

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly, Peer Reviewed Journal)

Visit: www.ijirset.com

Vol. 7, Issue 3, March 2018

A Review on Pollution Eating and Self-Cleaning Properties of Cementitious Materials

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ABSTRACT: Pollution controlling and smog-eating properties induced in a self-cleaning cementitious material were identified recently. Initially meant as a self-cleaning material, it was discovered that this material had the ability to reduce certain pollutants from surrounding air, and this reduction in the concentration of the pollutants depends upon the surrounding conditions and the amount of exposed area. These properties induced in cementitious material were mainly due to the photocatalytic action of TiO₂, which under the influence of sunlight acts as a catalyst and triggers chemical reaction due to that decomposition of dirt particles take place on the concrete's surface, also it reacts with certain pollutants that contribute to smog, breaking it under the presence of sunlight and accelerating their natural oxidation process. It is found that it is very effective against the Nitrogen oxides (NO_x), Sulphur oxides (SO_x) and many other harmful pollutants, which are mainly released due to the burning of fossil fuels and is one of the major constituents of smog. It decomposes NO_x effectively up to a great extent in the surrounding environment and to a height of about 2-3 meters above the surface. In simple words, this material showing photocatalytic property due to TiO₂, when irradiated with sunlight accelerates the decomposition process of pollutants and dirt clearing up the smog and ultimately cleaning the environment and that is the reason why the term self-cleaning and smog-eating is given to it. This material has already found relevant applications, and is being used in a variety of projects such as self-cleaning walls and in the reduction of urban pollutants and serves multiple purposes. Furthermore, the main focus of this paper is to explain the mechanisms involved and to understand the merits and demerits of using this cementitious material in a better way and also it aims at finding out ways in which it can contribute more to this new environmental friendly civil engineering world.

KEYWORDS: Self-cleaning, Smog-eating, Pollution eating, Photo-catalytic, Clean and green Environment.

I. INTRODUCTION

The current climatic situations all over the world are alarming. The deviations through which nature and the environment have gone through in the past few decades are very much observable and uncontrollable and have had harmful effects on the environment like; Glaciers have shrunk, ice on rivers and lakes is breaking up earlier, plant and animal ranges have shifted and trees are flowering sooner. These are the side effects of the magnified global warming. The Intergovernmental Panel on Climate Change (IPCC) tells in a report that, the temperature rise of 2.5 to 10 degrees Fahrenheit is expected over the next century [1]. Not only the rise in temperature, pollution has made the air unfit for breathing. The poor indoor air quality is now a common issue in almost all of the urban and industrial areas. Fumes from industries, emissions from vehicular exhausts, extensive burning of coal and the other fossil fuels, forest and agricultural fires and many other such activities has increased the public concern. One of the side effects of all these activities is smog. Smog is nothing but a type of air pollution formed from all these sources that react in the atmosphere with sunlight to form secondary pollutants that also combine with the primary emissions to form photochemical smog. The major air pollutants that are responsible for the formation of smog are Aldehydes, Nitrogen oxides (Nox), Sulphur oxides (Sox), Peroxyacyl nitrates, tropospheric ozone and VOC's [2]. In some of the most polluted cities like Delhi, smog is one of the major problems and its severity is often aggravated by stubble burning in neighbouring agricultural areas. On 8th November 2017, some monitoring stations reported an Air Quality Index of 999, way above the worst

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Vol. 7, Issue 3, March 2018

case category, Hazardous [3]. In such conditions, a cementitious material that has pollution-eating and self-cleaning properties when applied to infrastructural work will be very beneficial and can contribute to cleaning the environment and help in improving sustainability. This construction material with the help of its photocatalytic ability is able to accelerate the natural oxidation process of many pollutants leading to their faster decomposition and preventing them from accumulating and forming persistent compounds [4] [5] [6]. This photocatalytic cement has titanium dioxide (TiO₂) mixed with other pozzolanic ingredients. This cement, when exposed to sunlight, triggers a chemical reaction, which in turn results in breaking down of some of the major pollutants, which contribute to the formation of smog [7]. One of the major pollutants which are readily decomposed by this photocatalytic cement is Nitrogen oxides (Nox) and its compounds. Nox is a result of the burning of fossil fuels which further breaks down in the atmosphere and creates smog and is also responsible for the formation of ground-level ozone [8]. It has been found that it almost decomposes 25% - 45% Nitrogen oxides up to 2-3m near and around the surface [9] [10]. Construction materials which are both environment-friendly, as well as sustainable, are the need, of the current civil engineering world because until now, both, the construction materials and the construction processes are known to contribute a significant amount of pollutants to the air and the water resources. The endeavour for finding alternative construction materials that are environment-friendly and pose a lesser threat to living world has led to the exploration of this photocatalytic, self-cleaning, smog-eating cementitious material. Self-cleaning and pollution-eating buildings and road pavements may seem a part of the futuristic infrastructure but they are a part of realities in some parts of today's world [11]. This innovation in the field of civil and environmental engineering is very much based on the properties of TiO₂ which can be incorporated directly into the concrete or can be brought to work by applying coatings of the material over the surface of the buildings or the pavements [11] [12]. TiO₂ not only provides the self-cleaning and pollution-eating advantages but also being white in colour adds to the aesthetics of the buildings and constructions [13]. The main focus of this paper is to tell the readers about the advantages of using this cementitious material, and about its properties and the working principle, that are responsible for the self cleaning and pollution-eating behavior of this material, which are strongly supported by some case studies that will help in understanding the changes brought about and in nearby neighborhood by the use of this material.

II. HISTORY

Titanium dioxide TiO₂, possess photocatalytic properties that can decompose pollutants when irradiated by the ultraviolet rays, was known since 100 years ago [14]. It was discovered around 1970's that, titanium dioxide can be used to decompose pollutants present in water by electrolysis when illuminated upon by light, this phenomenon is known as 'Honda-Fujishima effect' [15]. During the 1980's, TiO₂ under the influence of ultraviolet light was being used to remove organic pollutants from water and products like titanium oxide coating films, composite materials, etc., were deployed for the purpose of water purification, antifouling protection and so on [16]. It was only during the 1990's that, photocatalytic cement-based materials came into play. The first official publication in this field was presented by L. Cassar et al. in 1997 [17]. Since then, a photocatalytic cementitious material has been used and developed with increasing innovative solutions from self-cleaning performances to depolluting effects. A no. of patents have been filed up to date based on this material, the main work is supposed to be done by Italcementi and Mitsubishi group, in which, 16 patents are of Italcementi, with a progressive development in the commercially available products [18]. During the early days this photocatalytic cementitious material was used as a building material for self-cleaning and antibacterial properties usually in Japan and Italy, but, after seeing the benefits of this cementitious material, it has been used from Italy, Japan to France, Netherland, Canada and in various cities of USA [19] [20] [21] [22] [23].

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Vol. 7, Issue 3, March 2018



Fig 1: Air France headquarters.



Fig 2: The Palazzo Italia in Milan.



Fig 3: A hospital shielded by tiles having smog eating abilities in Mexico City.



Fig 4: Cermak Road in Chicago, known as the 'greenest street in America'.

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Visit: www.ijirset.com

Vol. 7, Issue 3, March 2018

III. WORKING PRINCIPLE AND ITS MECHANISM

The cementitious material containing TiO₂ works on a basic simple principle of photocatalysis. The material gets activated under the influence of light and, subsequently, TiO₂ oxidizes the pollutants and this phenomenon is known as photocatalysis [24]. The pollutants oxidized get precipitated on the material surface, which can then be removed from the surface by rain or by cleaning/washing by water as shown in Fig 5.

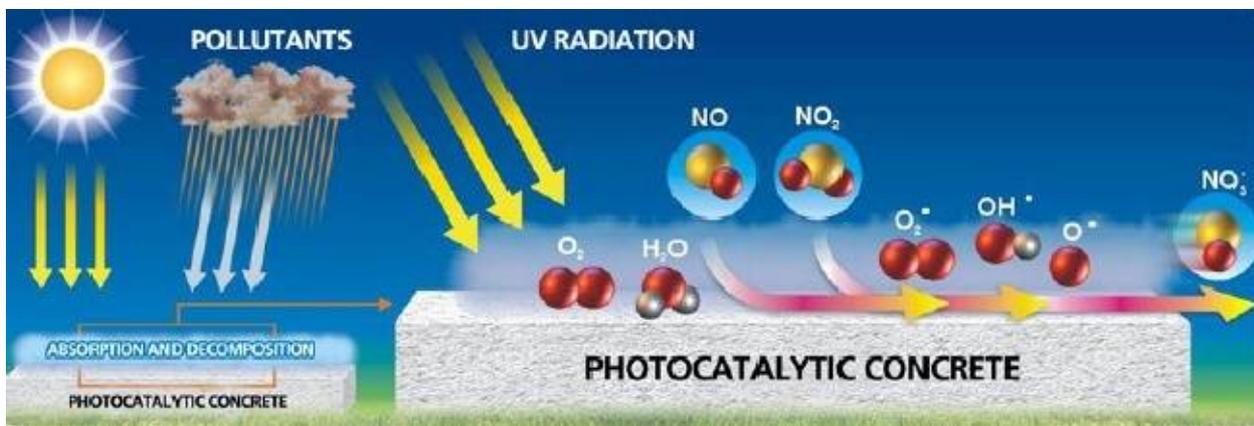


Fig 5: Oxidation of pollutants by Photo catalysis and then decomposition of the pollutant after precipitation over concrete surface.

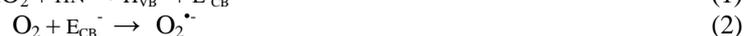
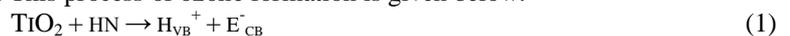
Harmful gases like SO_x, NO_x present in the atmosphere are removed efficiently with the help of TiO₂ incorporated system [25] [26]. In the presence of UV radiations, TiO₂ oxidizes an array of micropollutants - NO_x, SO_x, NH₃, CO, toluene, benzene, ethylbenzene, and o-xylene [27] [28]. NO in the atmosphere is converted into lesser harmful nitrogen compounds, nitrates and nitrites, with TiO₂ and cement mix combination, and the compound formed adheres to the surface and gets washed away with the rain [29] [30]. The nitrate compounds formed during this can also be easily consumed by the plants [31]. The mechanism involves, NO₂ gas formation as an intermediary step between the oxidation of NO to nitrates and nitrites ions, and it escapes from the photocatalytic surface, whereas in the combination of a catalyst with a cementing material, the escape of NO₂ is reduced as it gets entrapped with the nitrate salts [32]. Research conducted also shows that NO removal is much more efficient (20% more efficient) when hetero-catalyst is combined with the cement matrix, the reason being when catalyst alone is used NO₂ gas is formed but in the usage photocatalyst and cement system, nitrate ions are produced [31].



NO₂ IS OXIDIZED AND NITRATE REMAINS ADSORBED:



If the adsorbed nitrate is not washed or swiped away for many days from the surface then on being illuminated with sunlight it undergoes a renoxification process [33]. During that renoxification process along with the formation of NO_x, ozone formation also takes place which in itself is a harmful gas. This is the only disadvantage of using a TiO₂ mixed cementitious material, it is said to undergo a renoxification process on coming in contact with visible light if the adsorbed NO₃⁻ is not washed or swiped away for many days [33] [34] [35]. During the process, an alternative photochemical pathway is created which leads to the formation of NO₃ radical, because of a charge exchange reaction between the nitrate anion and the solid surface, followed by photochemical reaction of nitrate radical giving rise to oxygen radical, which in turn forms ozone [36]. This process of ozone formation is given below:

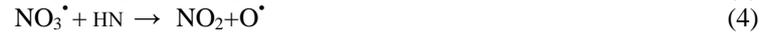
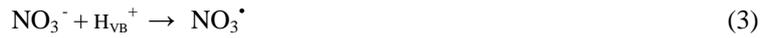


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Vol. 7, Issue 3, March 2018



This is one of the major problems why this material isn't being used worldwide regardless of the fact that it has so many benefits and also serves multipurpose. This review has stated some of the solutions for this problem such as; by using materials like modified TiO₂, Pt and Ni-doped TiO₂ and by using TiO₂ nanoparticles [37].

IV. CASE STUDIES

Cermak Road in Chicago (USA):

There's a road in Chicago known by the name of "Greenest Street in America" as this street is clearing up 20-70% air pollution within the material vicinity, in the local area [38]. Cermak road's project utilized coating of photocatalytic cementitious material containing TiO₂ for nearly all of its paving surfaces. Chicago is well known to be hit by heavy and vigorous storms, thus sewer overflows and washing away of stormwater along with hazardous compounds was also a concerned issue. Therefore, integration of photocatalytic cementitious material on the permeable pavements and roadways along with landscape design in the form of rain gardens and bioswales have helped in not only reducing harmful NO_x and SO_x content in the atmosphere but has also helped to mitigate hazardous overflows and pollution levels along with maintaining a clean surface. The self-cleaning and pollution-eating properties of this material are best utilized when in close proximity to the source of pollution. The Ontario's Ministry of Transportation data shows that 1sq meter of this material removes 60mg of NO_x per day [39].

These results show that photocatalytic concrete if applied to an area of about a football field, can remove emissions approximately equal to 1,19,000 cars-km per year [39]. Therefore, this case study clearly shows that using this material for infrastructural work in urban areas will make our cities cleaner and greener.



Photos of Cermak Street, 'The Greenest street of USA'.

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Vol. 7, Issue 3, March 2018

Street Jean Bleuzen, Vanves, France.

In 2009, a concrete road was planned to be constructed in Rue Jean Bleuzen, Vanves. The area had an estimated IMD of 13,000 automobiles throughout the day and is considered as the main business zone of Vanves, consequently, the air in the area was polluted to a certain level that was alarming. The street itself is relatively narrow and it has building constructed on both sides and gets a good share of sunlight in a day that sets the stage for abatement of air by photocatalysis. The concrete road is clearing the air in vehicle loaded area, owing to the incorporation of TX Aria®, a mortar based on the technology TX Active®, patented by FYM-Cementos Rezola, a firm group of Italcementi [40]. The concrete construction has a long span of 300m and is laid upon an area of 6 m² that involves sidewalks, kerbs and the road [41]. According to the air quality monitoring report by an external laboratory (Labortaire Regional de l'Quest Parisien), along with a 20% reduction in gas pollution, a betterment in acoustic pollution is recorded as well [42] [43].



Photos of Street Jean Bleuzen, Vanves, France.

Torre de Especialidades, Mexico City.

This project is based in the infamously polluted area of Mexico City, and it extends the scope of photocatalytic usage to vertical constructions. According to a report of WHO of 1992, the level of SO₂, particulate matter, CO and NO₂ exceeded the limit set in its guidelines. The hospital's 100 yards long facade is fitted with white tiles, that's incorporated with photocatalyst TiO₂ [21]. It's just not its self-cleaning action that's impressive, but its aesthetics is also being remarked as brilliant. The white of the exterior of the building is not getting dirty with time, making the whole construction unique in aesthetics also. The tile (proSolve370e) is designed and manufactured by Berlin-based architecture firm Elegant Embellishments, it's coated over with photocatalyst TiO₂, that gets activated with sunlight and starts its process of cleaning the air. The makers of the tiles stated that it counteracts the affect of 8750 cars in a day, in the area around the hospital and making the air relatively healthier to breathe [44].

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Visit: www.ijirset.com

Vol. 7, Issue 3, March 2018



Photos of Torre de Especialidades, Mexico City.

V. CONCLUSION

Recent researches on photocatalytic cementitious material in the last two decades have shown that how these materials can reduce the urban pollution up to some extent in parallel of being aesthetically sober and cleaner. These materials can be used for various purposes like in concrete pavements, rooftops, paving blocks and paving plates, coatings on buildings and sidewalks, for tunnel lining and ultra-thin white topping, etc. India has such a vast network of highways and roadways which can also be used as a potential site for pollution reduction; thus making the environment cleaner and greener. These materials are known to perform better if the source is in the close vicinity of the material and also under UV rays. Also, the article discussed the formation of ozone as a by-product under a certain set of conditions, which is an alarming issue related to this material. This issue can be resolved by using materials like modified TiO₂, Pt and Ni-doped TiO₂ and by using TiO₂ nanoparticles. The case study of the Cermak road shows that, along with reducing atmospheric pollutants, it also reduces water dissolved hazardous compounds effectively. This material can prove out to be worthy if implemented on a large scale by reducing the contaminants as well as by enhancing the aesthetical quality. Also, both the case study clearly showed that the efficiency of this cementitious material was found to be more in the case when it was used as a coating 20-70% as compared to the use of mortar containing TiO₂, where the efficiency was just around 20%. It is also being used in multiple vertical constructions, like in the case study of Torre de Especialidades, and it is observed the efficiency of the former is much better due to being closer to the source and getting sunlight for more period of time. Also, it is quite clear that this photocatalytically active cementitious material is being used in many parts of America and Europe, for making the environment cleaner, greener and a better place to live.

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Visit: www.ijirset.com

Vol. 7, Issue 3, March 2018

VI. SCOPE FOR FUTURE STUDIES

1. Future studies can be conducted to find out photocatalytic materials that have higher efficiencies and at the same time are economic.
2. Research studies can be done on inducing the photocatalytic properties by incorporating the photocatalytically active nano-particles of TiO_2 and in turn finding out their efficiencies.
3. Finding out catalyst and doping elements so as to increase the efficiencies along with making the cementitious material work more effectively under the visible spectrum of sunlight.
4. If used as a pavement material then along with observing the pollution reducing abilities, studies can be carried out on finding out durability, age of photocatalytic behaviour and resistance to abrasion.

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