

The Use of Photocatalytically Modified Concretes for the Degradation of Airborne Pollutants in Urban Areas

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Abstract :

In the course of a growing awareness for our environment, more and more limits for air pollutants are defined by legal regulations worldwide. Vehicletraffic is one of the major causes of frequently exceeding limits for particulate matter and nitrogen oxides (NOx) in heavy-traffic zones such as urban agglomerations. Besides prevention strategies such as driving bans, speed limits or cleaner engines there is the option to reduce existing airborne pollutants using photocatalytically active construction materials. For this purpose, Steag Power Minerals and Kronos have developed a photocatalytic concrete additive designed for the manufacture of pavers with air-cleaning properties "Photoment". Photoment was tested by Berlin University of Technology and is currently proving itself in field tests in several cities worldwide. In addition to presenting the product concept, this paper is intended to critically illuminate the measurement of specimens according to the ISO 22197-1 method and show alternative, more suitable measurement methods that meetpractical criteria.

Key Words : Photoment photocatalytically active concrete; photocatalysis rethought; TiO^2 + fly ash; photocatalytic pavers urban air pollution

1. Introduction

One of the central questions of our society is: how do we want to live in the future In no other area is the adaptability of a modern society so evident as in the built space of the cities. Cities have always been and always will be an engine for interests, innovation and interaction. In western countries, urbanization is progressing only slowly. The biggest challenge here is the optimization and update of existing structures. In the emerging and third countries, on the other hand, cities are growing rapidly into multimillion metropolises. Their infrastructural, ecological and economic development will become a central, global task for the future. Especially the challenge to stop the climate change will play a significant role [1].

1.1 Cities are the living space of the future

In the first decade of the 21st century, more than 50% of the world's population lived in cities for the first time. The United Nations predicts that by 2050 almost 70 % of the world population will live in an urbanised environment [2]. Within the context of a growing environmental awareness, which has a direct influence on our well-being and our health, more and more legal regulations for limits of air pollutants are being defined in many countries worldwide [3]. In the course of urbanisation, especially due to traffic pollution, limits for fine dust and nitrogen oxides

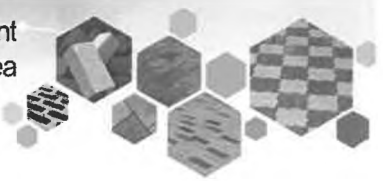
are often exceeded in heavy-traffic zones, such as metropolitan areas. The affected cities react to this with prevention strategies for air pollution control, such as speed limits, driving bans or environmental zones. In addition to improved engine technologies and the transformation to electric mobility, fast and simple secondary measures are required for the transition period of this transformation process to an emission-free traffic. The companies Steag Power Minerals and Kronos are convinced that urban city planning and design should pay particular attention to the available open spaces. With the idea of adding value to existing streets, pavements and squares, they intend to contribute to a smarter urbanisation of cities worldwide and improve the quality of life for their inhabitants. With the help of photocatalytic building materials, it is already possible to reduce existng air pollutants such as nitrogen oxides or volatile organic compounds (VOC). This technology requires large material surfaces, which are exposed to sunlight or artificial light and so get activated. The specific degradation of air pollutants is most efficient with high concentrations of harmful gases and at the same time high intensity of UV light – therefore surfaces in the immediate nearby the sources of pollutants are particularlysuitable, such as paving stones, concrete pavements, acoustic barriers or similar.

For this reason, Steag Power Minerals and Kronos developed a photocatalytic concrete additive in cooperation with the Technical University (TU) Berlin, suitable for the production of paving stones with air-cleaning properties. A large number of formulations were tested in the course of development. The Proctor specimens produced for this purpose were tested by Steag with respect to the concrete properties and colour fastness and at the Technical University of Berlin for photocatalytic activity, freeze-thaw resistance andabrasion resistance.

2. Method

2.1 Basic principle of photocatalysis

For a better understanding of the overall context, Amrhein et al. define the basic principles of photocatalysis as follows: "The photocatalytic degradation of airborne pollutants relies on the interaction between a photosensitive semi – conductor, such as titanium dioxide (TiO^2), and light of specific wavelengths, which excites part of the electrons present in this semiconductor. This process triggers complex redox reactions that can lead to the degradation of various organic and inorganic compounds, such as dirt or airborne pollutants. The most commonly used photosensitive semiconductor is titanium dioxide, for instance in the form of anatase, which can be excited by UV light (< 380 nm, UV-A) to convert nitrogen dioxides to harmless nitrate in several reaction steps in the presence of sufficient humidity and atmospheric oxygen. Thus, titanium dioxide enables both the degradation of airborne pollutants and pollutants and dirt deposits on the material surface. Furthermore, a superhydrophilic surface is created that can bring about an additional cleaning effect. This reaction essentially depends on light intensity, pollutant concentration and humidity. To increase the overall degradation of pollutants, the total surface of the photocatalytic material needs to be enlarged. Titanium dioxide with particles that are as fine as possible, and thus a high specific surface area available for the reaction, is generally used to increase efficiency. Fine particulate materials have a strong tendency to agglomerate. They are difficult to disintegrate during conventional mixing processes, which is why it is hardly possible to utilize the full potential of the large TiO^2 surface to enhance photocatalytic activity" [4].



2.2 Working principle of Photoment

In the article "Increasing efficiency in the degradation of airborne pollutants by photocatalytically modified concretes" thedevelopers involved in the Photoment project, Amrhein et al., describe the innovative effect of Photoment. "To prevent titanium dioxide from becoming less efficient due to agglomeration, Steag cooperated with Kronos to develop Photoment, an innovative concrete additive. Its main constituents are coal fly ash and custom titanium dioxide photocatalysts supplied by Kronos. A specially designed mixing process enables thorough disintegration of the titanium dioxide so that the photocatalytic components are evenly distributed during concrete mixing even without custom equipment. Agglomerations of titanium dioxide particles are broken up during mixing of the fly ash and the photocatalyst to create a homogeneous distribution of these particles whilst reducing charging of TiO^2 particles, which is usually observed in the conventional process. The SEM image and the element distribution reveal the homogeneous spread of titanium dioxide in the fly ash. In this mix, fly ash thus acts as a dispersing agent for the titanium dioxide. Furthermore, the use of Photoment results in good color fastness of the face mix compared to using pure fly ash.

Many studies prove the effectiveness of photocatalytic titanium dioxide in concrete products. The continuous improvement of photocatalytic concrete products concentrates on optimizing its use and determining favorable and adverse boundary conditions. Potential influential factors include the type and ratio of the photocatalyst but also the water/binder ratio, the cement grade, additives such as pigments, and the prevailing manufacturing conditions. When optimizing photocatalytic properties, key characteristics such as the compressive and split- ting tensile strength and freeze-thaw resistance of concrete products should be borne in mind" [4].

3. Result

The evaluation of the test results of Amrhein et al. clearly prove that the use of Photoment results in a significantly better compaction, which is due to an optimization of the particle size distribution in the ultra -fine grain range. In the tests carried out, it can be seen that the binders used react differently sensitive to a variation in watercontent from the outset. Increasing the water content almost always results in better compaction, which is due toan increased water film thickness and a reduction in capillary forces. The data show optimum compaction with the selected mixture at a photometric content of 55 kg/m^3. Fig. 1 illustrates that the more effective compaction of the mix achieved by adding 55 kg/m^3 of Photoment to the CEM I and CEM II/A-LL cements resulted in an improved 28-day compressive strength in all investigated cases.

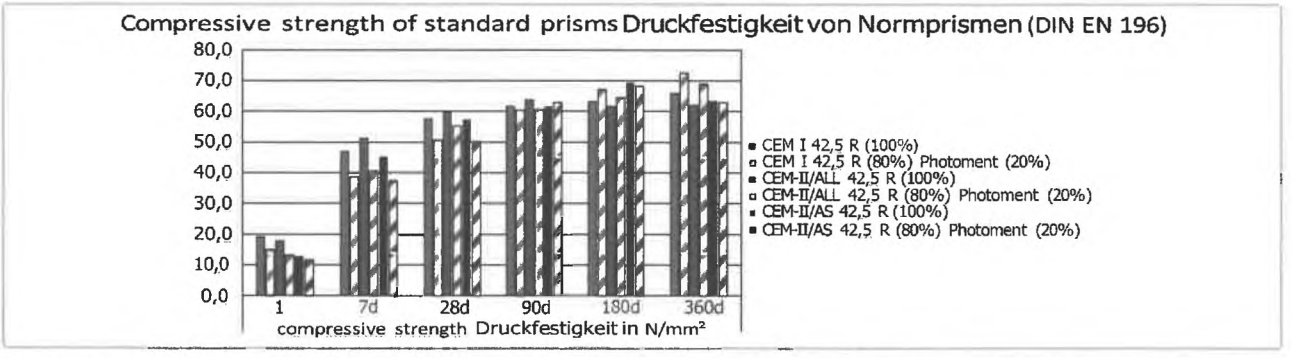


Figure 1. Strength curves of standard prisms according to DIN EN 196, with pure cement or 80% of standard cement and 20% of Photoment. Blue: CEM I 52.5 R red: CEM II/A-LL 42.5 R black: CEM II/A-S 42.5 R. Samples with 20% of Photoment appear in a hatched pattern.

02_ Inovative material applcation into BP

None of the specimens without Photoment revealed a photocatalytic degradation of nitric oxide. Fig. 2 and 3 show examples of curves to compare measurements for specimens with and without Photoment. This diagra m clearly proves that the nitric oxide concentration continues to decrease in line with extended light exposure although all of the specimens were pretreated by exposing them to UV light. When the UV light is switched off, nitric oxide concentrations again decrease to their original levels within only a few minutes.

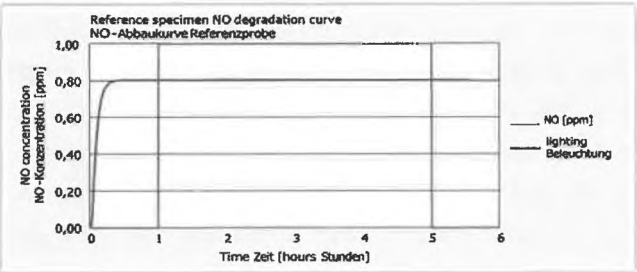


Figure 2. Nitrogen oxide degradation on reference specimens: The diagram shows the degradation curves of nitric oxide and the lighting sequence (on/off) over a period of six hours

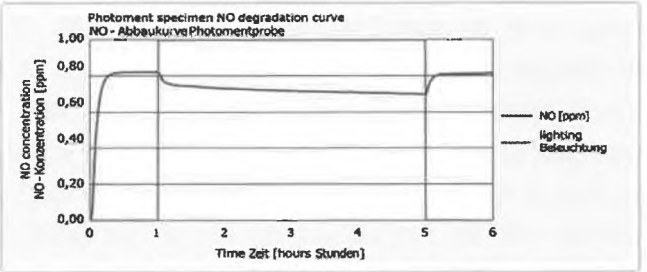


Figure 3. Nitrogen oxide degradation on reference specimens with 55 kg/m³ of Photoment, all other constituents unchanged

Fig. 4 illustrates the photocatalytic NO degradation for the specimens referred to above. It should be noted that the percentage recorded in this diagram is not an absolute measured value. Rather, it serves as a mere laboratory comparison within the series of specimens tested under identical measuring conditions. For this purpose, pollutant degradation after four hours of irradiation was recorded and compared. Deposition rates (i.e. the key parameter to measure nitrogen oxide degrading capability) were determined for selected specimens for use in simulations to model the degradation of nitrogen oxides. This diagram shows not only the expected dependency on the amount of Photoment but also proves that both the cement grade and water contents of the mixes have a significant influence on the photocatalytic effect of concrete. One of the possible causes of these differences is the altered surface structure resulting from the varying water ratios of the specimens. This effect is particularly pronounced in the specimens produced with a CEM I cement. As the water ratio increases, a larger amount of binder and thus photocatalytically active titanium dioxide accumulates on the specimen surface.

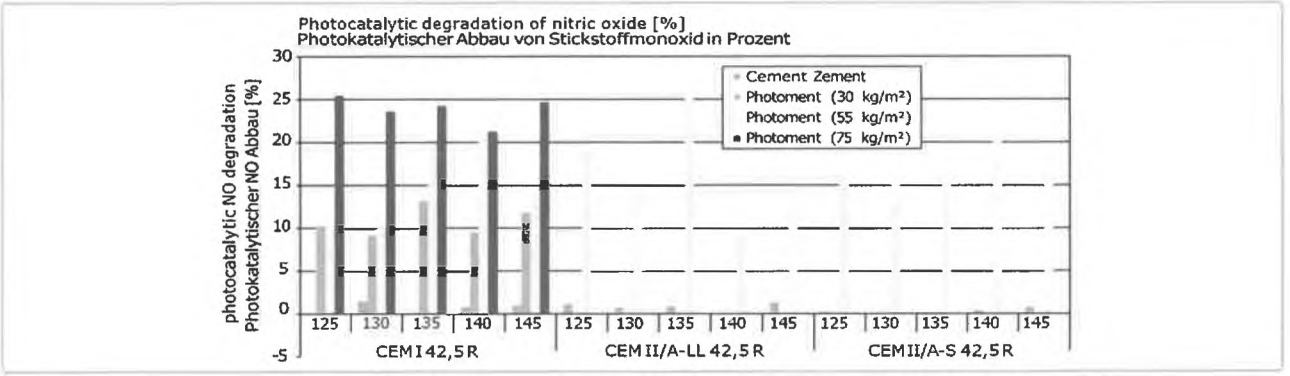
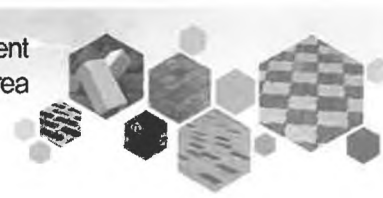


Figure 4. Photocatalytic nitrogen oxide degradation in the photoreactor, percentage decrease of the initial concentra- tion. Grey: reference (without Photoment) green: with 30 kg/m³ of Photoment yellow: with 55 kg/m³ of Photoment red: with 75 kg/m³ of Photoment



As expected, the photocatalytic degradation on the surfaces of the Proctor specimens increased in line with the Photoment ratio. However, no linear correlation exists between Photoment ratio and photocatalytic degradation. For example, the CEM I mixes show no change in photocatalytic activity both at very low (125 and 130 kg/m³) and very high (145 kg/m³) water ratios when the Photoment ratio is increased from 30 to 55 kg/m³. At water ratios of 135 and 140 kg/m³, however, the addition of Photoment results in staggered degradation rates. At a ratio of 55 kg/m³, optimizing the water ratio of the mix makes it possible to more strongly influence the photocatalytic degradation rate in some cases compared to modifying the Photoment ratio itself. This is why no differences are seen between Photoment ratios of 55 kg/m³ and 75 kg/m³ when the water content is set correctly.

4. Conclusion

Photoment is an innovative, photocatalytically active concrete additive designed for use in concrete products to degrade nitrogen oxides. Its use can lead to higher strengths despite the reduced ratio of standard cement. The optimized composition of ready-to-use Photoment makes its handling easier in terms of good conveying and (conventional or manual) batching properties in mixing systems. The comprehensive series of tests performed shows that the amount of the added photocatalyst is not the only factor that determines nitrogen oxide degradation, which is also influenced by the selection of the cement grade and water content of the concrete mix. The tests have shown that the best compressive strength, compaction and freeze-thaw resistance parameters were achieved at the optimal fresh concrete bulk density at which there is also a very high level of photocatalytic ac-tivity. To achieve a significant reduction in the pollutants contained in ambient air, photocatalysts should be used extensively near the sources of pollution, which is why squares, streets, parking facilities and side walks in heavy-traffic zones appear to be optimally suited for this purpose, for example in inner-city areas. Prof. Michael Bruse developed a simulation model for Bottrop "Innovation City" to prove the effectiveness of such measures depending on local surroundings and varying climatic conditions [5]. Further developments are being envisaged by STEAG Power Minerals for structural concrete and other building materials to leverage the full potential of photocatalytic construction materials to keep our air clean.

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