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Surface Modification of Photocatalytic Cementitious Composites with Polyacrylic Superabsorbent Polymers (SAP) †

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Abstract: This study focuses on developing new surface modification methods for photocatalytic cementitious composites. The question that was investigated was if superabsorbent polymers can act as an intermediate environment, intensifying the incorporation of TiO_2 particles on the surface of the tested material. Four variants of surface modification were designed: water dispersions of TiO_2 with non-saturated SAP, with SAP in a hydrogel form, and two reference series. Due to the use of SAP, the efficiency in air purification from NO_x under different light conditions compared to the reference series increased significantly, exceeding a 75% increase under a UV-A light and a 600% increase under visible light.

Keywords: superabsorbent polymers; SAP; cement composites; titanium dioxide; gaseous pollutants; photocatalysis

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1. Introduction

Air pollution caused by human activity is one of the most worrying problems in urban areas nowadays [1,2]. Due to an increase in the concentration of harmful gaseous pollutants, mainly nitric oxides, ozone, and others, methods to reduce their presence need to be developed. As urban areas occupy significant areas of land, any active air purification system would require a vast amount of energy to operate and would contribute to a reduction in the quality of life in its vicinity (noise generated by high-efficiency air turbines). Moreover, most pollutants are produced due to the activity of transport systems within city boundaries, contributing to the differences in their concentrations over different areas (residential areas, roads, and other transport pavements, etc.) [3]. Therefore, different solutions to the problem have been developed over the years, with one of them being the use of photocatalytic materials embedded into cementitious materials—a passive system that requires only the presence of solar radiation to operate and purify the air from pollutants [4,5]. As a significant part of urban areas is covered with different types of pavements, mostly made of various cementitious materials and exposed to solar radiation, such a passive system would not require any changes to the existing infrastructure other than replacing non-photocatalytic surfaces with photocatalytic ones.

For a photocatalytic reaction to occur, a photocatalytic material (a semiconductor—for example, titanium dioxide) needs to be irradiated (for instance, with solar radiation). Due to energy introduction, electrons (e−) from the semiconductor shift from the valence band (vb) to the conduction band (cb), leading to the formation of electron holes h+ (Equation (1)). The resulting pairs of charges initiate a reduction–oxidation process (Figure 1). In the presence of adsorbed oxygen and water (strong oxidants) it is possible to decompose a wide range of air pollutants due to the formation of hydroxyl radicals ($OH^\bullet$) and superoxide radicals ($O_2^{\bullet -}$) (Equations (2) and (3)) [6].

$$TiO_2 \xrightarrow{h\upsilon} TiO_2 + h_{vb}^{+} + e_{cb}^{-} \tag{1}$$

$$(H_2O)_{ads} + h^+ \rightarrow H^+ + OH^\bullet \tag{2}$$

$$(O_2)_{ads} + e^- \rightarrow O_2^{\bullet -} \tag{3}$$

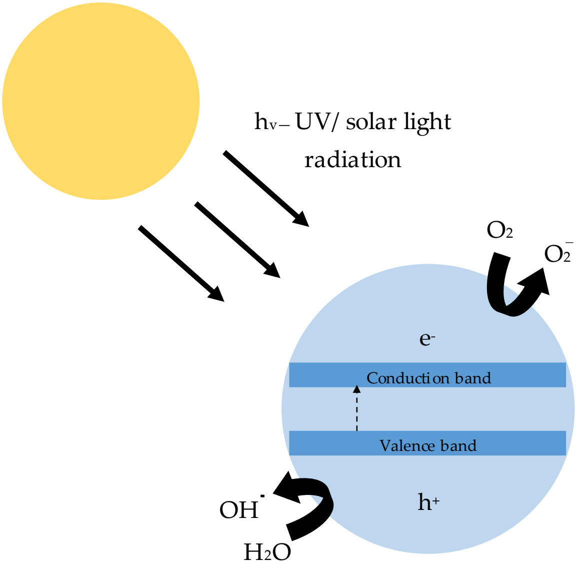

Figure 1. General mechanism of the photocatalytic reaction.

As shown, titanium dioxide grains, or other photocatalyst grains, must be exposed to UV/solar radiation for a photocatalytic reaction to occur. To accomplish this goal, cementitious materials incorporating that type of addition usually consist of two layers—one exposed to the external environment containing photocatalytic material and the other with no (or close to no) photocatalytic material. As photocatalysis occurs only in a near-surface material layer, dividing the composite into two parts reduces its overall cost without impacting its properties regarding air purification [7].

Due to its fine granulation (starting at 10 nm), titanium dioxide functions as nuclei for hydration products during the hydration of the binder. Due to this, the TiO_2 grains are usually covered with hydration products, limiting the effectiveness of the photocatalytic reaction of the hardened material (the TiO_2 grains must be exposed for it to occur) [8].

To improve the effectiveness of air purification from gaseous pollutants, the authors decided to investigate new methods of the surface modification of photocatalytic materials using polyacrylic superabsorbent polymers (SAP). Superabsorbent polymers can be described as cross-linked hydrogel networks which absorb water due to high osmotic pressure caused by the accumulation of ions within their structure [9]. Water absorption into the polymer network causes the SAP grains to increase their volume, pushing ions apart. With its network stretched out, the osmotic pressure decreases. Hydrogel obtained in that way can later desorb water stored in its volume under external pressure or due to changes in the properties of the desorption environment [10]. For that reason, SAP are usually used as an internal curing agent in cementitious materials, preventing the cement matrix's self-desiccation and promoting the hydration of the binder.

As the SAP hydrogel is introduced into the cement matrix, it desorbs water due to the high electrochemical activity of the environment. This process is prolonged (water desorbs from SAP during more than 30 days from its introduction into cementitious material) compared to water absorption time (usually 5–15 min in a water environment) as water desorption occurs during hydration and is limited by water pressure within the pore network and its microstructure [11].

The SAP also facilitates hydration in the direct vicinity of its grains. This effect was linked to the course of water desorption from the SAP grains. As water desorbs from SAP, it creates a thin film over the volume of a shrinking SAP hydrogel grain, which acts as an environment of intense hydration of the binder [9]. This phenomenon can be used to introduce various nanoparticles into cementitious material with the view of increasing their homogenous distribution within the cement matrix (Figure 2).

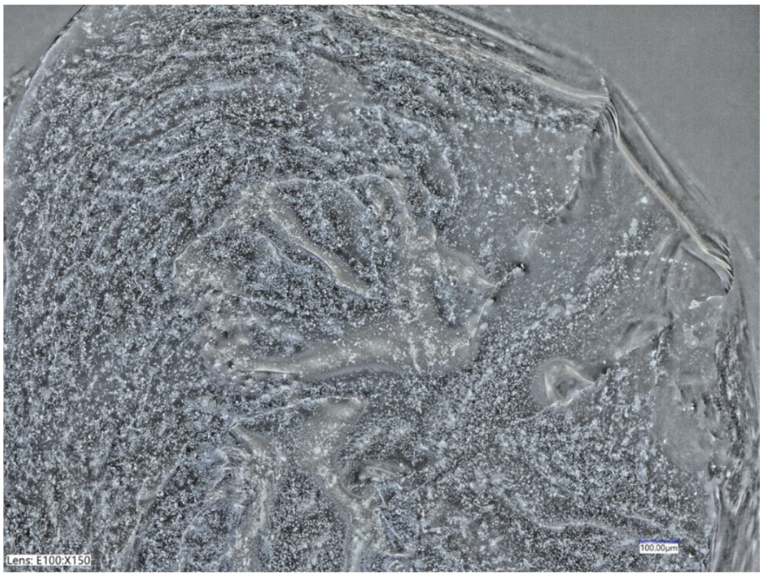

Figure 2. SAP hydrogel grain covered with nano-grains of titanium dioxide used in the study.

2. Materials and Methods

The main goal of the research was to increase the content of TiO_2 on the exposed surface of the material and obtain its homogenous distribution over the entire surface of the element. The phenomenon of adsorption of solid particles on the outer layer of the SAP grains was utilized to achieve it. In molds (in which samples for air purification tests were prepared), a thin layer of SAP (either in non-saturated or hydrogel form) was placed and sprayed over with 5–7 g of TiO_2 water dispersion. Next, the photocatalytic mortar of a proposed composition was poured into the mold (Figure 3).

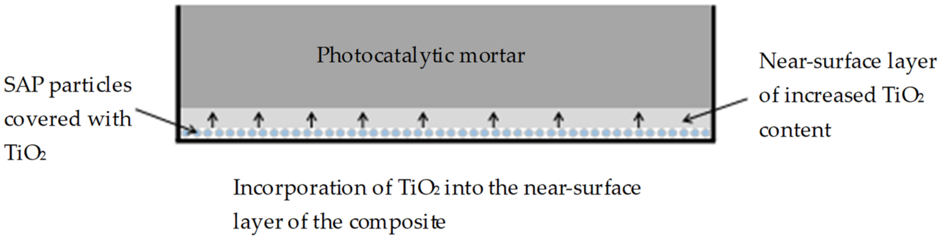

Figure 3. Method of surface modification with a reverse layer order—after demolding, the bottom surface was considered as an exposed surface and tested in air purification tests.

The ability to purify the air from harmful gaseous pollutants is an essential aspect of photocatalytic composites, so the viability of each solution was assessed through the air purification tests from NO and NO_x.

The cement used in this study—CEM II/A-S 52.5R (Ożarów, Poland)—met the requirements of EN 197-1 [12]. The study used two types of fire-dried quartz sand aggregates of different granulations—0.1/0.5 and 0.5./1.2 (Łajski, Poland)—which met the requirements of EN 13139 [13]. Two types of titanium dioxide were used: TiO_2 (A)—K7000 (Leverkusen, Germany) and TiO_2 (B)—P25 (Shanghai, PRC) of properties in the powder state presented in [6] (Table 1). TiO_2 (A) represented a VLA (visible light active) photocatalyst, while TiO_2 (B) represented a UV-A (UV light active) photocatalyst. VLA photocatalysts are active in both UV and visible light. However, their market price is several times higher than for

UV-A photocatalysts. Due to this fact, a mix of two photocatalysts was used so that the obtained photocatalytic material would have the capability to purify the air in both UV and visible light, with its overall price reduced.

Table 1. The content of crystalline phases and the size of crystallites (measured via XRD), and specific surface area (measured via BET).

Photocatalyst	Phase [%]		Size of Crystallites [nm]		Specific Surface Area [m^2/g]
	Rutile	Anatase	Rutile	Anatase	
TiO_2 (A)	-	100	-	10	246.8 ± 2.9
TiO_2 (B)	13	87	54	33	53.8 ± 0.2

Titanium dioxide was introduced into the mortar as a dispersion made of a portion of mixing water and a PCE superplasticizer (SP). As TiO_2 agglomerates in dry conditions, it was decided to use mechanical mixing and sonication to reduce its average grain size. Polyacrylic superabsorbent polymer (sodium acrylate and acrylic acid polymer) (Ludwigshafen, Germany) of properties described in [9] was used as a surface modification agent.

The water used in this study met the requirements of EN 1008 [14]. An additional mass of the PCE superplasticizer (SP) that met the EN 934-2 [15] requirements was added to mortars to modify their rheological properties (Myślenice, Poland). All described components were used to prepare a photocatalytic mortar. For each of the prepared series of samples, different surface modification techniques were applied (Table 2). The mass amount of dispersion was chosen so that the TiO_2 content in the composite would be 12.5 kg/m^3.

Table 2. Composition of the prepared mortar and information regarding the type of applied surface modification for each series of samples.

ID	Description	Cement [kg/m^3]	Water [kg/m^3]	0.1/0.05 [kg/m^3]	0.5/1.2 [kg/m^3]	TiO_2 Water Dispersion [kg/m^3]	SP [kg/m^3]
REF	Reference—no modification	780	255	574	574	72	3.3
REF—D	Reference—a layer of water TiO_2 dispersion						
SAP D	A layer of non-saturated ('dry') SAP covered in TiO_2 dispersion						
SAP H	A layer of water-saturated SAP hydrogel covered in TiO_2 dispersion						

The designed mortars were prepared according to the mixing procedure described in EN 196-1 [16]. The consistency of the mortar was tested based on EN 1015-3 [17]. Due to the low viscosity of the prepared mortar, only free flow was measured. After 24 h, samples were demolded and cured in the curing chamber (temperature 20 ± 2 °C, relative humidity RH $\geq$ 95%) until further tests. The tensile and compressive strength of the hardened mortar after two days were tested according to EN 196-1 [16] (Table 3) on 40 mm × 40 mm × 160 mm samples. As the considered surface modification techniques did not include the modification of the material's composition in its entire volume (only within an approx. 1–2 mm layer of the sample), it was assumed that the strength characteristics of the material would remain unchanged compared to the reference series.

The air purification from the nitrogen oxides test was performed according to the procedure developed during the 'Technology for the production of innovative self-cleaning prefabricated facade and surface elements that improve air quality' TECHMATSTRATEG-III/0013/2019 project. Tests were performed on 40 mm × 140 mm × 160 mm samples made from the designed photocatalytic mortar after 28 days of curing.

Table 3. Average compressive, tensile strength and consistency of prepared mortar.

Consistency—Free Flow [mm]	Compressive Strength [MPa]	Tensile Strength [MPa]
300	39.3 (CV = 4.4%)	5.9 (CV = 4.0%)

Before the test, the tested surface was cleaned of antiadhesive agent and other organic pollutants. It was sprinkled with distilled water, scrubbed, dried at 60 °C for two hours, and placed in the irradiation chamber for 16 h, with the test surface facing the light source, where the surface organic impurities were burned in UV-A radiation (irradiance 10 W/m^2). After that, the surface was cleaned with distilled water and dried at 60 °C for 2 h. The air purification tests were performed during the earliest two hours after the last drying cycle.

The sample was then placed in the glass reaction chamber with the tested surface facing the light source. The temperature in the glass reaction chamber during the experiment was kept at 25 ± 3 °C and the relative humidity at 40 ± 5%. The gas flow was maintained at a constant value of 2 L/min.

This study consisted of several stages, including filling the reaction chamber with nitrogen oxides to achieve a concentration of 100 ± 5 ppb (parts per billion, 10^{-9}), irradiating the sample with a UV-A light with an irradiance of 0.2 W/m^2, and measuring the concentration of nitrogen oxides while maintaining the gas flow. Then, the concentration of nitrogen oxides after switching off the light source while maintaining the gas flow was measured. In the next step, the reaction chamber was emptied of nitrogen oxides. Consecutively, the same procedure was performed for visible light with an irradiance of 115 W/m^2 and for a combined presence of UV-A and visible light with an irradiance of 0.2 W/m^2 and 115 W/m^2, respectively.

The nitrogen oxide concentration in the performed tests was approximately 100 ppb to model the actual NO_x concentration in Warsaw [6]. The UV-A and visible light irradiance were chosen as 0.2 and 115 W/m^2 to model the UV index of 8 (summer solar radiation conditions in the Polish territory) and the autumn/winter irradiance of visible light.

3. Results and Discussion

The introduction of an additional layer of SAP in either non-saturated or saturated (hydrogel) form significantly affected the distribution of TiO_2 on the surface of the mortar. An increase in the efficiency of air purification was observed for all light sources (Figure 4).

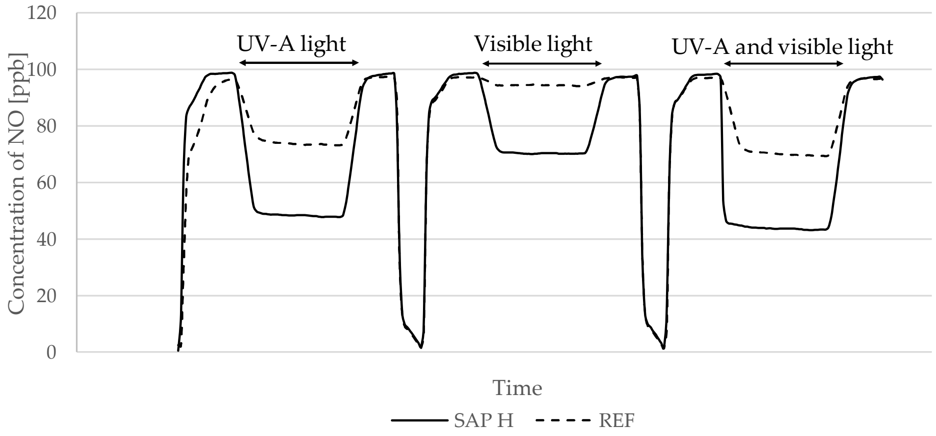

Figure 4. The efficiency of air purification from NO pollutants on a mortar sample formed in a mold with a layer of SAP hydrogel covered in TiO2 dispersion (SAP H) and reference series with no surface modification (REF). The test consisted of three parts: the study of the phenomenon of photocatalysis in UV-A light (first decrease in NO concentration), in visible light (second decrease in NO concentration), and in combined UV-A + visible light (third decrease in NO concentration). [ppb]—parts per billion, 10-9.

The photocatalytic mortar made with the SAP hydrogel layer showed the highest relative reduction of gaseous pollutants among the tested samples (Tables 4 and 5). The lowest coefficient of variation also characterized it. In the case of the photocatalysis intensity in visible light, compared to the reference series, the relative reduction of the NO concentration increased from 5.67% to 26.15%, and the relative decrease in NO_x concentration increased from 3.05% to 24.12%. The relative NO and NO_x concentration reductions increased to a slightly lower extent in the case of a layer made of non-saturated SAP. Spraying molds with dispersion alone also contributed to an increase in the relative reduction of the analyzed pollutants. However, this method was characterized by the highest coefficient of variation of all the tested series (from 18 to 37%). This observation suggests an uneven dispersion distribution on the surface of individual samples. The rheological properties of the dispersion itself are probably responsible for this phenomenon. When spraying the molds with a suspension with a viscosity similar to that of water, along with introducing the photocatalytic mortar into the mold, some of the dispersion previously placed flows out of the mold in an uncontrolled way, contributing to the uneven distribution of the photocatalyst on the surface.

Table 4. Relative reductions in NO concentrations in performed tests for all considered surface modification techniques.

ID	Description	The Relative Reduction in the Concentration of NO [%]					
		UV-A	**CV [%]**	**Visible Light**	**CV [%]**	**UV-A + Visible Light**	**CV [%]**
REF	No modification	26.85	10.58	3.50	16.85	30.87	9.36
REF—D	Water dispersion layer	33.64	18.02	5.67	24.95	37.77	18.75
SAP D	Non-saturated SAP with TiO_2 dispersion layer	48.05	7.11	24.41	16.89	52.93	6.01
SAP H	SAP hydrogel with TiO_2 dispersion layer	53.47	4.90	26.15	11.13	59.09	2.23

Table 5. Relative reductions in NO_x concentrations in performed tests for all considered surface modification techniques.

ID	Description	The Relative Reduction in the Concentration of NO_x [%]					
		UV-A	**CV [%]**	**Visible Light**	**CV [%]**	**UV-A + Visible Light**	**CV [%]**
REF	No modification	19.31	10.07	3.05	15.91	25.39	8.46
REF—D	Water dispersion layer	23.37	37.12	4.31	33.52	30.25	29.54
SAP D	Non-saturated SAP with TiO_2 dispersion layer	37.73	12.63	22.83	20.36	45.86	9.02
SAP H	SAP hydrogel with TiO_2 dispersion layer	44.23	12.01	24.12	13.31	51.88	4.12

The proposed surface modification method with SAP significantly affected the efficiency of purifying the air from NO and NO_x in visible light conditions. As one of the considered photocatalysts (K7000) is a VLA (visible light active) material, the SAP layer contributed to its better exposure to external radiation, increasing the overall efficiency of the material in purifying the air in conditions simulating common autumn/winter conditions.

Due to their properties, the SAP grains promote hydration in their direct vicinity [18]. This effect is linked with the kinetics of water desorption from the SAP structure—the formation of a thin water film on the outer layer of the SAP grain that acts as an environment of intense hydration/crystallization [9,19]. In the case of SAP covered with the TiO_2 grains, this phenomenon allowed for the immobilization of the TiO_2 grains in the near-surface layer and its crystallization on the surface, increasing its exposure to external radiation (Figure 5). However, due to water entrapment in the mold due to its continuous desorption from SAP during hydration, the porosity of the tested surfaces significantly increased. As the proposed surface modification method represents a first step in the development of surface modification methods for photocatalytic cementitious materials, in future iterations, the mold surface exposed to the SAP-TiO_2 layer is going to be prepared as a semi-permeable/sponge-like layer to limit the influence of the excess water released from SAP on the surface porosity.

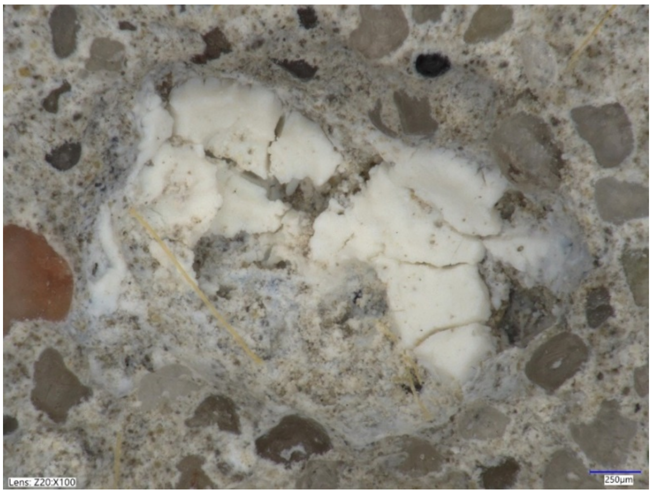

Figure 5. Micrograph of crystallized TiO_2 on the surface of the photocatalytic mortar.

4. Conclusions

Based on the performed research, several conclusions can be drawn:

- Modifying the surface of the composite solely with water dispersion of TiO_2 increased the efficiency of the photocatalytic reactions. However, due to the low viscosity of the modifying agent, this method of modification did not provide a homogenous distribution of TiO_2 on the surface of the cementitious composite (the coefficient of variation for that solution increased significantly);
- Surface modification with SAP, either in non-saturated or hydrogel form, increases efficiency in air purification from NO and NO_x pollutants under considered UV-A and visible light irradiance and allowed for the homogenous distribution of TiO_2 over the surface of cementitious material;
- Surface modification with the SAP hydrogel contributed to the highest reductions in concentrations of NO and NO_x under all considered light sources.

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