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Applicability of TiO_2 Penetration Method to Reduce Particulate Matter Precursor for Hardened Concrete Road Structures

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Abstract: Recently, air pollution is increasing sharply in Korea, caused by fine particulate matter. Nitrogen oxides (NOx) are particulate matter precursors that significantly contribute to air pollution. They are transmitted into the atmosphere by a large amount, especially in high-volume traffic areas. This pollutant is particularly harmful. Therefore, there are increasing efforts focused on NOx removal from the air. As the photocatalytic reaction of titanium dioxide (TiO_2) is the mechanism that eliminates NOx, the ultraviolet (UV) rays in sunlight and TiO_2 in existing concrete structure need to be contacted for reaction process. Generally, TiO_2 concrete is produced by mixing the concrete binder with TiO_2. However, a significant amount of TiO_2 in the concrete cannot be exposed to air pollutants or UV. Additionally, this technique may not be applicable to existing structures. Therefore, an alternative method that utilizes surface penetration agents is used to add TiO_2 to the concrete surface of the structures. This proposed method may not only be economical but also applicable to various types of structures. The applicability of the TiO_2 penetration application method to existing concrete road structures for reducing NOx is the purpose of this study. The penetration depth of TiO_2 particles was measured using scanning electron microscopy (SEM) combined with energy dispersive analysis of X-rays (EDAX). Additionally, the NOx removal efficiency was evaluated using the NOx analyzing system. The results of this study showed that the TiO_2 penetration method was advantageous in removing NOx effectively and securing economic feasibility.

Keywords: particulate matter precursor; nitrogen oxides (NOx); titanium dioxide (TiO_2); TiO_2 penetration method; NOx removal efficiency

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1. Introduction

A variety of air pollutants give harmful and negative effects on both environmental and human health. These air pollutants are produced from the combustion processes involved in space heaters, motor-vehicle traffic, and power generation, mostly in the large city areas. Most of the air pollution is typically caused by rapid urban development; thus, its negative impacts have become a significant concern for the public.

The air pollutants not only contribute to pollution, but they can also travel over vast distances in the atmosphere, and induce acid rain where chemical reactions produce.

The principal pollutants which generate from vehicles are nitrogen oxides (NOx), carbon monoxide, fine particulates, and volatile organic compounds (VOCs) [1]. Primarily, NOx is the general term for a highly reactive gases group [2]. Nitrogen oxides are produced in motor vehicles during the combustion process at high temperatures when fuel is burned. NOx causes many problems to the environment and health, such as urban smog due to photochemical reactions with hydrocarbons and the production of tropospheric ozone. It is one of the urgent concerns for the environmental problem worldwide [2]. Air pollution from exhaust gases may be effectively mitigated by eliminating the emission source. Therefore, photocatalytic materials have been used to eliminate NOx. These materials can be added to the building and pavement surface. Titanium dioxide (TiO_2) is photocatalytic material that is effective in the NOx removal. The photocatalytic reaction of TiO_2 is the mechanism that eliminates NOx, and hence the ultraviolet (UV) rays of sunlight are essential for the reaction of TiO_2 in concrete roads. Additionally, TiO2 is an excellent photocatalytic material that imparts biocidal, self-cleaning and smog-abating functionalities when added to cement-based materials [3]. To activate the TiO_2 during heterogenic photocatalysis, a wavelength lower than 387 nm of UV light needs to be presented. Moreover, the intensity of the light is vital to optimizing the photocatalytic activity.

Fujishima et al. (1999) and Hashimoto et al. (2000) show good effectiveness for NOx removal by combining cementitious with other construction materials [4,5]. Consequently, in modern air-pollution control technologies, TiO_2 photocatalysts has been used [6]. It has been shown that paving blocks with TiO_2 have been used in Japan to reduce the NOx from automobile exhaust gases. According to Beeldens (2006), in Belgium, separate parking lane construction at the Leien of Antwerp used TiO_2 containing pavement blocks. After one year of use, the purification efficiency rate reduced to 20% [2]. Most of the studies have focused on TiO_2 concrete produced by mixing the concrete binder with TiO_2. As solar photocatalysis of TiO_2 is the mechanism that removes NOx, UV rays of sunlight and TiO_2 in concrete road need to be contacted for reaction process. A study on TiO_2 concrete paving blocks showed that a considerable amount of TiO_2 was not exposed to pollutants or UV light. Kim et al. (2014) showed that penetration method using surface penetration agents is an alternative method to produce TiO_2 in concrete without mixing with the concrete binder. The purpose of the penetration method is to position the TiO_2 into concrete structures' surface [7].

Replacement of cementitious materials with TiO_2 may effectively reduce the automobile pollutants. However, a large portion of the photocatalyst reaction may not be activated inside the concrete structure that is unexposed to sunlight. Furthermore, this method can be applied only in upcoming projects that require concrete mixture for their construction. Accordingly, the penetration method may be an effective and economical alternative that applies to various types of new and existing concrete structures.

This paper intends to evaluate the applicability of the TiO_2 penetration method for existing concrete structures, such as concrete pavement, L-type ditch, interlocking block, and permeable block, to remove NOx, which is a fine-size particulate matter precursor. Accordingly, NOx removal efficiencies were evaluated along with the penetration depth and distribution characteristics of TiO_2 particles.

2. Literature Review

2.1. Characteristics of Photocatalytic Reaction of TiO_2

NOx is the generic term of a highly reactive gases group. It contains oxygen and nitrogen in varying amounts. Mostly, nitrogen oxides are odorless and colorless. When fuel is burned in the combustion process at high temperature, nitrogen oxides are generated. The primary sources of NOx come from the objects which consume the fuel such as vehicles, commercial, electric utilities, residential and other industrial. NOx is the generic term for nitrogen dioxide (NO_2), nitric oxide (NO), and mono-nitrogen oxides. Typically, in large cities with a high volume of traffic areas, nitrogen oxide is transmitted into the atmosphere adding to air pollution with a highly significant amount. Delany et al. (1982) revealed that the nitrogen oxides concentration ranges from 10 to 500 ppb in the unpolluted troposphere, whereas range of 100 ppb in polluted urban air [8]. However, the NOx concentration in the high volume traffic area has increased to approximately 1000 ppb recently [7].

Air pollution gives adverse effects on environmental and human health; therefore, it has become a significant public concern in the rapid urban development of the increasing level of air pollution. Many studies have reported on the modern air-pollution control technologies that use TiO_2 photocatalyst for NOx removal in air pollution [6]. TiO_2 is a metal and has three different molecular structures, i.e., anatase, rutile, and brookite. It is abundantly present in nature. TiO_2 is a natural oxide of the element titanium with insignificant toxicity, and negligible biological effects [9]. To active the TiO_2 in heterogenic photocatalysis, a wavelength lower than 387 nm of UV light needs to be presented. Moreover, the intensity of light intensity is vital to optimizing the photocatalytic activity. In normal daylight, the photocatalytic reaction does take place. Currently, most of the research are focused on the application of TiO_2 that can be active in the visible light range. Figure 1 depicts the oxidation-reduction process at active TiO_2 sites, most widely indicated in the literature [7]. Hashimoto et al. (2000) show that a free radical of O_2- is generated from a UV-A irradiation of TiO_2 in the presence of oxygen [4]. The UV-A has 315~400 nm of wavelength. Nitrates were formed by superoxide ions which subsequently react with nitrogen oxides [4,6].

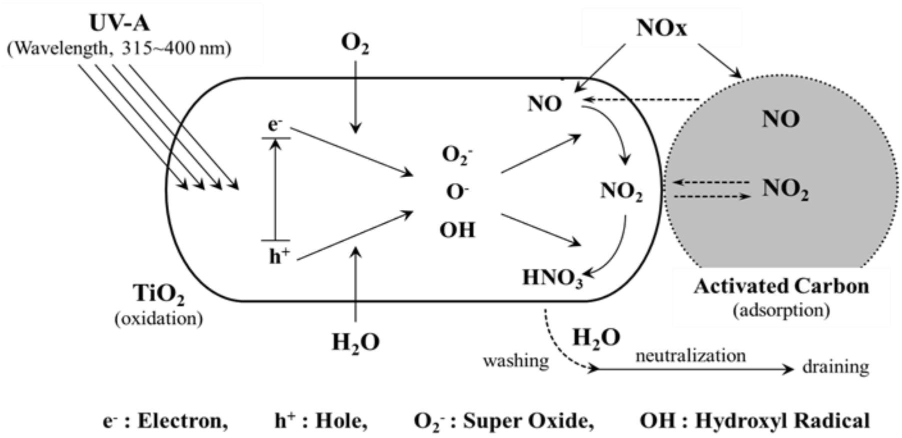


Figure 1. Photocatalytic reaction and NOx removal process of TiO_2.

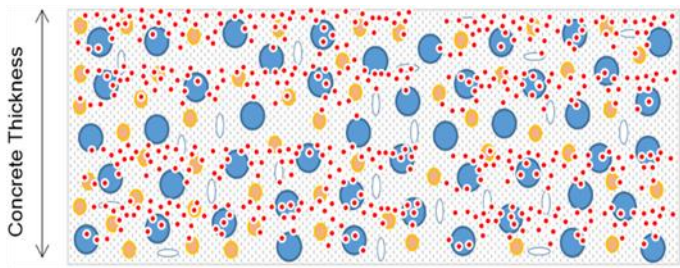
2.2. Current Status of TiO_2 Application

In recent years, titanium dioxide (TiO_2) has been commonly applied in the production of photoactive concrete materials capable of degrading a wide range of air contaminant such as nitric oxide (NO), VOC, etc. [10]. Fujishima et al. (1999) reveal favorable results of nitrogen oxides removal by combining TiO_2 photocatalyst with cementitious and other construction materials [4]. Consequently, many studies show that in modern air-pollution control technologies, TiO_2 photocatalyst has been used [6]. TiO_2 containing paving blocks were utilized at a roadside in Japan for NOx reduction from automobile exhaust gases. In Japan, in 12 h with a UV and wind speed intensity of 0.6 mW/cm^2 and 0.036 m/s, respectively, the paving blocks were eliminating NOx of 45 mg/m^2 [6]. At the Leien of Antwerp, pavement blocks which contain TiO_2 were used for separate parking lanes in Belgium. The air purifying efficiency and also the durability of this method were evaluated in situ. After one-year use, purification efficiency rate was 20% [2].

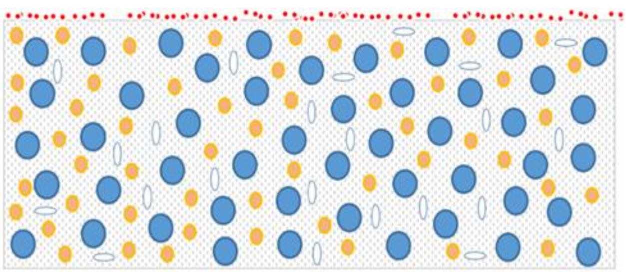
In summary, many studies overseas reported that TiO_2 concrete can be produced by mixing the concrete binder with TiO_2 material. Otherwise, a solar photocatalysis reaction is needed to break down NOxs' structure. Therefore, the TiO_2 in concrete needs exposure to UV rays to be activated, which are utilized for road structure. However, a considerable portion of TiO_2 in concrete is not in contact with the pollutant or the sunlight. Therefore, wasteful quantities of the TiO_2 additive are used, which is not economical. The TiO_2 penetration method is an alternative method besides mixing the TiO_2 with the concrete binder [11]. The penetration method aims to attach TiO_2 to the surface of the structure [11]. The two methods of TiO_2 penetration are: mixing the TiO_2 with the binder and spraying the TiO_2 on the surface with a surface penetration agent. The distribution of TiO_2 in the concrete was measured by using EDAX (energy dispersive X-ray spectroscopy). It distributed up to a 3 mm depth from the specimen surface. In the mixing method, TiO_2 particles were evenly distributed, while in the penetration method, a large amount of TiO_2 particles were distributed close to the surface.

2.3. Application Methods of TiO_2 Materials into Existing Concrete Road Structures

Mitigation methods of particulate matter precursor include various techniques such as mix substitution, coating, and penetration into the concrete structure. Figure 2 represents the schematic of the above methods. In European countries and Japan, a method of mixing TiO_2 is used to replace some parts of cement [2,4]. However, a large amount of particulate matter precursor reduction material should be used in the mixing method as compared to the coating and penetration methods. Thus, this may increase the initial cost of construction. If a large amount of material is distributed on a surface, NOx is better removed. In the case of mix substitution, air pollutants cannot be effectively removed because they cannot contact with the atmosphere as they are farther from the surface. Thus, this method is less efficient than the coating and penetration methods. Additionally, since mixing TiO_2 with the binder can only be applied in upcoming structures, it may not be suitable for the existing concrete structures. The coating method requires a pre-treatment process to improve the attachment of the coating agent and also the surface to be well-developed, which is disadvantageous in terms of the economical aspect. The coating method can be applied only on the surface, and it may be removed or affected by external forces such as rain, wind, or snow. The penetration method is applied to concrete structures by penetrating the particulate matter precursors into the concrete using a surface penetration agent, which contains less amount of TiO_2 material to some extent. It can be applied for NOx removal and is also economical. The surface penetration agent penetrates the entrained air through capillary voids by gravity and the capillary force acting in a vertical direction and hence, pulls the particles into the concrete [12]. Since the size of the TiO_2 particle is 21 to 260 nm, and the entrained air void size is about 70 to 1000 nm, the TiO_2 particles can penetrate through the capillary pore. Figure 3 shows the ideal penetration and distribution of TiO_2 particles in existing concrete structures. The penetration method can ensure economic feasibility due to the reduction of particulate matter precursors from the surface to a certain depth. It can secure long-term performance and durability since the particle matter penetrates into the concrete structures.

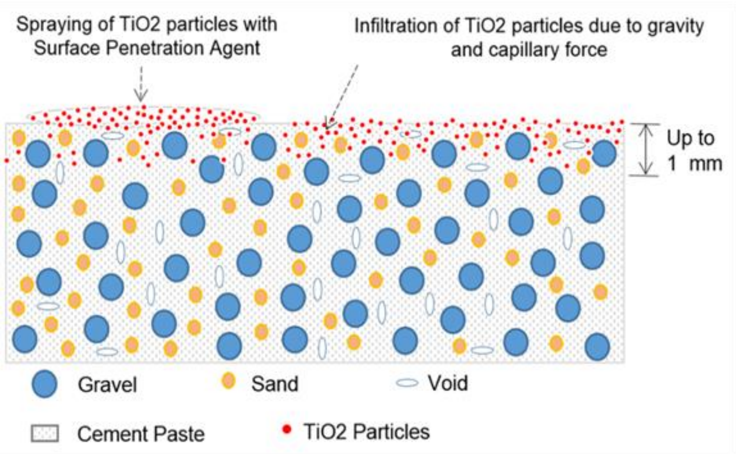


(**a**)



(**b**)

Figure 2. *Cont.*



(**c**)

Figure 2. Application methods of particulate matter precursor reduction materials: (**a**) concrete mixing with TiO_2, (**b**) TiO_2 coating on concrete surface, and (**c**) TiO_2 penetration into concrete structures.

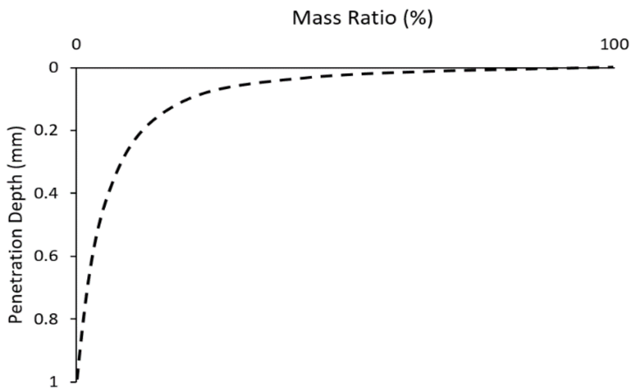


Figure 3. Ideal penetration and distribution of TiO_2 particles in existing concrete structures.

3. Evaluation of Penetration and Distribution of TiO_2

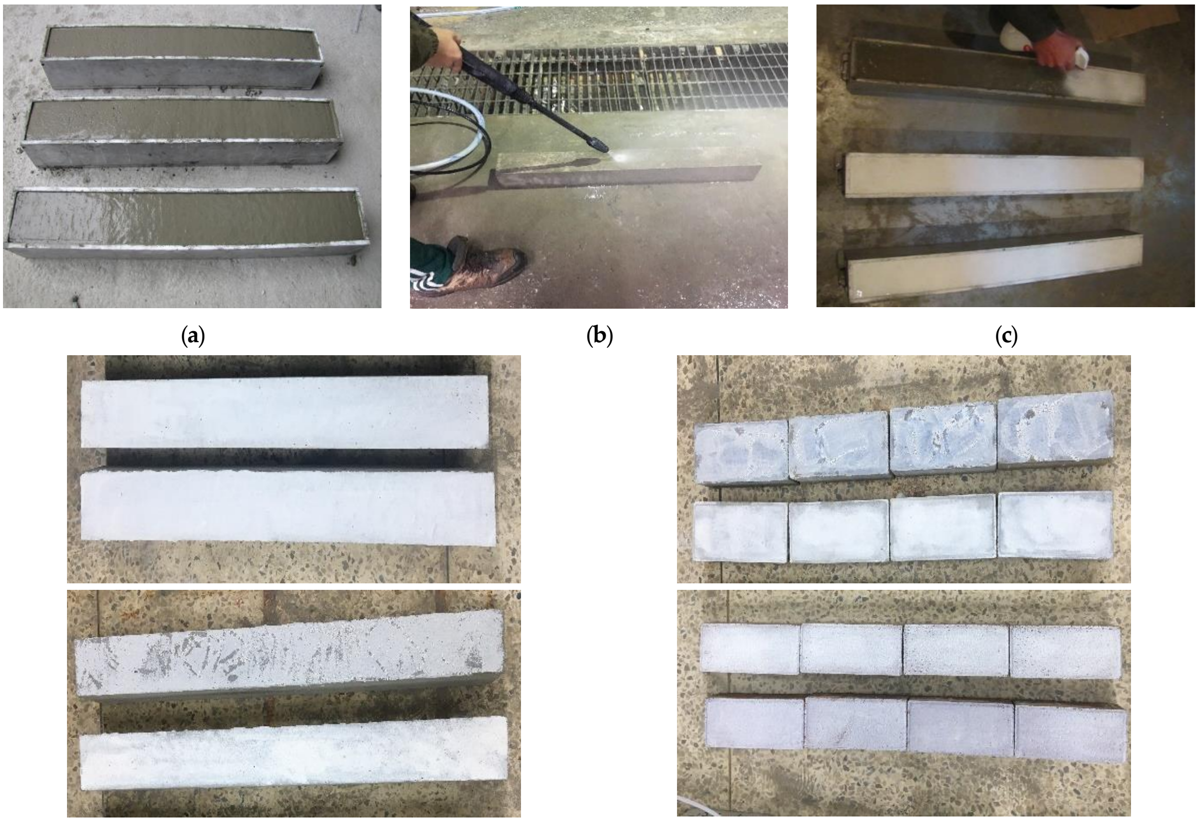
3.1. Specimen Preparation

Table 1 shows the mixture proportioning of the concrete structures such as concrete pavement and L-type side ditch. Concrete specimens used for pavement and L-type side ditch were prepared according to specification suggested by Korea Expressway Corporation, and typical interlocking blocks and permeable blocks were used in this study. According to the product's specification, permeable blocks contained a void content of around 20%, which allows water to infiltrate directly through the surface to the subsurface. On the other hand, the interlocking blocks contained less than 7% void content similar to that of ordinary concrete specimens.

Figure 4 shows the process of specimen preparation for the TiO_2 penetration method. An anatase-type of TiO_2 mixed with silane-siloxane surface penetration agent in the ratio 8 to 2 (application amount, 500 g/m^2) was sprayed on the existing concrete structures such as pavement, L-type side ditch, interlocking block, and permeable block. After curing for 3 days, residual TiO_2 particles on the concrete surface were removed by washing with water to evaluate the penetration and distribution characteristics of the TiO_2 penetration method.

Table 1. Mixture proportioning of concrete structures used in this study.

Type of Concrete Structures	Gmax (mm)	fck (MPa)	Slump (mm)	Air (%)	W/C (%)	S/a (%)	Contents (kg/m^3)				AE Water Reducing Agent
							W	C	S	G	
Pavement	25	35	40	5~7	45	42	148.5	330	759	1067	C × 0.3%
L-type side ditch	25	24	40	5~7	45	47	166	370	863	1001	C × 0.3%



(a) (b) (c)

(d) (e)

Figure 4. Specimen preparation of TiO_2 penetration method: (**a**) Concrete placement (10 × 10 × 80 cm^3), (**b**) Latency and dust removal using high-pressure spray, (**c**) TiO_2 sprayed on concrete (500 g/m^2 with surface penetration agent), (**d**) Concrete pavement and L-type side ditch, and (**e**) Interlocking block and permeable block.

3.2. Test Methods to Evaluate the Penetration and Distribution of TiO_2

The penetration and distribution characteristics of the TiO_2 penetration method was evaluated using scanning electron microscopy combined with energy dispersive analysis of X-rays (SEM/EDAX). The mass ratio was measured at different depths until the mass ratio of the material was not reached. The higher amount of TiO_2 material at penetration depth close to the surface is expected in significantly reducing particulate matter precursors.

Figure 5 represents the measurement process of the field radial injection electron microscope. The specimen is placed in the SEM/EDAX after platinum (Pt) plating to place potential on the specimen. Electronic microscopes use electron beams instead of rays to create vacuum conditions inside the microscope, and then the specimen is analyzed. Component analysis is performed to check the penetration and penetration depth. The mass ratio of the amount of Ti to the amount of concrete was computed.

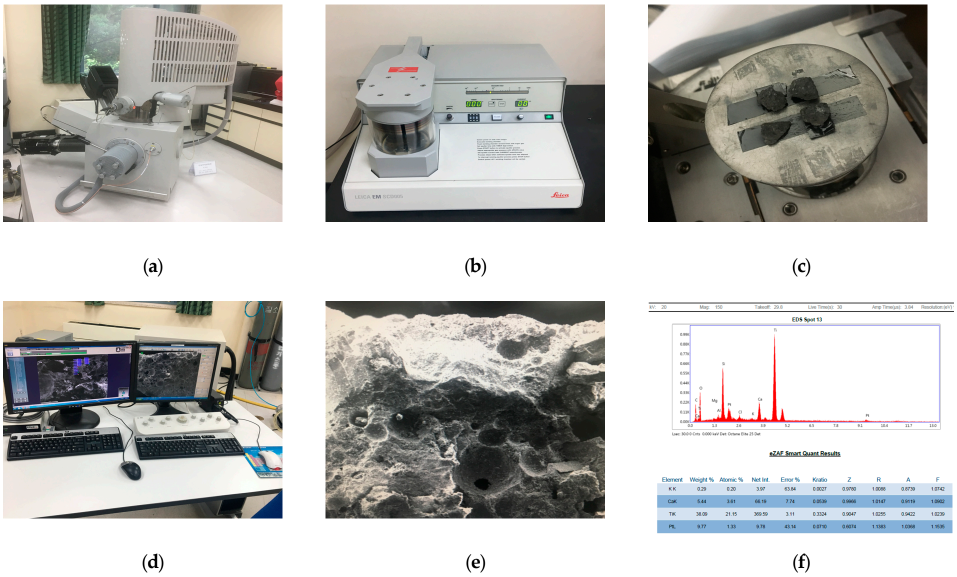


Figure 5. Procedure for evaluating the penetration and distribution of TiO_2: (**a**) SEM/EDAX equipment, (**b**) Pt coating, (**c**) Setting for test, (**d**) Convert to image, (**e**) Image analysis, and (**f**) Detection of mass ratio.

3.3. Characteristics of Penetration Depth and Distribution of TiO_2 Paticles

The TiO_2 mass ratio at 0.1 mm depth from the concrete surface was investigated to evaluate the TiO_2 penetration and distribution characteristics using SEM/EDAX. In addition, the mass ratio at the concrete surface was estimated based on the TiO_2 mass ratio at 0.1 mm depth. The penetration and distribution of TiO_2 particles in existing concrete structures are presented in Table 2. The mass ratios measured at 0.1 mm depth of TiO_2 applied to concrete pavement, L-type side ditch, interlocking block, and permeable block are 38%, 43%, 50%, and 15%, respectively. Additionally, the predicted mass ratio of TiO_2 on the concrete surface was 40%, 57%, and 55%, respectively. For permeable block, the predicted mass ratio of TiO_2 could not be estimated since the particles penetrated the entire cross-section due to the high porosity. These results showed that TiO_2 particles, which are particulate matter precursor-reducing material with silane-siloxane type surface penetration agent, can be efficiently penetrated and distributed in existing concrete road structures.

Table 2. Penetration and distribution of TiO_2 particles in the existing concrete structures.

TiO_2 Type	Types of Concrete Structure	Type of Surface Penetration Agent	Mixing Ratio of Penetration Agent and TiO_2	Mass Ratio at 0.1 mm Depth from Surface (%)	Predicted Mass Ratio at the Surface (%)
Anatase	Concrete pavement	Silane-siloxane	8:2	38	40
	L-type side ditch			43	57
	Interlocking block			50	55
	Permeable block			15	-

4. NOx Removal Efficiency Using TiO_2 Penetration Method

4.1. Test Method to Evaluate the NOx Removal Efficiency

Figure 6 shows the NOx removal evaluation system for photocatalytic concrete following the ISO 22197-1 [7,13]. UV-A lamps which have a wavelength ranged from 315 to 400 nm are used in the NOx removal evaluation system since UV rays reaching the surface of the earth generally have a wavelength in the range of 290 to 380 nm. In addition, the NOx concentration in roadside areas is 170 ppb on an average and 854 ppb at a maximum. This concentration is higher than that measured in other areas by 2.5 times. Therefore, the NOx removal efficiency was fixed at 1000 ppb as per ISO 22197-1, which is similar to the highest NO concentration in the roadside areas.

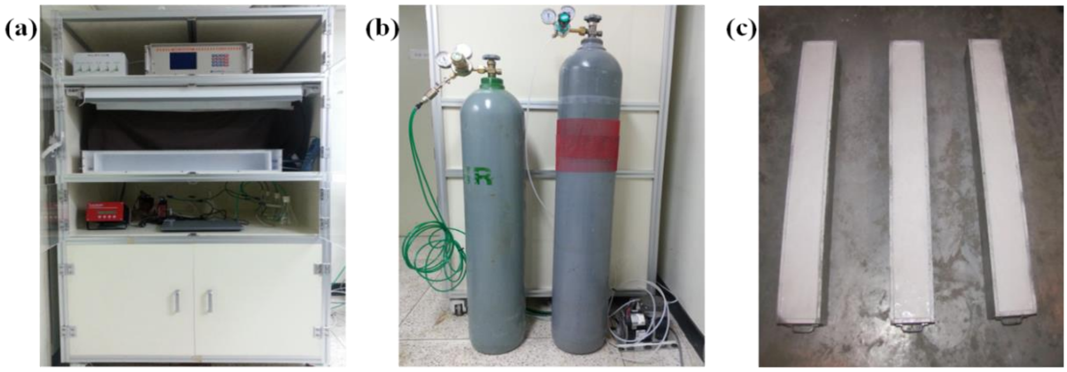


Figure 6. NOx analyzing system: (**a**) NOx removal efficiency tester, (**b**) Synthetic air and NO source (NO 30 ppm/N_2), and (**c**) Specimen preparation.

4.2. NOx Removal Efficiency Based on Surface Predicted Mass Ratio of TiO_2

Figure 7 shows the NOx removal efficiency of the TiO_2 penetration method when applied to various existing concrete structures measured using the NOx analyzing system. In this case, the application amount of TiO_2 mixed with surface penetration agent was 500 g/m^2. The initial NOx removal efficiency was when the residual TiO_2 particles on the surface were not removed. For concrete pavement, L-type side ditch, interlocking block, and permeable block, the initial NOx removal efficiencies were 52.3, 55.1, 53.3, and 55.4%, respectively. In addition, NOx removal efficiencies measured after removing the residual TiO_2 particles on the concrete surface decreased in approximately a range of 5% to 16% compared to initial measurement. For TiO_2 penetration method, the NOx removal efficiency of above 50% can be achieved during the initial period of application; however, the efficiency reduces when the residual TiO_2 particles on the surface are removed due to rainfall, snowfall, wind, etc. Therefore, long-term NOx removal efficiency can be secured when a large amount of TiO_2 particles are penetrated and distributed from the concrete surface to a proper depth. Furthermore, it was shown that the NOx removal efficiency increased when the TiO_2 mass ratio increased due to the proper penetration and distribution of TiO_2 particles in the concrete structures. For permeable block, however, a similar trend for NOx removal efficiency was not observed.

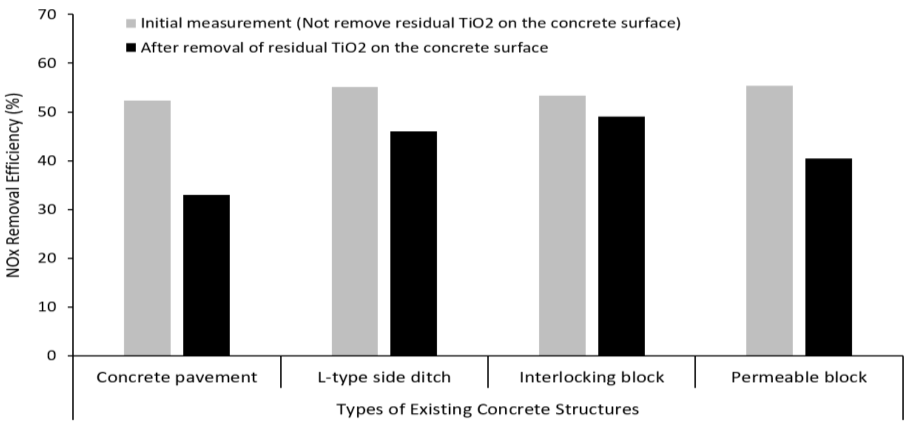


Figure 7. NOx removal efficiencies using TiO_2 penetration method when applied to various existing concrete structures (application amount of TiO_2 with surface penetration agent: 500 g/m^2).

4.3. NOx Removal Efficiency Based on Application Amount of TiO_2

The NOx removal efficiency was measured when the application amounts of TiO_2 mixed with the penetration agent was varied to 300 g/m^2, 500 g/m^2, and 700 g/m^2, as shown in Figure 8. Overall, it was confirmed that a high NOx removal efficiency was measured when the predicted mass ratio at the concrete surface was high. In the case of concrete pavement, the NOx removal efficiencies were less than 40%, even when the TiO_2 application amount was increased. Moreover, the predicted mass ratio was relatively lower than that of the L-type side ditch and interlocking block. For the L-type side ditch and interlocking block, NOx removal efficiencies of approximately 50% were observed when the applied amounts of TiO_2 with the surface penetration agent was 500 g/m^2 or more. Additionally, the NOx removal efficiency increased significantly when the application amounts were increased from 500 to 700 g/m^2 in all experimental cases.

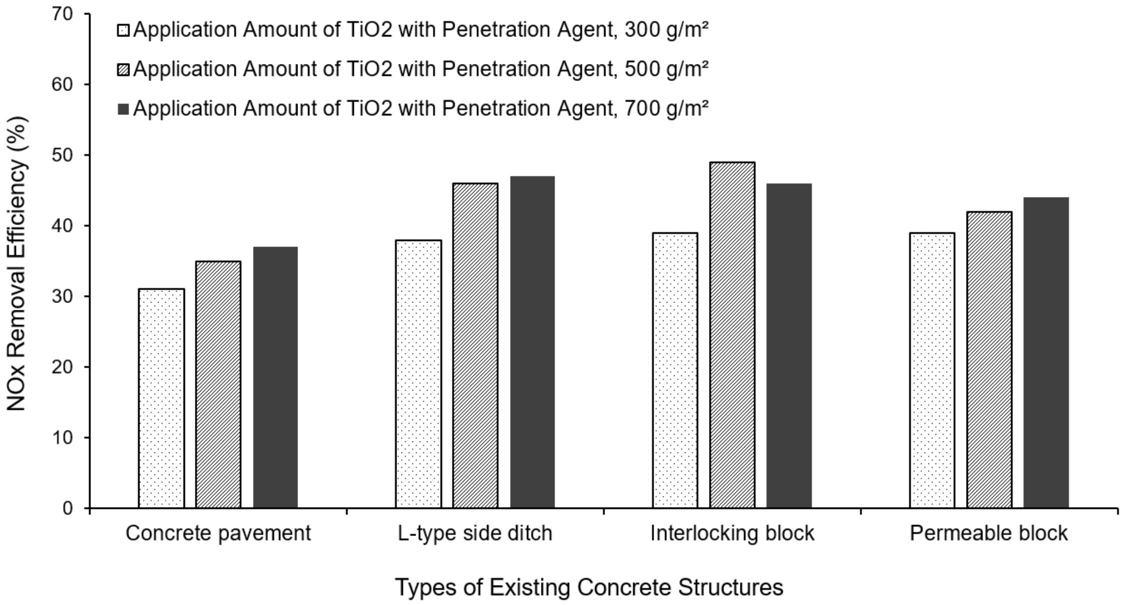


Figure 8. NOx removal efficiencies for various application amount of TiO_2.

5. Conclusions

This paper intends to evaluate the applicability of the TiO_2 penetration method to reduce NOx, which is the particulate matter precursor emitted into the atmosphere by vehicles. This method was applied to existing concrete road structures such as concrete pavement, L-type side ditch, and concrete blocks. Several important conclusions were achieved and are summarized below.

The TiO_2 mass ratios at 0.1 mm depth from the concrete surface were investigated to evaluate the TiO_2 penetration and distribution characteristics using SEM/EDAX. TiO_2 particles with silane-siloxane-type surface penetration agents can efficiently penetrate and be distributed in the existing concrete road structures.

Long-term NOx removal efficiency can be obtained when a large amount of TiO_2 particles are penetrated and distributed from the concrete surface to a proper depth. Additionally, the NOx removal efficiency increased when the TiO_2 mass ratio increased due to the proper penetration and distribution of TiO_2 particles into the concrete structures.

A high NOx removal efficiency was measured when the predicted mass ratio at the concrete surface was high. For the L-type side ditch and interlocking block, a NOx removal efficiency of approximately 50% was obtained when the applied amounts of TiO_2 with surface penetration agents were 500 g/m^2 or more. Additionally, the increase in NOx removal efficiency was insignificant when the application amounts were increased from 500 to 700 g/m^2.

This study indicates that the TiO_2 penetration method can be applied to various existing concrete structures such as concrete pavement, side ditch, and concrete blocks as an alternative method to remove NOx, which is the particulate matter precursor in a high volume traffic area.

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