Cementitious materials and photocatalysis

Luigi Cassar
CTG Italcementi Group – Via G. Camozzi 124 – 24121 Bergamo (Italy)

Summary

While the primary function of concrete is structural, its pervasiveness in our society lends it to other functions and creates the need for it to maintain its integrity and aesthetic quality. Therefore, concrete with added functionality – for example, self-cleaning characteristics and the ability to remove pollutants – is desirable.Heterogeneous photocatalysis by semiconductor particles or coatings has now reached a high level of development and is a promising technology for the reduction of global environmental pollutants. Among the various semiconductor materials, TiO_2 in the form of anatase has attracted wide interest, due to its strong oxidising power under near-UV radiation, its chemical stability when exposed to acidic and basic compounds, its chemical inertness in the absence of UV light, and its absence of toxicity. TiO_2 has proved effective in the reduction of pollutants such as NO_x aromatics, ammonia, and aldehydes. Surprisingly, the use of TiO_2 in combination with cementitious materials has shown a favourable synergistic effect in the reduction of pollutants. These new materials have already found relevant applications in self-cleaning building walls and in the reduction of urban pollutants[(1,2)]. Several examples of applications possessing self-cleaning and depolluting abilities resulting from the photocatalytic properties of titanium dioxide contained in the cement matrix are shown.

Introduction

Photocatalysis plays a primary role in biological processes and environmental control activities. In particular, until the early 1900s, the production of both energy and materials were derived directly and indirectly from sunlight. In the 20th century, the demographic boom, the creation of new materials and the increasing oil and nuclear power exploitation for energy purposes led to an ever-increasing gap between nature and society.

We have been switching rapidly from a world where nature reproduces itself through light to a world of materials that must be made inert to guarantee stability. The need for a cleaner environment and better living standards urges us to change our mind about an environmentally-friendly use of sunlight. In this respect, photochemistry as applied to construction materials might turn out to be a winning solution. It is important to stress that the amount of solar energy impinging on the Earth's surface is about 5×10^{24} J per year, or more than 10^4 times the worldwide yearly consumption of energy.

A promising field where photochemistry is gaining ground from both a technological and economic point of view is the elimination of environmental pollutants. In recent years, scientific and engineering interest in the application of photocatalysis to semiconductors has been growing exponentially if we just consider the worldwide growth of patents and the 800-plus patent applications that have been published. This technology can contribute to improving our living standards, particularly within the urban context.

Results of tests performed enabled us to conclude that cementitious materials containing titanium dioxide, mainly in the form of anatase, when irradiated with adequate light, enhance the oxidation efficiency on the organic substances with which they come into contact. Based on experimental evidence, we can affirm that a building element containing cement to which TiO_2 has been added is capable of maintaining its aesthetic appearance unchanged over time, thereby contributing to reducing the dirtiness of surfaces exposed to specific polluting environments. Moreover, effectiveness in urban pollutant mitigation has been confirmed both in the laboratory and in the field.

Typical pollutants against which the photocatalytic system cement + TiO_2 can mitigate are NO_x, SO_x, NH_3, CO, volatile organic compounds such as benzene and toluene, chlorinated organic compounds, aldehydes, and polycondensate aromatic compounds. With respect to the improvement in our living standards, we believe that a massive and continuous use of photocatalysts in construction materials may be a new way of contributing to minimising contaminants that attack our urban environment.

1. Photocatalysis

Heterogeneous photocatalysis[3,4] is based on the irradiation of a semiconductor photocatalyst in contact with a liquid or a gaseous environment. TiO_2, ZnO, and CdS are widely used examples. The electronic structure of semiconductors is characterised by a filled conduction band and an empty valence band separated by a bandgap of energy (E_g). The absorption of a photon of energy equal to or larger than E_g promotes an electron from the valence band to the conduction band, leaving a hole in the valence band. The valence-band hole can oxidise electron donor molecules adsorbed on the surface, whereas the conduction-band electron can reduce acceptor molecules. For instance, the valence-band hole can react with water to produce a highly reactive hydroxyl radical, OH•. The conduction-band electron can be trapped by an adsorbed oxygen molecule to yield a superoxide ion, O_2– (Fig. 1). The efficiency of the whole photochemical process is a complex function of several parameters.

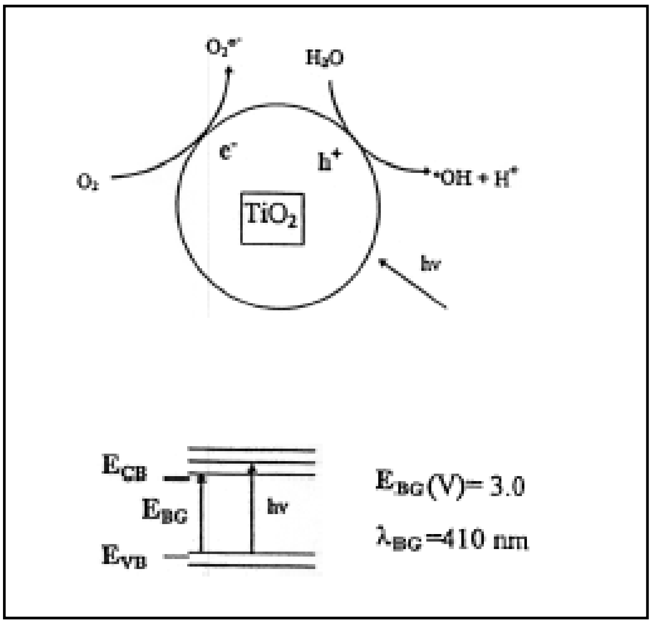

Figure 1: Photo-activation of TiO_2

One of the basic tenets of photochemistry is that, by absorption of photons, energy is injected in quanta of energy much larger than the ambient thermal energy. In addition, regardless of the intensity of the light, the energy of each photon is the same. For instance, the energy of photons in light at a wavelength shorter than 400 nm (blue and near-UV) is equivalent to a thermal energy of more than ~100*kBT* at room temperature. This is enough to overcome huge activation-energy barriers and to decompose most organic compounds, provided that the redox potentials are adequately matched.

Over the last few years, scientific and engineering interest in the application of photocatalysis by semiconductors has been growing exponentially, as illustrated by the huge growth in patents on the subject. In 2003, more than 800 international applications were published, and according to a recent estimation, more than 2000 companies are presently active in the photocatalysis market, mostly in Japan[5]. The elimination of environmental pollutants is the main concern of this effort (Fig. 2).

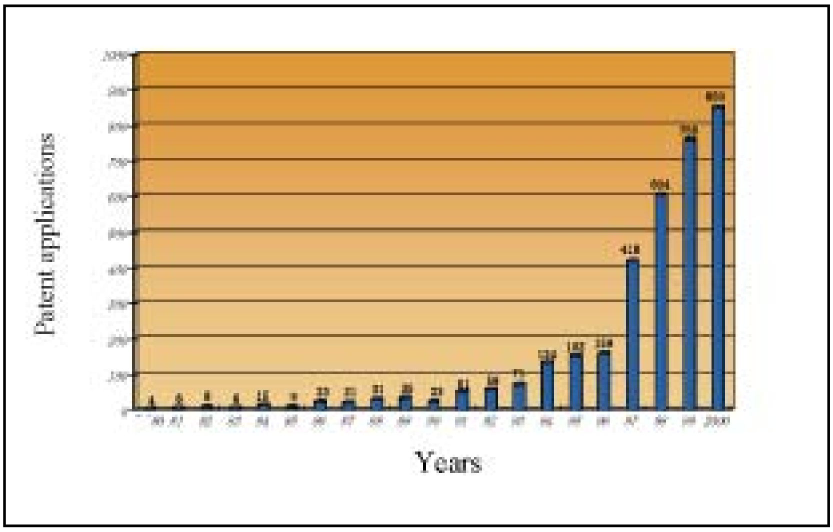

Figure 2: Number of photocatalyst patents applications

Titanium dioxide is the most widely used inorganic pigment for varnishes and plastics. The main crystallographic forms of TiO_2 are anatase and rutile, the former being photocatalytically much more active than the latter. The bandgap of anatase is of the order of 3.0 eV, which corresponds to a wavelength of 400 nm. Thus, the pigment used in industrial products is essentially rutile, in order to avoid photodamage. On the other hand, the high photoactivity of anatase has led to the development of a wide range of applications as photocatalytic coatings on various substrates such as glass and ceramic tiles that can photodegrade various noxious or malodorous chemicals, smoke, and cooking oil residues under low-intensity near-UV light[6-9]. Antibacterial tiles with TiO_2 coatings photocatalytically modified with Ag and Cu metal particles have also been developed, and the technology has been extended to silicone rubber used for medical devices and other polymer substrates[10]. TiO_2 surfaces exposed to near-UV light were also found to have an alternate distribution of hydrophilic and oleophilic submicrometre-sized regions (~500 nm), leading to surprising amphiphilic properties[10]. Furthermore, under UV irradiation, these surfaces become progressively superhydrophilic, presumably due to light-induced Ti^{3+} defect sites[11]. Thus, water droplets spread out and, if the substrate is glass, become transparent. This is the basis for antifog coatings. The holes photogenerated in the valence band of TiO_2 have a very strong oxidising power (3.0 V) and are able, for instance, to totally oxidise (to CO_2 and water) methane and ethane or partially oxidise higher hydrocarbons. In fact, this has been known for more than 30 years,[12,13] and since then, a wealth of compounds including alkanes, halogenated compounds, acids, surfactants, herbicides, and organometallics have been shown to be photodegradable by TiO_2[3,6].

2. Cement containing photocatalysts

A system comprising TiO_2 and cement has been studied recently within the framework of a strategy for alleviating environmental pollution through the use of construction materials containing photocatalysts. This technology for the photocatalytic degradation of organic pollutants is aimed at maintaining the aesthetic characteristics of concrete structures,[14–16]) particularly those based on white cement. The main reason for discoloration of cementitious materials is the accumulation of coloured organic compounds on their surfaces.

Suitable amounts of TiO_2 have been introduced into cement mixes to render the surface of the resulting structures photocatalytically active. In order to verify the photocatalysis, experiments focusing on the oxidation of several kinds of aromatic organic compounds have been carried out.[17] For instance, white cement disks have been impregnated with a phenanthroquinone solution (0.1 mg/cm2), yielding homogeneously yellow surfaces. Accelerated irradiation tests were then performed with a solar simulator (100 h of irradiation, corresponding to 1 year of sunlight). As shown in Fig. 1, rapid restoration of the clean surface was obtained.

These results open the way to the widespread development of self-cleaning concrete and mortar-coated walls. TiO_2-cement composites are expected to maintain their aesthetic characteristics unchanged over time, in particular the colour, even in the presence of aggressive urban environments. In fact, a white cement containing TiO_2 has already been used for the construction of the Dives in Misericordia Church in Rome[18] (Fig. 3), completed in 2003; the Cité des Arts et de la Musique in Chambéry, France (Fig. 4), completed in 2000; a school in Mortara, Italy, completed in 1999; and several buildings in Europe and Africa. Cementitious paints containing photocatalysts have also been developed [19] and applied on residential buildings (completed in 1997) in Italy.

Figure 3: Dives in Misericordia Church – Rome
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Figure 4: Cité des Arts et de la Musique - Chambéry

A particularly interesting aspect of TiO_2-cement composites is that there is a clear synergy between the cement and TiO_2 that makes cement an ideal substrate for environmental photocatalysis. Many photo-oxidising compounds, such as NO_2 and SO_2, are acidic. The basic nature of the cement matrix is particularly suitable for fixing both the polluting reagent and the photo-oxidation products at its surface.

3. Photocatalysis and the removal of NO_X

Photocatalysis has recently gained considerable recognition as a reliable method of NO_X abatement under mild experimental conditions, employing sunlight as a low-cost renewable energy source. Research under way at our laboratories and at other research institutions shows that cementitious material containing TiO_2 has very good potential application as a resolving technology in pollution control. [1,18,19]

The mechanism of nitrogen oxide removal by photocatalysis is not simple. It is assumed that NO in the air is oxidised when the catalyst is exposed to light. Through the intermediate step of nitrogen dioxide (NO_2), it is then converted to nitrate. When NO_2 is formed, part of the gas may escape from the photocatalytic surface but, in the presence of the cement matrix, the gas may be effectively entrapped together with the nitrate salt formed.

Laboratory tests of photoconversion of NO_x were carried out on films of:

- TiO_2 mixed with cement (5% by cement weight)
- cement matrix without photocatalyst
- TiO_2 powder.

Figure 5 summarises the tests carried out in the dark. NO_x is considered as a residual amount; a percentage is referred to an initial concentration of 100%. In this case, the observed concentration decrease is only due to adsorption. It is probable that such absorption is attributed to the ability of hydroxides present in the cement matrix.

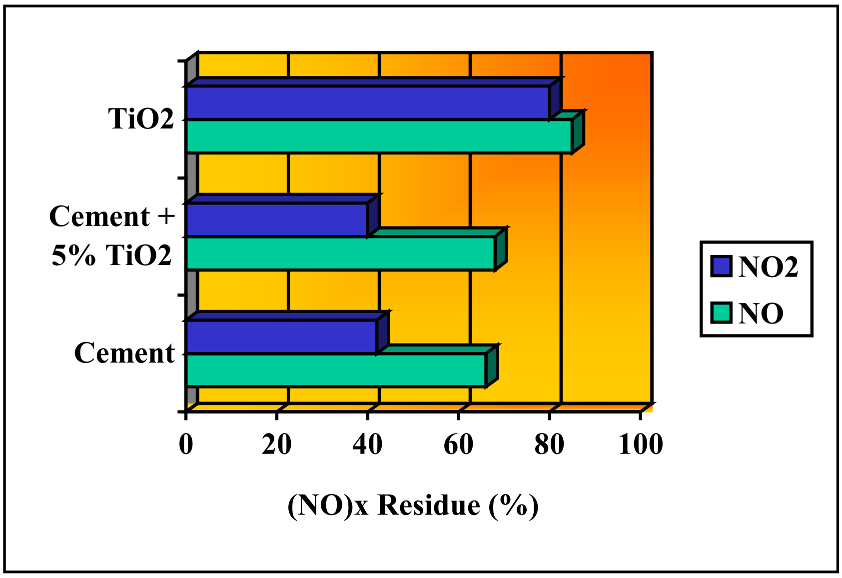

Figure 5 : NO_x treatment in the dark

Photochemical tests after 7 h of light of the samples, still considered as a percentage as referenced to an initial concentration of 100%, are reported in Figure 6. It can be noted that the removal of NO_x by action of the photocatalyst plus the cementitious matrix is higher than the removal obtained with the photocatalyst alone.

The reason for this is that on the surface NO is oxidised to NO_2 by O_2 and TiO_2:

$$NO \xrightarrow[O_2]{TiO_2} NO_2 \qquad (1)$$

NO_2 is oxidised and remains on the matrix as nitrate :

$$NO_2 \xrightarrow[O_2]{TiO_2} NO_3- \qquad (2)$$

Furthermore, the examination of the data of Fig. 6 shows that also the cementitious matrix without TiO_2 has a certain catalytic effect, as often observed in the case of organic substrates, probably due to the presence of photocatalytic oxides, in small amounts, in the matrix itself.

However, the main function of the cement matrix is its ability to absorb NO_2 by transforming it into nitrate and nitrite. TiO_2 introduced into the cement matrix is active in the transformation of NO to NO_2 and then to nitrate.

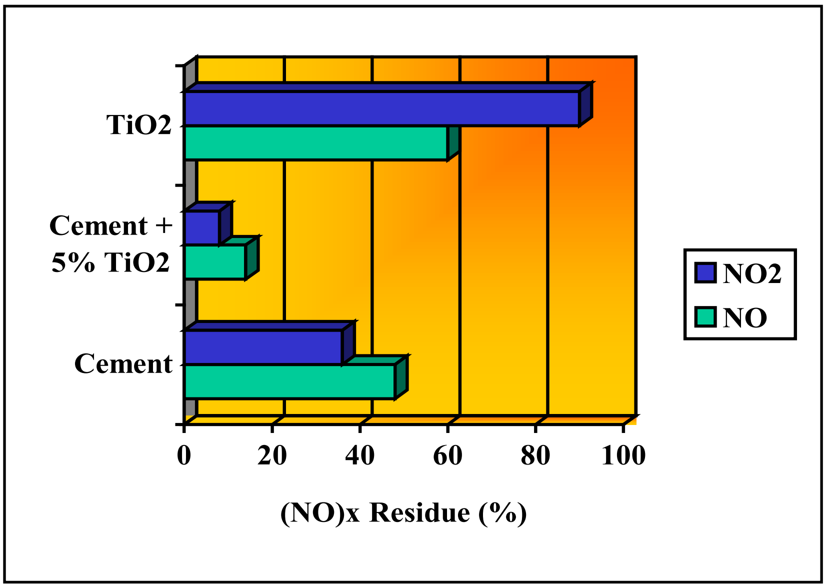

Figure 6: NO_x treatment under UV light

In the absence of cement or other basic compounds NO is transformed into NO_2. To give an efficient abatement of NO_x the photocatalytic cement must posses both a high NO_2 absorption rate and a high NO_2 absorption capacity, so that it can trap large volumes of NO_2.[20] These data, carried out in a photocatalytic chamber of 1.5 litres, have been confirmed in a quantitative way in two different chambers respectively of 450 litres and 35 m3. The results confirmed good performance with regard to abatement of NO_x and allow us to plan a large test in a real environment.

In Segrate (Milan) and in Bergamo the application of the photocatalytic mortar has been carried out on 220 m of an urban road with about 6000 m^2 of available surface, and a vehicle traffic rate of 1200 units/h. These types of test are probably the most comprehensive experimental tests concerning pollutant abatement by using photocatalytic cementitious products.

The results were encouraging since the measured abatement of NO_x was about 50% when the environmental conditions were a summer sunny day with wind speed lower than 0.7 m/s and lux higher than 90.000. The results have to be evaluated as very positive considering the limited photocatalytic surface available.

It is noteworthy that two years after the application the mortar had still maintained its photocatalytic activity. Furthermore, important information was obtained from these experiments: the abatement of NO_x with our photocatalytic system forms mainly NO3– and only a minor quantity of the more toxic NO_2–, whereas without the photocatalyst the NO_2– is predominant.

Conclusions

Results of tests undertaken allowed us to conclude that cementitious materials containing titanium dioxide mainly in the form of anatase, when irradiated with adequate light, enhance the oxidation efficiency of organic and inorganic substances with which they come into contact. Experimental evidence confirmed that a building element containing cement to which TiO_2 has been added is capable of maintaining its aesthetic appearance unaltered in time thus contributing to reducing the dirtiness of surfaces exposed to specific polluting environments. Furthermore, the capability of reducing urban pollutants was confirmed both in laboratory and field applications.

Examples of pollutants which can be destroyed by the photocatalytic system cement + TiO_2 are: $NO_{x,}$ SOx, NH3, CO, volatile organic carbons such as benzene and toluene, organic chlorides, aldehydes and polycondensated aromatics. Therefore we believe that massive and continuous use of photocatalysts in construction materials can be a new way of contributing to minimising contaminant attack in the urban environment.

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