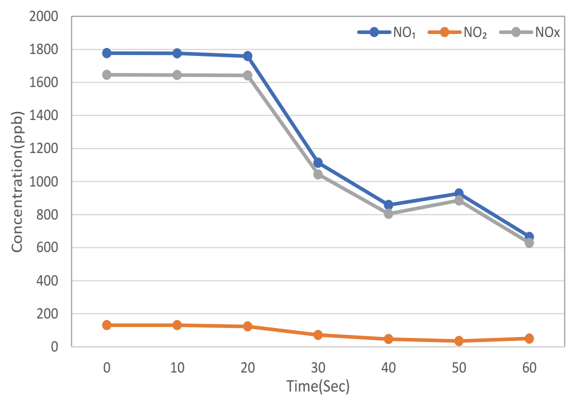
The NO_1, NO_2, and NO_x removal efficiencies of the No. 2 mix with a TiO_2 mixing ratio of 5% under normal surface treatment were 58.79%, 60.57%, and 57.21%, respectively, and 62.58%, 61.72%, and 61.85%, respectively, for sample No. 2 with a washed surface. Shown as Fig. 9, the NO_1, NO_2, and NO_x concentrations displayed decrease trend in the case of No. 2 with the both normal and washing surface treatments over 60 seconds. And rapid decrease trends were observed after 10 second for normal surface treatment case (Fig. 9(a)) and after 20 second for washing surface treatment case (Fig. 9(b)).

The NO_1, NO_2, and NO_x removal efficiencies of the No. 3 mix with 10% TiO_2 were 61.99%, 56.19%, and 61.68%, respectively, for the general/normal surface treatment and 69.93%, 63.40%, and 69.51%, respectively for the washing surface treatment. Changes in NO_1, NO_2, and NO_x concentrations discharged over a 60-min period for sample No. 3 (10% TiO_2) were reduced after 20 s for the general/normal surface treatment, compared with 10 s for samples whose surfaces had been washed.

The NO_1, NO_2, and NO_x removal efficiencies for the No. 4 mix with a TiO_2 mixing rate of 5% were 64.51%, 58.81%, and 61.86%, respectively. The concentrations of NO_1, NO_2, and NO_x discharged for 60 min from the No. 4 sample did not change greatly during the first 20 s, but then decreased rapidly after 40 s (Fig. 11).

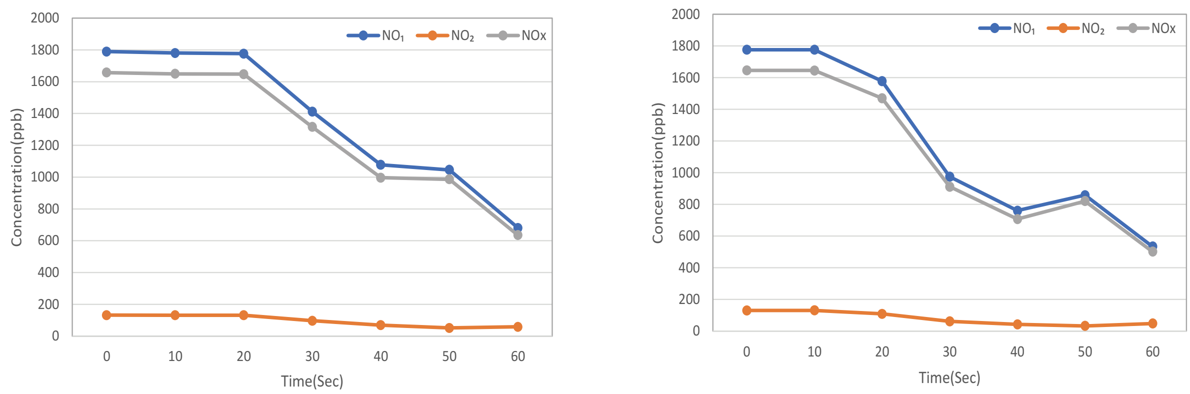


(a) No. 2: 5% (general/normal)



(b) No. 2: 5% (washing)

Fig. 9 Results of the NO_x removal test for the No. 2 mix (5% TiO_2) prepared using general/normal and washing surface treatments



(a) No. 3: 10% (general/normal)

(b) No. 3: 10% (washing)

Fig. 10 Results of the NO_x removal test for mix No. 3 with 10% TiO_2 prepared with a general/normal surface treatment or washing surface treatment

The NO_1, NO_2, and NO_x removal efficiencies for the No. 5 mix with 10% TiO_2 applied as a diluted spray were 74.49%, 57.10%, and 73.84%, respectively. The concentrations of NO_1, NO_2, and NO_x discharged for 60 min in the No. 5 mix decreased rapidly after 10 s (Fig. 12).

The NO_x concentration changes over measurement time showed that the values of NO_1 and NO_x increased slightly form 40 to 50 seconds (Figs. 8~12). These are an error form concentration measurements at the inlet and outlet of the NO_x removal efficiency test equipment, however the error did not significantly affect the trend of the overall removal efficiency.

This study also examined the NO_x removal efficiency according to the percentage of TiO_2 additive, the surface treatment method, and the fabrication/fixing method; NO_1, NO_2, and NO_x results were averaged for each mix. The average removal efficiency for mix No. 1 with a TiO_2 mixing ratio of 0% was 0.57%. The average removal efficiencies of NO_x for mix No. 2 (5% TiO_2) were 58.86% and 62.05%, with general/normal and washing surface treatments, respectively; for the No. 3 mix (10% TiO_2), the average removal efficiencies were 59.94% and 67.61%, respectively (Fig. 13).

For the No. 4 (5% TiO_2) and No. 5 (10% TiO_2) mixs involving a diluted spray of TiO_2 onto the block surface, the average NO_x removal efficiency was 61.72% and 68.48%, respectively (Fig. 14).

The NO_x removal efficiency was high, up to 58% or more on average; this was due to the rapid progression of the reaction. The size of the pollutant reactor was small, and the concentration of NO_x gas was injected in small amounts at 1.4 ppm. Accordingly, in terms of the removal efficiency of NO_x, samples with a mixing ratio of 10% (No. 3 and 5) were superior to samples with a TiO_2 mixing ratio of 5% (No. 2 and 4). This

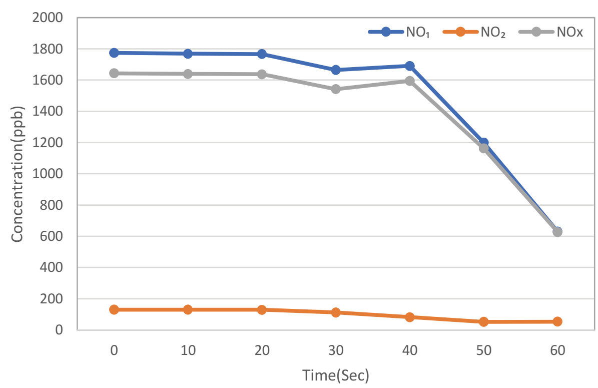


Fig. 11 Results of the NO_x removal test for mix No. 4 with 5% TiO_2 incorporated as a diluted spray

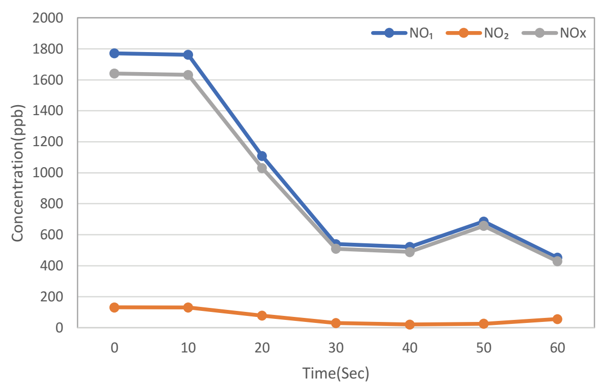


Fig. 12 Results of the NO_x removal test for the No. 5 mix with 10% TiO_2 applied as a diluted spray

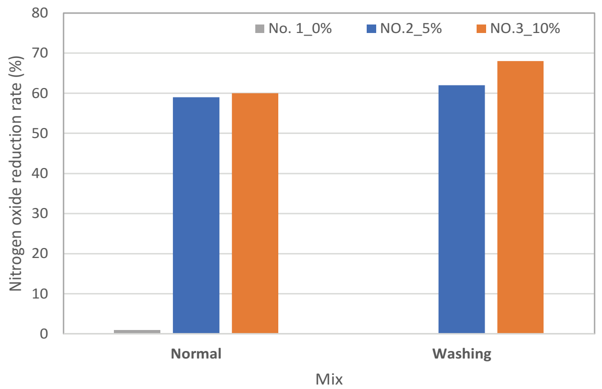


Fig. 13 NO_x removal efficiency of fixing method 1 (mixing) for mixs No. 2 (5% TiO_2) and No. 3 (10% TiO_2) with normal surface treatment and washing surface treatment

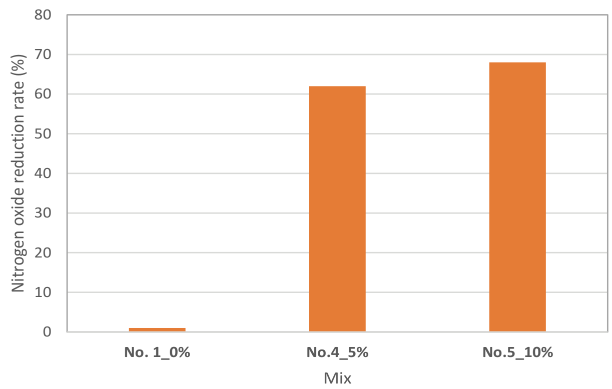


Fig. 14 NO_x removal efficiency from 5% (No. 4) and 10% (No. 5) TiO_2 samples prepared using the diluted spray method

Table 4 NO_x removal efficiency according tho the fixation method of TiO_2

No.	TiO_2 mixing ratio (%)	Fixing method	Surface treatment	Removal rate (%)			
				NO_1	NO_2	NOx	Mean
1	-	-	-	0.56	0.61	0.55	0.57
2	5	Mixing	Normal	58.79	60.57	57.21	58.86
			Washing	62.58	61.72	61.85	62.05
3	10	Mixing	Normal	61.99	56.16	61.68	59.94
			Washing	69.93	63.40	69.51	67.61
4	5	Diluted spray	-	64.51	58.81	61.86	61.72
5	10	Diluted spray	-	74.49	57.10	73.84	68.48

indicates that a higher mixing ratio of TiO_2 yields a better NO_x removal effect. Based on the efficiency of NO_x, mixing (washing) and diluted spray are appropriate treatment for the fixing method of TiO_2. And comparing these methods, the diluted spray method can be used in terms of NO_x removal efficiency (Table 4).

Ⅳ. Conclusions

This study evaluated the effect of TiO_2 on the removal of NO_x from exhaust gas by air purification concrete blocks. The compressive strength was assessed according to the mixing rate of TiO_2, and the removal efficiency of NO_x was assessed according to the mixing ratio and fixation method of TiO_2. The results are as follows.

1. Compared to the mix not applying TiO_2, compressive strengths in the mixs with 5% and 10% TiO_2 were reduced by 4.93% and 1.05%, respectively. However, the change in compressive strength was not large. Therefore, the addition of TiO_2 did not significantly affect to the compressive strength.
2. In this study, it was observed that the NOx removal efficiency was improved as the addition rate of TiO_2 increases. And, the mixing (washing) and diluted spray methods provided better NOx removal efficiency, compared to the one by the fixing method (normal). Therefore, the diluted spray method can be employed in the manufacture of air purification concrete blocks.
3. The study did not evaluate the change of NOx removal efficiency for long-term period. In future study, there is a need to evaluate the NOx removal efficiency for long-term period with the TiO_2 addition rate. Also, the addition rate of TiO_2 were applied up to 10% of cement weight, though, there is a need to examine if it is cost-effective method to apply more than 10% of TiO_2.

ACKNOWLEDGMENT

This work was supported by the research grant (sabbatical research) of the Kongju National University in 2019.

REFERENCES

1. Jung, Y. W., S. H. Lee, and J. O. Choi, 2015. Characteristics of concrete sidewalk block manufactured using stone powder sludge and photocatalytic agent. *Journal of the Korea Academia-Industrial Cooperation Society* 16(6): 4237-4244 (in Korean).
2. Kim, H. J., 2000. Development of materials to remove nitrogen compounds (NOx) of cement. *Conference of Cement Association* 153: 50-54 (in Korean).
3. Kim, H. J., 2010. A study on the development of functional concrete using permeating agents and photocatalyst. Ph.D. diss., Jeonbuk National University.
4. Kim, H. J., Y. K. Kim, and S. J. Kwon, 2018. Evaluation of durability and self-clearing in concrete impregnated with photocatalyst-colloidal silica. *Journal of the Korea Institute for Structural Maintenance and Inspection* 22(5): 47-54 (in Korean). doi:10.11112/jksmi.2018.22.5.047.
5. Kim, H. W., B. W. Jung, J. Y. Park, Y. J. Choi, and W. J. Kim, 2001. A basis study on development of photocatalystic block to purify polluted air. *Journal of Korean Concrete Institute* 13(2): 1117-1122 (in Korean).
6. Kim, T. H., 2010. Study on characteristics of TiO_2 catalyst for DeNOx. Ph.D. diss., Kangwon National University.
7. Kim, Y. K., S. J. Hong, K. B. Lee, and S. W. Lee, 2014. Evaluation of NOx removal efficiency of photocatalytic concrete for road structure. *International Journal of Highway Engineering* 16(5): 49-58. doi:10.7855/IJHE.2014.16.5.049.
8. KS L 5105, 2007. Testing method for compressive strength of hydraulic cement mortars.
9. KS L 5201, 2016. Portland cement.
10. KS L ISO 22197-1, 2016. Fine ceramics (advanced ceramics, advanced technical ceramics) - Test method for air-purification performance of semiconducting photocatalytic materials - Part 1: Removal of nitric oxide.
11. Park, J. Y., H. W. Kim, B. W. Jung, Y. J. Choi, Y. H. Kim, and H. J. Kim, 2001. An experimental study on the NOx removal properties of photocatalystic paint. *Journal of Korean Concrete Institute* 13(2): 1123-1128 (in Korean).
12. Youn, Y. S., S. S. Seo, S. H. Cho, P. S. Kim, and T. K. Kim, 2013. The empirical evaluation on the NOx removal of photocatalytic plaster. *Journal of Korean Concrete Institute* 25(2): 305-306 (in Korean).