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Air purification by cementitious materials: Evaluation of air purifying properties

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ABSTRACT

This paper addresses the evaluation of the photocatalytic properties of concrete containing titanium dioxide (TiO₂). Here, the assessment of the air purifying abilities of the hardened concrete regarding the degradation of nitric oxide (NO) is of major interest. A setup for measuring the performance of these photocatalytic active concrete products will be presented. The test setup uses the UV-A induced degradation of NO and is oriented on the draft version of the ISO standard TC 206/SC N [1]. By means of this test setup, the influence of boundary conditions like irradiance, relative humidity, surface texture, flow rate and pollutant concentration on the degradation mechanism is investigated and a suitable measuring procedure is suggested for evaluating the performance of concrete products having photocatalytic activity. The suggested measuring procedure is used for the analysis of own developed mortar mixtures and a comparative analysis of already available concrete products on the European market.

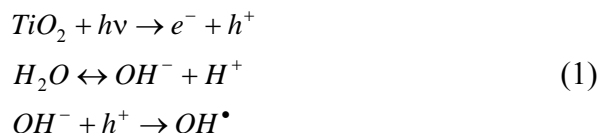
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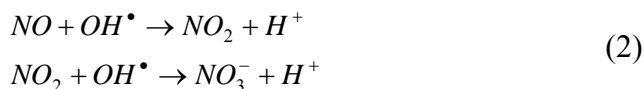
1. INTRODUCTION

The beneficial effects of the photocatalytic activity of titanium dioxide (TiO₂) have been applied to various materials since the middle of the 1990s. In the beginning, more attention was paid to the 'self cleaning' effect of the TiO₂ treated surfaces than to the 'decomposing' effect of organic and inorganic compounds. Nevertheless, the decomposing effect becomes more important in the near future as air pollution caused by road traffic and industry is one of the major problems in metropolitan and urban areas. In particular, the emission of nitric oxide (NO), which is generated during the combustion of fossil fuels, is a critical point as the limit values for nitrogen dioxide and oxides of nitrogen are reduced by 20% with coming into force of the council directive 1999/30/EC [2]. In this respect, the photochemical conversion of nitrogen oxides (NO_x) to nitric acid due to heterogeneous photocatalytic oxidation (PCO) is a beneficial contribution to the overall reduction of NO [3]. Therefore, the degradation of nitric oxide or more general of nitrogen oxides, also referred to as DeNO_x-process (denitrogenization), delivers a suitable model to assess the ability of surfaces for air purification.

The working principle of the degradation process is based on the optoelectronic properties of TiO₂ as semiconductor. Electrons can be transferred from the valance band to the conduction band by photons in the UV-A range. The UV-A absorption creates electron holes which are responsible for the formation of hydroxyl radicals. The formation of hydroxyl radicals results from the presence of water at the surface of the photocatalyst [4]:



The formed hydroxyl radicals are acting as a strong oxidant and can therefore degrade organic and inorganic compounds in further reactions. In the considered case, the NO is absorbed at the surface of the photocatalyst and degraded by the formed hydroxyl radicals:



As reaction product of the degradation of NO, nitrate ions are formed. These ions are flushed from the surface of the photocatalyst as a weak nitric acid. The removal of reaction products from the active sites of the photocatalyst is necessary as intermediates produced during the photocatalytic oxidation process will occupy the active sites of the catalysts surface and result in the deactivation of the catalyst. Under practical conditions, reaction products are flushed from the concrete surface by rain. This flushing process maintains the performance of the product regarding NO degradation.

2. TEST SETUP

As the research was started, the preliminary standard ISO TC 206/SC N [1] served as a sound basis for the measurements. Actually, the standard is applicable for advanced technical fine ceramics but in this case it satisfies the needs for measurements on concrete specimen as well. Therefore, its recommendations were largely followed for the practical conduction of the experiments on concrete and the design of a suitable test setup. The designed test setup consists of:

- reactor cell housing the sample
- UV-A light source
- NO_x analyzer and
- gas supply.

2.1 Reactor cell

The gas reactor forms the core of the experimental setup. The reactor cell allows a planar sample of the size of 100 x 200 mm² to be embedded. A schematic representation of the gas reactor is given in Figure 1.

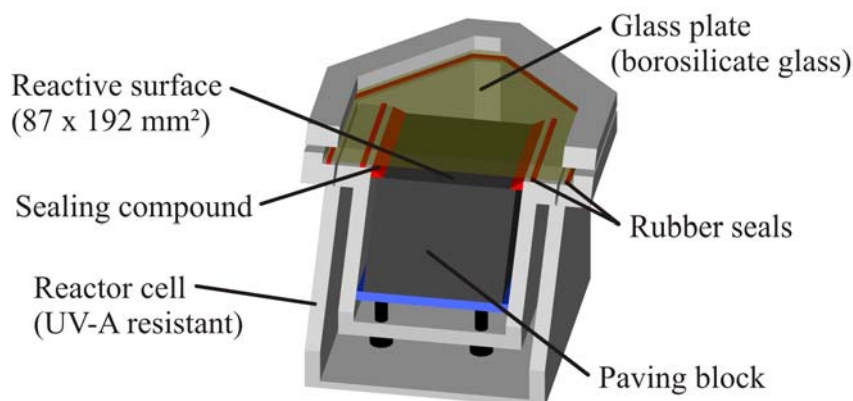


Figure 1: Schematic diagram of the reactor cell.

During the development of the reaction cell, some special requirements have been identified. Due to the use of UV-A light as well as NO as pollutant, a non-adsorbing material which can withstand UV-A light of high irradiance was chosen. Furthermore, a glass plate made from borosilicate glass, allowing the UV-A radiation to pass through, is used to tightly close the reactor cell. Within the reactor, the planar surface of the test specimen is fixed parallel to the covering glass plate leaving a slit of 3 mm height to allow the gas passing through. The active sample area used for degradation is 100 mm in width and 200 mm in length, which allows placing standard paving blocks in the reactor cell. The sample and the reactor is sealed by means of profiles and seals in that way that the sample gas can pass the reactor only in longitudinal direction through the slit between the sample surface and the covering glass plate.

2.2 Gas supply

As mentioned in the beginning, nitric oxide (NO) is used as model pollutant. The applied gas is composed of 50 ppmv NO stabilized in nitrogen (N₂). The gas is mixed with synthetic air (20.5 V.-% of oxygen (O₂) and 79.5 V.-% of nitrogen (N₂)) in order to obtain a concentration of 1 ppmv NO which is applied as pollutant to the sample. The NO concentration is monitored by a NO analyzer, connected to the outlet of the reactor box. The inlet of the synthetic air is split into two parts whereof one part is passing a gas-washing bottle in order to maintain a constant relative humidity of 50%. Using a valve before the split, changes in the relative humidity can be controlled. Before the gas passes the reactor, the volume flow of the gas is adjusted to 3 l/min, which corresponds to a flow velocity of 0.17 m/s along the samples surface.

2.3 Light Source

The applied UV-A light source uses three fluorescent tubes of each 25 W emitting UV-A radiation in the range of 300 to 400 nm with a maximum peak at about 345 nm. All fluorescent tubes can be adjusted in irradiance. With the help of a calibrated UV-A radiometer, the distribution of the irradiance was determined within the test setup (see Figure 2a). The reactor cell was placed according to the irradiance distribution within the test setup in order to ensure 10 W/m² at the sample surface (see Figure 2b).

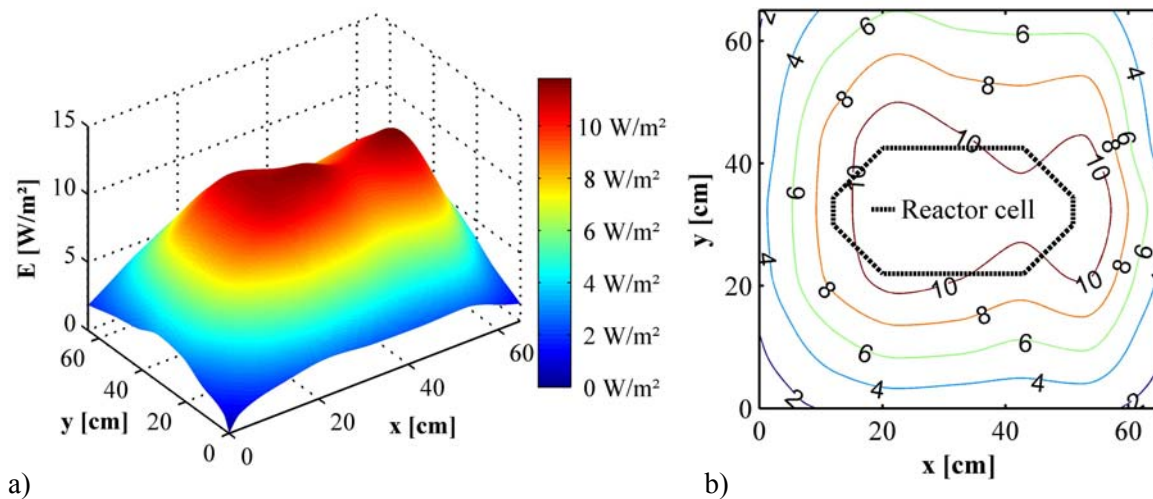


Figure 2: Distribution of the UV-A irradiance within the test setup (a) and the resulting placement of the reactor cell (b).

2.4 Analyzer

For the gas analysis, a chemiluminescent NO_x analyzer like described in ISO 7996 was deployed. The analyzer is measuring the NO_x and NO concentration in steps of 5 sec while the corresponding NO_x concentration is computed by the difference of the previous two. During the measurement the analyzer is constantly sampling gas with a rate of 0.8 l/min. The detection limit of the deployed analyzer is at about 0.5 ppbv.

3. INFLUENCING FACTORS

The degradation of NO and therewith the performance of the photocatalytic reaction is governed by physicochemical parameters. In the following, a short and descriptive explanation of the influencing factors irradiance, relative humidity, pollutant concentration and flow rate is given. The remaining boundary conditions in Figure 3 are 50% relative humidity, 3 l/min flow rate, 1 ppmv pollutant concentration and 10 W/m² irradiance.

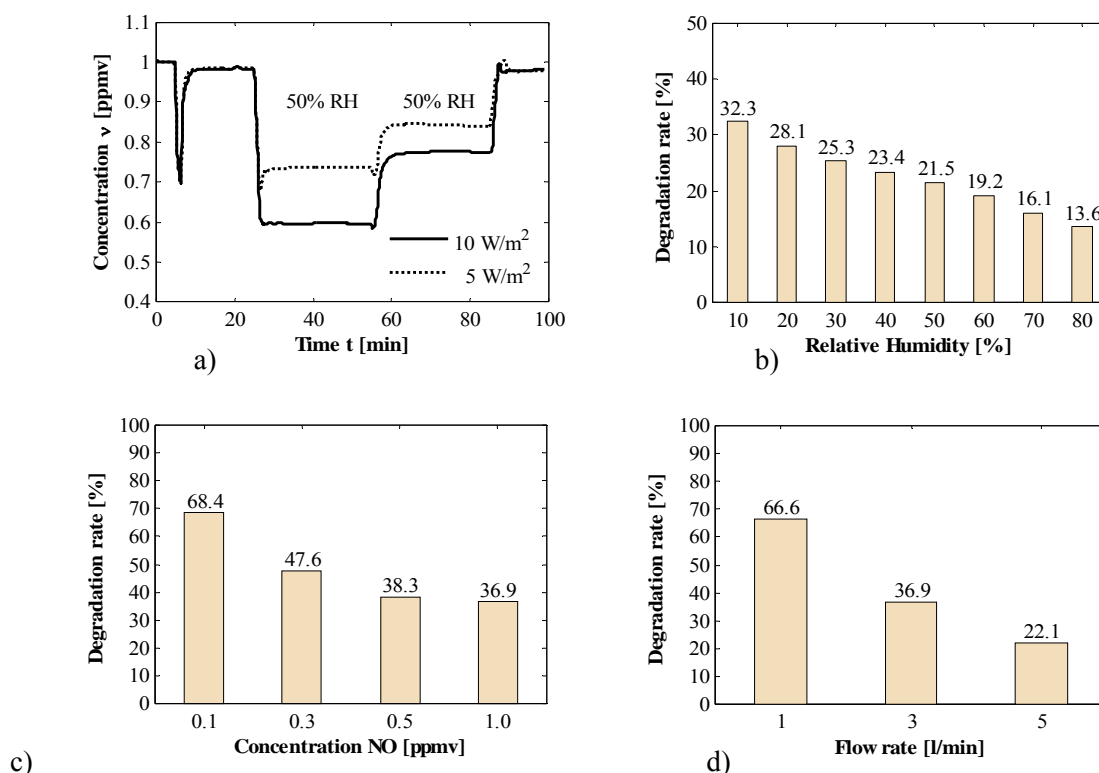


Figure 3: Variations of the degradation rate depending on variations of: irradiance (a); relative humidity (b); pollutant concentration (c) and flow rate (d).

3.1 Irradiance

The degradation process of NO molecules is caused by the photocatalytic activity of TiO_2 in the anatase modification. This photocatalytic behavior is caused by the optoelectronic properties of this semiconductor. According to the explanation of the photocatalytic process given in the introduction, the UV-A light shows the most suitable range regarding the wavelength (λ) to start the photo-induced oxidation process. But not only the wavelength is influencing the efficiency of the system but also the light intensity or irradiance (E) has an effect on the degradation rate. According to Herrmann [4], the increase in the photocatalytic activity caused by increased irradiance can be divided into two regimes: i) for $E \leq 250 \text{ W/m}^2$ the reaction increases proportional to E and ii) for $E > 250 \text{ W/m}^2$ the photocatalytic activity grows as the square root of E . Figure 3a shows the dependence of the NO removal on the irradiance for low values of the irradiance.

The averaged irradiance of a cloudless summer day amounts to approximately 60 W/m^2 for Central Europe. Values of 10 W/m^2 for the UV-A irradiance can easily be achieved on cloudy days depending on the degree of cloudiness. Based on these values, the theoretical functional capability is ensured even for cloudy weather conditions with low values of UV-A irradiance.

3.2 Relative Humidity

The influence of the humidity depends to a large extent on the type of material used. According to Beeldens [6], the hydrophilic effect at the surface is gaining over the oxidizing effect when high values of the relative humidity are achieved. The water molecules are adsorbed at the surface and prevent therefore the pollutants to reach the TiO₂ at the surface. Figure 3b gives an overview over the achieved degradation rates depending on the relative humidity. It is evident from Figure 3b that with increasing relative humidity the total efficiency of the system regarding the degradation of NO is decreasing.

3.3 Pollutant Concentration

The influence of the pollutant concentration on the NO degradation plays an important role when paving blocks are compared among each other. Figure 3c shows the influence of varying NO inlet concentrations on the achievable degradation rates for a paving block containing TiO₂ as photocatalyst. It is obvious from Figure 3c that increasing inlet concentrations are resulting in lower degradation rates whereas lower pollutant concentrations are acting performance enhancing. Furthermore, changes of the pollutant concentration in the lower range are resulting in remarkable higher changes of the degradation rate than changes in the range of higher concentrations. Therefore, also a limiting value exists which will not be undergone.

3.4 Flow Rate

The flow rate or the therewith connected exposure time of the pollutant on the active surface of the concrete product can vary under practical conditions extensively as the wind speed as well as the wind direction is changing by time. Under laboratory conditions various flow rates can be realized which are resulting in different simulations of environmental conditions and therefore in unequal conditions for comparative tests. Figure 3d shows the results for varying flow rates on the NO degradation. High flow rates are reducing the exposure time of the model pollutant on the active surface and the degradation rate is reduced subsequently, whereas lower flow rates are enhancing the degradation rate by a longer exposure time of the model pollutant.

4. EXPERIMENTS

4.1 Mortar Tests

For conducting the experiments, two different TiO₂ powders from different suppliers have been selected. A coarse powder (TiO₂ A) and a powder having a higher specific surface area (TiO₂ B) are used (see Table 1). In order to achieve comparability, a reference mortar has been designed. The workability of the designed reference mortar allows achieving comparable compaction efforts in the lab. Test mortars containing 3%, 5% and 10% TiO₂ are produced. The TiO₂ content is based on the binder content of the reference mortar and will be the same for both tested powders as the binder of the reference mortar will be constant to ensure a comparison of the selected powders. The mix design of the composed mortar mixes is given in Table 2.

Besides varying powder contents of the applied TiO₂, the application technique of the powder was changed during the experiments. Applying the TiO₂ as dry powder or water based suspension turned out to be appropriate for the experimental tests in the lab. The dry powder was added combined with the binder, whereas the suspension was added with the mixing water.

Table 1: Powder characteristics

	TiO ₂ A	TiO ₂ B
d _{0.1} [μm]	1.2	0.6
d _{0.5} [μm]	2.7	2.1
d _{0.9} [μm]	6.5	7.1
Specific surface [cm ² /g]	7,916	11,910
Specific surface [m ² /cm ³]	3.115	4.645

Table 2: Composition of the tested mortar mixes

Material	Amount [kg/m ³ fresh concrete]					
	Mix 1 2/7	Mix 3/8	Mix 4	Mix 5/9	Mix 6/10	
CEM I 52.5N	600.0	600.0	600.0	600.0	600.0	600.0
TiO ₂ A	60.0	30.0	18.0	-	-	-
TiO ₂ B	-	-	-	60.0	30.0	18.0
Sand 0-2	1300.0	1300.0	1300.0	1300.0	1300.0	1300.0
Water	250.0	250.0	250.0	250.0	250.0	250.0

Thin slabs having a thickness of 2 cm have been produced in the lab in order to keep the efforts of the sample production as low as possible. Producing thin slabs for testing the photocatalytic efficiency is possible as the massive core of a double-layer paving block is not influencing the NO removal performance of the system. The hardened slabs have been tested using the test setup described in section 2. Constant boundary conditions are used for performing the test. The flow rate is adjusted to 3 l/min, the relative humidity to 50% and a pollutant concentration of 1 ppmv is applied. A detailed explanation of the applied test procedure is given by Hüsken et al [7]. The UV-A irradiance was chosen to be 10 W/m². The test results of the NO degradation process are depicted in Figure 4.

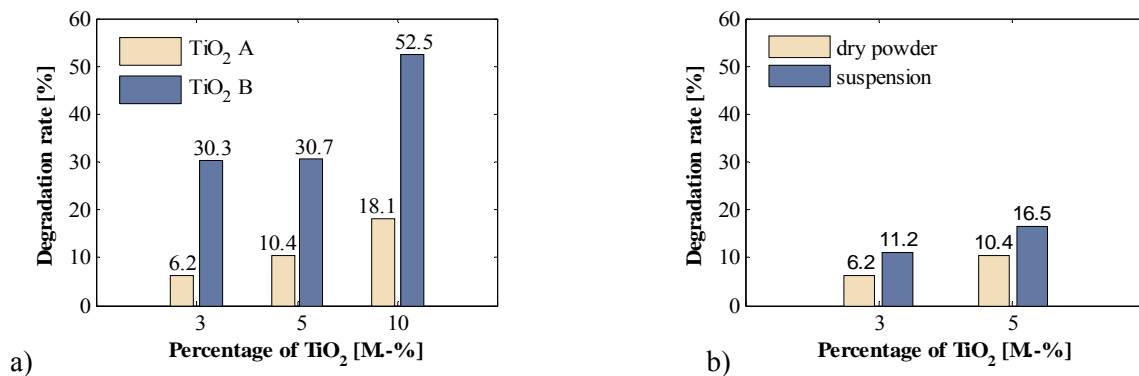


Figure 4: Variations on the degradation rate in dependence on: the fineness of the powder (a) and the kind of application (b).

The test results are clearly showing that the finer TiO₂ B yields higher conversion rates than the coarser TiO₂ A. This is line with the expectations based on the higher specific surface area of the powder TiO₂ B (see Table 1), which is about 30% higher. Furthermore, it is obvious that with increasing powder content the degradation rate is also growing. But this effect is much more clear for the coarse TiO₂ A than for the finer TiO₂ B. Here, the higher fineness of the TiO₂ A is not only increasing the degradation of NO, but is also causing problems regarding a homogeneous distribution of the powder when the powder is mixed dry with the cement. This inefficient distribution of the powder is visible on the ground side of the sample of Mix 6 (see Figure 5). Here, the undistributed TiO₂ formed a kind of flow mark in the sample. If these flow marks are located in the center of the sample, the high amount of TiO₂ concentrated here is not available for the degradation process as this process is only taking place at

the surface of the sample. To avoid the formation of agglomerates or remarkable flow marks, the distribution of the TiO_2 within the mortar can be improved when the powder is added as suspension with the mixing water.

The beneficial effect of applying the powder as suspension is shown in Figure 4b. The advantage of a better distribution of the powder is reflected by the higher degradation rates of the slabs containing 3% and 5% TiO_2 as suspension (Mix 8 and Mix 7). These slabs are produced having the same TiO_2 content as the comparable powder mixtures solely the application method of the TiO_2 was changes. A doubling of the conversion rate was almost possible for the mixes containing 3% TiO_2 . Comparable observations are also possible for the mix containing 3% of the TiO_2 B powder. Here, the conversion rate could be increased from 30.3% of the mix using the dry powder to 39.1% of the mix containing the suspension.

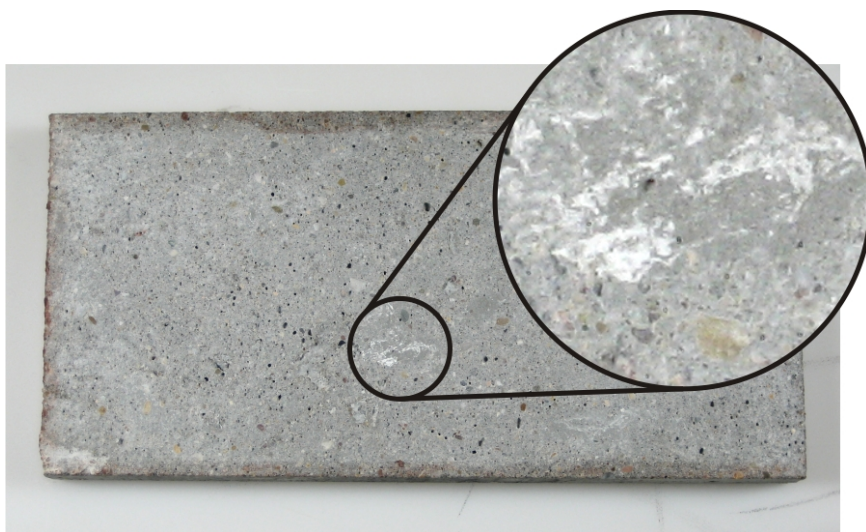


Figure 5: Formation of agglomerates on the grinded surface of a tested mortar sample (Mix 6).

4.2 Comparative study

Products containing titanium dioxide are commercially available since the middle of the 1990s. The production of the first concrete paving blocks containing TiO_2 started in 1997 in Japan. Regarding the current market situation in Europe, a wide variety of cement based products containing titanium dioxide can be found for horizontal and vertical application. Based on the patents owned by Mitsubishi Materials Corporation [8] and Italcementi S.p.A. [9], products with different properties are available on the European market.

These products show varying amounts of titanium dioxide, having preferably the active anatase structure, but also the application of blends of titanium dioxide having anatase and rutile structure is comprised in the patents. These products are promoted regarding their photocatalytic capabilities under laboratory conditions. A comparative assessment in terms of the efficiency of different products as well as application techniques has not been carried out so far.

The comparison of different products is rather difficult as different test procedures are used by the manufacturers. These test procedures differ in their execution and therefore a comparison of different products is questionable. Therefore, a representative profile of economically

available products (see Table 3) of the European market was selected and tested using the test setup described in section 2. The same constant boundary conditions are used as already mentioned in section 2 and 4.1.

In Figure 6, the degradation of NO is given as mean values for every sample series. A wide spectrum of conversion rates was obtained by the measurements. Samples of the series D 2 achieved the by far highest conversion rates and therewith have the highest air purification ability. Next, the series D 4 showed the second highest results. Here, it has to be considered that for later application of this slurry seal the actual active surface will be reduced by the percentage of the asphalt matrix. Series D 4 depicts the only sample which is not representing the surface as it is in later application. For direct comparison, a sample of cut asphalt containing the slurry seal and being in service already for some time would have been required. With a notably lower conversion rate the series D 1 follows in this sequence. Finally, series D 3 and D 5 only achieved low degradation rates. For these products it becomes questionable if the increased production expense and the likely higher market price can be justified by the slight air purification effect.

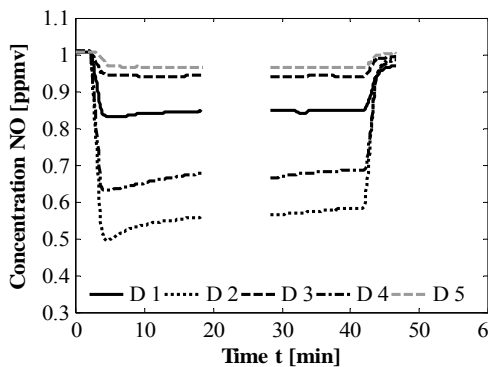


Table 3: Sample denomination and description

Code	Samples	Type of sample
D 1	2	Concrete paving block (outside storage area)
D 2	2	Concrete paving block taken from test area
D 3	3	Concrete paving block taken from production
D 4	3	Casted slabs of cementitious asphalt slurry seal
D 5	1	Concrete paving block taken from production

Figure 6: Test results

For all samples it can be noticed that with higher maximum conversion rates the beginning conversion progresses faster and the decline over time becomes more apparent. However, the decline was approaching a constant degradation rate in all cases. This effect could be explained by an initial saturation of the reactive surface by intermediate and end products.



Figure 7: Staining of concrete paving blocks due to algae formation: untreated sample (a); paving of untreated paving blocks (b); paving block containing TiO₂ in the functional top layer (c)

Although the results of the samples of series D 5 are not sufficient regarding the degradation of NO, one paving block was placed at a location with humid conditions and low natural light where the staining of an already existing paving by algae is a typical problem (see Figure 7). After a short period of time, the reference sample (a) of Figure 7 was covered with algae on its lateral side as well as its top side. This process also occurred on the lateral side of the concrete paving block containing TiO₂, but here only up to the level of the core mix which is not containing photocatalytic active TiO₂. The remaining lateral side of the functional top-layer as well as the top side of the paving block is not covered with algae as here the photocatalytic material is preventing the fouling by algae. This exposition of concrete paving blocks at a location, which is not suitable for the degradation of NO caused by high humidity and low natural light, showed another potential of photocatalytic products regarding the prevention of undesirable staining due to algae growth.

5. CONCLUSION

This paper addresses the properties and the evaluation of air purifying properties of concrete products containing photocatalytic active titanium dioxide (TiO₂). For evaluating the air purifying abilities of these concrete products, a suitable test setup was developed which is based on the degradation of nitric oxide (NO) described in the ISO standard TC 206/SC N [1]. By means of the setup, the influencing parameters on the degradation process of NO are investigated. With respect to the number of influencing parameters and their partial major influence on the measurement, it is advisable to agree a common test standard using equal boundary conditions. Based on these findings as well as specifications in the literature and standards [1], a suitable test procedure is suggested.

Using the described test procedure, mortar mixes with two different TiO₂ are designed and tested regarding their NO degradation efficiency. The degradation rate of the designed mixes is depending on the amount of TiO₂ used as well as on the fineness of the TiO₂. Here, higher amounts of TiO₂ are enhancing the performance of the products regarding NO degradation. The application of finer TiO₂ is showing a bigger effect on the degradation rate than higher amounts of TiO₂.

Furthermore, a comparative study on cementitious products was carried out in order to assess the efficiency of different products available on the European market. It can be noticed that the European market provides a variety of products, showing air purifying abilities. However, their efficiency in regard to NO degradation was found to vary in a notable scale. There are products achieving mean degradation rates of about 40% under the above described optimum laboratory conditions, whereas other products almost show no effect using the same conditions. Hence, the assessment of concrete products for projected constructions becomes more important. With the proper selection of air purifying products a contribution for the environment and an active remedy for atmospheric pollution can effectively be achieved. For large areas like parking lots or broad sidewalks and bicycle lanes, in particular the total conversion can be influenced notably by the selection of the paving stones.

Also, more fundamental research on the influencing factors is necessary to reliably model the degradation process. Here, especially long run experiments for the evaluation of the duration and durability of the NO degrading process are of special interest. The presented results are

used as a basis for later measurements and the modeling of the degradation process as well as its influencing parameters by using an appropriate reaction model.

Finally, the current patent situation makes it difficult to enter the market with new ideas without breaching existing patent rights. One of the promising opportunities would be the expansion of the degrading effect from the active surface into deeper layers of the top layer by means of e.g. UV-A transmitting glass particles and surface layers having a porous structure. Besides the application of photocatalytic active concrete products for the degradation of NO, the prevention of staining by algae growth seems to be a promising field for this type of functional concrete products.

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