AIR PURIFYING BLOCKS BASED ON PHOTOCATALYSIS

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ABSTRACT

Nitrogen oxides in exhaust gases from automobiles have been causing so serious air pollution in urban areas that the products with a NOx removal capability have been required. The pavement blocks laid on the road have locational advantages as an air purifying material. We have developed an interlocking paving block with an oxidative NOx removal capability by means of a photocatalytic activity of titanium dioxide, and confirmed the performances under a UV intensity of the outdoor level. The photocatalytic concrete blocks with a brand name NOXER worked in the humidity and NOx concentration ranges of the roadside environment and was actually implemented in a couple of sites in Japan. We are also researching the way to apply photocatalytic technology for another construction materials such as sound-proof walls.

1. INTRODUCTION

The atmospheric NOx pollution due to exhaust gases from automobiles has become more serious particularly in the heavy traffic areas. NOx removal measures such as automobile emission control and traffic reductions have been implemented but are not successful in reducing the total amount of emission. With all possible emission reduction measures, areas of high NOx concentration may still remain where the emitted NOx should be preferably removed. In spite of the demand for the atmospheric NOx removal, virtually no technology have met the requirements until now. The practical solutions of purifying the environment with photocatalytic titanium dioxide have been widely studied in recent years [1]. It can remove NOx from the roadside environment with the help of solar energy as reported by Ibusuki and Takeuchi [2]. Roadside NOx removal technologies other than photocatalyst include the soil-based air cleaning system, the adsorption method and the flue gas deNOx method with a concentrator. They have problems with maintenance and the driving energy consumption. Plants can absorb NOx but require much spaces, have less performance than photocatalyst and pause when leaves fall. The photocatalytic technology, however, has no driving energy, less maintenance actions and can work throughout a year. Though the photocatalyst can oxidize the atmospheric NOx and extract as nitrate ions in the same manner as the atmospheric oxidization process of the vehicle emitted NO [3], the oxidization at the photocatalytic titanium dioxide
surfaces is a very rapid process with active oxygen species such as hydroxyl radicals (OH·) and super oxide anion (O₂⁻) formed in the presence of oxygen and sunlight.

\[ \text{NO} \rightarrow \text{NO}_2 \rightarrow \text{NO}_3^- \]

In the oxidation NO₅ removal process, resulting nitrate ions are accumulated in the substrate material, rinsed by the rain and removed from the system. Possible fixing means of the photocatalyst include fluorocarbon polymer sheet materials [4] and paint materials [5]. This technology is characterized by a global environment conscious and fossil fuel free nature, and expected to be used as a road material or a road equipment which easily become popularized. The following advantages are suggested when the technology is realized as pavement blocks [6].

(1) The block can be used as flat outdoor surfaces, where sunlight and rains necessary for the activation and regeneration are available.
(2) The block is installed close to the NO₅ emission sources and reacts with the pollutants under a higher concentration.
(3) The block is adopted as a pavement of the roadside without any additional space for the NO₅ removal.

We will discuss in this paper with the photocatalytic, NO₅ removing cement based pavement block.

2. EXPERIMENTAL METHODS

2.1 PREPARATIONS OF SPECIMENS

The paving blocks have a surface layer of the titanium dioxide contained in a special cement mortar which is monolithically formed with the substrate by the vibration press. Blocks can be produced in various shapes by selecting the form type. A typical example is shown in Photo 1.

![Photo 1](image)

Specimens had 5 to 7 mm thick surface layer containing photocatalytic titanium dioxide on a monolithic substrate without titanium dioxide. Aggregates, cement, photocatalytic titanium
dioxide and water were mixed and placed in the form with vibration and pressed to have 60 mm in total thickness, 100 mm in width and 200 mm in length. The block formed a porous skeleton applicable as a permeable interlocking block. The specimens were subsequently cured at room temperature for 1 month and subjected to the test. The concept of the atmospheric NO\textsubscript{x} removal by the block is schematically shown in Figure 1.

![Diagram of NO\textsubscript{x} removal](image)

*Figure 1  NO\textsubscript{x} removal schematic of the paving block*

### 2.2 EVALUATION OF THE NO\textsubscript{x} REMOVING PERFORMANCES

The NO\textsubscript{x} removing performance test was carried out with an apparatus as shown in Figure 2. A block specimen with a surface area of 200 cm\textsuperscript{2} was set in a reaction vessel as shown in Figure 3, where an simulated emission gas made by mixing a dry air and a dilute NO gas with the flow controllers to have a NO\textsubscript{x} concentration of 1.0 ppm was passed through at a flow rate of 3 l/min. The reactor vessel was made of PVC and had a upper window of the UV transparent Pyrex glass. A gap between the glass and the block surface was 5 mm to allow the photocatalyst a sufficient contact with the air. Temperature of the test was the room temperature of 25 °C and

![Diagram of test setup](image)

*Figure 2  System of evaluating NO\textsubscript{x} removing performances*
the relative humidity of the simulated emission gas was 50 % except for a test series where humidity was a variable. UV with an intensity of 6 W/m² (UV-A: 315-400 nm) was applied on the specimen by a pair of 10 W black light. The NO₅ concentration was determined by a chemiluminescence NO₅ analyzer (Monitor Labs, INC. ML9841). From the differences in concentrations at the inlet and the outlet, the amount of NO₅ removal was obtained and the NO₅ removal ratio, a ratio of the concentrations of the outlet to that of the inlet, was calculated. Measurement was continued for 12 hours and the concentrations of NO₅, a sum of NO and NO₂, was recorded.

![Figure 3 Reaction vessel for NO₅ removing performance evaluation](image)

The outdoor performance test was carried out with the same reaction vessels settled outdoors for three days under the same gas flow and natural UV environment. The roadside air was introduced in the reactor vessel at a flow rate of 3 l/min and the difference in radiation conditions with direct sunshine and with a sunshade screen was compared.

### 2.3 MECHANICAL PROPERTIES OF THE BLOCK

1. Skid resistance test
   The British Pendulum Skid Resistance Tester specified in the ASTM E303 was applied on the block surfaces under dry and wet conditions.

2. Flexural strength test
   Flexural strength was tested according to the JIS A 5306.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 PERFORMANCES IN THE LABORATORY TEST

Dependence of the NO₅ removal upon relative humidity is shown in Figure 4. In the humidity
range from 10 to 80%, NOx was removed, thereby the blocks can work under the normal atmospheric humidity ranges. At higher humidity, the NOx removal performance decreased probably because the water adsorbed on the photocatalytic surfaces interfered the adsorption of NOx.

![Graph showing NOx removal ratio vs. relative humidity](image)

Figure 4  Dependence of NOx removal upon relative humidity  
(UV intensity: 6 W/m², NO feed concentration: 1.0 ppm)

![Graph showing NOx removal ratio vs. UV intensity](image)

Figure 5  Relationship between UV intensity and NOx removal  
(NO feed concentration: 1.0 ppm)

Relationship between UV intensity and NOx removal is shown in Figure 5. The UV wavelength ranged from 300 to 400 nm and the NOx concentration of the inflow air was 1.0 ppm. The NOx
removing performance was confirmed when the UV intensity was from 1 to 12 W/m². Effect of NOₓ adsorption can be seen in a small amount of the removal when UV intensity became zero, therefore, adsorption effects can be neglected in the NOₓ removal performance test. Since the UV intensity of a direct sunlight in summer is 20-30 W/m² and the minimum UV intensity in cloudy winter days is 1 W/m², the photocatalyst can work throughout a year.

Relationship between NO concentration in the inflow gas and the NOₓ removal is shown in Figure 6. The NO concentration was varied from 0.05 ppm to 1.0 ppm whereas the NOₓ removal was almost constant throughout the concentration range that corresponds to those observed as the current roadside level. Removal of low concentration NOₓ in the real atmosphere is thus realistic.

![Figure 6](image_url)

**Figure 6  Relationship between NO concentration and the NOₓ removal (UV intensity: 6 W/m²)**

### 3.2 PERFORMANCES IN THE OUTDOOR TEST

(1) NOₓ removal test under sunlight

Though the black lights were used as an UV source in the laboratory test, this experiment was carried out under time-dependant variable UV intensity with a 1 ppm of NO gas flow and the amount of NOₓ removal was determined. NOₓ removing blocks worked quite well either in a sunlight UV level as shown in Figure 7. The nocturnal performance without a sunlight was almost zero. Direct sunlight are not necessary because the working UV intensity range where the blocks show constant NOₓ removal ratio is as low as 1 W/m² as given in the diffused reflection or artificial light sources. Since the currently available mercury lamps have sufficient UV intensity for the photocatalytic reactions, these artificial light sources can be applied to the NOₓ removing blocks in tunnels or in nocturnal uses.
Figure 7  NO\textsubscript{x} removal in the outdoor
(NO concentration: 1 ppm, gas flowrate: 3.0 l/min)
Feb. 1998 at OMIYA, SAITAMA, JAPAN
UV intensity UV-A (365 nm)

(2) Atmospheric NO\textsubscript{x} removal at roadside
Roadside air containing NO\textsubscript{x} was introduced in the reaction vessel which was subsequently exposed to the sunlight. Flow rate of the roadside air was 3 l/min and the NO\textsubscript{x} concentration at the outlet was determined. The result of NO\textsubscript{x} removal is shown in Figure 8. When the radiation condition was varied from covering to direct sunlight, resulting NO\textsubscript{x} concentrations at the outlet were greatly decreased, thus, it was possible that the NO\textsubscript{x} removing block can be

Figure 8  NO\textsubscript{x} removal at a roadside environment (suburbs of Tokyo)
Temperature: 17 °C, Relative humidity: 47 %
used in the roadside environment and can show as much performance as those obtained in the laboratory tests. The NO$_x$ removing blocks are now subjected to the outdoor exposure test to check the long term performance, by which further improvement can be expected. Some evidences of neutralizing the acidic drainage by alkaline particles in the roadside air has been obtained [7], and it may be expected that the decomposition of the substrate block is not significant because the amount of nitric acid originated from the oxidation of the atmospheric NO$_x$ is so small.

3.3 PROPERTIES AND THE CONSTRUCTION OF THE BLOCKS

The NO$_x$ removing blocks can be laid in the same manner as used for the conventional interlocking blocks since the test results of the mechanical properties such as flexural strength and skid resistance were satisfactory as shown in Table 1.

Table 1  Mechanical properties of the NO$_x$ removing block (permeable interlocking block)

<table>
<thead>
<tr>
<th></th>
<th>Measured value</th>
<th>Standard values</th>
<th>Test methods</th>
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</thead>
<tbody>
<tr>
<td>Flexural strength</td>
<td>4.63 N/mm$^2$</td>
<td>more than 2.9 N/mm$^2$</td>
<td>JIS A 5306</td>
</tr>
<tr>
<td>Skid resistance test</td>
<td>wet 65-70 BPN</td>
<td>more than 65 BPN</td>
<td>ASTM E303</td>
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<tr>
<td></td>
<td>dry 80-85 BPN</td>
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</tbody>
</table>

4. EXAMPLES OF CONSTRUCTION OF THE NO$_x$ REMOVING BLOCKS

The NO$_x$ removing block NOXER has been applied to a couple of sites in Japan. In the redevelopment project of Narashino city, NOXER was widely applied to the pavement as shown in Photo 2, while it was used in the roadside of Kawasaki city contaminated by the emission gases as shown in Photo 3. These applications are characterized by the use of the

Photo 2  Construction at Narashino City

Photo 3  Construction at Kawasaki City
permeable substrate block taking into considerations of rain infiltration to minimize the sewer road.

5. CONCLUSIONS

The atmospheric NOₓ pollution has become serious in the urban roadside. The NOₓ removing paving blocks with a titanium dioxide surface layer have developed. The photocatalytic removal of the atmospheric NOₓ was confirmed. The NOₓ removing performance and physical properties of the paving block were measured and the followings are resulted.
(1) The NOₓ removing block was able to remove the low concentration NOₓ of a roadside level.
(2) The block worked under a normal humidity range between 10 to 80 %.
(3) The block worked under as low UV intensity of 1 W/m² as those in cloudy winter days in Japan. Thus the block can be expected to work throughout a year.
(4) The block performance under a sunlight UV level was confirmed by the outdoor tests.
(5) Since the block has equal mechanical properties and durability with that of the normal blocks, it can be placed and used in the conventional manner.

The photocatalytic block is a long-life product but now subjected to a long term test to confirm the roadside performance and the degradation over time which may be reflected in the subsequent development. In order to process continuous automobile emission under the limited sunlight, the roadside photocatalytic product should have both more efficient photocatalytic capability and a large surface area resulting in a new product, for example, photocatalytic sound absorbing boards.

REFERENCES