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Study on Photocatalytic Cement as Solution for Pollution Control

KEYWORDS: Air pollution, Photocatalytic, Concrete, Gas chromatography, RhB

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ABSTRACT *In recent years, environmental concerns of pollution and resource depletion represent major concerns for society. Air quality in the vicinity of large cities is linked with serious health hazards. Many of these health hazards are associated with nitrogen oxides (NOx) and volatile organic compounds (VOCs) in the air, which in turn are caused by high traffic volumes and combustors. These pollutants may also travel long distances to produce secondary pollutants, such as acid rain or ozone (Beeldens 2006).*

The product TX Active (Titanium dioxide used as catalyst), is a patented portland cement developed by Italcementi Group and produced in North America by its U.S. subsidiary, Essroc. The key to TX Active's properties are photocatalytic components that use the energy from ultraviolet rays to oxidize most organic and some inorganic compounds. Air pollutants that would normally result in discoloration of exposed surfaces are removed from the atmosphere by the components, and their residues are washed off by rain. So, this new cement can be used to produce concrete and plaster products that save on maintenance costs while they ensure a cleaner environment.

This paper presents an overview of the principle of photo catalysis and the application in combination with cement, as well as the results of the laboratory research especially towards air purifying action. The implementation of this type of material in urban and interurban areas is not only ecofriendly but also a great savage for society.

Introduction

Among the necessary evils those being faced by modern societies, as we commonly quote as modern problems which are challenging the very existence of human society itself are the three great "P"s. They are Population, Poverty and Pollution. Yet again among the various kinds of pollutions, the air pollution is not only perilous but also fatal in its finest terms.

In the present context, Air pollution is a major crisis that modernization and urbanization is facing. On a daily basis civil, industrial and military activities generate an enormous amount of organic and inorganic pollutants which inevitably end up in our atmosphere, soil, rivers and oceans. Air pollution abatement strategies are essentially based on electrostatic filters and membranes to reduce fine suspension particulate matters (SPM), chemical derivatives, mutagens and materials derived out of catalytic processes to purify air from hazards like SO_x, NO_x, CO, vaporized organics and formaldehyde like substances.

When a photo catalyst is incorporated in a concrete, it decomposes organic materials like dirt, mold, algae, bacteria, allergens, air pollutants, smoke, tobacco etc in the presence of light. The catalyzed compounds break down into Oxygen, Carbon dioxide, Water, Sulfates, Nitrates, and other substances that are either beneficial or have a relatively minor effect on the environment. This type of concrete having a photocatlyst in it is known as photocatalytic concrete or self-cleaning concrete, which is a green construction material.

A photcatalytic concrete along with its structural qualities like an ordinary concrete is a strong depollutant. Titanium dioxide (TiO_2) or titania is the photocatalyst material mixed with the concrete. In the presence of light, titania creates a charge that disperses on the surface of the photcatalyst, and reacts with external substances to decompose organic compounds. The products of the reaction can easily be washed with water. Rain or simple rinsing can easily remove the reaction products and the building looks clean and beautiful like a new one. Titanium dioxide can be employed in all types of concrete, including plaster and mortar.

Along with TiO_2, other photocatalysts like ZnO, WO_3, $FeTiO_3$ and $SrTiO_3$ can also be utilized in concrete for the same purpose. As the sunlight strikes the concrete surface, most organic pollutants are neutralized; this would otherwise discolor the concrete surfaces. As already mentioned, the photocatalyst is not spent as it breaks down the pollutants, rather it continues to work indefinitely.

Experimental objective

- The major objective of this project was to review of the available results of existing research on the use of photocatalysts for reduction of air pollutants.
- The data from the Photo-catalytic Innovative Coverings Applications for De-pollution Assessment (PICADA) project of the European Union was to be gathered and analyzed in addition to the other related work.
- The data assessment was to include the effectiveness of the construction material using TiO_2, the extend of the pollution reduction, and the transport mechanisms and the fate of TiO_2 after being introduced into the environment.
- In addition, the cost of addition of TiO_2 to construction material was to be estimated.
- Finally, based on best available information, a recommendation was to be provided whether to consider incorporating TiO_2 into exterior and interior construction material.

This paper focuses on the application of TiO_2 as photocatalytic material in concrete blocks. The addition of TiO_2 in building materials adds an additional property to the road/any structure. Purification of the air, which is in contact with the surface, is obtained when the surface is exposed to UV-light (present in daylight).

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Materials used

The basic materials required for mixing concrete are:

- Ordinary Portland Cement
- Fine Aggregate [Sand]
- Coarse Aggregate
- Titanium Di oxide (Catalyst)

All the material should be of the same standard used for mixing conventional concrete. Photocatalytic cement is no different. However specifications of TiO_2 should be considered.

Mix Design

Concrete Mix Design:

- Normal mix design procedures are applicable to photocatalytic concrete¼ACI 211, etc.
- Same attention as concrete produced with OPC.
- Water cement ratio- The water cement ratio must be optimum according to the grade of concrete chosen and mix design has to be done.
- Quality aggregates – The quality of aggregates must be high.

For Concrete Production manufacturing procedures same as normal concrete, however extra care should be taken to avoid contamination.

Concrete Curing:

- All concrete must be properly cured to attain maximum strength, reduce permeability, obtain durable concrete and attain desired properties - photocatalytic concrete is no different.

Experimental Program

Fresh Concrete Properties	Hardened Concrete Properties
• Workability • Rheology • Heat generation • Finishability	• Compressive Strength • Flexural Strength • Durability • Air Void System • Permeability

Specific Gravity Test on Photocatalytic Cement

The specific gravity is normally defined as the ratio between the weight of a given volume of material and weight of an equal volume of water.

Apparatus

Le Chaterlier"s flask, weighing machine, kerosene (free from water).

Procedure

(I) Dry the flask carefully and fill with kerosene or naphtha to a point on the stem between zero and 1 ml.

(II) Record the level of the liquid in the flask as initial reading.

(III) Put a weighted quantity of cement (about 60 gm) into the flask so that level of kerosene rise to about 22 ml mark, care being taken to avoid splashing and to see that cement does not adhere to the sides of the above the liquid.

(IV) After putting all the cement to the flask, roll the flask gently in an inclined position to expel air until no further air bubble rises to the surface of the liquid.

(V) Note down the new liquid level as final reading.

Slump test and apparatus

Workability is often referred to as the ease with which a concrete can be transported, placed and consolidated without excessive bleeding or segregation. The slump is a measure indicating the consistency or workability of cement concrete. It gives an idea of water content needed for concrete to be used for different works. A concrete is said to be workable if it can be easily mixed, placed, compacted and finished. A workable concrete should not shown any segregation or bleeding. Segregation is said to occur when coarse aggregate tries to separate out from the finer material and a concentration of coarse aggregate at one place occurs. This results in large voids, less durability and strength. Bleeding of concrete is said to occur when excess water comes up at the surface of concrete. This causes small pores through the mass of concrete and is undesirable. By this test we can determine the water content to give specified slump value. In this test water content is varied and in each case slump value is measured till we arrive at water content giving the required slump value. However, this test is not a true guide to workability. For example, a harsh mix cannot be said to have same workability as one with a large proportion of sand even though they may have the same slump.

Apparatus

Iron pan to mix concrete, slump cone, spatula, trowels, tamping rod and a graduated cylinder.

Procedure

Four mixes are to be prepared with water-cement ratio (by mass) of 0.50, 0.60, 0.70 and 0.80, respectively.

1) Mix the dry constituents thoroughly to get a uniform colour and then add water.
2) Place the mixed concrete in the cleaned slump cone mould in 4 layers, each approximately ¼ of the height of the mould. Tamp each layer 25 times with tamping rod distributing the strokes in a uniform manner over the cross-section of the mould. For the second and subsequent layers the tamping rod should penetrate in to the underlying layer.
3) Strike off the top with a trowel or tamping rod so that the mould is exactly filled.
4) remove the cone immediately, raising it slowly and carefully in the vertical direction.
5) As soon as the concrete settlement comes to a stop, measure the subsidence of concrete in mm which will give the slump.

Note: Slump test is adopted in the laboratory or during the progress of work in the field for determining consistency of concrete where nominal maximum size of aggregate does not exceed 40mm. Any slump specimen which collapses or shears off laterally gives incorrect results and if this occurs the test is repeated, only the true slump should be measured.

Compression test and apparatus

Compressive strength of concrete: Out of many test applied to the concrete, this is the utmost important which gives an idea about all the characteristics of concrete. By this single test one judge that whether Concreting has been done properly or not. For cube test two types of specimens either cubes of 15 cm X 15 cm X 15 cm or 10cm X 10 cm x 10 cm depending upon the size of aggregate are used. For most of the works cubical moulds of size 15 cm x 15cm x 15 cm are commonly used.

This concrete is poured in the mould and tempered properly so as not to have any voids. After 24 hours these moulds are removed and test specimens are put in water for curing. The top surface of these specimens should be made even and smooth. This is done by putting cement paste and spreading smoothly on whole area of specimen.

CO_2 analysis by gas chromatography:

Materials and Methods [Preparation of Materials]

Cement used in this study is an Ordinary Portland Cement (OPC). Only the portion that passed through a 2.36 mm sieve will be use for making the surface layer. The recycled aggregate (RA) is also used in this study. It is a crushed waste sourced from a temporary recycling facility. The maximum

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size of the recycled fine aggregate used is 2.36 mm. The sand that was used is fine natural river sand commercially available in Malaysia. Chemical material candidate is Titanium dioxide (TiO_2). The best source of titanium dioxide is Anatase sourced commercially available, which was used due to its high purity and accurate specifications. It is commonly used in the industry and research community, hence would be useful for comparison with works of other materials (Poon and Cheung, 2007).

Sample proportions: The samples were fabricated in steel moulds with internal dimensions of 20 × 10 ×5 cm. The wet mixed materials were weighed between 400 and 500 g for each sample depending on the different materials. The steel moulds were filled by hand compaction. After 1 day, the samples were removed from their moulds and tested for CO_2 photo degradation at 15, 30, and 60 days with GC gas equipment.

Mix proportions : Mixes were prepared with Aggregates, TiO_2, water and sand. This study focuses on effectiveness of depollution, so a series of mixes were prepared to find out the effects of titanium dioxide and proportions on CO_2 removal efficiency. Mixes with varying cement to aggregate ratios, ranging from 1:2, 1:2:5 and 1:3 were prepared. As well as varied percentage of TiO_2 were taken. A large amount of the mixes were prepared by utilizing aggregate sizes from 300 to 2.36 mm. The varying amounts of TiO_2 were studied by preparing samples with the TiO_2 Anatase content ranging from 5- 10% as shown.

Equipments: The central part of the experimental setup used is a gas reactor allowing a sample of size 10× 20 cm^2 to be fixed. The reactor is made from materials which are non-absorbing to the applied pollutant and can hold up UV-A light of high irradiance. The reactor is tightly closed with a glass plate made from borosilicate glass allowing the UV-A radiation to pass through with almost no conflict. The surface of the specimen is fixed parallel to the covering glass inside the reactor, leaving a slot of 0.3 cm for the gas to pass through it; the sample gas only passes the reactor through the slot between the sample surface and the glass cover in longitudinal direction. All structural designed parts inside the box are to allow laminar flow of the gas along the sample surface and to put off distribution. Two 10W UV-A fluorescent lamps with wavelengths 366 nm were used to supply photo irradiation to activate the photo catalyst. Two types of sensors were used, temperature and humidity sensor. The tool that was used to analyses the result of CO_2 removal efficiency by computer is GC gas. The schematic illustration of the reactor cell and the test setup is specified in Figure.1.

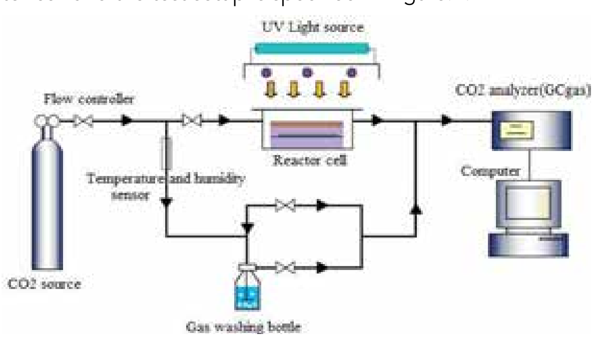

Fig.1.Gas Chromatography equipment for testing CO_2 photodegradation.

Depollution – NO_x oxidation test and modeling
NO_x oxidation experiments have been carried out in a continuous fixed bed flow reactor according to the Italian Standard UNI 11247. The scheme of the lab plant used is illustrated in Figure 2. The photocatalytic reactor consists of a Pyrex glass chamber having a total volume of 3.58 m^3, where the specimen under testing can be located on the bottom part supported by a proper sample holder. The gas inlet tube allows the air/NO_x mixture to flow directly onto the specimen upper surface whilst the gas outlet tube is positioned underneath the sample holder.

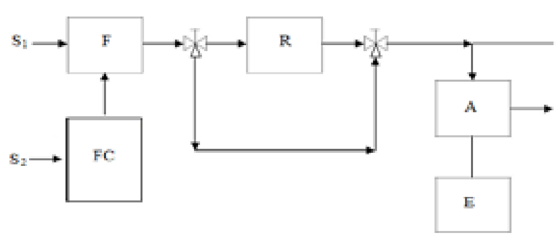

Fig.2.Lab plant flow chart for NO_x oxidation.

S1 is the NO_x cylinder, S2 the air cylinder, F and FC the mass flow meters for NO and air respectively, R the photocatalytic reactor, A the chemiluminescence analyzer and E the software/computer.

The system was kept at room temperature: 25 ± 1°C. U.V. light was provided by an OSRAM ULTRAVITALUX lamp having a main emission in the U.V.-A field distributed around a maximum intensity wavelength of about 365 nm. The lamp – sample distance was set to achieve on the upper sample surface an average irradiance of 20 ± 1 W/m^2. A schematic diagram of the photocatalytic reactor equipped with the U.V. lamp is illustrated in Figure 3.

The gas mixture used for the oxidation experiment came from a cylinder containing 40 ppm of NO (nitric oxide) and 20 ppm of NO_2 in air. Through the other air cylinder and the mass flow meters, the desired flow rates and inlet NO concentration were adjusted. The experiments were carried out at an inlet NO concentration of 500 ppb for a flow rate equal to 3 l min-1, 2 l min-1 and 1.5 l min-1, in order to evaluate the effect of the residence time.

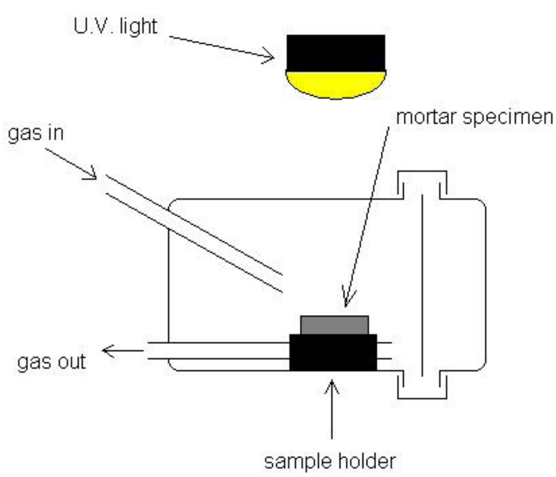

Fig.3.Photocatalytic reactor scheme for NO_x oxidation.

All the oxidation experiments have been performed according to the following procedure. The disk sample was wrapped in a sealing film in order to let the upper surface free and protect the side surface. After introducing the disk sample in the photocatalytic reactor the gas stream (at given flow rate) was switched on and the system let to stabilise for half an hour in the dark in order to achieve a constant NO concentration. The U.V. light was then switched on and the NO/NO_2 concentrations monitored for a further 90 minutes.

N-TiO_2 has been selected for a further study in order to iden-

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tify the role of surface water in the photocatalytic oxidation of NO and investigate the different reaction regimes as well as the possible deactivation phenomena. The pure photocatalyst has been deposited on the surface of glass beads and tested in a photocatalytic powder layer reactor.

Self-cleaning effect – Rhodamine B (RhB) test

Cement paste samples prepared were coated with 20 l of a 0.5 g/l aqueous rhodamine B solution. The area coated was approximately 1.2 cm^2, see Figure 4, and the samples conditioned for 30 min. The sets cured for one single day were used to evaluate the influence of a different light exposure during the conditioning time. Three of the six discs per set (one set with m-TiO_2, one with n-TiO_2 and one without photocatalyst) were conditioned for 30 minutes under daylight, the remaining three were coated and

conditioned for 30 minutes in darkness. All three sets were subsequently irradiated with a UVItec LI-208.m lamp (2 tubes 8W each, main wavelength 312nm). The sets cured for fourteen days were used to evaluate the influence of the cement aging. Three of the six discs per set (one set with m-TiO_2, one with n-TiO_2 and one without photocatalyst) were conditioned for 30 minutes under daylight and irradiated with the same UVItec LI-208.m lamp. In all the experiments the distance between samples & lamp was 10 cm.

Limitations and Solutions

1. They are generally limited to new structure. This is because the additive has to be mixed in with concrete mixture. Some have resorting to adding a two inch layer of concrete to existing structures, but this method has its own challenges. For the most part, until now if you wanted a self cleaning concrete substrate, you had to build it from scratch. That is one of the reasons why we developed Self Clean Masonry Sealer. Now you can easily bring all the asthetic and green benefits of self cleaning concrete to existing structures. Self Clean Masonry Sealer can be used of make existing paver walkways, cement driveways, brick patios, stone walls and concrete buildings self cleaning.

2. Self cleaning concrete is expensive. The raw material that makes concrete photocatalytic is not cheap. When this additive is mixed in with the concrete mixture the great majority of it is buried within the mass of the concrete and will never see the light of day. Only the surface of the photocatalytic concrete is exposed to the UV rays of the sun and thus self cleaning. Therefore the expensive ingredient is wasted in the mass of the structure. We solved this problem by creating a penetrating sealer that brings the photocatalytic properties of the raw material only to the surface, where it is needed and not inside the concrete, where it is wasted. At 120 Rs per kg, you can make existing and new substrates self cleaning for as little as Rs 10 per square foot.

Discussion

Application of TiO_2 photocatalysis to cement and concrete provides an efficient strategy to simultaneously obtain: self-cleaning of building facades, retardation of natural surface ageing as well as air pollution mitigation, simply with the support of sunlight, atmospheric oxygen and water present as humidity and/or rain water. In this project, performances in degrading rhodamine B, RhB, (a common industrial test to evaluate self-cleaning activities), ability to retard natural ageing caused by processes such as soiling and erosion and performances in oxidising nitrogen oxide gaseous pollutants, NO_x, are presented for two different TiO_2 samples tested in cement and mortars, together with an insight into the fundamental chemistry about TiO_2 photosensitised reactions responsible for the degradation processes involved.

Discolouration of RhB on TiO_2 in cement involves not only a proper photocatalytic mechanism (TiO_2 – sensitised photoreaction) but also a dye – sensitised pathway. In the first mechanism light activates TiO_2 through promotion of electrons from the valence band to the conductance band. Adsorbed water and oxygen react with valence band positive holes (left after promotion) and conductance band electrons respectively to generate hydroxyl radicals, HO·, which ultimately degrade the adsorbed dye. In the second mechanisms, electrons in the HOMO level of the dye undergo transitions to the LUMO level and are subsequently injected into the conductance band of TiO_2. These electrons are therefore used by oxygen to generate oxidative species which degrade the already partially reacted dye. Dye – sensitised pathways are predominant when the system TiO_2/RhB is irradiated with visible light. The lower energies available from visible light are insufficient to induce photo-activation of TiO_2 but they can lead to dye sensitisation and degradation of colour by this mechanism. In these conditions, if RhB adsorbs on the TiO_2 surface through the positively charged amino groups (most likely since TiO_2 surfaces in highly alkaline conditions are negatively charged), a selective stepwise de-ethylation of RhB amino groups occurs. This mechanism is responsible for a sequence of structurally similar degradation products which absorb radiation at progressively lower wavelengths (hypsochromic shift in the UV-vis diffuse reflectance spectra). These findings, related to the photocatalytic degradation of RhB on photoactivated TiO_2 supported on cementitious materials, match very well what is already observed for slurry suspensions in terms of influence of the incident radiation.

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