

NO_x photocatalytic degradation on gypsum plates modified by TiO₂-N,C photocatalysts

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In presented studies the photocatalytic decomposition of NO_x on gypsum plates modified by TiO₂-N,C photocatalysts were presented. The gypsum plates were obtained by addition of 10 or 20 wt.% of different types of titanium dioxide, such as: pure TiO₂ and carbon and nitrogen co-modified TiO₂ (TiO₂-N,C) to gypsum. TiO₂-N,C photocatalysts were obtained by heating up the starting TiO₂ (Grupa Azoty Zakłady Chemiczne Police S.A.) in the atmosphere of ammonia and carbon at the temperature: 100, 300 i 600°C. Photocatalyst were characterized by FTIR/DRS, UV-Vis/DR, BET and XRD methods. Moreover the compressive strength tests of modified gypsum were also done. Photocatalytic activity of gypsum plates was done during NO_x decomposition. The highest photocatalytic activity has gypsum with 20 wt.% addition of TiO₂-N,C obtained at 300°C.

Keywords: photocatalysis, modified gypsum, NO_x.

INTRODUCTION

In recent years, a lot of efforts were made to obtain various building materials (cementitious, gypsum, brick materials, etc.) exhibiting self-cleaning, self-sterilizing, bactericidal and anti-fog properties¹. One of the employed methods involves inducing photocatalytic activity of the building materials by loading them with highly photoactive oxides^{2, 3}. Recent findings in nanomaterials development field led to formation of nano size materials, such as titanium dioxide, which possesses a strong oxidizing capability⁴. Moreover, in order to additionally enhance the TiO₂ photoactivity and consequently its effectiveness in removal of larger variety of the pollutants, the titania can be additionally modified with non-metals or metals^{3, 4}. The possibility to incorporate titanium dioxide nanoparticles in construction materials (cement, plaster, concrete, etc.) has been recently investigated, leading to the development of commercial products like TioCem⁵⁻⁷.

Besides direct mixing of TiO₂ powder with the building materials, other techniques, including sputtering, spray coating and sol-gel dip coating^{8, 10}, have also been used to incorporate the photocatalysts onto the building materials. However, these coatings often have weak adhesion to the substrates, rendering their poor durability¹¹.

The most popular group of the building materials, exhibiting self-cleaning properties are cements¹²⁻¹⁴. Little attention is given to the other group such as gypsum, which are widely applied interior walls and ceilings coatings¹⁵. The constantly increasing air quality demands, enforced by the EU^{16, 17} gave rise to the investment in the research of new photocatalytic construction and building materials focused on the reduction of pollutant concentration levels, not just in the outdoor atmosphere but also in indoor environments¹⁸. The atmosphere inside buildings can be gradually contaminated by various chemical species, such as NO_x, SO_x or VOC (volatile organic compounds), deriving from traffic and industry sources¹⁹. Especially the adverse effects of atmospheric nitrogen oxides (NO_x) on human and environmental health are well-known²⁰. The nitrogen oxides are present

indoor by the contamination from the exterior air that enters through ventilation systems or windows²¹. The additive of photocatalyst such as TiO₂ to gypsum, which is a natural, environmentally friendly and fireproof material, with good acoustic performance, offers promising potential in elimination of nitrogen oxides, in indoor environments²².

This paper focusing on the de-polluting effect of gypsum plasters added with titanium dioxide simultaneously modified with carbon and nitrogen, based in the degradation of NO₂. Moreover, the impact of photocatalytic additive to gypsum material on compressive strength was also presented.

EXPERIMENTAL

Sample preparation

The gypsum plate was obtained by addition of 10 and 20 wt.% of unmodified and modified titanium dioxide to gypsum. The unmodified, pure titanium dioxide was mainly anatase TiO₂, supplied by Grupa Azoty Zakłady Chemiczne "Police" S.A., Poland. Modified titanium dioxide was obtained by modification of unmodified titanium dioxide in the carbon and nitrogen atmosphere by method described below.

Firstly, the pure TiO₂ was rinsed with 240 ml of ammonia water (2.5 wt%) and then distilled water until pH value reached 6.8. Acquired suspension was filtered and then obtained TiO₂ slurry was pre-dried for 24 hours at 105°C to remove ammonium residues and water molecules adsorbed on the surface of titanium dioxide powder. Secondly the carbon and nitrogen modification of titanium dioxide was performed. The quartz crucible with 15 g of pre-dried TiO₂ was placed in a central part of tubular furnace and heated up to 100, 300 and 600°C (5°C/min) in argon gas flow (100 ml/min, gas grade purity of 99.9995% (Messer, Poland)). In the point of maximal calcination temperature argon flow was closed. The TiO₂ sample was kept in programmed temperature for 1.5 h and gaseous ammonia with a flow of 200 ml/min was

passed through a glass scrubber with n-hexane. After that time the furnace was firstly cooled down for 1 h in argon flow (100 ml/min) and then automatically to room temperature without argon flow. Prepared samples were micronized using analytical grinder IKA A11 basic (IKA, Germany).

Gypsum plates were obtained by mechanical grinding of gypsum with 10 or 20% wt. of photocatalysts in agate mortar during 20 minutes. Prepared mixtures were blended with distilled water (water to gypsum ratio g/w = 0.8). The obtained pastes were poured into silicone moulds (20 mm x 20 mm x 6 mm) and dried to constant mass at 40°C. The sample codes for modified gypsum plates in Table 1 are presented.

Sample characterization

The characteristic of obtained carbon and nitrogen modified photocatalysts ($\text{TiO}_2\text{-N,C-100}$, $\text{TiO}_2\text{-N,C-300}$, $\text{TiO}_2\text{-N,C-600}$) was precisely presented in our earlier publication. UV-Vis/DR, FTIR/DRS, XRD analysis were done. Moreover the BET specific surface were calculated and carbon and nitrogen content in the photocatalysts

were also measured²³. The most important data in Table 2 are presented.

The compressive strength tests of modified gypsum were done on the several series of cylinder specimens. Similarly to gypsum plasters, prepared mixtures were blended with distilled water, with water-gypsum ratio (w/g) 0.8. Successor, received pastes were poured into cylindrical silicone moulds (16 mm x \varnothing 15 mm). Acquire samples were removed from the molds and dried at 40°C, during for 72 hours. Dried specimens were placed into exsiccator for 24 hours, before being tested for compressive strength.

NO_x decomposition tests

The NO_x decomposition test were done in the reactor which scheme in Figure 1 is presented. A cylindrical Pyrex glass vessel ($\varphi \times H$, 5 cm x 32 cm) was used as the photoreactor for the degradation of NO_x and a four gypsum plates (each at dimensions 20 mm x 20 mm x 6 mm, each) were located inside the vessel. Reactor was surrounding by UV lamp 4 x 22W (Philips) and placed inside thermostatic chamber. The emission spectrum of the lamp in Figure 2 is presented. The irradiation

Table 1. Sample codes for gypsum plates modified by titanium dioxide

Sample code	Material composition	Treatment temperature [°C]	TiO ₂ loading [wt %]
g	gypsum	–	–
g+TiO ₂ -10%	gypsum/starting TiO ₂	100	10
g+TiO ₂ /N,C-100-10%	gypsum/TiO ₂ -N,C photocatalysts	100	10
g+TiO ₂ /N,C-300-10%	gypsum/TiO ₂ -N,C photocatalysts	300	10
g+TiO ₂ /N,C-300-20%	gypsum/TiO ₂ -N,C photocatalysts	300	20
g+TiO ₂ /N,C-600-10%	gypsum/TiO ₂ -N,C photocatalysts	600	10

Table 2. Characteristic of carbon and nitrogen modified TiO₂

Photocatalyst	S _{BET} [m ² /g]	Anatase crystallite size [nm]	Nitrogen content [wt%]	Carbon content [wt%]
TiO ₂ -N,C-100	219	6.7	1.27	0.12
TiO ₂ -N,C-300	206	7.7	0.97	0.05
TiO ₂ -N,C-600	24	50.0	0.22	0.14

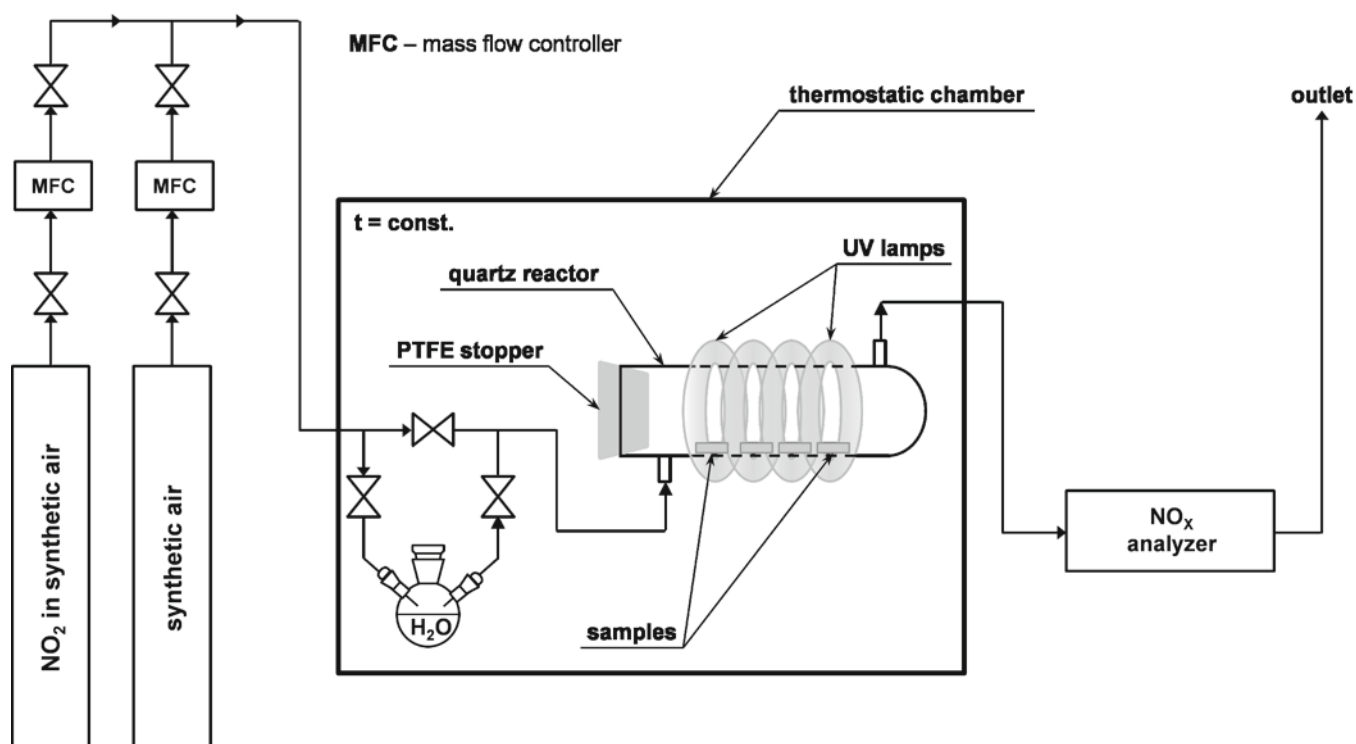


Figure 1. Scheme of photoreactor for NO_x decomposition

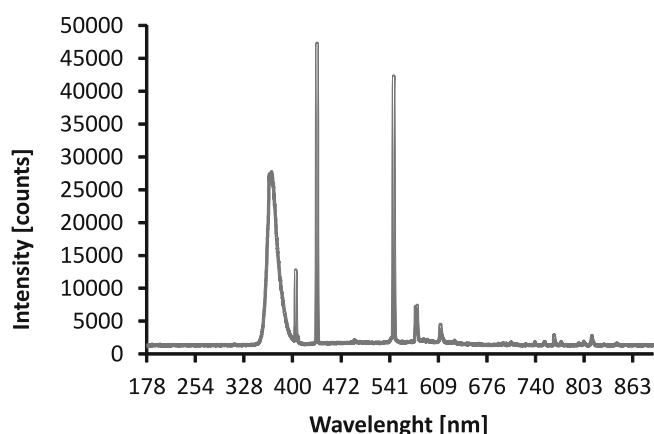


Figure 2. Emission spectrum of UV lamps

intensity amounted 100 W/m² of UVA and 4 W/m² of visible light. NO_x degradation was carried out at 25°C using an air stream containing 25 ppm NO₂ as feedstock with flow 500 ml/min. The flow of gases was control by mass flow meters. An on-line chemiluminescent NO_x analyzer (T200, Teledyne) continuously monitored NO and NO₂ concentrations for gas analysis in the outlet.

RESULTS AND DISCUSSIONS

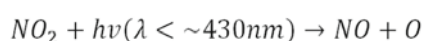
NO_x decomposition

Photocatalytic activity of obtained modified gypsum plates was tested during NO_x decomposition. In the reactor four gypsum plates with dimensions 20 mm x 20 mm x 6 mm were placed. Then the gas containing 25 ppm of NO₂ was continuously pass through the reactor for 1 hour to obtained equilibrium state. After that time UV lamps were switch on and 1 hour irradiation starts. In Figure 3 the absolute concentration of NO₂, NO and NO_x is presented. In Figure 3a) the photolysis effect can be observed. In Figure 3b) degradation of NO_x in presence of gypsum plate modified by addition of 20 wt% of TiO₂-N₂C modified at 300°C is presented. As it can be seen in Figure 3 a) when the light was on the concentration of NO₂ decrease while concentration of NO increased, but the concentration of NO_x stayed on the same level. Its mean that photolysis occur. But when gypsum plates modified by TiO₂ was placed inside the reactor and the light was switch on the concentration of NO₂ decrease while concentration of NO increased but not so much like during photolysis and moreover the concentration of NO_x also decreased. Its mean that TiO₂-N₂C modified gypsum decomposed NO_x.

In Figure 4 the conversion of NO₂ is presented. The amount of produced NO and oxidized NO₂ is shown. During photocatalytic decomposition of NO₂ several reaction may occur. The efficiency and selectivity of NO₂ reaction were calculated as following²⁴:

$$NO_2 \text{ conversion} = \left(1 - \frac{NO_{2,out}}{NO_{2,in}}\right) \times 100\%$$

Undesirable NO during decomposition of NO₂ occurred due to photolysis of NO₂ under the influence of UV irradiance:



Moreover NO₂ can react with the water vapor producing NO, as follows²⁵:

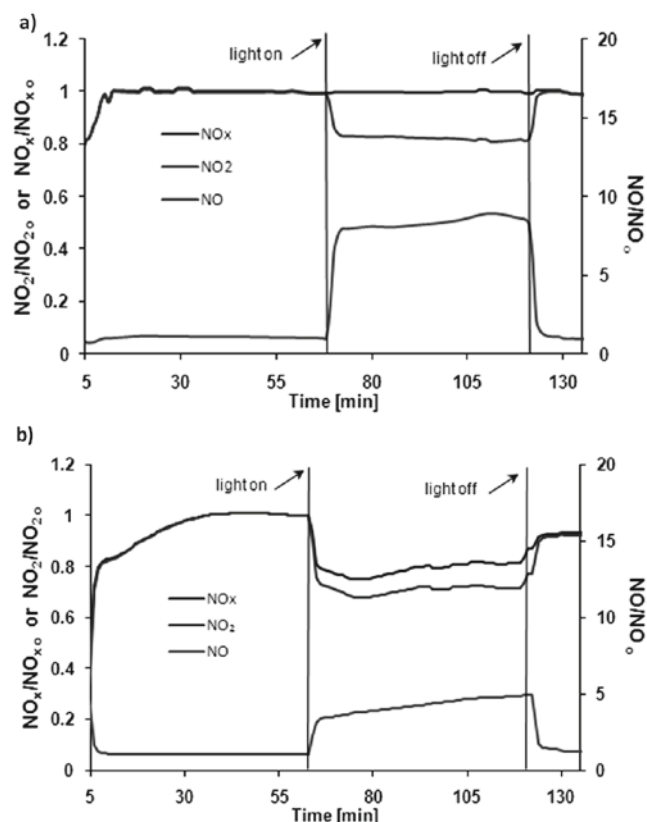
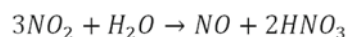


Figure 3. Time-course of the changes in concentration of NO, NO₂ and NO_x: a) as a results of photolysis and b) in the presence of g+TiO₂-N₂C-300-20%; inlet concentration of NO₂: 25 ppm, inlet flow rate: 500 ml/min, reaction temperature: 25°C where [NO]_x = [NO] + [NO₂]



The amount of produced NO was calculated by using the following equation:

$$NO_{produced} = \frac{NO_{out} - NO_{in}}{NO_{2,in} - NO_{2,out}} \times 100\%$$

NO₂ may be also partially converse to oxidative forms (NO₃)

$$NO_{2,oxidized} = NO_2 \text{ conversion} - NO_{produced}$$

As it can be seen in the case of pure gypsum and with the case of plates containing less active photocatalyst such as TiO₂-N₂C modified at 100 and 600°C under UV light irradiation NO₂ pass to NO, probably because of photolysis process. In the case of plates containing 10 wt% and 20 wt% of TiO₂-N₂C-300 the photocatalysis occur, because it can be observed the decreasing of NO₂

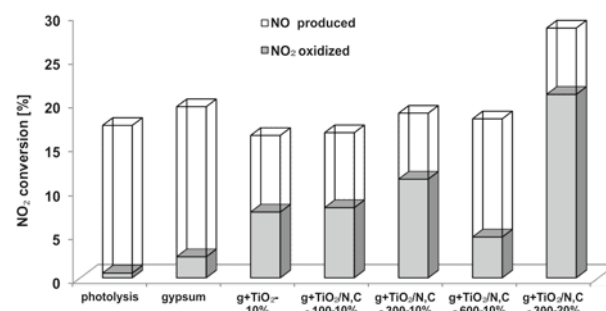


Figure 4. NO₂ conversion on various modified gypsum plates under UV light irradiation

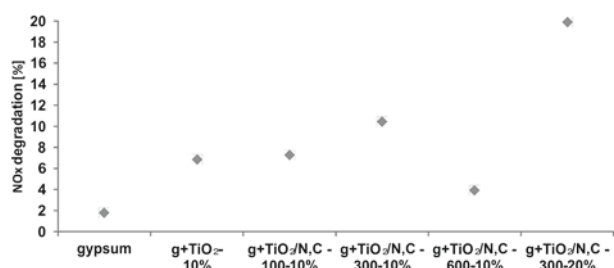


Figure 5. Degradation of NO_x on modified gypsum under UV light irradiation

concentration and also the amount of produced NO is not so high and even three times less than in the case of photolysis. NO₂ is probably oxidized to NO₃⁻ which is adsorbed on modified gypsum surface.

In Figure 5 the degradation of NO_x is presented. In the case of gypsum plates containing TiO₂-N,C modified at 100 and 600°C NO₂ cross in NO and concentration of NO_x keeps on the same level. In the case plates containing 10 wt% and 20 wt% of TiO₂-N,C-300, NO₂ cross in NO₃⁻ which is adsorbed on plates surface and concentration of NO₂ decrease.

As it can be seen that there is no NO_x degradation on pure gypsum. The highest degradation of NO_x is when plates contain 10 wt% and 20 wt% of TiO₂-N,C modified at 300°C. The explanation may be the fact that this photocatalyst has high surface area, amounted 206 m²/g and content of 0.97 wt% of nitrogen, mainly these are ammonia groups –NH₃⁺ presents on the surface of photocatalyst and only 0.05 wt% of carbon groups, FTIR/DRS spectra in Figure 6 is presented. Presence of ammonia on the surface of photocatalysts caused alkalinity of the surface and acidic NO₂ is easier adsorbed.

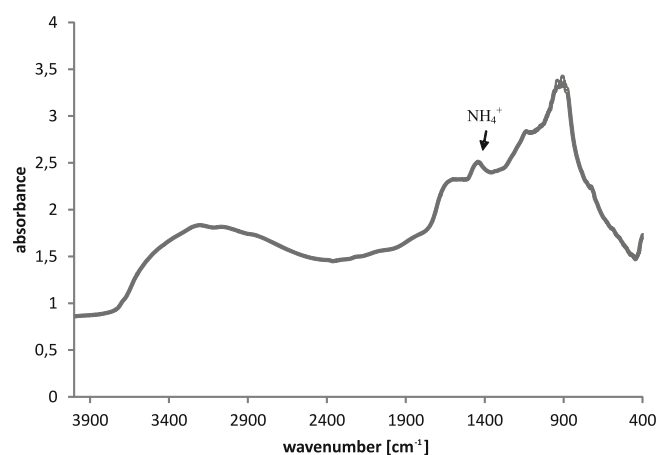


Figure 6. FTIR/DRS spectra of TiO₂-N,C photocatalyst modified at 300°C

The compressive strength analysis

The values of compressive strengths of gypsum modified by 10 wt% addition of TiO₂-N,C in Table 3 are presented. Additionally, a distinctly growing tendency in compressive strength of gypsum cylinder specimens can be observed with the treatment temperature of prepared co-modified photocatalysts. According to the XRD analysis anatase crystallite size was appointed. The anatase crystallite size of carbon and nitrogen modified TiO₂ in Table 2 are presented. It can be seen that there is

dependence between the crystallite size of photocatalyst and the compressive strength of gypsum cylinders specimens modified by these photocatalysts. In general, tested results indicated that the compressive strengths gradually increased with the size of TiO₂ particles. Consequently, sample designed as g+TiO₂/N,C-600-10%, which contained the largest sized of TiO₂ particles (50 nm) revealed the highest values of compressive strength (6.64 MPa). Similar observation was reported by Haruehansapong et al.²⁶, for cement mortars containing nanosilica with various sizes. They confirmed that medium particle size of nanosilica (40 nm) improvement the compressive strength of cement mortars.

CONCLUSION

The addition of TiO₂-N,C to gypsum has influence on photoactivity and the compressive strength of these new materials. The higher activity during NO_x degradation has gypsum modified by addition of 20 wt% of TiO₂/N,C modified at 300°C. The explanation may be the fact that this photocatalyst has high surface area, amounted 206 m²/g and content of 0.97 wt% of nitrogen, mainly these are ammonia groups –NH₃⁺ presents on the surface of photocatalyst and only 0.05 wt% of carbon groups. Presence of ammonia on the surface of photocatalysts caused alkalinity of the surface and acidic NO₂ is easier adsorbed. On the other hand the highest value of the compressive strength (6.64 MPa) has sample designed as g+TiO₂/N,C-600-10%, which contained the largest sized of TiO₂ particles (50 nm).

Table 3. Compressive Strength of modified gypsum

Sample code	Compressive Strength [MPa]
g	5.84
g+TiO ₂ /N,C-100-10%	3.66
g+TiO ₂ /N,C-300-10%	4.52
g+TiO ₂ /N,C-600-10%	6.64

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LITERATURE CITED

1. Fujishima, A.X., Zhang & Tryk, D.A. (2007). Heterogeneous photocatalysis: from water photolysis to applications in environmental cleanup. *Int. J. Hydrogen Energy* 32(14), 2664–2672. DOI: 10.1016/j.ijhydene.2006.09.009.
2. Lackhoff, M., Prieto, X., Nestle, N., Dehn, F. & Niessner, R. (2003). Photocatalytic activity of semiconductor-modified cement-influence of semiconductor type and cement ageing. *Appl. Catal. B-Environ.* 43(3), 205–216. DOI: 10.1016/S0926-3373(02)00303-X.
3. Meng, T., Yu, Y., Qian, X., Zhan, S. & Qian, K. (2012). Effect of nano-TiO₂ on the mechanical properties of cement mortar. *Constr. Build. Mater.* 29, 241–245. DOI: 10.1016/j.conbuildmat.2011.10.047.
4. Beydoun, D., Amal, R., Low, G. & McEvoy, S. (1999). Role of nanoparticles in photocatalysis. *J. Nanopart. Res.* 1, 439–458. DOI: 10.1023/A:1010044830871.
5. Hunger, M., Husken, G. & Brouwers, J. (2008). Photocatalysis applied to concrete products – part 1: principles and test procedure. *Zkg. Int.* 61, 77–85.

6. Bolte, G. (2009). Innovative building materials-reduction of pollutants with TioCem. *Zkg. Int.* 62, 63–70.
7. Toma, F.L., Bertrand, G., Klein, D. & Coddet, C. (2004). Photocatalytic removal of nitrogen oxides via titanium dioxide. *Environ. Chem. Lett.* 2(3), 117–121. DOI: 10.1007/s10311-004-0087-2.
8. Carneiro, J.O., Teixeira, V., Martins, A.J., Mendes, M., Ribeiro, M. & Vieira, A. (2009). Surface properties of doped and undoped TiO₂ thin films deposited by magnetron sputtering. *Vacuum* 83(10), 1303–1306. DOI: 10.1016/j.vacuum.2009.03.028.
9. Rachel, A., Subrahmanyam, M. & Boule, P. (2002). Comparison of photocatalytic efficiencies of TiO₂ in suspended and immobilized form for the photocatalytic degradation of nitrobenzenesulfonic acids. *Appl. Catal. B-Environ.* 37(4), 301–308. DOI: 10.1016/S0926-3373(02)00007-3.
10. Boccaccini, A.R., Rossetti, M., Roether, J.A., Zein, S.H.S. & Ferraris M. (2009). Development of titania coatings on glass foams. *Constr. Build. Mater.* 23(7), 2554–2558. DOI: 10.1016/j.conbuildmat.2009.02.019.
11. Ramirez, A.M., Demeestere, K., De Belie, N., Mäntylä, T. & Levänen, E. (2010). Titanium dioxide coated cementitious materials for air purifying purposes: preparation, characterization and toluene removal potential. *Build. Environ.* 45(4), 832–838. DOI: 10.1016/j.buildenv.2009.09.003.
12. Lackhoff, M., Prieto, X., Nestle, N., Dehn, F. & Niessner, R. (2003). Photocatalytic activity of semiconductor-modified cement – influence of semiconductor type and cement ageing. *Appl. Catal. B-Environ.* 43(3), 205–216. DOI: 10.1016/S0926-3373(02)00303-X.
13. Meng, T., Yu, Y., Qian, X., Zhan, S. & Qian, K. (2012). Effect of nano-TiO₂ on the mechanical properties of cement mortar. *Constr. Build. Mater.* 29, 241–245. DOI: 10.1016/j.conbuildmat.2011.10.047.
14. Yousefi, A., Allahverdi, A. & Hejazi, P. (2013). Effective dispersion of nano-TiO₂ powder for enhancement of photocatalytic properties in cement mixes. *Constr. Build. Mater.* 41, 224–230. DOI: 10.1016/j.conbuildmat.2012.11.057.
15. Pereira, A., Palha, F., Brito, J. & Silvestre, J.D. (2011). Inspection and diagnosis system for gypsum plasters in partition walls and ceilings. *Constr. Build. Mater.* 25(4), 2146–2156. DOI: 10.1016/j.conbuildmat.2010.11.015.
16. U.E., Directive 2008/50/EC of the European Parliament and of the Council on ambient air quality and cleaner air for Europe, Official Journal of the European Union, L152/1, 2008.
17. Berglund, B., Brunekreef, B., Knoppel, H., Undvåij, T., Maroni, M., Mblhave, L. & Skov, P. (1991). Effects of Indoor Air Pollution on Human Health – Report no. 10, Commission of the European Communities, Luxembourg.
18. Zhao, J. & Yang, X.D. (2003). Photocatalytic oxidation for indoor air purification: a literature review. *Build. Environ.* 38, 645–654. DOI: 10.1016/S0360-1323(02)00212-3.
19. Todorova, N., Giannakopoulou, T., Karapati, S., Petridis, D., Vaimakis, T. & Trapalis, C. (2014). Composite TiO₂/Clays Materials for Photocatalytic NO_x Oxidation. *Appl. Surf. Sci.* DOI: 10.1016/j.apsusc.2014.07.020 (In press, Accepted Manuscript, Available online 12 July 2014).
20. Kampa, M. & Castanas, E. (2008). Human health effects of air pollution. *Environ. Pollut.* 151, 362–367. DOI: 10.1016/j.envpol.2007.06.012.
21. Kukadia, V. & Palmer, J. (1998). The effect of external atmospheric pollution on indoor air quality: a pilot study. *Energy Build.* 27, 223–230. DOI: 10.1016/S0378-7788(97)00044-3.
22. Wu, Z., Wang, H., Liu, Y. & Gu, Z. (2008). Photocatalytic oxidation of nitric oxide with immobilized titanium dioxide films synthesized by hydrothermal method. *J. Hazard. Mater.* 151(1), 17–25. DOI: 10.1016/j.jhazmat.2007.05.050.
23. Janus, M., Bubacz, K., Zatorska, J., Kusiak-Nejman, E., Czyżewski, A., Przepiórski, J. & Morawski, A.W. (2014). Induced self-cleaning properties towards Reactive Red 198 of the cement materials loaded with co-modified TiO₂/N,C photocatalysts. *React. Kinet. Mechanism Catal.* In press, DOI: 10.1007/s11144-014-0749-4.
24. Nguyen N.H. & Bai, H. (2014). Photocatalytic removal of NO and NO₂ using titania nanotubes synthesized by hydrothermal method. *J. Environ. Sci.* 26, 1180–1187. DOI: 10.1016/S1001-0742(13)60544-6.
25. Ballari, M.M., Yu, Q.L. & Brouwers, H.J.H. (2011). Experimental study of the NO and NO₂ degradation by photocatalytically active concrete. *Catal. Today.* 161, 175–180, DOI: 10.1016/j.cattod.2010.09.028.
26. Haruehansapong, S., Pulngern, T. & Chucheeepsakul, S. (2013). Effect of the particle size of nanosilica on the compressive strength and the optimum replacement content of cement mortar containing nano-SiO₂. *Constr. Build. Material.* 50, 471–477. DOI: 10.1016/j.conbuildmat.2013.10.002.