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EFFECT OF TIO_2 AND ZNO POWDER MIXTURES ON MECHANICAL AND PHOTOCATALYTIC PERFORMANCE OF HIGH PERFORMANCE CONCRETE

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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 (TiO_2) 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 TiO_2 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 (NO_x) degradation of modified HPC in TiO_2 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 NO_x 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 NO_x gases. The nitrogen oxides family, grouped under the formula NO_x, mainly includes nitrogen moNO_xide (NO) and nitrogen dioxide (NO_2). They can contribute to various environmental problems and have health consequences [2]. There are several methods to reduce NO_x, in particular photochemical oxidation by the use of photocatalysts [3].

Among the many nanoparticles studied over the last ten years, titanium oxide (TiO_2) 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]. TiO_2 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 TiO_2, making it increasingly recognized as a suitable alternative to TiO_2. 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 TiO_2-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 TiO_2 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-

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	TiO_2	P_2O_5
%	18.7	4.5	3.4	65.9	1.3	4.3	0.8	0.3	0.1

TABLE 1. Chemical analysis of CEM I 42.5 R (% by weight).

Samples	Technical Sand %	Quartz flour %	Silica fume %	Super-plasticizer %	Water %	Binder		
						Cement (C) %	TiO_2 %	ZnO (Z) %
R	41	13.92	7.47	1.25	7.31	29.05	0	0
CT1	41	13.92	7.47	1.25	7.31	28.05	1	0
CT2	41	13.92	7.47	1.25	7.31	27.05	2	0
CT3	41	13.92	7.47	1.25	7.31	26.05	3	0
CZ0.3	41	13.92	7.47	1.25	7.31	28.71	0	0.34
CZ0.6	41	13.92	7.47	1.25	7.31	28.38	0	0.67
CZ1	41	13.92	7.47	1.25	7.31	28.05	0	1
CT1Z0.6	41	13.92	7.47	1.25	7.31	27.38	1	0.67
CT2Z0.3	41	13.92	7.47	1.25	7.31	26.71	2	0.34

TABLE 2. Formulation of HPC samples.

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 TiO_2 and ZnO in proportions varying from 1 to 3% by weight.

Titanium dioxide (TiO_2) and zinc oxide (ZnO) used in this research were produced by the Czech manufacture Precheza. TiO_2 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 m^2/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 TiO_2 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 accordance with ČSN EN 12390-3 on prismatic specimens $40 \times 40 \times 160$ 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 $\pm 10\,\%$ 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 $\pm 10\,\%$ from their average, all of the results are rejected. The tests were carried out using a mechanical press of the BRIO HAANICE® type with a capacity of 400 kN.

Nanoparticles of ZnO and TiO_2 were suspended in distilled water (2.5 g/dm^3) 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/cm^2 TiO_2 or ZnO respectively. Photocatalytic activity was determined using standard ISO 22197-1 methodology (total flowrate $3dm^3/min$, initial concentration of NO 1 ppm, relative humidity 50%, UV intensity $1mW/cm^2$).

The photocatalytic performances of TiO_2 and ZnO nanoparticles were studied by NO_x degradation under UV irradiation for 2 hours (Fig. 1). TiO_2 showed a significant NO_x degadation 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 $1dm^3/min$, initial concentration of NO was 1 ppm, relative humidy 50%, intensity of UV light 1 mw/cm^2.

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,

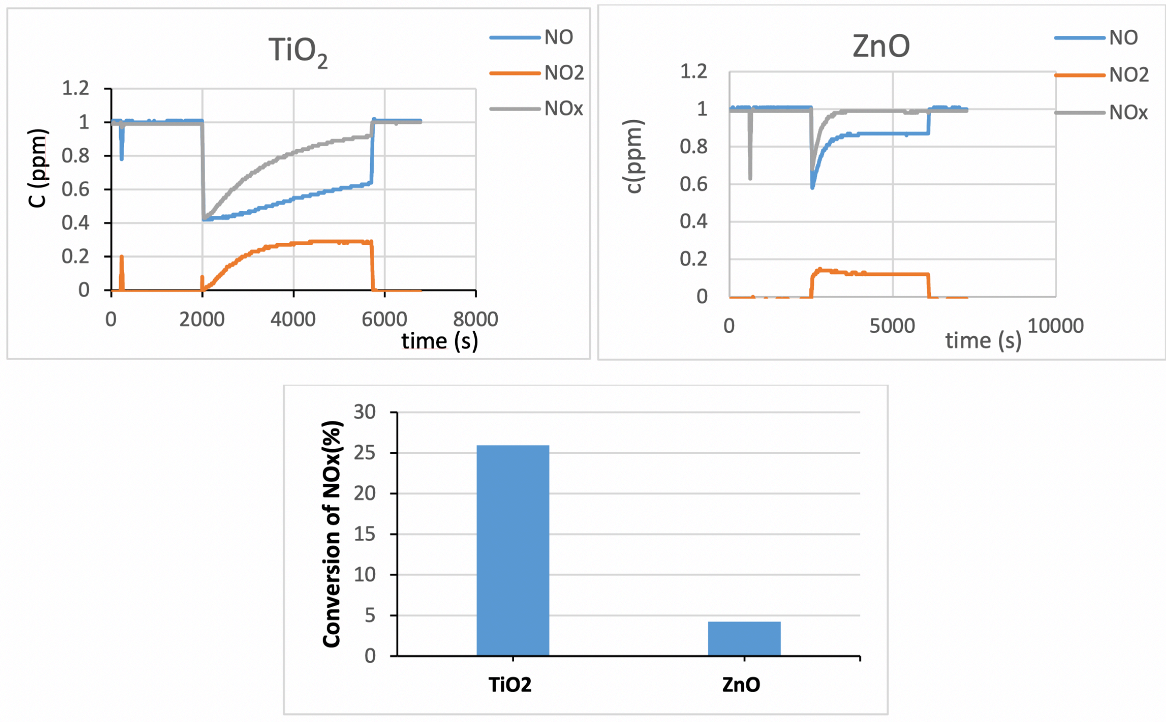

Figure 1. NO_x abatements for TiO_2 and ZnO nanoparticles under UV irradiation.

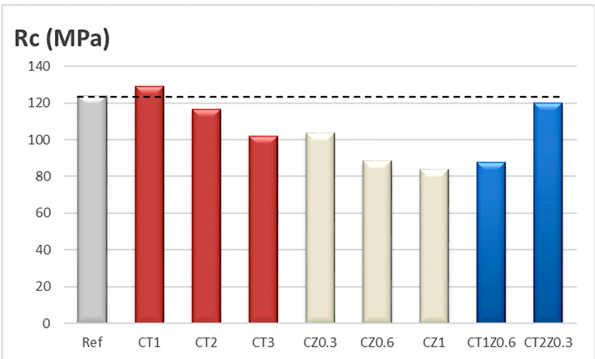

Figure 2. Compressive strength of HPC samples.

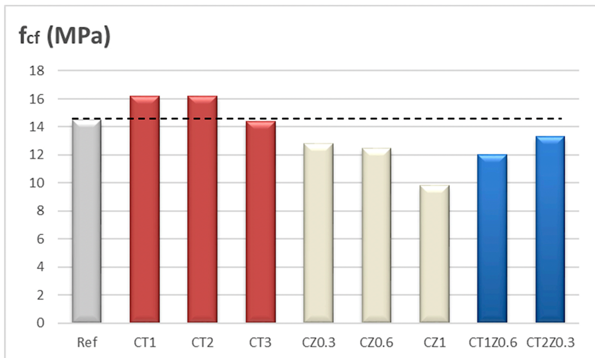

Figure 3. Flexural strength of HPC samples.

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 TiO_2 (1%) in the concrete increased its compressive strength compared to the reference concrete. On the other hand, from 2% of TiO_2 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% TiO_2 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 TiO_2 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 TiO_2, 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 TiO_2 nanoparticles in cement mortars, the strength initially increased rapidly compared to the reference mortar until the dosage reached 2% by weight of TiO_2, 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.

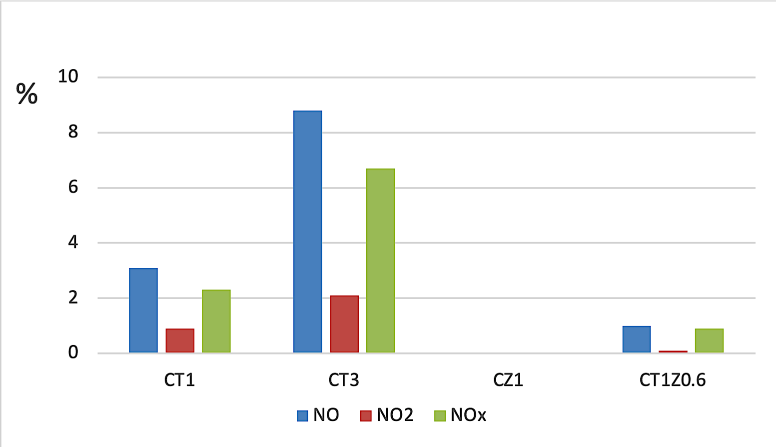

FIGURE 4. NO_x removal under UV irradiation over CT1, CT3, CZ1 and CT1Z0.6.

3.2. NO_x decomposition

The photocatalytic activity of HPC samples containing TiO_2 and ZnO was evaluated under UV irradiation by photodegradation of NO_x (Figure 4). The maximum NO, NO_x removal obtained was 8.8 and 6.7%, respectively, for CT3 sample. CT1Z0.6 sample removed an average of 0.1% of NO_x and 1% of NO, however, CZ1 showed no photocatalytic reaction. On the other hand, the produced amount of toxic intermediate NO_2 is very low, which is crucial in environmental application [21]. It is clear that concretes incorporating TiO_2 have been shown to be superior to the photodegradation of NO_x compared to those containing ZnO. B. Bica et al. [22] showed that with the same percentage of TiO_2 and ZnO introduced in the concrete, the concretes incorporating the TiO_2 presented a more degradation of the NO_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_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_x removal rate with a higher TiO_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.

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