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Field study of NO_x degradation by a mineral-based air purifying paint

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ABSTRACT

This paper studies the performance of a mineral-based transparent air purifying paint. The air pollutants removal efficiency of this photocatalytic paint was first determined following the ISO 22197-1 procedure under laboratory conditions. Subsequently, its air pollutants removal efficiency under realistic conditions was determined by outdoor monitoring with a duration of 20 months, applying a new monitoring protocol. The weather conditions, including temperature, wind flow, humidity, precipitation, and NO_x concentration were continuously monitored. The efficiency of the photocatalytic paint was analyzed. The influence of the environmental parameters on the air pollutant removal efficiency as well as long term performance was discussed. The results show the excellent air purifying efficiency of this new paint, nevertheless the environmental parameters show dramatic effects on its long term performance. Furthermore, this study also confirmed the robustness of the proposed air purification performance monitoring protocol.

1. Introduction

Exposure to harmful gases such as nitrogen oxides (NOx) and sulphur oxides (SO_x) or particulate matters (PM) has been associated with adverse health effects [1]. Due to the increase in concentrations of these harmful gases in large urban areas, the air quality is becoming a pressing issue, despite strict regulations on pollutant emissions [2]. Therefore, more and more attention is being paid to the removal of these pollutants. One of the most promising removal methods is the application of heterogeneous photocatalysis. Heterogeneous photocatalytic oxidation (PCO) has been studied for several decades and shown as an effective method for water or air purification [3] or selfcleaning [4,5]. Some metal oxide semiconductors like TiO₂ and ZnO are photocatalysts which are commonly used for PCO applications [6-9]. Among them, TiO₂ is widely used because of its many appropriate characteristics [10]. TiO₂ has two main crystal forms of anatase and rutile with a band gap of 3.2 eV and 3.0 eV, respectively. Anatase has some more superior characteristics than rutile, such as a more favorable conduction band location for conjugate reactions and being able to form very stable surface peroxide groups during PCO reactions, which makes anatase the preferable choice to be used as photocatalyst [11].

Extensive studies on the photocatalytic oxidation of NO_x have been carried out in the past years. Hashimoto et al. [12] studied the effect of using a titania-zeolite composite catalyst for the photocatalytic oxidation of NO and found a combination of TiO₂ and zeolite of 7:3 by weight results in the highest PCO rate. Devahasdin et al. [13] studied the reaction kinetics of NO photocatalytic oxidation with an inlet concentration of 20-200 ppm. Ichiura et al. [14] studied the PCO of NO_x using composite sheets containing TiO₂ and metal compounds like CaO and MgO from which the CaO treated TiO₂ indicated to have the greatest NOx conversion rate. Wang et al. [15] studied the reaction mechanism of PCO of NOx with an inlet concentration of 20-168 ppm using TiO₂ supported on woven glass fabric. Yu and Brouwers [16] evaluated the influence of environmental conditions on the photocatalytic oxidation of NO under visible light irradiation, and proposed a kinetic model to predict the photocatalytic behavior of NO_x [17]. Kuo et al. [18] studied the PCO of NO_v under visible light using carboncontaining TiO₂ and the effect of the wavelength of the light was investigated. Ballari et al. [19] investigated the synergetic effect of photocatalytic oxidation of NO and NO2 and observed a combined photocatalysis and photolysis of NO2, especially under a relatively high humidity level. Luévano et al. [20-22], developed TiO2 based photocatalysts modified by, for instance, WO3 and these new photocatalysts showed excellent NO_x degradation performances. In addition, the effect of different substrates was also evaluated. Ballari et al. [23] evaluated the air decontamination performance of several modified TiO₂ under visible light irradiation and proposed a radiation flux balance model to address the radiation absorption of the photocatalyst. Liu et al. [24] synthesized visible-light responsive carbonated-doped anatase TiO2 using sol-gel method and found that the carbonate dopants can help to promote the charge carrier's separation and serve as the photosensitizer for the absorption of visible light. Aghighi and Haghighat [25] confirmed the great effect of humidity on the photocatalytic efficiency.

However, up till now, the performance of photocatalytic materials

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Fig. 1. (a) Picture of the photocatalytic set-up (b) schematic overview of the PCO test (1. NO gas supply; 2. Synthetic air; 3. Mass controller meter; 4. Humidifier; 5. Humidity controller; 6. Temperature and relative humidity sensor; 7. Light source; 8. Reactor; 9–10. Valves; 11. NOx analyzer; 12. Computer; 13. Vent).

under realistic outdoor conditions has been investigated in a very limited manner. Maggos et al. [26] performed a field study by building artificially a street canyon with a width/height ratio of 0.4, using a relatively high inlet NO concentration produced by a gas generator. Different NOx removal efficiencies of 36.7%-82.0% were observed, depending on the wind direction and street direction. Boonen and Beeldens [27] suggested that the translation from the laboratory results to the real site is still difficult because of the great of number of parameters. Furthermore, large scale projects to demonstrate the effectiveness of the photocatalytic materials on site are highly needed. De Melo et al. [28] evaluated the efficiency of photocatalytic pavement in the filed for a one-year duration in Brazil and found a dramatic reduction of NO_x degradation efficiency after one year. Ballari and Brouwers [29] performed a full demonstration project of air purifying pavement in the Netherlands and reported a fast reduction of NO_x degradation efficiency where the photocatalyst is applied as surface coating on pavement stones. Folli et al. [30] performed a field study of air purifying paving elements containing TiO2 and observed that under ideal weather conditions (i.e. summer time) the monthly average NO concentration was around 22% lower than in the reference area, in contrast to a very high lab NO degradation of over 78%. Gallus et al. [31] performed a photocatalytic de-pollution field study in the Leopold II tunnel in Brussels. Three monitoring campaigns during the period June 2011 and January 2013 were performed. Photocatalytically active coating was applied to the side walls and ceiling of the tunnels. In contrast to the laboratory results, the field results showed no significant reduction of NO_x in the tunnel test and an upper limit of NOx reduction of 2% was observed. Besides, a serious deactivation of the photocatalytic material under the heavily polluted tunnel was observed. Yang et al. [32] investigated the durability of TiO₂ coated aggregates for concrete applications and observed a 30% photocatalyst removal after only 10 cycles of artificial washing.

The above reviewed literature shows the following distinguishable remarks: (1) photocatalysis offers distinctive advantages regarding air pollutant removal, for instance, no extra energy input is required and large surfaces can be applicable [33]; (2) environmental conditions play an essential role on the air pollutants degradation efficiency, reflected by the very varied performance of the photocatalytic coatings in various field studies, although those coatings in general show excellent efficiency under laboratory conditions [31,33]; (3) it is difficult to design a reliable field monitoring protocol as well as evaluation methods [30].

The presented project aims at the evaluation of the air pollutants removal efficiency of a newly developed mineral based transparent photocatalytic paint and development of a new protocol for monitoring the air purification performance under outdoor conditions. Firstly, the air pollutants degradation performance of the mineral paint was evaluated under laboratory condition following the standard ISO 22197-1 [34], using NO as a model pollutant. Then, the photocatalytic paint was coated onto a panel with the size of 100 cm \times 65 cm, and lime render was applied as the substrate for the paint. A second panel with the same

size using the same lime render as substrate was coated with the mineral paint but containing no photocatalyst, as a control panel. In addition, this photocatalytic paint was applied on a polycarbonate panel at a later stage, to investigate the effect of the substrate on the air pollutants NO_x removal performance, by collecting and analysing the produced NO₃⁻ ions. The detailed experimental description and the monitoring principle are presented in Sections 2 and 3, respectively. The panels were mounted outdoors for 20 months during which the photocatalytic oxidation of air pollutants was monitored. In addition, environmental parameters, including temperature, wind flow, irradiance, humidity, water precipitation and NOx concentration were continuously measured through the whole monitoring period. The results are presented and discussed. The air purifying performance of the developed paint under real outdoor condition is correlated with the environmental parameters. Furthermore, key influential parameters are evaluated.

2. Laboratory assessment

The photocatalyst used in this coating was provided by Joma International (Norway) and the mineral base paint was provided by Keim (The Netherlands). The new mineral-based air purifying paint was developed primarily applying sodium silicate as a mineral binder and additives containing about 5% bio-based copolymers where the TiO_2 photocatalyst is pre-mixed. The amount of photocatalyst was kept low enough to ensure the transparency of the paint.

The air pollutant removal activity of the photocatalytic paint was firstly assessed under fully controlled laboratory conditions, following the ISO 22197-1 [34]. A custom-made plug-flow experimental set-up was used with nitrogen oxide as the model pollutant. The picture of the setup is shown in Fig. 1a, including the light source, environmental parameters control panel, gas source and the reactor. Panels with a surface size of 200 mm \times 100 mm were first coated with the mineral based air purifying paint, applying the lime render and/or polycarbonate as the substrate. Subsequently, the samples were irradiated by UVA light for 5 h, then washed by demi-water for 2 h and finally oven dried. The following testing conditions were applied: 10 W/m^2 of UVA irradiance, 50% of relative humidity, 3 L/min of flow rate, 1 ppm of NO inlet concentration. The exposure testing sample surface was $200 \text{ mm} \times 100 \text{ mm}$ with the reactor height of 3 mm, namely the distance between the reactor cover and the surface of the testing sample. The duration of the measurements was set to 1 h under irradiation. Prior to irradiating the sample with UVA light, the system was conditioned until a constant NO concentration was acquired, to reach NO adsorption saturation on the surface of the testing sample. A schematic overview of the PCO experiment is shown in Fig. 1b.

The NO degradation results are firstly interpreted by using:

$$NO_{x \ con}(\%) = \frac{[C_{NO_x}]_{in} - [C_{NO_x}]_{out}}{[C_{NO_x}]_{in}} \times 100\%$$
(1)



Fig. 2. Results of the lab test following ISO standard. On the left is the lime render panel and on the right is the polycarbonate panel.

where C_{NOxin} is the inlet concentration of NO_x (here only NO) [ppm], C_{NOxout} is defined as the average NO_x concentration that exits the system of the last 5 min of the measurement time [ppm].

The results of these tests are shown in Fig. 2. The NO_x removal efficiency of the lime render panel is 48.2% and the efficiency of the polycarbonate panel is 34.2%. The higher efficiency of the lime render panel can be attributed to the rougher surface which results in more available photocatalytically active sites. Furthermore, it should be noted that the generation of NO_2 during the experiments is very low, confirming again the excellent air pollutant removal ability. It is suggested in Ref. [29] that a NO_x removal of 45% can be achieved under ideal weather conditions with a paving stone that has a NO_x removal of 38% under ISO 22197-2 condition. Therefore, a decent air purifying performance applying the present photocatalytic paint can be expected under outdoor conditions.

Furthermore, the reactive uptake coefficient was also evaluated. The reactive uptake coefficient is defined as the ratio of number of collisions that lead to reaction over all collisions of the gas-phase reactant with a reactive surface and it is calculated by following equation [35]:

$$\gamma = \frac{4 \cdot k_{\text{rxn}}}{\overline{\nu} \cdot S_{\text{active}}/V}$$
(2)

where V is the volume of the reactor $[m^3]$, $\bar{\nu}$ is the mean molecular velocity of the reactant $[m \cdot s^{-1}]$ and k_{rxn} is the first-order rate coefficient $[s^{-1}]$. $\bar{\nu}$ is calculated using,

$$\overline{\nu} = \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M}} \quad [m \cdot s^{-1}]$$
(3)

where R is the ideal gas constant (R = $8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature [K] and M is the molecular mass of the reactant [kg·mol⁻¹], and k_{rxn} is calculated with,

$$k_{rxn} = -\frac{\ln\left(\frac{c_{(NO)out}}{c_{(NO)in}}\right)}{t_{rxn}}$$
(4)

where $t_{\rm rxn}$ is the reaction time of the gas-phase reactant and the sample [s].

The dimensionless reactive uptake coefficient considers the surface reaction rate, while independent on the geometry of the reactor. Therefore, it can be directly used to indicate the performance of a given air purifying sample. The computed reactive uptake coefficients of the samples are 14.5×10^{-4} and 9.2×10^{-4} . According to Ifang et al. [35], photocatalytic materials should possess a minimum reaction uptake coefficient value of 1×10^{-5} in order to show air purifying effect. A reaction uptake coefficient value of this magnitude will not significantly improve the urban air quality. The excellent NO_x reaction uptake ability under laboratory condition confirms again that a relatively good performance can be expected under realistic outdoor conditions.

3. Outdoor monitoring

3.1. Monitoring principle

As discussed in the previous section, in the reported field studies, measurement of the NO_x concentrations before and after application of photocatalytic products has often been used [29,30]. But this method shows certain disadvantages, for instance, it is rather difficult to interpret the local air quality by discontinuous samplings of the air at certain height level; the control streets or campaign sites in some field studies lack representativeness [36]; a short monitoring period does not provide a reliable spectrum of the effect of the environmental conditions on the air pollutant removal efficiency [29].

Hence in the present study, a new protocol is proposed to assess the outdoor air pollutant removal efficiency of the developed mineralbased transparent paint. Photocatalytic oxidation can be divided into three main steps: (1) mass transport and adsorption of pollutants from the bulk air to the surface of catalyst; (2) photocatalytic reaction on the catalyst; (3) desorption and mass transport of the reaction products. Extensive investigations on the photocatalytic oxidation mechanism have shown that NO in the gas form oxidizes to the final product, NO₃ in liquid form through a number of reaction steps and intermediate, including NO2 in gas form [13,17,37-40]. Laufs et al. [41] reported HONO production from NO2 under dark condition, especially under high humidity condition, but the produced HONO can be very efficiently removed once UV irradiation is applied. However, Gandolfo et al. [42] observed the production of gas phase HONO by photocatalytic oxidation of NO2 under UV light irradiation, nevertheless, the production level is rather limited.

This indicates that the efficiency of NO removal can be interpreted if the amount of the produced NO_3^- (and possible NO_2^-) can be relatively precisely quantified. In this case, if one can ensure that the produced NO_3^- (and possible NO_2^-) can be efficiently collected, then the evaluation of the NO degradation by the photocatalysis becomes feasible. In this project, this principle is first applied, and a monitoring setup is designed for this purpose that will be described in detail in the following section.

3.2. Description of the monitoring setup

The roof of the podium building (one floor) of the educational building Vertigo on the campus of Eindhoven University of Technology (Eindhoven, The Netherlands) was selected as the field study site because of the following reasons. This building is adjacent to the main traffic road and located within a campus containing a good number of residential/office buildings, as shown in Fig. 3, so this situation is representable to a typical Dutch city environment. A full weather station is installed on the roof of this building so the full spectrum of the environmental parameters could be collected. Furthermore, an online NO_x concentration could be continuously collected during the whole monitoring



Fig. 3. Picture of the monitoring site (Google map[@]) (the red arrow marked building is Vertigo, the white arrow pointing to the main traffic road Professor Doctor Dorgelolaan). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

period.

The setup of the outdoor monitoring is shown in Fig. 4. Two panels of $100 \,\mathrm{cm} \times 65 \,\mathrm{cm}$ were prepared with lime render (No. 1 and 2 in Fig. 4) and one panel with polycarbonate (No. 3 in Fig. 4). The panels No. 1 and No. 3 in Fig. 4 were then coated with the mineral based transparent photocatalytic paint, and mounted to a back support. The other panel of lime render (No. 2 in Fig. 4) was coated with only the base of this transparent paint (i.e. without photocatalyst) and was used as a reference panel. The panels were fixed to the handrail of the roof, about 60 cm from the roof, facing to the south. Rain water reaching the surface of the panels was collected by a 2L bottle hanging beneath the panels. The water in the bottles was collected weekly and the panels were washed with distilled water to reset the amount of ions on the panels. In case of heavy rains, the collection frequency was adjusted in order to avoid possible water loss due to overflowing. The adopted artificial washing procedure was to make sure each week's measurement only measured the ions collected by the panels in that week and not from the previous weeks.

3.2.1. Ion chromatography calibration

The ions in the collected liquid were determined by employing an ion chromatography (Thermo Scientific Dionex TM ICS-1100 Ion chromatography). Calibrations were made in order to quantify the tested species, including Fluoride, Chloride, Nitrite, Bromide, Nitrate, Sulfite, Phosphate and Sulphate.

Based on the calibration lines, the ions in the collected liquid can be reliably quantified. Furthermore, the used demi-water was analyzed in order to determine whether the demineralized water is suitable for the washing of the samples. The goal was to find any impurities, which could affect the final results. It is shown that no significant impurities were found, thus demineralized water was used in further experiments.

3.2.2. Washing efficiency analysis

The washing efficiency was firstly assessed as it is reasonable to raise the question whether artificial washing once or more times is efficient enough to collect the produced ions from the surface of the panels. The PCO panel was washed several times in order to determine how much water has to be used in order to get representative results.



Fig. 4. The setup of the panels outside on the roof of the Vertigo building, Eindhoven. 1: PCO lime render panel, 2: Reference panel, 3: PCO polycarbonate panel, 4: air tube connected to NOx analyzer.



Fig. 5. The washing efficiency test on the measurement on 2.10.2015.



Fig. 6. The washing efficiency test on the measurement on 9.10.2015.

The ion masses of these washings were compared to the reference panel. Figs. 5 and 6 show the washing efficiency results based on two dates (2.10.2015 and 9.10.2015).

The results show that two sets of washing is relatively sufficient to wash most of the ions adsorbed on the surface of the PCO panel. This was obvious in case of sample washed on 2.10.2015. Three sets of washing were required on 9.10.2015 in order to get to the same level as on REF panel. Therefore, 4 sets of washing were eventually applied in order to wash both panels effectively throughout the whole monitoring period.

3.2.3. Post-monitoring analysis

This field study intended to assess the performance of the air purifying paint under real conditions. Under complex weathering, the testing sample would undergo significant changes, both physically and chemically. Therefore, a post-monitoring analysis study was planned. The samples placed outdoor for the field study was subjected to a series of experiments under fully controlled laboratory conditions. The chemical composition of the sample, including the elemental composition and chemical structure, was evaluated by using X-ray fluorescence (XRF) and X-ray diffraction (XRD) instruments. The air pollutant degradation performance of the exposed sample was assessed by lab test following the ISO 22197-1.

3.3. Pre-air quality monitoring

A pre-air quality monitoring was performed between March 2015 and May 2015 before the commencement of the real monitoring campaign on the performance of the photocatalytic paint. The aim was to check the robustness and stability of the monitoring system. Furthermore, the analysis was performed in order to evaluate the suitability of the environment for the analysis of photocatalytic efficiency of panels coated with the developed photocatalytic mineral paint. Some typical results, selected one week in March, are shown in Fig. 7.

The NO_x concentrations at the location next to the panels were measured continuously using an online HORIBA 370 NO_x analyzer (see the sampling point, labelled with No. 4 in Fig. 4). The NO_x analyzer measures the NO and NO₂ concentration every 5 s. Besides the NO_x collection from the own analyzer, NO and NO₂ data were also taken from public institute of people's health and environment (RIVM, The Netherlands) [43] (see Fig. 8). These data were measured at the Genovevelaan Street in Eindhoven (about 4 km from the monitoring site in the present study).

These data show that the NO_x concentration varies significantly during the day. Although in the peak hours, the concentration reached up to 115 ppb, this high concentration is very exceptional. Nevertheless, it can be seen that in most of the time the NO concentration is below 20 ppb. The measured NO_2 concentrations are in most of the time higher than NO, as expected. But in peak values, it is clearly seen that NO concentration is higher, indicating the direct effect of car emissions. Furthermore, it can be seen that although the day-today NOx concentration values measured at the monitoring site are different from the values taken from RIVM, the trend as well as the range of the measured pollutants are very similar. This confirms the reliability of the site monitoring.

The following conclusions can be drawn based on the pre-air quality monitoring campaign:



Fig. 7. The NO_x concentration collected on one week (18–25 March 2015).

- A continuous air pollution (NO_x) monitoring for the Vertigo building (TU/e) was performed between March and May 2015, the measurement showed the NO_x collection using the online analyser was reliable.
- The NO_x concentration was correlated with the monitored concentration level by other governmental organizations, and the comparison shows the reliability of the own measurement at the monitoring site.
- Full weather conditions were collected.
- The NO_x concentration is clearly related to the traffic next to the Vertigo building.

3.4. Air quality monitoring and results analysis

3.4.1. NO_x concentration monitoring

The real field study monitoring study began in July 2015 and ended in November 2016, covering the full four seasons. Within this period, the NO_x concentration and other weather conditions were continuously monitored and the nitrates from the panels were periodically collected. The NO_x analyser measured NO_x concentration based on the amount of molecules NO_x compared to the amount of air molecules, i.e. with the unit of ppm. To express NO_x concentrations in $\mu g/m^3$, the measured values were converted using Eq. (5):

$$C\left(\frac{\mu g}{m^3}\right) = \frac{M \times C_{ppm} \times P}{R \times T}$$
(5)

where M is the molar mass of the calculated gasses (NO or NO₂) in grams per mole, C_{ppm} the concentration in ppm, P is the pressure (101325 Pa for 1 atm), R is the gas constant 8.314 and T the

temperature in Kelvin (for these calculations the average of each day was used).

The collected NO_x concentration data are shown in Figs. 9 and 10, where Fig. 9 shows the average values of every single day and Fig. 10 shows the highest values of every single day. A clear difference in concentration between the two figures can be observed, which shows that the NO_x concentration can increase for short times. The EU goal is to have, on average, not more than $40 \,\mu g/m^3 \, NO_2$ (annual mean) and not more than 18 h per year in which the concentration is $200 \,\mu g/m^3$ or more [44]. It was calculated that over the year only for 4.2 h the $200 \,\mu g/m^3$ limit was exceeded. In addition, according to Fig. 9, the NO_x concentration on average indeed did not reach $40 \,\mu g/m^3$ in most days. Nevertheless, these low concentrations clarify that the amount of nitrates measured could have been higher if the same test would have been performed in more polluted areas [45].

3.4.2. Weather monitoring

The data of the weather condition close to the panels were collected and shown in Figs. 11–15. The weather can have a large influence on the PCO reaction [16,46]. The humidity shown in Fig. 14 shows that the average humidity in Eindhoven is almost every day very high. Most of the time the RH is over 60% and often it even reaches over 80%. Such a high humidity level negatively influences the PCO efficiency [47,48]. The wind is relatively strong as the average wind speed is in general higher than 2 m/s, while according to Gallus et al. [31] a wind speed value of 1 m/s would provide good air removal efficiency. In addition to the very high humidity and wind speed, during the autumn and winter, the irradiance was low. In this period, the light intensities are in general lower than 50 W/m², about 20–30 W/m². While according to [49],



Fig. 8. NO/NO₂ measurement by RVIM (2015).



Fig. 9. Average values of NO, NO₂ and NO_x measured on each days between 16 and 10-2015 and 28-10-2016.



Fig. 10. Highest values of NO, NO_2 and NO_x measured on each days between 16 and 10-2015 and 28-10-2016.

about 9% of the irradiance of solar radiation outside the atmosphere is UV light, which means a rather low UV light intensities of about 2–3 W/m² in the monitoring site. Folli et al. [45] reported that a UV irradiance value of 6.9 W/m^2 can provide an adequate NO abatement. This indicates that the acquired low UV irradiance value in this research would provide a rather poor photocatalytic effect. In overall, these poor weather conditions would contribute to rather low photocatalytic

activities [50].

3.4.3. Results analysis

The amount of nitrate ions in the rain water and washing water collected by the panels are presented in Fig. 16. It has to be emphasized that nitrite was also analyzed in the collected water, but the amount was too low to be detectable. Therefore, only the amount of nitrate is



Temperature average

Fig. 11. Average Temperature of each day between 15 and 10-2015 and 27-10-2016.



Fig. 12. Average amount of irradiance of each day between 15 and 10-2015 and 27-10-2016.

shown here. In addition to the total nitrate amounts, the amount of rain water collected by each panel is also shown since the total amount of ions collected in the rain water immensely depends on these amounts. The photocatalytic activity of the PCO panel with lime render as the substrate is visible for most of the measurements as its nitrate amount exceeds those of the reference panel. Nevertheless, in some weeks, the nitrate amount from the reference panel exceeds that of the PCO lime render panel. For example, in the first week of August 2016, the collected nitrate from the reference panel is obviously more than that from the PCO panel. This can be explained by the weather condition, as can be seen from Fig. 15 that it rained a lot in this week which resulted in very low or almost no photocatalytic effect due to supersaturation of the panels. It was found [30] that it is very hard to reconcile NO abatement entirely with a photocatalytic process under the conditions of little sun and substantial rain. Considerable pollution wash-off by rain is clearly observed in Fig. 16, especially when correlating the collected nitrate by the reference panel with the weather conditions shown in Fig. 15, which is also confirmed by Folli et al. [30].

It is also rather obvious that the activity of the PCO lime render panel decreases over the entire monitoring period. Initially the activity was supposed to increase during the summer time of 2016. However, the overall collected data did not show any extra high difference in nitrate amounts, possibly attributed to the high amount raining and deactivation of the photocatalyst. The reason for the deactivation will be further analyzed in the following sections.

The polycarbonate panel (No. 3) was installed at a later stage, in June 2016. It did not show significant differences in nitrate amounts in the first weeks after installation, compared to the reference panel. However, after the first three weeks, the photocatalytic activity started increasing. This can be explained by the time needed for the activation of the photocatalysts which were partly covered by the binder in the mineral paint. The coverage of the photocatalysts causes inhabitation of photocatalytic oxidation of air pollutants. In fact, the nitrate amounts surpass those of the lime render PCO panel. This higher activity indicates as well the deactivation of the PCO lime render panel. The lab scale measurements showed that the lime render panel should have had a higher efficiency (See Section 2) indicating that if there would have been no deactivation, the lime render panel should have had a higher activity. Next to the nitrate amounts also the amount of rain water is higher, which can be explained by the different penetration depths in the panel attributed to the difference in the rendering materials. While this higher amount of rain water can have contributed to the higher nitrate amounts, the increase is too large to be only caused by the amount of rain.

In the whole monitoring period of 471 days, a total of 497.3 mg of nitrate was collected by the reference panel and 831.3 mg of nitrate by the photocatalytic lime render panel. In the whole monitoring period of 105 days, the photocatalytic polycarbonate panel collected 365.0 mg against 97.2 mg collected by the reference panel in that period. These results show on the one hand the effectiveness of the photocatalytic oxidation of NO_x by the mineral paint, and on the other hand the deactivation of the photocatalysts on the lime-based panel over time.

Figs. 17 and 18 show separately the amount of nitrate measured from the water used to wash the panel and the rain water collected by the panels. It can be seen the majority of nitrate is collected by the natural rain flushing and the artificial washing only helps to collect the produced nitrate. This shows that artificial washing can be skipped in the future research applying this principle. As on the other hand, artificial washing does not really contribute much to the collected ions and on the other hand, artificial washing in fact alters the pollutants degradation efficiency because the surface becomes wet after washing which causes inactivation within certain time period.

In addition, the absolute amount of the NO₃⁻ that are removed by rain and artificial washing are calculated, by deducting the same amount of nitrate collected by the reference panel and the results are shown in Fig. 19. These figures show very evident the air purification efficiency of this mineral-based transparent coating. It is clear that the degradation efficiency becomes dramatically lower when there is a large quantity of rain water, which causes the competition between water molecular and NO_x molecular [25].





Fig. 13. Average wind speed of each day between 15 and 10-2015 and 27-10-2016.



Fig. 14. Average humidity of each day between 15 and 10-2015 and 27-10-2016.

3.5. Post-monitoring analysis

3.5.1. Correlations between photocatalytic activity, surface wetness and humidity

After the full field monitoring, a post-monitoring analysis study was performed to the lime-render PCO panel. The testing samples were cut from the original big panels used for the outdoor monitoring, to the size of 100 mm \times 200 mm, matching the size of the photocatalysis reactor. The experiments were carried out under the laboratory condition to one specimen that was extracted from the large photocatalytic lime render panel. This specimen was washed and dried before each experiment series. The effect of two different influential parameters were investigated, including the relative humidity and surface wetness to simulate the outdoor conditions.

The sample was made surface wet by washing the same way as applied to the large panel during the outdoor monitoring. The surface dry condition was achieved by drying the sample at 60 °C in an oven overnight. The results show that the NO_x removal efficiency is lower when the panel piece is wet, namely 4% compared to 8%. Comparing the results of the panel after 2 years' exposure to outdoor to that of the newly prepared panel (see Section 2), it is clear that the NO_x degradation efficiency dramatically reduced. This can be explained by deactivation and potential loss of photocatalytic active sites by either loss of the photocatalyst, and surface modification, which will be analyzed in the following section. In addition, the produced intermediate NO₂ is evidently more than that of the newly prepared panel (0.08 ppm vs. 0.04 ppm), especially considering the drastically reduced NO removal content, indicating further the reduced active sites.

Two RH values of 50% and 80% were applied to the panel under both dry and wet conditions. In this case, the drying was done by leaving the sample under ambient conditions for three days. In both surface wet and dry cases, the PCO efficiency first decreases when the humidity is increased from 50% to 80% but then slowly increases during the experiment. However, under the wet scenario, the difference is much smaller, which can be explained by the fact that the water on the panel contributes to the humidity inside the reactor and that the efficiency is already rather low. Before the humidity was increased, the PCO efficiencies were 16.1% under dry condition and 6.5% under wet condition. The end PCO efficiencies after the humidity was increased are 7.5% and 4.6%, respectively. The reason why the PCO efficiency of the sample under the natural surface dry state at the same RH of 50% is higher than that of the surface dry condition after drying at 60 °C overnight in an oven might be due to the longer drying. This means not only the surface humidity but also the moisture inside the matrix of the substrate affects the photocatalytic performance, indicating a longer air purification performance recovery after a rain period.

3.5.2. Minerology and elemental analysis of the coating after monitoring

After the full demonstration, elemental composition and phase content of the aged coating were analyzed employing X-ray fluorescence (XRF) and X-ray diffraction (XRD), respectively. The quantitative XRF analysis was performed using a PANalytical Epsilon 3 XRF device. The result shows that the sample contains: CaO 45.2%, MgO 7.5%, TiO₂ 0.1%, Br 4.2% and LOI 42.1% among a few other trace elements.

The XRD analysis was performed by using a Bruker D8 advance powder X-ray diffractometer with a Cu tube (20 kV, 10 mA) with a scanning range from 5° to 65° (20), applying a step 0.02° and 0.2 s/step measuring time. The qualitative analysis was carried out by using the Diffracplus Software (Bruker AXS) and the PDF database of ICDD. The results are shown in Fig. 20. It is clearly shown that calcite is the primary phase in the tested coating. All major peaks correspond to the calcite crystal structure. Only a very small trace of dolomite (MgCa $(CO_3)_2$) peak can be seen. No detectable TiO₂ is observed, which is in line with the XRF analysis. While in the original photocatalytic paint, also shown in Fig. 20, it can be clearly seen that the broad peaks around 25 and 38 indicate the existence of anatase nanocrystals and the sharp peaks at 28 and 40.5 rutile.

It is surprising to observe that the initially applied photocatalysts were almost entirely disappeared from the XRD and XRF analysis. This can be possibly explained by the following reasons. Firstly, the gradual reaction of lime binder to calcite which over time overgrows the surface of the photocatalyst. Karatasios et al. [51] observed a uniform and





Fig. 15. Precipitation of each day between 15 and 10-2015 and 27-10-2016.



Fig. 16. The amounts of nitrate ions measured in the wash and rain water, and the amount of water collected.

compact carbonated layer of about 5 µm on the surface of TiO₂ modified lime mortar after only 4 weeks curing. In addition, the TiO₂ induced photocatalysis accelerated the carbonation due to the locally increased CO₂ concentration resulting from photocatalytic oxidation of organic matters, which is further confirmed by Diamanti et al. [52] who reported an increased carbonation coefficient from 20 mm/year of plain concrete to 24 mm/year of concrete containing 5% of TiO₂ by mass of cement. The carbonation process of Portland cement based concrete leads to a continuous but slight reduction of the photocatalytic activity under normal curing conditions and a dramatic reduction under accelerated carbonated condition [53]. Secondly, the weathering including rain and wind and artificial washing over the entire monitoring time (20 M) might cause the removal of part of the coating. Chen and Poon [54] observed a continuous NOx removal efficiency reduction at the increase of concrete age and found that TiO₂ is not chemically involved in the concrete matrix, but the continuing hydration of cement leads to a gradual reduction of porosity and crystal surface which is adverse for the photocatalytic activity. These factors in overall contribute to a significantly reduced photocatalytic performance, which can be both seen from the gradually reduced nitrate production over time during the monitoring period and the evidently reduced NO_x removal efficiency under the laboratory condition test after the monitoring. From this study, it is shown deactivation of photocatalyst is a serious issue that affects the long term stability of air purifying performance of the paint. Gallus et al. [31] performed the field study using the Leopold II tunnel in Brussels and also observed a significant deactivation, caused by the heavily polluted tunnel in that specific condition. It can be concluded that it is critical for the application of photocatalytic material to have a proper location together with an appropriate substrate to achieve a desired air purifying performance.

4. Conclusions and recommendations

In this research, a mineral-based transparent photocatalytic paint was developed and its NO_x degradation efficiency was assessed under laboratory conditions following ISO 22197-1. Furthermore, the NO_x removal efficiency of this paint under realistic outdoor conditions was investigated through an outdoor field study for almost two years. A new air purification quality monitoring protocol was proposed. The air pollutant removal efficiency was interpreted by using the measured NO_3^- that was produced by the photocatalytic oxidation of NO. The full weather parameters were collected and their relation with the NO_x degradation performance was analyzed. From the obtained results the following conclusions can be derived:

- Both lab-scaled test and the outdoor experiment confirm that the transparent mineral paint can be used for making photocatalytic surfaces.
- Measuring the nitrate amount in the collected liquid is an effective method to determine the air purification activity.



Fig. 17. Nitrate amounts measured in the water collected after washing the panels.



Fig. 18. Nitrate amounts measured in the rain water collected by the panels.

- The activity of the panels is lower with very high humidity, low irradiance and no raining.
- The NO_x concentrations at the monitoring site are, in general, relatively low. With higher NO_x concentrations the amount of nitrate formed could have been higher.
- Deactivation of the photocatalytic coating on the lime render panel is observed, most probably caused by the overgrowth of calcite on the surface of the photocatalyst.

This research demonstrates that this innovative mineral-based transparent paint can be applied for outdoor air pollutants removal purpose. Furthermore, the proposed monitoring principle and test protocol work relatively well. Besides, the applied weather parameters collection system shows robustness. Nevertheless, much more effort is further needed on this topic, especially considering the limited time within the current project. The following topics should be addressed in the future research:

- The chosen monitoring site, the building on the campus of Eindhoven University of Technology, in general possesses a very good air quality, reflected by the very low NO_x concentration. A more polluted area can be better selected for this aim to increase the contrast;
- The weather conditions are very complex, which makes it very difficult or impossible to derive effective correlation between the

 NO_x removal and environmental parameters. Much more studies including big data study and mathematical modelling are needed;

• The stability of the paint as well as the substrate play a significant role on the performance, especially considering the interaction between the used substrates and the used base materials, which increases the complexity of the performance evaluation. This should be considered more carefully.

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Fig. 19. Total absolute nitrate amounts collected by the panels.



Fig. 20. X-ray diffractions of the aged coating.

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