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Estimation of Nitrogen Oxides (NOx) Removal Efficiency for TiO_2 Concrete

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Abstract: Nitrogen oxide (NOx) is a significant precursor of particulate matter (PM), particularly in high-traffic areas. Accordingly, this study aimed to reduce the presence of nitrogen oxide (NOx) along roadsides. Titanium dioxide (TiO_2) is used as a photocatalyst to remove NOx through a chemical reaction. Typically, concrete and TiO_2 are mixed to create TiO_2 concrete. However, air pollutants or UV rays cannot be allowed to come into contact with a significant amount of TiO_2. Thus, the TiO_2 surface penetration method was used to fix TiO_2 to the surface of the concrete. In this method, surface penetrants and TiO_2 are combined and sprayed onto the concrete surface, enabling the possibility of NOx reduction using relatively less TiO_2. When the fixation method is applied to vertical concrete structures, however, a peeling issue arises. To address this, a pressurized TiO_2 fixation method was applied to vertical concrete structures. This method uses external force to penetrate and fix TiO_2 to a specific depth. In the instance of the pressurized TiO_2 fixation method, which was tried for the first time, penetration depth was used to ensure long-term durability as well as NOx removal efficiency. To investigate TiO_2 distribution characteristics, the penetration depth and mass ratio of TiO_2 particles in TiO_2 concrete were measured using a scanning electron microscope (SEM/EDX). In addition, NOx removal efficiencies were evaluated using the NOx analyzing system (ISO 22197-1 standard). The experimental results showed that NOx removal efficiency increased with an increasing TiO_2 mass ratio. When the TiO_2 fixation method was used, the NOX removal efficiency was 32% when the TiO_2 mass ratio at the surface was 50%, and the efficiency was 61% when the TiO_2 mass ratio was 70%. This is attributed to the increase in NOx removal efficiency as TiO_2 content at the concrete surface increases. This study analyzed and forecasted the NOx removal efficiency of TiO_2 concrete based on the mass ratio of TiO_2 on the surface. As the TiO_2 mass ratio increased, the NOx removal efficiency improved, and it was determined that the surface TiO_2 mass ratio significantly influences the NOx removal efficiency. Consequently, this study developed an equation to estimate NOx removal efficiency, making it possible to determine a suitable maintenance interval for TiO_2 concrete.

Keywords: particulate matter; nitrogen oxide (NOx); TiO_2 concrete; TiO_2 mass ratio at surface; SEM/EDX; NOx removal efficiency

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1. Introduction

Particulate matters (PMs) constitute a serious problem because they are a global phenomenon. PMs are complexes of airborne solids and liquids, and they are classified as PM_{10} (diameter = 10 μm or less) and $PM_{2.5}$ (diameter = 2.5 μm or less) (United States Environmental Protection Agency, US EPA). PMs are harmful to the human body, and they can also generate secondary pollutants that can be converted to PMs through chemical reactions with air pollutants discharged into the atmosphere [1]. The PMs are classified into PM_{10} in the solid state emitted from the pollution sources (primary emission) and

PMs released in gaseous form from sources; they become $PM_{2.5}$ through chemical reactions with other substances in the air (secondary generation). For $PM_{2.5}$, nitrogen oxide (NOx), sulfur oxide (SOx), ammonia (NH_3), and other pollutants emitted from automobile exhaust gases and factory manufacturing processes combine with water vapor (H_2O) and ozone (O_3) to form PMs through chemical reactions [2]. The NOx is detected in large volumes compared to other air pollutants, and it accounts for ~58% of road-mobile pollution sources (CO, NOx, SOx, PM_{10}, and $PM_{2.5}$, etc.). Thus, there is an urgent need to develop measures to remove roadside NOx [3].

To this end, methods that employ titanium dioxide (TiO_2) have been developed to reduce NOx. Figure 1 shows that TiO_2 is a photocatalyst converted from the valence band to the conduction band when irradiated with a UV wavelength energy of 3.2 eV or more and 387.5 nm or less, which is similar to the principle of solar cells. Here, electrons (e^-) are formed in the conduction band, and holes (h^+) are formed in the valence band. On the surface of TiO2 particles, the electrons and holes react with water (H_2O) and oxygen (O_2) to form a superoxide anion (O_2^-) and a hydroxyl radical (OH·). The generated hydroxyl radical (OH·) has a particularly high oxidation/reduction potential for oxidizing organic substances, and it decomposes viruses, bacteria, and odor substances in the air into water (H_2O) and carbon dioxide (CO_2). Further, the hydroxyl radical (OH·) removes the NOx, SOx, and volatile organic compounds (VOCs) [4].

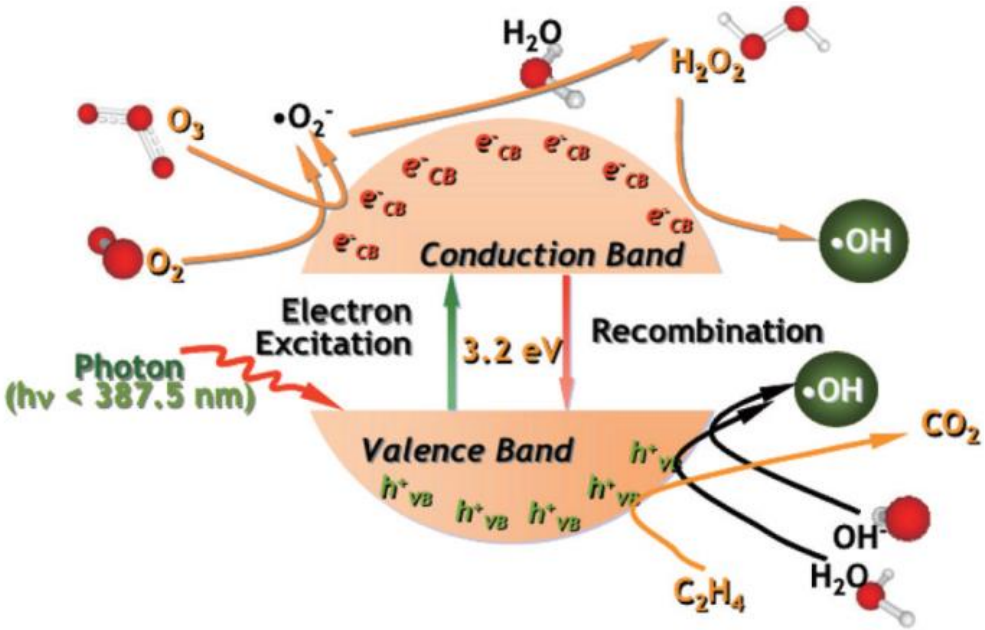


Figure 1. Photocatalytic reaction (Takeuchi, 2000 [4]).

The NOx in the atmosphere is oxidized by the active oxygen when TiO_2 is exposed to UV light, and it forms nitric acid through a photocatalytic reaction. The reacted nitric acid accumulates on the TiO_2 surface and deteriorates its function; however, TiO_2 continues to react with NOx and can be used permanently if nitric acid is washed away by rain [5].

Given these characteristics of TiO_2, research has focused on removing NOx by applying TiO_2 in concrete and environmental engineering fields. For TiO_2, anatase (with a diameter of approximately 21 nm), which has an anatase crystal structure, is applied in this study. TiO_2 causes a catalytic reaction upon receiving ultraviolet (UV) light from a light source such as sunlight or a UV lamp, and it decomposes and removes harmful substances such as NOx, organic compounds, and bacteria that cause pollution by forming radicals with a strong oxidizing power from water or oxygen when the photocatalyst interacts with UV rays [6].

Due to its ability to photocatalytically address both organic and inorganic air pollutants, TiO_2 in the form of ultrafine particles has attracted a lot of attention as a coating for

concrete pavement in recent years. Despite these promising advantages, the durability and wear resistance of TiO_2 coatings have not been assessed. Therefore, the environmental impact of the concrete photocatalyst was evaluated using a spectrophotometer. To find out how different TiO_2 ratios affected the strength and radiation resistance of the samples, the outcomes were compared to those of conventional concrete. TiO_2 was added to ordinary concrete in varying amounts of 0.5, 1.0, and 1.5% with respect to cement weight to provide a remedy. The strength metrics were investigated over a range of TiO_2 ratios and time durations. When TiO_2 is added to concrete, the compressive strength of the concrete increases by 0.5% before decreasing again by 1% and 1.5%. Additionally, according to spectrophotometric experiments, adding 0.5% TiO_2 to concrete increases absorption. This proves that TiO_2 absorbs the energy from photon present in the environment [7].

There are three main categories of TiO_2 concrete application methods: TiO_2 substitution mixture in which a part of cement is replaced with TiO_2, TiO_2 coating in which a TiO_2 and coating agent are mixed, and a TiO_2 surface penetration method in which TiO_2 and a surface penetrant are mixed and penetrated through gravity and capillary forces. However, when TiO_2 penetration technology is applied to vertical concrete, gravity peels it off. To address this issue, a study by Ahn et al. (2021) employed a pressurized fixation method to infiltrate and immobilize TiO_2 in vertical concrete [8].

Although many studies have investigated the NOx removal efficiency of TiO_2 concrete; the NOx removal efficiency was only experimentally verified based on the application method rather than establishing a standardized quantification. As a result, there is a lack of quantitative performance verification for NOx removal efficiency in TiO_2 concrete. Therefore, in this study, the NOx removal efficiency for each TiO_2 fixation technology will be assessed. The result of this study will propose the determination of NOx removal efficiency from the TiO_2 mass ratio using the TiO_2 fixation method. The NOx removal efficiency can be inferred when the TiO_2 mass ratio approaches the limiting standard, and the TiO_2 fixation method can be rebuilt through the goal of NOx removal efficiency. Consequently, the TiO_2 penetration depth may be used to determine the long-term durability, and the TiO_2 mass ratio and NOx removal efficiency can be used to estimate the maintenance period of TiO_2 concrete.

2. Literature Review

The NOx adsorption rate increased when TiO_2 particles were irradiated with light and 60% of nitrogen dioxide (NO_2) was captured on the TiO_2 surface in the form of nitric acid (HNO_3); this confirmed the NOx oxidation potential of TiO_2. TiO_2 was applied to the exterior walls of buildings and road construction in Europe, which reduced the NOx on the roadside in the city. Since the early 2000s, Italy has promoted the application of TiO_2 to various road facilities and buildings. Gian Luca Gerrinni et al. (2012) effectively reduced pollutants by treating cement-based paint with TiO_2 in the Umberto I tunnel in Rome, Italy; they achieved an ~20% reduction in NOx at the center of the tunnel and verified the possibility of reducing pollution levels in outdoor conditions. Furthermore, TiO_2 road pavement construction in Milan and TiO_2 block pavement construction on Borgo Palazzo Street in Bergamo helped to effectively reduce the NOx concentration by 30–40% [9].

Beeldens et al. (2016) constructed a photocatalyst block pavement on an area of 10,000 m^2 in Antwerp, Belgium to verify the effect of photocatalytic pavement in actual conditions. Only the top 5–6 mm of the block contained anatase TiO_2, and the pavement was designed with temperature, humidity, light intensity, and contact time as variables. The experiment results indicated that the best results were realized by applying high temperature, low relative humidity, high light intensity, and long contact time. Furthermore, the on-site NOx removal efficiency was identified, and the durability of the efficiency was measured. About a 20% reduction was obtained as a result of on-site NOx removal efficiency measurement after one year of construction [10].

Maggos et al. (2007) conducted field experiments and measurements after applying TiO_2 photocatalytic paint to an actual parking lot for removing pollutants and NOx emitted

from vehicle exhaust gases. A chamber similar to a parking lot was built to examine the performance of the material, and a reduction of NOx concentration was confirmed [11].

Kim et al. (2018) applied a TiO_2 surface penetration method after mixing the photocatalyst TiO_2 with a surface penetrant to the 150 m long retaining wall of the Gyeongbu Expressway in South Korea. A change in NOx concentration based on weather and traffic volume was evaluated after the TiO_2 surface penetration method was applied. The NOx removal efficiency on the first day in relatively cloudy weather was 11.1%; the NOx removal efficiency on the second day in clear weather was 21.2%. In addition, the NOx removal efficiency related to the average hourly traffic volume in the section where TiO_2 surface penetration method was applied decreased by about 18% compared to the reference section [12].

Ahn et al. (2020; 2021; 2022) applied various methods of mixing TiO_2 and surface penetrant to reduce NOx emissions from road mobile pollution sources. For a horizontal concrete structure, the TiO_2 surface penetration method was applied using gravity and capillary force. In the case of vertical concrete structures, the TiO_2 surface penetration method did not achieve proper penetration due to the effects of gravity, resulting in peeling off. Static and dynamic pressurized TiO_2 fixation methods were applied to address this issue. For a static pressurized TiO_2 fixation method, 0.2, 0.3, and 0.4 MPa were applied from 0.1 MPa equal to an atmospheric pressure of 1 atm to more than 0.2, 0.3, and 0.4 MPa to select a pressurization criterion. The experiment was conducted with pressing times of 5, 10, and 15 s to verify changes based on pressing time. An electric hammer with striking energy of about 16.95 J was used for a dynamic pressurized TiO_2 fixation method. Pressing times of 1, 3, and 5 s with a constant pressure were applied. A penetration depth of 1 mm and a NOx removal efficiency of about 61% were obtained for a pressurization time of 15 s and a pressurization amount of 0.4 MPa when applying a static pressurized TiO_2 fixation method. The dynamic pressurized TiO_2 fixation method showed a penetration depth of 0.5 mm and a NOx removal efficiency of 51% when a striking energy of 16.95 J and a pressing time of 5 s were applied. Consequently, the long-term performance and NOx removal efficiency were verified, and the possibility of field application was confirmed (Ahn et al., 2020; 2021). The surface of TiO_2 concrete deteriorates over time based on the service period. Thus, the NOx removal efficiency based on the road surface deterioration of TiO_2 concrete was examined. The dynamic pressurized TiO_2 fixation method, which can be easily used in the field, was applied to this end, and the road surface deterioration was simulated through an environmental resistance test. The penetration depth and NOx removal efficiency decreased as the test progressed, which suggests that long-term durability and easy field application can be achieved by securing a TiO_2 penetration depth and NOx removal efficiency even if the road surface deteriorates [13,14].

3. Methods and Tests

L-shaped gutters, median strips, and retaining walls, which are roadside existing concrete structures and open places that emit high volumes of pollutants, were selected as the subjects of application for reducing NOx. For roadside concrete structures, the specimens were prepared by applying a mixing ratio that satisfies the standard of the Korea Expressway Corporation presented in Table 1. Three specimens for compressive strength and flexural strength were prepared, and their physical properties at the age of 28 days were examined. The concrete structure's strength standard (target compressive strength: 21 MPa) was satisfied by achieving the compressive and flexural strengths of 27.62 MPa and 4.19 MPa respectively. In addition, the laitance layer on the surface of the concrete structure was removed for efficient penetration, and fine substances in the concrete pores were removed by a high-pressure water spray (nozzle pressure: 140 bar).

Table 1. Concrete structure mixture design (Ahn et al., 2020 [13]).

Type	G_{max} (mm)	F_{ck} (MPa)	Slump (mm)	Air (%)	W/C (%)	S/a (%)	Contents (kg/m^3)				AE Agent (%)	Water-Reducing Agent (%)
							Water	Cement	Fine Aggeregate	Coarse Aggregate		
Concrete Structure	25	21	40	6	50	42	150	300	762	1044	0.01	0.7

G_{max} = Maximum Coarse Aggregate Size, F_{ck} = Target Compressive Strength, S/a = Fine Aggregate/Total Aggregate Ratio.

The mixing ratio, spraying amount, TiO_2 material, and surface penetrant were chosen based on the fundamental study of Ahn et al. (2020) [13]. For the TiO_2 solution, the optimum mixing ratio of 8:2 was used for TiO_2 and the surface penetrant; the optimum spray amount was 500 g/m^2. Anatase TiO_2 (with a diameter of approximately 21 nm), which has a commonly used anatase crystal structure, was used for TiO_2. In addition, a silane-siloxane-type surface penetrant was used.

TiO_2 has been applied to existing concrete structures via surface penetration, and static and dynamic pressured TiO_2 fixation methods. The TiO_2 surface penetration method is applied to horizontal concrete structures as shown in Figure 2a. The surface penetrant penetrates the entrained air while attracting and fixing TiO_2 through gravity and capillary forces acting perpendicular to the concrete structure surface. However, when applying the TiO_2 surface penetration method to the surface of a vertical concrete structure, the surface penetration effect becomes insufficient due to gravity. As a result, the TiO_2 does not penetrate and flow down to the floor as intended. To solve this problem, pressurized TiO_2 fixation methods are applied as shown in Figure 2b,c, where TiO_2 and the surface penetrant are mixed, penetrated, and then fixed by applying an external force. Figure 2b shows the static pressurized TiO_2 fixation method. The experiment is conducted based on the principle of applying pressure higher than atmospheric pressure to facilitate the penetration of TiO_2 to a certain depth from the surface. A pressure ranging from 0.1 MPa equal to an atmospheric pressure of 1 atm to 0.4 MPa was used; the pressurization times of 5, 10, and 15 s were applied accordingly. For a dynamic pressurized TiO_2 fixation method in Figure 2c, penetration and fixation were performed using an electric hammer that has a hit energy of 16.95 J; pressurization times of 1, 3, and 5 s were set as variables.

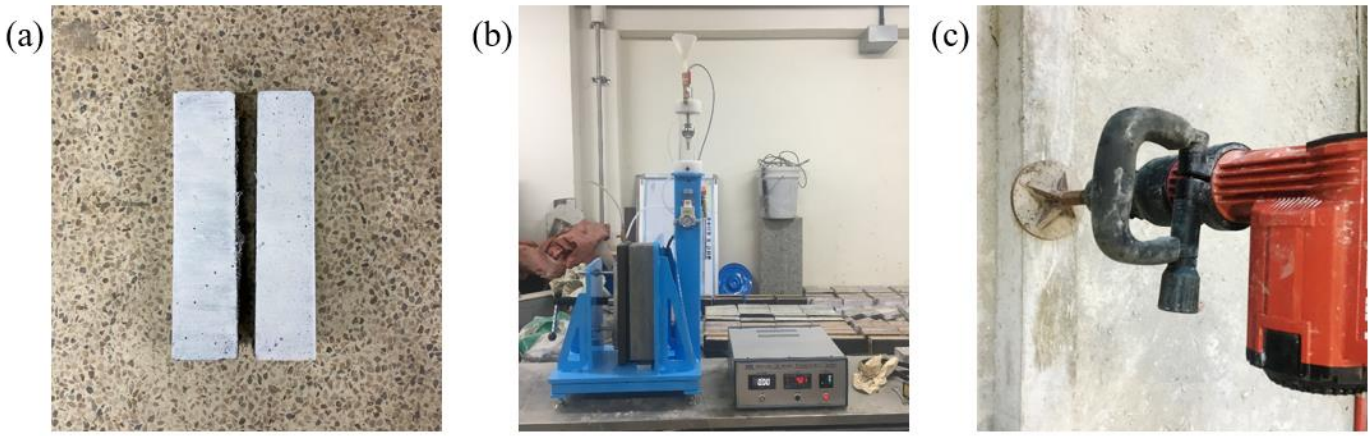


Figure 2. TiO_2 Fixation Method: (**a**) TiO_2 Penetration Method, (**b**) Static Pressurized TiO_2 Fixation Method, (**c**) Dynamic Pressurized TiO_2 Fixation Method.

The illustration in Figure 3 expresses the penetration depth measurement using the scanning electron microscope (SEM/EDX), with Figure 3a showing the equipment and visualizing the penetration depth analysis. The platinum (Pt) plating pretreatment was performed in order to apply an electric potential to the specimen, and after making the

inside a vacuum state, component analysis was performed through an electron beam. In addition, the shape of the sample, observation of the microstructure, distribution of constituent elements, and qualitative and quantitative analysis can be reviewed. In Figure 3b, specimens with a size of 0.5–1 cm were collected and tested. The objectivity and reliability were achieved using the average value of the test results of about three or more specimens for each test case. In addition, as shown in Figure 3c, the TiO_2 penetration depth and TiO_2 mass ratio for each penetration depth of TiO_2 concrete were analyzed; the TiO_2 mass ratio at the surface was derived from the distribution trend of the TiO_2 material by the penetration depth. Thus, the degree of TiO_2 residue that can reduce NOx on the surface of TiO_2 concrete is reviewed.

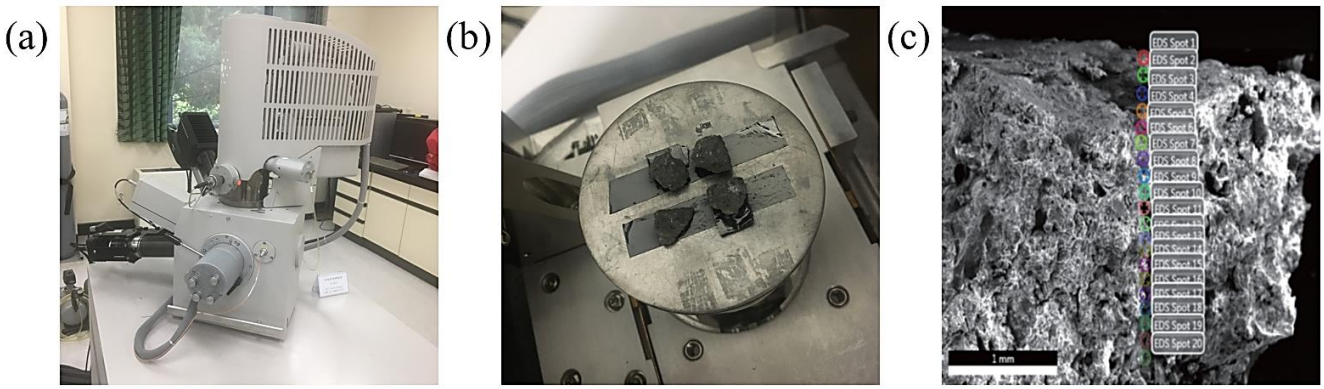


Figure 3. Procedure for Using the SEM: (**a**) SEM Equipment, (**b**) Setting Specimen, (**c**) Component Analysis.

Figure 4 describes the NOx analyzing system. The equipment for the NOx analysis is illustrated in Figure 4a, and the procedure of the system that represents the experimental setup is depicted in Figure 4b. The NOx removal efficiency was measured using the NOx evaluation equipment manufactured based on the ISO 22197-1 standard (Test method for air-purification performance of semiconducting photocatalytic materials-Part 1: Removal of nitric oxide). For the experimental environment, a temperature of about 25 °C and relative humidity (RH) of 50% were maintained. The NOx concentration was adjusted by mixing nitrogen monoxide (NO) and high-purity air. A UV lamp with a wavelength of 315–400 nm was installed for TiO_2 activation. According to Kim et al. (2014), the concentration of nitrogen oxide (NOx) in the roadside area can reach 854 ppb, which is 2.5 times higher than the concentration in general areas, with the maximum value occurring when the number of commuting vehicles increases. For the NOx concentration, 1000 ppb (1 ppm) was similarly used to represent the actual roadside maximum concentration. After the NOx concentration was stabilized, TiO_2 was activated through a UV lamp. After the reaction was completed, the NOx removal efficiency was analyzed through the concentration of the stabilization step.

In the case of TiO_2 concrete performance in service, the TiO_2 material distributed on the surface decreases with the progress of surface deterioration, followed by the decrease in NOx removal efficiency as depicted in Figure 5. concept. This was verified through an environmental resistance test.

The freezing–thawing resistance test (KS F 2456) [15] and scaling test (ASTM C 672) [16] were performed to examine the deterioration of TiO_2 concrete specimens. The freezing–thawing resistance test was conducted using the water-thawing method (Method B) after freezing in the air. It takes 2 h 50 min for one cycle of the freezing process of reduction from 6 °C to −23 °C, and the thawing process of raising the temperature from −23 °C to 6 °C. The freezing–thawing resistance tests were performed 300 times in total, and the relative dynamic modulus of elasticity was examined every 30 cycles. Tests were performed until 300 cycles were reached or the initial measured elastic modulus of 60 % was reached. The TiO_2 penetration distribution and NOx removal efficiency were measured at 0, 150, and 300 cycles to examine the NOx removal efficiency of TiO_2 concrete based on

surface deterioration. Concrete specimens measuring 100 × 100 × 400 mm were used for this purpose.

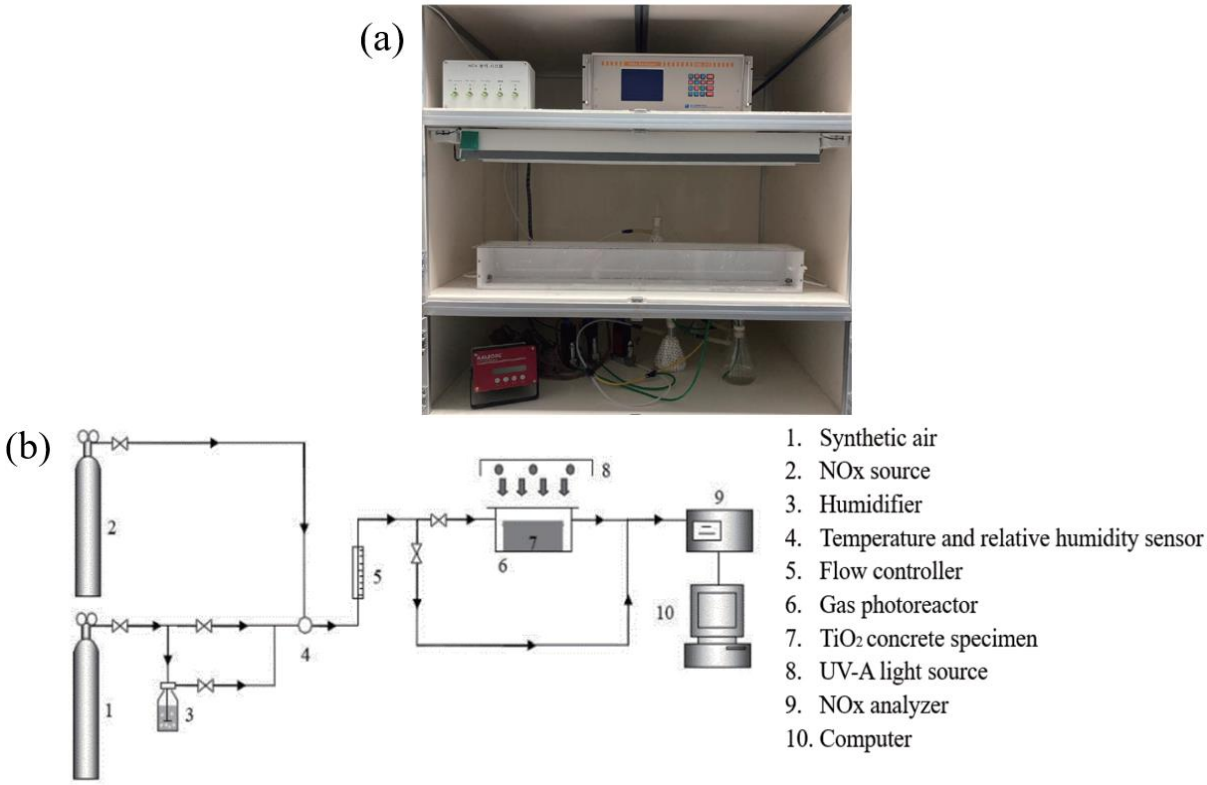


Figure 4. NOx Analyzing System: (**a**) NOx Removal Efficiency Tester, (**b**) Schematic Representation of the Experimental Setup.

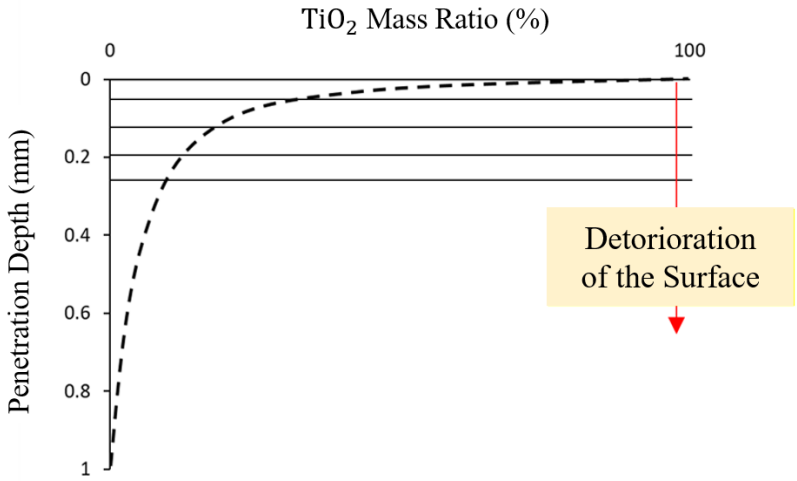


Figure 5. Concept of TiO_2 Distribution based on Surface Deterioration.

The scaling test was performed using the ASTM C 672 test method. $CaCl_2$ was prepared at a ratio of 4 g per 100 mL of distilled water to maintain a constant water level above the specimen. One cycle of the experiment was performed by freezing at −18 ± 3 °C for 16–18 h and thawing at 23 °C for 6–8 h. The surface peeling resistance tests were performed for 50 cycles in total. The concrete surface evaluation was performed at 0, 25, and 50 cycles, and concrete specimens measuring 100 × 100 × 400 mm were fabricated to examine TiO_2 penetration distribution and NOx removal efficiency.

4. Experimental and Analysis

Under the same conditions, the TiO_2 surface penetration and static and dynamic pressurized TiO_2 fixation methods were tested. 500 g/m^2 was used by combining the surface penetrating agent with an 8:2 concentration ratio of TiO_2. As a result, even if the application technology differs, it is possible to compare and demonstrate as follows.

The TiO_2 mass ratio according to the penetration depth was measured until it was no longer detected when the TiO_2 mass ratio according to the penetration depth of each specimen was evaluated with a scanning electron microscope (SEM/EDX). The trend of the TiO_2 mass ratio according to penetration depth was used to display the TiO_2 mass ratio of the surface. As the TiO_2 mass ratio increases near the surface, TiO_2 is observed to be more effective in reducing NOx, and the experimental results are shown in Figures 6–13.

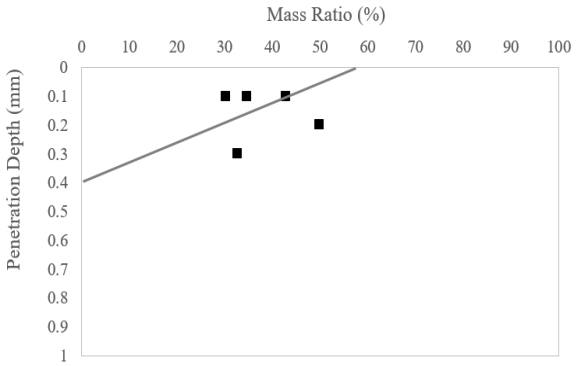
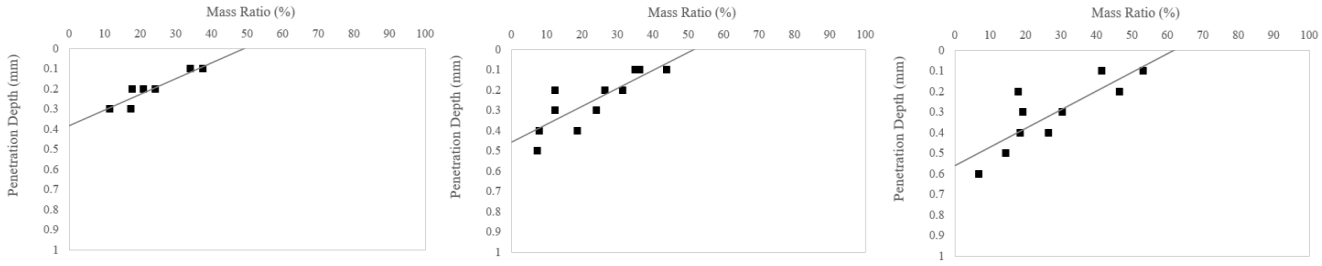
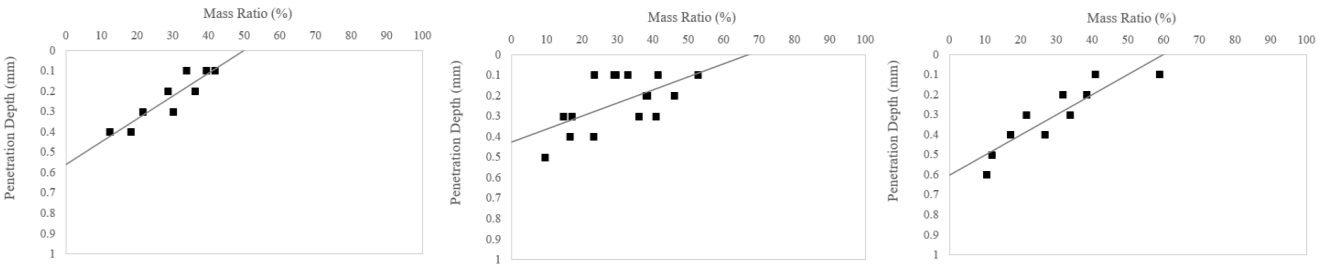


Figure 6. TiO_2 distribution of the TiO_2 surface penetration method.



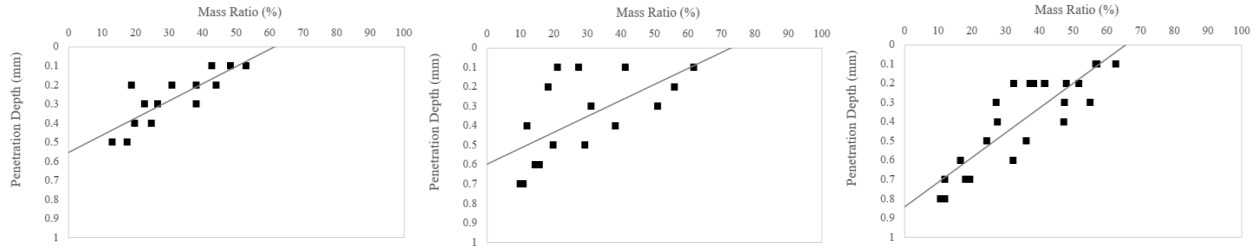
(**a**) Pressure Time of 5 s (**b**) Pressure Time of 10 s (**c**) Pressure Time of 15 s

Figure 7. TiO_2 distribution of the static pressurized TiO_2 fixation method applying a pressure of 0.1 MPa.



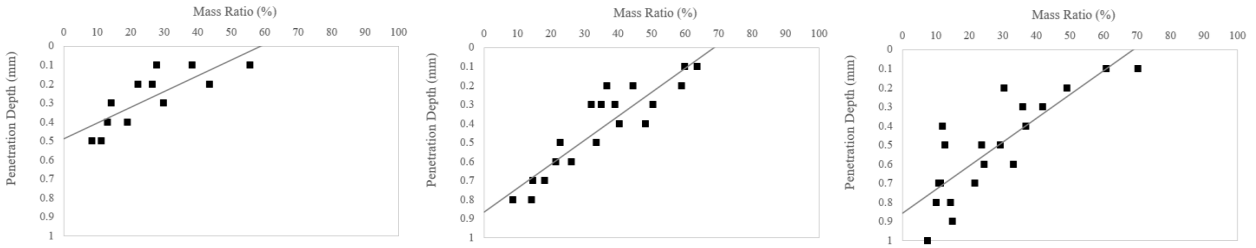
(**a**) Pressure Time of 5 s (**b**) Pressure Time of 10 s (**c**) Pressure Time of 15 s

Figure 8. TiO_2 Distribution of the static pressurized TiO_2 fixation method applying a pressure of 0.2 MPa.



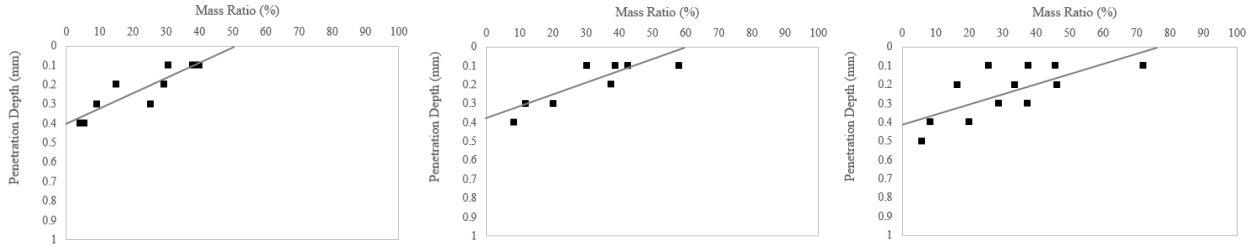
(**a**) Pressure Time of 5 s (**b**) Pressure Time of 10 s (**c**) Pressure Time of 15 s

Figure 9. TiO_2 distribution of the static pressurized TiO_2 fixation method applying a pressure of 0.3 MPa.



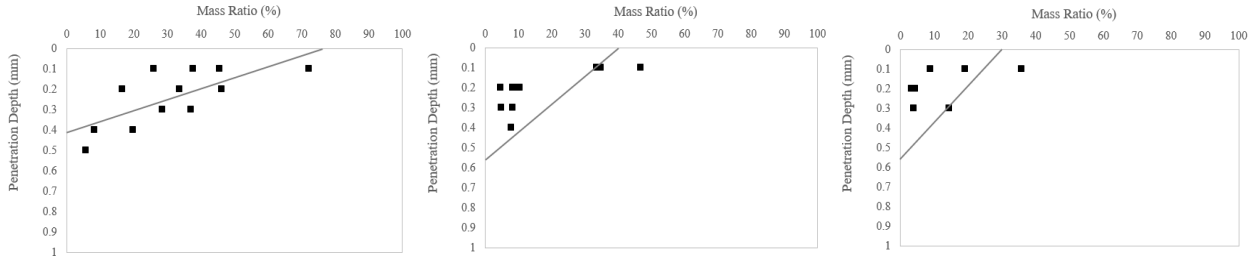
(**a**) Pressure Time of 5 s (**b**) Pressure Time of 10 s (**c**) Pressure Time of 15 s

Figure 10. TiO_2 distribution of the static pressurized TiO_2 fixation method applying a pressure of 0.4 MPa.



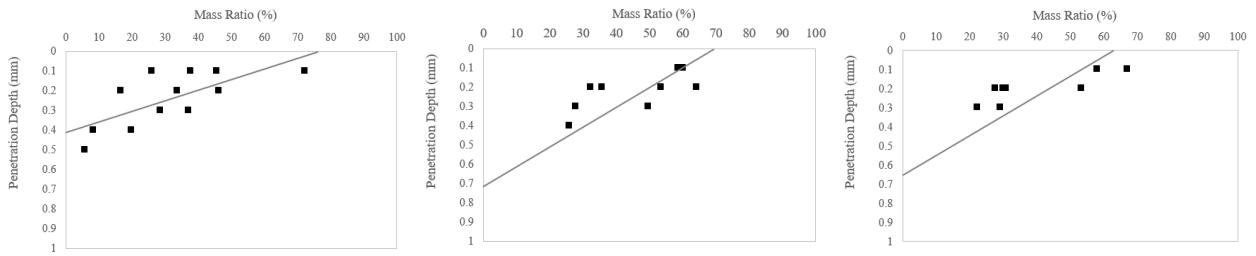
(**a**) Pressure Time of 1 s (**b**) Pressure Time of 3 s (**c**) Pressure Time of 5 s

Figure 11. TiO_2 Distribution of Dynamic Pressurized TiO_2 Fixation Method, Applying Energy of 16.95 J.



(**a**) 0 cycle (**b**) 150 cycle (**c**) 300 cycle

Figure 12. TiO_2 distribution of the freezing–thawing resistance test.



(**a**) 0 cycle (**b**) 25 cycle (**c**) 50 cycle

Figure 13. TiO_2 distribution of the scaling test.

Gravity and capillary force penetrate and fix the TiO_2 material when the TiO_2 surface penetration method is applied to a horizontal concrete structure. In Table 2, TiO_2 penetration depth of 0.3 mm, 57% TiO_2 mass ratio at the surface, and a 45% NOx removal efficiency were observed. The experiment confirmed the possibility of field application by achieving long-term performance through the establishment of a sufficient TiO_2 penetration depth and fixation. Additionally, the NOx removal efficiency further supported the viability of field application.

Table 2. Results of applying the TiO_2 penetration method.

Target	Fixation Method	Applied Pressure	Penetration Depth (mm)	TiO_2 Mass Ratio at Surface (%)	NOx Removal Efficiency (%)
Horizontal Concrete Structure	TiO_2 Surface Penetration Method	0.1 MPa (Gravity)	0.3	57	45

Table 3 summarizes the experimental results using pressurized TiO_2 fixation method. The TiO_2 penetration depth and NOx removal efficiency tended to increase with the amount of pressurization and pressurization time when the static pressurized TiO_2 fixation method was applied to vertical concrete structures. This is because the TiO_2 material reacts more with NOx when it increases on the surface. In the case of the static pressurized TiO_2 fixation method, the NOx removal efficiency was a minimum of 32% and a maximum of 61%. The surface TiO_2 mass ratios were a minimum of 50% and a maximum of 72% as confirmed through experiments.

Table 3. Results of applying the pressurized TiO_2 fixation method.

Target	Fixation Method	Applied Pressure	Pressure Time (s)	Penetration Depth (mm)	TiO_2 Mass Ratio at Surface (%)	NOx Removal Efficiency (%)
Vertical Concrete Structure	Static Pressurized TiO_2 Fixation Method	0.1 MPa	5	0.3	50	32
			10	0.5	51	32
			15	0.6	61	34
		0.2 MPa	5	0.4	50	28
			10	0.5	67	41
			15	0.6	60	51
		0.3 MPa	5	0.5	61	42
			10	0.7	72	48
			15	0.8	65	49
		0.4 MPa	5	0.5	59	49
			10	0.8	69	49
			15	1.0	70	61
	Dynamic Pressurized TiO_2 Fixation Method	16.95 J	1	0.4	50	28
			3	0.4	60	51
			5	0.5	62	51

The NOx removal efficiency was guaranteed by the dynamic pressurized TiO_2 fixation method to be at least 28% for 1 s and up to 51% for 5 s, as well as a mass ratio of TiO_2 on the surface of at least 50% for 1 s and up to 62% for 5 s. The dynamic pressurized TiO_2 fixation method showed about twice the NOx removal efficiency when it was applied for 1 s compared to that when it was applied for 3 s. The NOx removal efficiency appears to show

similar trends after applying the pressure time of 3 s and 5 s. The distribution of the TiO_2 material based on a pressurization time of at least 3 s standard no longer affects the NOx removal efficiency; therefore, in the case of the dynamic pressurized TiO_2 fixation method, the optimum pressurization time is achieved when a pressurization time of 3 s is applied. When the static and dynamic pressurized TiO_2 fixation methods are applied to vertical concrete structures, and it is penetrated and fixed through a certain TiO_2 penetration depth, it is easy to apply the method in the field based on the NOx removal efficiency.

The TiO_2 penetration depth and NOx removal efficiency based on the road surface deterioration of vertical concrete structures were examined after applying the dynamic pressurized TiO_2 fixation method. Environmental resistance tests were used on roadside concrete structures because they were exposed to the outside environment. As shown in Table 4. The freezing–thawing resistance test and scaling test results indicated that the TiO_2 penetration depth and NOx removal efficiency tended to decrease as the road surface deteriorated. However, the long-term durability of TiO_2 concrete was achieved through the TiO_2 penetration depth and NOx removal efficiency even in the final cycle. Even if the concrete surface deteriorates through the secured TiO_2 penetration depth, NOx removal efficiency can be secured due to the TiO_2 being penetrated to a certain depth. This is expected to contribute to PM reduction when applied to the field by confirming the practical use of TiO_2 concrete and securing the NOx removal efficiency. Figure 14 shows the total NOx removal efficiency and TiO_2 Mass Ratio by combining all the results.

Table 4. Results of applying the environmental resistance test using the dynamic pressurized TiO_2 fixation method.

Type of Structure	Fixation Method	Type of Environmental Resistance Test	Cycle	Penetration Depth (mm)	TiO_2 Mass Ratio at Surface (%)	NOx Removal Efficiency (%)
Vertical Structure	Dynamic Pressurized TiO_2 Fixation Method	Freezing–Thawing Test	0	0.5	78	51
			150	0.4	40	29
			300	0.3	30	11
		Scaling Test	0	0.5	78	51
			25	0.4	70	43
			50	0.4	63	36

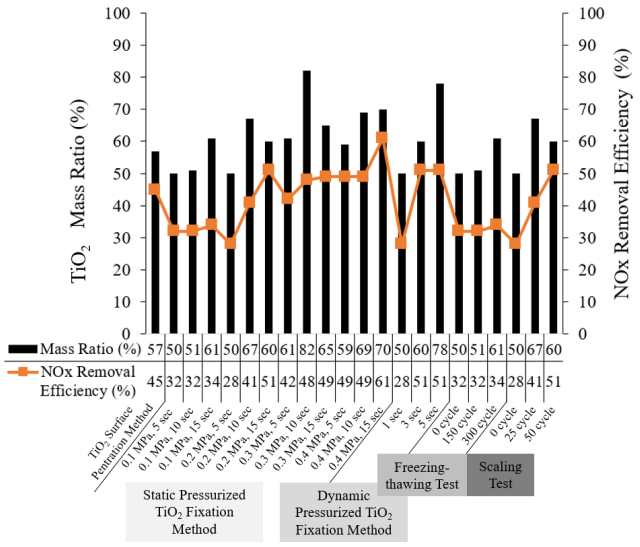


Figure 14. TiO_2 mass ratio and NOx removal efficiency by the TiO_2 fixation method.

Experimental results based on the TiO_2 fixation method and surface deterioration were reviewed. The TiO_2 penetration depth, TiO_2 mass ratio at surface, and NOx removal efficiency tend to increase with an increase in the pressurization amount and time of fixation method. In contrast, the TiO_2 penetration depth, TiO_2 mass ratio at the surface, and NOx removal efficiency tend to decrease with surface deterioration. As a result, the mass ratio of TiO_2 on the concrete surface was analyzed in relation to NOx removal efficiency.

The relationship between the TiO_2 mass ratio at the surface and NOx removal efficiency was examined by performing multiple regression analyses through the application of the TiO_2 surface penetration method, static, dynamic pressurized TiO_2 fixation method, and experimental results based on surface deterioration. This is expressed in Equation (1), and the R-Square is 0.782, as shown in Figure 15. This implies that the NOx removal efficiency can be estimated through the TiO_2 mass ratio at the surface irrespective of the TiO_2 fixation method applied. In addition, it will be possible to apply it more efficiently by examining the change in NOx removal efficiency attributed to the surface deterioration of TiO_2 concrete.

$$NO_x \text{ Removal Efficiency (\%)} = 0.718 \times TiO_2 \text{ mass ratio at surface (\%)} - 2.1682 \quad (1)$$

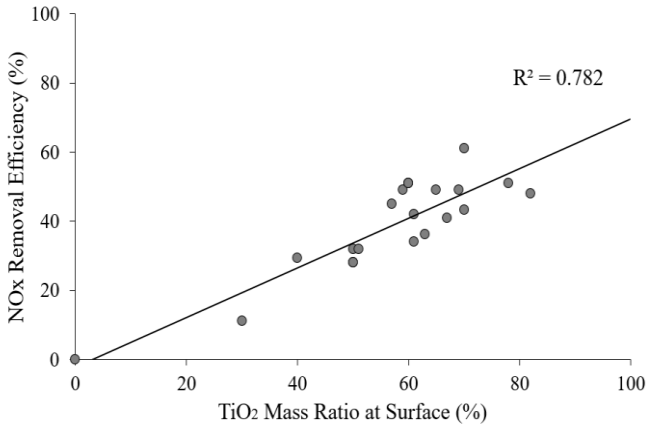


Figure 15. Relationship between the TiO_2 mass ratio at the surface and the NOx removal efficiency.

5. Conclusions

This study reviewed the long-term performance, durability, field applicability, and NOx removal efficiency of TiO_2 concrete to which different fixation methods were applied. Additionally, the NOx removal efficiency was predicted through the TiO_2 mass ratio at the surface. The main conclusions are as follows.

The long-term performance was obtained through the TiO_2 penetration depth. The NOx removal efficiency can be obtained based on the TiO_2 penetrated to a specific depth, even if the concrete surface deteriorates as a result of the secured TiO_2 penetration depth. TiO_2 was fixed by applying the TiO_2 fixation method to the horizontal and vertical roadside existing concrete structures. In addition, the TiO_2 fixation method developed through the verification of the NOx removal efficiency is considered suitable for field application.

Static pressurized TiO_2 fixation methods resulted in 61% NOx removal efficiency and 70% surface TiO_2 mass ratio when applying 0.4 MPa pressure and 15 s pressure time. When a hit energy of 16.95 J and a pressure time of 5 s was used in dynamic pressurized TiO_2 fixation methods, 51% NOx removal efficiency and 62% surface TiO_2 mass ratio were observed. For static and dynamic pressurized TiO_2 fixation methods, the TiO_2 penetration depth, TiO_2 mass ratio at the surface, and NOx removal efficiency tended to increase with an increase in the amount of pressurization and pressurization time. The opposite trend was confirmed for the TiO_2 concrete road surface deterioration based on the experimental results.

The NOx removal efficiency can be predicted through the TiO_2 mass ratio at the surface even if various methods are applied during the production of TiO_2 concrete. The NOx removal efficiency tended to improve with the TiO_2 mass ratio, and it was determined that the surface TiO_2 mass ratio had a significant impact on the NOx removal efficiency, leading to the development of the NOx removal efficiency estimate equation. In addition, by assessing the surface TiO_2 mass ratio and NOx removal efficiency of TiO_2 concrete, the maintenance time of the TiO_2 fixation method can be chosen.

The TiO_2 fixation method attained the fixation and long-term performance through the TiO_2 penetration depth, and the durability was confirmed through an environmental resistance test. The NOx removal efficiency was verified through an experiment, and the result suggests easy applications to the field. The use of TiO_2 concrete on-site is expected to contribute to the reduction of PM.

6. Recommendations for Future Research

Until now, research has been limited, and several experiments have not been carried out. Therefore, it is concluded that further experiments should be carried out by researchers in various areas to enhance the understanding and knowledge of this subject. Furthermore, research should be conducted to predict the NOx removal efficiency regardless of TiO_2 material, as well as the outcome. In the future, more data should be collected through various experiments to improve the predictability of the NOx removal efficiency through the mass ratio of TiO_2 on the surface.

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