EFFECT OF TiO₂ AND ZNO POWDER MIXTURES ON MECHANICAL AND PHOTOCATALYTIC PERFORMANCE OF HIGH PERFORMANCE CONCRETE

FOUAD AMOR*, LENKA INGRISOVÁ*, ZUZANA RÁCOVÁ*, MICHAL BAUDYSb, PETR HÁJEKα

α Czech Technical University in Prague, Faculty of Civil Engineering, Department of Building Structures, Thákurova 2077/7, 166 29 Prague 6, Czech Republic
b University of Chemistry and Technology Prague, Department of Inorganic Technology, Technická 5, 166 28 Prague 6, Czech Republic
* corresponding author: fouad.amor@fsv.cvut.cz

ABSTRACT.
The development of new modified cement-based materials is increasingly becoming a necessity for improving the durability and surface performance of building materials. Titanium dioxide (TiO₂) photocatalyst has been widely used in building materials science due to its ability to break down pollutants. Zinc oxide (ZnO) is often considered a substituent for TiO₂ because of its photocatalytic and photoluminescent properties. A new inorganic nanocomposite photocatalyst, based on titanium and zinc oxides, is introduced in this work in order to study its compatibility with High Performance Concrete (HPC). This research aims to study the mechanical and photocatalytic behavior of mixtures based on nanoparticles in HPC. The study of the efficiency in the nitrogen oxides (NOₓ) degradation of modified HPC in TiO₂ and ZnO with different percentages is studied. The studies have shown that the introduction of titanium dioxide in HPC presents a significant efficiency for the NOₓ degradation and a positive effect on the mechanical properties than zinc oxide, and thus represents potential contribution to sustainability of concrete structures.

KEYWORDS: High performance concrete, nanoparticles, photocatalysis, titanium dioxide, zinc oxide.

1. INTRODUCTION
Atmospheric pollution is an alteration in the quality of the air, which is due to one or more gaseous substances or particle materials present in concentrations and for a period of time sufficient to create a toxic or eco-toxic effect. The presence of these toxic gases in the atmosphere is due to industrial activity and road transport [1]. In this study, we are focused on emissions and reduction of NOₓ gases. The nitrogen oxides family, grouped under the formula NOₓ, mainly includes nitrogen monoxide (NO) and nitrogen dioxide (NO₂). They can contribute to various environmental problems and have health consequences [2]. There are several methods to reduce NOₓ, in particular photochemical oxidation by the use of photocatalysts [3].

Among the many nanoparticles studied over the last ten years, titanium oxide (TiO₂) and zinc oxide (ZnO) have aroused particular enthusiasm because of their many properties. Their photocatalytic properties have allowed them to be used for self-cleaning, self-disinfection and environmental clean-up applications [4–6]. TiO₂ is currently the most efficient catalyst in this field thanks to its strong photocatalytic activity under UV irradiation. ZnO has a bandgap similar to that of TiO₂, making it increasingly recognized as a suitable alternative to TiO₂. ZnO is the subject of intensive research because of its remarkable properties which promote the development of photo-induced phenomena [7, 8]. The interest of this study is to mix these two oxides to form a nanocomposite which can be used to improve the photocatalytic activity of concrete. The photocatalytic activity of the TiO₂-ZnO system is increasingly being studied with the aim of finding a more efficient material for photocatalytic applications [9, 10]. S. Mayén-Hernández et al. [11] studied the photocatalytic activity of mixed oxides of TiO₂ and ZnO with different Ti/Zn ratios, they concluded that the Ti/Zn ratio of 0.5 exhibited the best photocatalytic performance. Furthermore, the incorporation of mixed oxides into the cement matrix stabilizes the distribution of hydration products (C-S-H) and improves mechanical surface properties [12–14].

The objective of this work aims to evaluate the effect of the inclusion of mixed oxides based on Zn and Ti on the hydration of High Performance Concrete by following the mechanical evolution and the photocatalytic performances as a function of time.

2. MATERIALS AND METHODS
2.1. MATERIALS
The HPC has been developed and optimized in recent years at CTU Prague [15] and it is the self-
consolidating fine grain concrete without fibres. The components of the raw material used are: cement I 42.5 R, silica fume, technical sands with maximum grain size of 1.2 mm, silica flour, water and superplasticizer. These materials come mainly from local sources.

Table 1 illustrates the chemical composition of CEM I 42.5 R cement used for the hydration of HPC with the addition of the mixed oxides TiO₂ and ZnO in proportions varying from 1 to 3% by weight.

Titanium dioxide (TiO₂) and zinc oxide (ZnO) used in this research were produced by the Czech manufacture Precheza. TiO₂ powder consists of 99 wt% of pure Anatase and also some traces of sulphates (0.7 wt%). The specific surface area is about 70-100 m²/g.

### 2.2. FORMULATION AND EXPERIMENTAL METHODS

For the development of this study, 9 series of HPC mixtures were produced, each group consisting of 4 prisms. The concretes were mixed with different percentages of the TiO₂ and ZnO nanoparticles according to Table 2. After 28 days of hardening in water, the samples were dried for 24 hours at the room temperature.

The flexural and compressive strength tests were carried out according to ČSN EN 12390-3 on prismatic specimens 40 × 40 × 160 mm in accordance with the instructions of standard ČSN EN 12390-1 [16]. After 28 days of curing under water, each specimen is first subjected to a 3-point flexion test. Then, the two half-test pieces are tested in compression until they break. The compressive strength of a formulation is the arithmetic average of the four individual results obtained from four determinations made on a set of two prisms. If any of the four results vary by more than ±10% from the average, that result is discarded and the arithmetic mean is calculated from the remaining three results. If any of the three results vary by more than ±10% from their average, all of the results are rejected. The tests were carried out using a mechanical press of the BRIOS HAANICÉ type with a capacity of 400 kN.

 Nanoparticles of ZnO and TiO₂ were suspended in distilled water (2.5 g/dm³) and after 15 minutes of ultrasonic pretreatment were prepared drop casted layers on the soda lime glass (dimension 10 × 5 cm) containing 0.5 mg/cm² TiO₂ or ZnO respectively. Photocatalytic activity was determined using standard ISO 22197-1 methodology (total flowrate 3dm³/min, initial concentration of NO 1 ppm, relative humidity 50%, UV intensity 1nmW/cm²).

The photocatalytic performances of TiO₂ and ZnO nanoparticles were studied by NOx degradation under UV irradiation for 2 hours (Fig. 1). TiO₂ showed a significant NOx degradation capacity which has reached 26%. On the other hand, ZnO was less reactive and had a value of 4%.

Photocatalytic activity of concrete samples was determined in stirred flow through reactor. Due to the expected lower photocatalytic activity, total flowrate was decreased to 1dm³/min, initial concentration of NO was 1 ppm, relative humidity 50%, intensity of UV light 1 mw/cm².

### 3. RESULTS AND DISCUSSION

#### 3.1. COMpressive AND FLEXURAL STRENGTH

Figures 2 and 3 showed the evolution of the addition of mineral powders on the compressive and flexural strength of HPC mixtures. The values of the compressive strength of concrete mixture Ref, CT1, CT2,
CT3, CZ0.3, CZ0.6, CZ1, CT10.6 and CT2Z0.3 are respectively 124, 129.2, 116.5, 102.1, 103.8, 88.4, 84, 87.6 and 120.2 MPa. The addition of a small amount of TiO2 (1%) in the concrete increased its compressive strength compared to the reference concrete. On the other hand, from 2% of TiO2 the strength slightly decreased. The flexural strength value of unmodified concrete (Ref) was 14.5 MPa. As in the compressive strength measurements, the addition of 1 and 2 wt% TiO2 increased the flexural strength and decreased slightly for the CT3 to reach a value nearly equivalent to the Ref sample of 14.4 MPa. The highest values of the flexural strength were obtained for the samples with 1 and 2% by weight of TiO2 of the value of 16.2 MPa. The lower value of flexural strength was observed in the sample with 1% by weight of ZnO.

In general, the substitution of cement by nanoparticles led to a slight decrease in mechanical strengths. Unlike TiO2, the mechanical properties of concrete strongly depend on the amount of this nanoparticle used. According to Wang et al. [17], with increasing the dosage of TiO2 nanoparticles in cement mortars, the strength initially increased rapidly compared to the reference mortar until the dosage reached 2% by weight of TiO2, then there is a slowdown in the percentage of that increase.

The incorporation of nanoparticles into the cement matrix led to increases and slight decreases in compressive and flexural strengths except for samples containing only zinc oxide which showed a significant decrease. The retarding effect of zinc on the hydration of cement, has a direct effect on the mechanical strength [18–20]. These results are not surprising since the added nanoparticles do not have the same performance as Portland CEM I cement.
3.2. NO\textsubscript{x} DECOMPOSITION

The photocatalytic activity of HPC samples containing TiO\textsubscript{2} and ZnO was evaluated under UV irradiation by photodegradation of NO\textsubscript{x} (Figure 4). The maximum NO, NO\textsubscript{x} removal obtained was 8.8 and 6.7\%, respectively, for CT3 sample. CT1Z0.6 sample removed an average of 0.1\% of NO\textsubscript{x} and 1\% of NO, however, CZ1 showed no photocatalytic reaction. On the other hand, the produced amount of toxic intermediate NO\textsubscript{2} is very low, which is crucial in environmental application [21]. It is clear that concretes incorporating TiO\textsubscript{2} have been shown to be superior to the photodegradation of NO\textsubscript{x} compared to those containing ZnO. B. Bica et al. [22] showed that with the same percentage of TiO\textsubscript{2} and ZnO introduced in the concrete, the concretes incorporating the TiO\textsubscript{2} presented a more degradation of the NO\textsubscript{x} for various test conditions and even with low percentages. These results are not surprising since the ZnO powder used in this work was not very reactive to photodegradation.

4. CONCLUSIONS

Different mixtures of HPC with the nanoparticles in substitution with cement have been prepared and their mechanical properties and capacities to degrade nitrogen oxides have been studied.

The introduction of nanoparticles into the cement matrix resulted in increases and slight decreases in compressive and flexural strengths, except for samples containing only zinc oxide which showed a remarkable decrease. The addition of TiO\textsubscript{2} up to 2\% by weight in the HPC did not decrease the mechanical properties but even increased the compressive and flexural strength.

All samples showed photocatalytic degradation under UV irradiation, except for concrete containing 1\% ZnO, achieving a higher NO\textsubscript{x} removal rate with a higher TiO\textsubscript{2} dosage in concrete. The incorporation of zinc oxide alone into the cementitious matrix deteriorates the properties of the concrete. On the other hand, titanium oxide alone or mixed with zinc oxide can be used as additions to HPC by substitution of cement to produce a material with photocatalytic and durable properties.

ACKNOWLEDGEMENTS

The authors would like to thank the program "Mobility Faculty of Civil Engineering", Projects "Mobility Czech Technical University in Prague" for the financial support given in order to support this original research.

REFERENCES


