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### Preliminary experimental study on the effects of surface-applied photocatalytic products on the durability of reinforced concrete



Alessandra Fiore<sup>a,\*</sup>, Giuseppe Carlo Marano<sup>a</sup>, Pietro Monaco<sup>a</sup>, Alessandro Morbi<sup>b</sup>

<sup>a</sup> Technical University of Bari, DICAR, Via Orabona 4, 70125 Bari, Italy <sup>b</sup> Italcementi Group S.p.A, Bergamo, Italy

#### HIGHLIGHTS

• The effect of photocatalytic products on concrete durability was tested.

• The photocatalytic activity of titanium dioxide was used.

• The durability of concrete in terms of carbonation resistance was improved.

• Surface-applied photocatalytic products provide protection for steel bars in concrete.

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#### ABSTRACT

The aim of this paper is to assess, by the results of suitable experimental tests, the durability performances of surface-applied concrete layers that incorporate a photocatalytic material such as titanium dioxide. The use of photocatalytic materials for air purification has been developing rapidly in the last decades. Within this framework, the proposed experimental study is particularly significant considering that, although there are many advantages in applying photocatalytic construction materials, during the TiO<sub>2</sub>-photocatalysis a large variety of organics, viruses, bacteria, fungi, algae can be totally degraded and mineralized to CO<sub>2</sub>, H<sub>2</sub>O and harmless inorganic anions. The mineralized amounts of CO<sub>2</sub>, deriving from both the photocatalytic oxidation itself and the external ambient, can progressively activate a chemical deterioration due to carbonation. It is then important to investigate the resistance properties of photocatalytic concrete products against carbonation.

The effects of the photocatalytic activity on the durability of concrete have been assessed by using accelerated carbonation and corrosion of reinforcing steel tests. In order to keep the photocatalytic process ongoing, specimens with finish coatings containing  $TiO_2$  were put in direct contact with air (water in the form of humidity) and were subjected to light radiation.

Results show that photocatalytic concrete products applied on the surface of concrete improve the property of carbonation resistance and reduce the corrosion propagation rate of reinforcing bars with respect to the case of cement coatings without any photocatalysts. The adopted experimental procedure can give a first contribution in order to understand if the photocatalytic activity of titanium dioxide creates a photocatalysed system acting as a protective barrier against the deterioration processes.

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#### 1. Introduction

Reinforced concrete (RC) has been used as the main structural material in the construction industry for many years. Nevertheless in the last decades the rapid deterioration of RC structures due to alkali-aggregate reaction, chloride-induced corrosion and carbonation has caused engineers to seek new ways to rehabilitate aging structure and to improve durability properties of concrete under aggressive environments. Among the countermeasures adopted against the deterioration of reinforced concrete structures, the use of composite materials has shown great potential in the area of durability of RC structures. The cementitious-polymeric composite materials are used for the modification of concrete surfaces and include finish coatings, barrier penetrants, linings, liquid-applied membrane waterproofing materials and permanent forms, which allow to eliminate or control chemical degradation factors in RC structures [1]. Considerable research has been carried out on concretes containing binary cements based on fly ash or silica fume which have shown advantages such as improved durability [2,3]. Polymer-coated reinforcing bars, including epoxy-coated reinforcing bars, FRP reinforcements

<sup>\*</sup> Corresponding author. Tel.: +39 080 5963743; fax: +39 080 5963719. *E-mail address:* a.fiore@poliba.it (A. Fiore).

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and continuous fiber reinforcing materials, are employed as corrosion-resistant materials [4,5]. Also the use of corrosion inhibitors is resulted to be an effective method in order to control rebar corrosion [6,7].

Only recently technical codes have introduced the durability and reliability issues, which both rank amongst the most decisive structural performance characteristics. In particular Model Code 2010 specializes in the durability design of concrete structures [8]. The objective is to identify agreed durability related models and to prepare the framework for the standardization of performance-based durability design approaches. According to this innovative approach, structural design should take into account environmental actions leading to the degradation of concrete and embedded steel.

In this framework this paper presents the results of a systematic study on assessing the effects of photocatalytic concrete products on the durability of reinforced concrete. Until now photocatalytic materials have been applied on concrete pavement surfaces and external building surfaces in urban areas mainly to reduce air pollution caused by road traffic and industry. In fact the use of titanium dioxide as photocatalyst mainly allows, under the UV-A part of the sunlight, the photochemical conversion of nitrogen oxides (NO<sub>x</sub>), emitted in the atmosphere by car traffic and transport, to low concentrated nitrates due to heterogeneous photocatalytic oxidation [9,10]. The reaction products in the form of nitrate compounds are water soluble and will be flushed from the active concrete surface by rain. The nitrate compounds can be finally extracted from the rain water by a standard sewage plant.

In addition the nature of the cement matrix is particularly suitable for incorporating titanium dioxide  $(TiO_2)$  powders and other photo-oxidation products. As a result a variety of products containing TiO<sub>2</sub> are already available on the European market and their capacity to mitigate air pollution is widely proven.

Differently from the above approaches, this paper presents the results of experimental tests carried out in order to evaluate the durability properties of photocatalytic concrete products in terms of carbonation of concrete and corrosion of reinforcing steel [11–13].

In fact the photocatalytic oxidation activated by the titanium dioxide not only allows the conversion of nitrogen oxides, but in general is capable of degrading a wide range of pollutants, both of organic and inorganic nature, under the influence of UV or solar light. In particular the photocatalytic oxidation can decompose the volatile organic compounds to harmless substances such as CO<sub>2</sub> and H<sub>2</sub>O [10]. Part of these reaction products can be transferred to solid  $CaCO_3$  in the outer pore system and the mineralized  $CO_2$ can be consumed by the carbonation. This effect is reduced by the contemporary production of H<sub>2</sub>O, so that it is difficult to establish the quantity of CO<sub>2</sub> involved in the carbonation process. On this topic it is worth noting that a special phenomenon, termed "photoinduced superhydrophilicity" has been discovered in the last years, according to which trapping of holes at the TiO<sub>2</sub> surface causes an high wettability [14]. In conclusion cover concrete during the photocatalytic degradation process can be exposed to some amounts of CO<sub>2</sub>, deriving both from the photocatalytic oxidation itself and the external ambient [15], which can activate a chemical deterioration due to carbonation.

It is then important to assess the carbonation resistance of photocatalytic concrete products in order to be sure to use their airpurifying properties without reducing the durability performance of the structure. This topic can be investigated just by suitable experimental tests, due to the different internal and external factors which can affect the amount of carbonation occurring with a given cement paste composition, such as water/cement ratio, chemical composition of the cement paste, curing time, internal and/or external relative humidity, external temperature, carbon dioxide concentration and texture of the surface [16,17]. The goal of the study is to assess the carbonation resistance of photocatalytic concrete coatings during the photocatalytic activity itself, reproducing real external ambient conditions. In the experimental setup photoactivity is produced thanks to the interaction between cement mortar surface containing TiO<sub>2</sub>, UV radiation and H<sub>2</sub>O (water in the form of humidity). In this case the reaction products are represented by hydroxyl radicals, hydrogen and/or superoxide ions [10]. The described experimental procedure can give a first contribution in order to understand if the application of photocatalysts in coatings of reinforced concrete structures can create a photocatalysed system acting as a protective barrier against the deterioration processes.

#### 2. Experimental details

#### 2.1. Concrete mix and casting of test specimens

Sixteen cubes ( $10 \times 10 \times 10 \text{ cm}^3$ , Type A specimen) and three reinforced slabs ( $20 \times 10 \times 5 \text{ cm}^3$ , Type B specimen) were cast for this experimental investigation (Fig. 1). Type CEM 32.5R II-A/LL Portland Cement (with Matera limestone) was used in the concrete mix for the test specimens. Table 1 gives the chemical properties of the concrete. Figs. 2 and 3 show the sections of Type A and B specimens respectively.



Fig. 1. Casting of test specimens: (a) Type A specimens; and (b) Type B specimens.

#### Table 1

Mixture proportions of concrete. Mix components Weight (%) Weight (kg/m<sup>3</sup>) CEM 32.5R II-A/LL Matera 100.0 300 Sand (0-4)VC 58.0 983.1 Fine aggregate (4-10)VC 13.0 225.6 Course aggregate (10-20)VC 29.0 4896 0.70 210 Water CRETV-M [03-1] additive 0.33 1.00



Fig. 2. Section of Type A specimen.

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