A REVIEW ON DEVELOPING SELF-CLEANING CEMENTITIOUS MATERIALS

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ABSTRACT

At present, the photocatalytic properties of TiO_2 are known worldwide. Research on cement composites materials achievement with self-cleaning properties (using the photocatalytic character of TiO_2) is a field of real interest. The purpose of this article was to present a synthesis of the research results reported in the specialty literature. The results of the theoretical analysis have shown that the properties of the concrete are positively influenced as long as the amount of nanoparticles is not in excess. In the case of an excess of TiO_2 nanoparticles, or their insufficiency, the effect on the concrete property is inversely.

Keywords: concrete; self-cleaning; nanoparticles of TiO_2; photocatalysis.

REZUMAT

În prezent, la nivel mondial, sunt cunoscute proprietățile fotocatalitice ale TiO2. Cercetările privind realizarea unor materiale compozite cementoase cu proprietăți self-cleaning (folosindu-se caracterul fotocatalitic al TiO_2) reprezintă un domeniu de real interes. Scopul acestei lucrări a fost să prezinte o sinteză a rezultatelor cercetărilor raportate în literatura de specialitate. Rezultatele analizei teoretice au arătat că proprietățile betonului sunt influențate pozitiv atâta timp cât cantitatea de nanoparticule nu este în exces. În cazul unui exces de nanoparticule de TiO_2 sau dacă acestea sunt insuficiente, efectul asupra proprietăților betonului este invers.

Cuvinte cheie: beton; autocurățare; nanoparticule de TiO_2; fotocataliză.

1. INTRODUCTION

Titanium dioxide (TiO_2) is a crystalline substance with photocatalytic properties. This property is based on the fact that, under the action of sunlight or UV radiation, an oxidation-reduction reaction occurs. This substance can be found in three forms of crystallization, namely: anatase, rutile and brukite. The use of the anatase form of TiO_2 has the most advantages compared to other substances with photocatalytic properties: it is chemically stable at the action of acids and bases, has the ability to decompose both organic and inorganic substances, has a relatively low price and it is not toxic. Due to the decomposition capacity of organic and inorganic substances, it contributes to the depollution, sterilization and elimination of unpleasant odors (Folli et al., 2015; Guo et al., 2009; Guerrini, 2012; Ravesloot, 2012; Awadalla et al., 2011).

TiO_2 has been used since the 20th century in the fields of pharmacy, cosmetics and paint preparation due to its effect called "chalk-effect". TiO_2 properties have been known since the 1950s, but their exploitation in practical applications have only begun in 1972 (purification of water) by Fujishima and Honda. After showing the capability of TiO_2 to purify the water, attention was directed to other uses of TiO_2, namely in the production of materials that have both anti-microbial, antibacterial and anti-algic properties. In 1995, one of the most important properties, namely the superhydrophilic effect on a specified surface of a composition of TiO_2-SiO_2 in the presence of UV rays, was accidentally discovered. This effect is produced by the oxidation-reduction reaction of H_2O, forming OH^- groups. Due to the multitude of OH^- formed groups, the water that reaches the surface of the TiO_2-SiO_2 material forms lamellar droplets that clean the impurities on the surface of the material. Unlike TiO_2 where the photocatalytic effect ceases without UV radiation, for the TiO_2-SiO_2 compositions the photocatalytic effect continues for hours even after the removal of the UV radiation source (Chen and Poon, 2009; Eshaghi et al., 2011; Ohtani, 2011; Chen et al., 2005).

Unlike TiO_2 where the photocatalytic effect ceases in the absence of UV radiation, in the case of TiO_2-SiO_2 compositions the photocatalytic effect continues for hours even after removal of the source of UV radiation.

The first official publication on the production of self-cleaning cement materials was recorded in 1997 by Luigi Cassar (Luigi Cassar et al.; Mujkanovic et al., 2016; Smits et al., 2013).

Buildings are exposed to various weather conditions, atmospheric pollutants, and microorganisms, resulting in deterioration in terms of both mechanical properties and operational safety, as well as an aesthetic appearance, which implies direct and indirect costs at some point. At the same time, buildings also have the advantage of exposure to sunlight, UV radiation, having large exposed surfaces, which led to the idea of creating facades that may self-heal, so that they could self-sustain. Thus, the first attempts were made using white cement-based materials to which TiO_2 was added. The first relevant results were reported in 1996, and in 2003 the Dives Church in Misericordia in Rome was inaugurated, the first building with self-healing properties. Other buildings / elements made using self-cleaning cement materials are: The Phillip and Patricia Frost School of Music, USA, Torre de Especialidades Hospital, Mexico City, The Sarajevo Bridge, Barcelona, Spain, Mortara School, Italy, Cité de la Musique, Chambéry, France, pavements and pedestrian areas in the cities of Kawasaki, and Saitama, Japan, Bergamo, and Northern, Italy, artistic monuments, sculptures at St. Anthony Falls Bridge, Mineapolis. There are reports showing that by the year 2003 approximately 5000 constructions in Japan were built using TiO_2 nanoparticles enriched with cementitious composite matrices (Janus and Zajac, 2016). In 2015, the latest use of cementitious composite material was made by building the famous Palazzo Italia Expo 2015, Milan, Italy, which was awarded with the American Concrete Institute's "The Excellence Award 2016".

Currently, the use of TiO_2 nanoparticles at the most of their efficient use and with all their properties, is achieved either by coating surfaces with TiO_2 dispersion solutions, by coating surfaces with a superficial cement composite with TiO_2 addition or by making some elements fully from concrete enriched with TiO_2. The latter case is the least favorable from the point of view of the high consumption of nanoparticles, some of which are not exploited due to the positioning in the depth of the composite mass.

The purpose of this article is to synthesize the current state of research in the field and to study the possibility of producing cementitious materials with self-cleaning properties in the laboratory.

2. INFLUENCE OF TiO_2 NANOPARTICLES ON MORTAR AND CONCRETE PROPERTIES

2.1. Properties of fresh concrete

Research has shown the influence on the properties of fresh concrete TiO_2 nanoparticles are introduced in the mixtures (the most commonly used type of nanoparticles being "Degussa P25"). By introducing TiO_2 nanoparticles in the mixtures an increase in the amount of water is required in order to achieve the standard consistency of ordinary concrete (Janus and Zajac, 2016; Zhao et al., 2015) and a decrease in workability and initial and final setting time (Janus and Zajac, 2016; Sorathiya et al., 2017; Zhang et al., 2010).

This can be explained based on the catalytic effect of the nanoparticles on the cement hydration reaction and on the fact that they can function as possible concentrates of the hydration products.

However, some research shows that replacing cement with a maximum of 1% TiO_2

does not significantly affect the fluidity of the cement mortar (Zhang et al., 2010; Kadri and Duval, 2002), even if it has been used or not as an addition.

Other researches have also indicated that: the porosity of the cement paste is reduced and the distribution of the pores in the paste (Janus and Zajac, 2016; Sorathiya et al., 2017) increase both the hydration heat and the hydration rate of the cement (Janus and Zajac, 2016; Zhang et al., 2010), the structural orientation of the cement crystals CH (Janus and Zajac, 2016) and their size (Ma et al., 2015).

2.2. Properties of hardened concrete

Changing the composition of the mortar and fresh concrete by adding, or replacing a part of the cement with TiO_2 nanoparticles are also influenced by the properties of the cementitious materials in hardened state. Ma and other researchers (Ma et al., 2015; Lucas et al., 2013; Meng et al., 2012; Jalal, 2012) have shown that mechanical properties of the material are improved if the amount of TiO_2 nanoparticles is not added in excess, due to the smaller crystal's CH sizes and the formation of a larger and better organized C-H-S gel. Excessive TiO_2 addition, however, results in a decrease in the performance of the composite. Most references in the literature mention a fluctuation of the mechanical properties, especially compressive strength. Although it is improved at small ages (7 days) (Janus and Zajac, 2016; Zhang et al., 2010; Odedra et al., 2014: Jalal, 2012; Khushwaha et al., 2015), at older ones, there are random variations that cannot be mathematically correlated directly with the nanoparticle content. Some research indicates that the mechanical strength of the composite is not adversely affected to a maximum of 6% TiO_2 added (Zhang et al., 2010), other studies reduce this percentage to 5% (Janus and Zajac, 2016), 3% or even 1% (Sorathiya et al., 2017). The compressive strength behaviour of the self-cleaning materials has been explained by some researchers with consideration to the agglomeration of nanoparticles, the modification of the porosity of the cement matrix and the appearance of some "weaknesses" in the mass of the composite. Controversially, other studies show that even with the addition of TiO_2 there is even an increase in compressive strength, which can vary between 59% and 76% (Sorathiya et al., 2017). Figure 1 shows the compressive strength synthesis of some of the relevant literature research on self-cleaning materials reported in the literature (Janus and Zajac, 2016; Zhang et al., 2010).

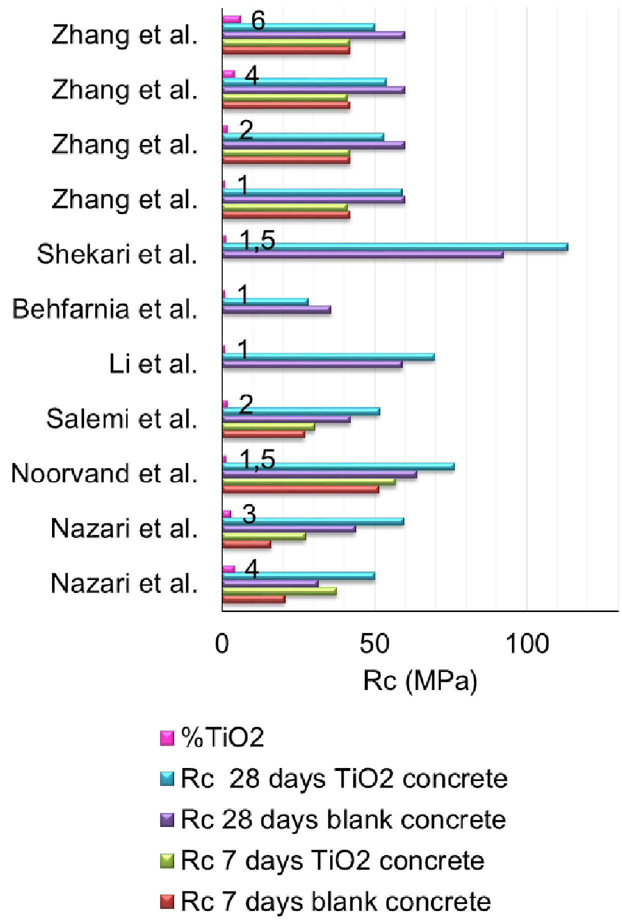

Fig. 1. Influence of TiO_2 on the compressive strength (literature review)

The majority of studies have concluded an acceleration of the maturing process of registering a concrete lower the compressive strength increases within 7-28 days compared to the blank concrete, as shown in figure 2.

In terms of flexural strength, it has been reported in the literature that due to a better structure of the material, this parameter is also improved, provided by the fact that the hydration-hydrolysis reactions of the cement granules are not hindered by excess nanoparticles (Ma et al., 2015; Lucas et al., 2013; Jalal, 2012).

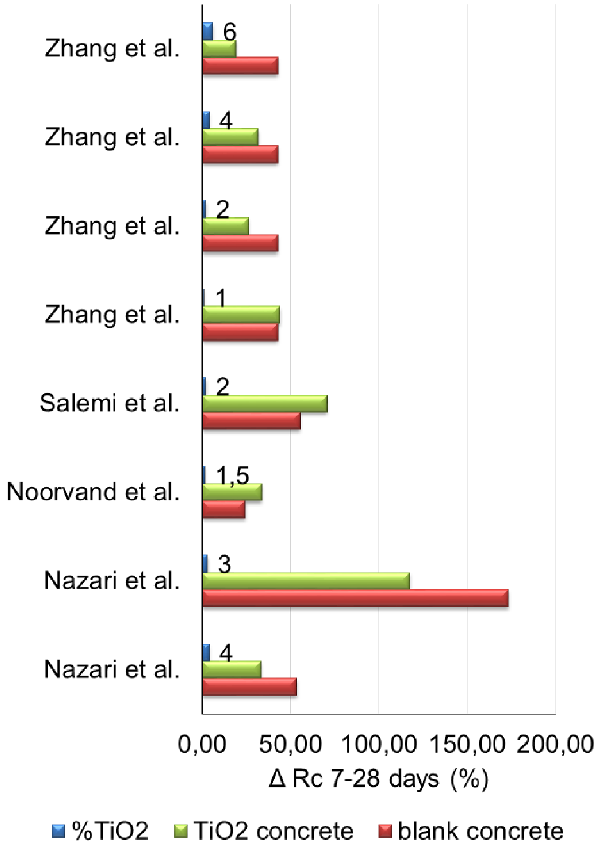

Fig. 2. Influence of TiO_2 on the increase of compressive strength within 7-28 days (literature review)

As a result of lower porosity of the material, there is also an increase in frost-thaw resistance (Janus and Zajac, 2016; Salemi et al., 2014; Fiore et al., 2013) (probably due to the reduction in water absorption (Ma et al., 2015)), a decrease in the carbonation depth (Janus and Zajac, 2016), is found, but this finding is still controversial, resistance to chemical corrosive action and a 180% increase in abrasion resistance of concrete with 1% TiO_2 nanoparticles compared to the ordinary concrete samples (Janus and Zajac, 2016; Fiore et al., 2013).

When exposed to heat and when reaching 750°C, nanoparticulate concrete loses its photocatalytic property as a result of altering the crystalline structure of TiO_2 from anatase to rutile, but no changes were reported compared to control concrete mixes.

3. INFLUENCE ON THE ENVIRONMENT

Although there is still much controversy over the influence of TiO_2 nanoparticles on the properties of fresh and hardened concrete, the contribution of the nanoparticles cannot be disputed in terms of water and air purification capabilities, also antibacterial, anti-algic, antimicrobial and antifungal effects, and self-cleaning ability of superhydrophobic surfaces (Benedix et al., 2000; Cassar, 2005; de Marco et al., 2012; Hashimoto et al., 2005; Huang et al., 2012; Janus and Zajac, 2016; Ma et al., 2015; Sassolini et al., 2014).

The antibacterial, antimicrobial and antifungal effect of TiO_2 is also analysed and documented in the literature (Ma et al., 2015) for some of the most common microorganisms (Cladophora, Chlorella vulgaris, Escherichia coli, Aspergillius niger), cementitious composites with the addition of TiO_2 nanoparticles are effective for disinfection, sterilization and purification of surfaces, water and air from sensitive public spaces (hospitals, schools, restaurants, airports, etc.). Furthermore, research has shown that surfaces retain and regenerate their aesthetic appearance and colour under the action of UV radiation (Hashimoto et al., 2005; Janus and Zajac, 2016; Kumar et al., 2013; Mujkanovik et al., 2016; Ohama and Van Gemert, 2011) and maintain their self-cleaning capability even after continuous exposure to UV for 1500 hours, thereby reducing maintenance costs, water consumption pollution by detergents. As far as air pollution, Luigi Cassar called the concrete with TiO_2 "smog-eating concrete". Sassolini and other researchers (Sassolini et al., 2014) consider that the realization of TiO_2 nanoparticle cement surfaces is a passive form of safety technology to increase (CBRN) safety as a result of self-decontamination capability of surfaces. Research results (Chen and Li, 2007; Ohama and Van Gemert, 2011) have shown that TiO_2 contributes to the elimination of CO, NO_x, SO_x, NH_3, aromatic hydrocarbons, VOC. The mechanism for eliminating them is not simple and, at present, not entirely clear. As a result, there are already many locations worldwide where either buildings, pavements and concrete pedestrian areas with TiO_2 nanoparticles are being built to reduce urban pollution but also military and strategic interest projects.

Over the past 15 years, some specific analysis methods have been standardized on the effect of air, water purification, self-cleaning and antibacterial effects. Most of these are Japanese and Italian national standards, some of them being assimilated also internationally.

4. CONCLUSIONS

Based on the above mentioned, it can be concluded that:

- TiO_2 nanoparticles have water and air purification properties, antimicrobial, antifungal and anti-algic in the presence of UV.
- Photocatalyzed, a TiO_2-SiO_2 composition becomes superhydrophilic, as a result of the oxidation-reduction reaction of H_2O a multitude of OH^- groups being formed and the water that reaches the surface of the TiO_2-SiO_2 material does not form droplets but the lamellae reducing impurities. The photocatalytic effect continues for hours, even days after removing the UV source.
- UV activated TiO_2 nanoparticles facilitate the decomposition of organic pollutants (fats, oils, aromatic hydrocarbons) into much simpler compounds that can be easily washed out by rainwater, while driving dust particles deposited on the superhydrofil surface.
- Inorganic pollutants of nitrogen, sulphates, acids, air, water or solids are transformed by oxidation / neutralization reactions into stable compounds, oxides / salts, which are then washed by rainwater.
- Photocatalytic activation mechanisms are not yet fully understood.
- In hardened state of the concrete, TiO_2 nanoparticles cause acceleration of hydration-hydrolysis processes, modification of the internal organization of hydrosilicate gel and crystals of cement hydration products, reduction of porosity.
- In the concrete hardened it was found the growth of resistance mechanical, resistance to freeze-thaw, abrasion, or chemical agents.
- It is obvious that for obtaining a cementitious composite material with preliminary TiO_2 addition, it is necessary to establish the optimum quantity of photocatalytic nanoparticles that are added into the mix, so that the mechanical performances are not affected and an analysis of the parameters that affect this type of material, because there is still controversy in the literature.

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