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# Influence of nanomaterial (Zinc Oxide) on the durability of conventional concrete

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**Abstract- This research seeks to present a nanomaterial that can provide self-cleaning property to conventional concrete, since the pollutants found in the air are also the cause of some concrete pathologies that affect its durability, such as carbonation, acid etching, and acid rain. The main objective of this research was to counteract the deterioration of concrete constructions using zinc oxide as a self-cleaning material for conventional concrete. For which, experimental tests were carried out, such as the rhodamine B test, exposure to polluting gases and the phenolphthalein test, carried out on mortar samples, and the compressive strength test, carried out on concrete specimens. Finally, the results allowed us to conclude that zinc oxide works as a photocatalytic material and gives concrete a self-cleaning property, which allows it to keep its surface free of contaminants that normally remain impregnated and damage it, in addition to being able to observe that this aggregate decreases the resistance of the concrete by a certain percentage, so it is recommended that it be used as a mortar rather than as concrete in structural elements.**

**Keywords- Concrete constructions, photocatalytic, zinc oxide, self-cleaning, deterioration.**

## I. INTRODUCTION

For many years it has been possible to observe how environmental pollution has been increasing throughout the world, affecting soil, water, and air. According to the article by Vignolo (2020), the main pollutants present in the air are: carbon monoxide (CO) of which 86% is produced by transport emissions, nitrogen oxides (NO, $NO_2$, $NO_X$) with 62 % from transport emissions and 30% from combustion for energy generation, sulfur dioxide ($SO_2$) with 93% due to the burning of fossil fuels and particulate matter (PM) [1], which can include particles that are especially harmful to concrete. Regarding the well-known greenhouse gas $CO_2$ [2], which is produced mainly by the combustion of fossil fuels and the respiration of the animal species itself, it is vital for the planet, thus complying with the so-called carbon cycle [3], however, for many years now this has lost its balance in nature because it has been unbalanced by having more $CO_2$ emissions than the planet can absorb, becoming one of the main causes of global warming and which it also influences the deterioration of concrete in processes such as carbonation [4].

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The effects that these contaminants have on the durability of concrete can be seen in the different pathologies caused by them. A clear example of them is carbonation [5], which is directly caused by gases found in the air, chemical attack by acids, which is generated by combining polluting gases and humidity that may exist in the environment, which causes them to adhere to the surface of the concrete and begin to deteriorate the surface of the concrete.

What can be seen in many parts of the world, and one of the best known, is the so-called acid rain [6], whose effect we can observe in many buildings, and depending on the type of agent that can be found in the polluted air, whether they are sulfates, aggregates, etc., these could generate other types of chemical attacks on concrete [7]. These pathologies become more and more noticeable with the passage of time, and this is because air pollution in the world continues to increase.

According to MeteoSim (2019), the capitals and their respective countries that have the highest pollution according to their concentration of PM 2.5 in $\mu g/m^3$, which is a very dangerous pollutant. This, due to its potential incorporation into organisms via inhalation since these are suspended in the air; that is why they are responsible for a large number of health problems. According to the mentioned article, we can find in Figure 1 that Delhi - India occupies the first place with respect to the most polluted capital, in addition we can find Lima - Peru a little higher than what would correspond to half of all those countries.

According to GreenPeace (2019), there is a total list of the 12 countries that have the most sulfur dioxide emissions measured in kilotons per year, with India as the main emitter in first place, being in 2019 when it was reported that it was responsible for 21% of $SO_2$ emissions worldwide. Regarding the emission of $NO_2$ in the period from 1980 to 2016, measured in millions of tons per year, there is a greater emission in Africa and East Asia, as well as a decrease in Europe and Russia, due to what if a new study was carried out to evaluate this issue would give us a better perspective of the current reality [8].

Finally, we have the main $CO_2$ emitting countries, measured in millions of tons per year, which continue to increase their level of pollution over the years, this due to the industrialization that exists in them and that has been growing, thus the countries with the greatest economic powers are the ones that pollute the most. First, we have China, followed by the United States, countries where the industrial sector forms a large part of the national economy [9].

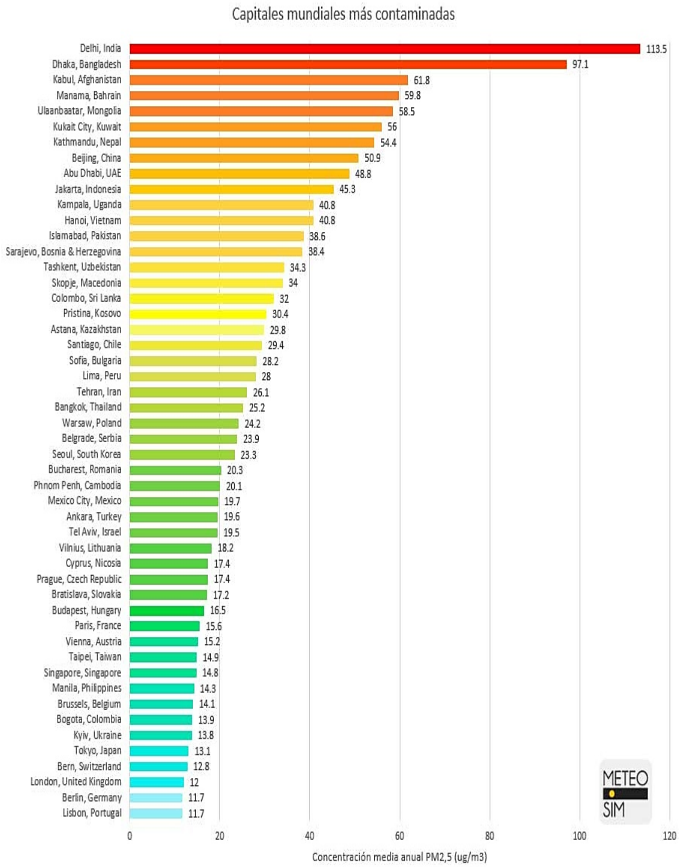



*Fig. 1* Pollution of world capitals according to their average annual concentration of PM 2.5. Source: [15]

In Peru, although it is not such a polluted country compared to others, the amount of pollutants in the air is notorious, in addition to being able to be seen in buildings as can be seen in Figure 2, these pollutants being able to damage them due to the different pathologies explained above, for which they must be constantly maintained and repaired. In an ESDA study (Environmental Performance Study) carried out by the Ministry of the Environment that was published in 2015, being the most recent of the data in Peru on air pollution, it shows us how throughout from 2002 to 2012, some of the emissions of polluting gases have increased, as well as some have been maintained, where the amounts emitted by Peru are appreciated in thousands of tons[10].

*Fig. 2* Lima buildings impregnated with pollution. Source: self-made

In relation to the aforementioned environmental attack suffered by urban structures, different authors have been investigating alternatives to counteract the aforementioned attack. Such is the case of Qu et al. (2021), who developed a method for the creation of hydrophobic mortar using bacteria grown in liquid cultures, being B. subtilis 3610 and E. coli (BL21 (DE3)) from ATCC the bacteria used for the study, using in turn two types of culture medium (Luria/Miller LB-Medium and LB Plus from Sigma Aldrich) for the investigation of its influence on the hydrophobic performance of bacteria. Samples of the hydrophobic mortar were prepared considering the culture liquid where the bacteria were found as part of the total volume of water that had to be added to the mixture, thus obtaining that all the samples added with bacteria had a greater contact angle with the water, being almost identical in the use of both bacteria, so it was possible to conclude that hydrophobic concrete can be prepared with bacteria that do not present innate hydrophobicity.

On the other hand, Molina-Prieto (2016) developed a study in which he evaluated the application of nanotechnology for the conservation of architectural and urban heritage. This study was based on an experimental campaign, where two metallic nanoparticles (iron oxide and zinc oxide) were tested as additives to the concrete mix. In this way, the author concluded that the metallic nanoparticles generate a filter that blocks ultraviolet light, reducing the conditions.

Angelomé and Angelomé (2019) worked with the incorporation of nanomaterials, as well as the monitoring and implementation of new treatments in the construction industry. To do this, they compared the various nanomaterials that had different uses, the technical sheets taught us the application either in concrete, cement ceramics, solar cells, paints, coatings, among others, and thus be able to determine the best benefit of its application. In the same way, Haurie Ibarra (2018), studied the applications of nanotechnology in construction materials, for which he made nanotechnology applications in cement-based elements by means of nanoparticle modification, reviewed the various nanoadditives that exist, and also made applications of nanotechnology in coatings, whether hydrophilic and hydrophobic, photocatalytic resistant to UV radiation, anti-corrosion, anti-graffiti, among others. Thus, both authors were able to conclude that by incorporating Zinc oxide nanoparticles into a compound, this improves its resistance to UV light, ensuring a surface sealing layer that helps preserve maximum moisture during the setting process, as well as being photocatalytic.

Based on the problematic reality expressed previously, the different pathologies that affect the durability of the concrete and that are consequent of the high air pollution that exists today were detailed. Therefore, the importance of this study lies in making known a self-cleaning nanomaterial, which, when added to conventional concrete, can help counteract the effects of polluting gases and particles that deteriorate concrete, as well as reduce the presence of these, thus contributing to the care of the environment by purifying the air at a certain level. That is why this research work seeks to reach the following main objective: "Counteract the deterioration of concrete constructions using zinc oxide as a self-cleaning material for conventional concrete", therefore, the following research question is posed: How to determine the influence of Zinc oxide on the durability of conventional concrete?

## II. METHODS

In the development of this work, 2 types of specimens were manufactured for their respective analysis, which are detailed in the following section:

### *A. Standard concrete specimens*

Conventional concrete test tubes with resistance f'c=210 $kg/cm^2$, dimensions: diameter 4" and height 8" were made as indicated by the ASTM C192 standard. As well as mortar samples with dimensions 10cm * 10cm * 4cm.

### *B. Concrete specimens with zinc oxide aggregate*

Concrete test tubes will be made with a percentage of: 4%, 7% and 9.5% of Zinc oxide aggregate to a conventional concrete mix, with dimensions: 4" diameter and 8" height. As well as mortar samples with the same percentages, and with dimensions 10cm * 10cm * 4cm.

The percentages were chosen based on previous work with zinc oxide, applied to mortars and rigid pavements, which served as a reference to know from what percentage zinc oxide began to be functional as a photocatalytic material, as well as prior tests were carried out on the final simples with higher percentages to be able to have the other reference limit, already having these data it was decided to take an interval between 2% to 11% of zinc oxide aggregate, since below the lower limit the concrete did not show much self-cleaning capacity , and above the upper limit considerable resistance began to be lost, as well as the setting time of the concrete being extended much more.

Once the limits were defined, more previous works were reviewed to avoid redundancy with respect to the choice of percentages and thus be able to ensure that a contribution is being made to these previous studies, thus being 4%, 7% and 9.5% the percentages chosen to make the samples. The procedure followed for each of the tests carried out is detailed below:

Prior to the preparation of the study specimens, a documentation guide was prepared where data from various scientific articles, thesis works and standards were collected, which would serve as a guide for the tests to be carried out on the specimens, as well as to give us a better perspective of the progress that have been made, in order to ensure that a contribution is being made with respect to the research topic. Wooden formworks were made for the mortar samples, these being different for each percentage of aggregate in order to ensure that there is no possible combination of the different types of samples, which were 12 in total with the respective percentages of 0%, 4%, 7% and 9.5% Zinc oxide aggregate, once the formwork was finished, we proceeded with the elaboration of the mortar samples, leaving them to dry for 48 hours for their subsequent stripping and immediate curing, which was carried out for 7 days. Once cured, the mortar was left to dry for 72 hours in order to begin the tests for Rhodamine B, phenolphthalein, and exposure to polluting gases.

The Rhodamine B test was carried out by adding 0.3 gr to 120 gr of water to spray it on the surface of the samples, this with the purpose of verifying the photocatalytic capacity of Zinc oxide as established by the UNI 11259-2008 standard. The test with phenolphthalein was carried out in order to corroborate if the aggregate helps to reduce the probability of carbonation in concrete structures, spraying 8 ml of phenolphthalein on each sample after leaving them exposed to the elements for 1 month; this test does not have standards that govern the method or any standard that can be used as a reference directly linked to the tests in particular, but there are many tests that demonstrate its effectiveness. And finally, for the exposure test to polluting gases, the samples were exposed to the burning of different materials such as plastics, rubber, and gasoline, for 20 minutes; for this test, the UNE 127197-1:2013 standard was used as a reference, which helps us to evaluate the performance of air purification in precast concrete products, referring to the elimination of nitrogen oxides, and also the AFNOR NF EN 16846-1 standard that helps us with the analysis to determine the effectiveness of the removal of volatile organic compounds / odors in the air.

The results of these samples were documented in an observation guide that was carried out at 0hr, 4hr, 8hr, 24hr, 28hr, 32hr and 48hr, with constant exposure to sunlight in order to activate the photocatalytic process, and in case of the test with polluting gases, at the end of the process water was sprayed to simulate rain and thus see the results of the cleaning due to the photocatalysis process.

Regarding the concrete test tubes, the preparation was carried out in the concrete laboratory of the "Universidad Privada del Norte - Breña headquarters", leaving the test tubes to dry for 48 hours and subjecting them to curing immediately for 28 days to thus reach their maximum resistance, after being cured, the compressive strength test was carried out on each of the specimens with the different percentages of aggregate following the ASTM C39 standard using 3 specimens for each percentage and documenting the results in our observation guide.

Finally, for the analysis of the obtained results, bar graphs, dispersion and comparative tables were used, in order to be able to appreciate how the photocatalytic performance of Zinc oxide is in the mortar samples, thus appreciating how it helps to counteract the deterioration of concrete constructions due to polluting agents found in the environment, at what level does it do so and how would this help to reduce air pollution in cities, as well as the way in which it influences the compressive strength of concrete, in order to determine if its use is more convenient as a mortar that is used in the coating of structures, or as an option to replace conventional concrete in the buildings.

## III. DISCUSSION OF RESULTS

### *A. Rhodamine B test*

Once the dissolved Rhodamine B was applied on the surface of the mortar samples, in a circular area of 22 +/- 2 $cm^2$ as indicated by the standard, the parameter "a" was recorded, which is like a coordinate in the system CIE L*a*b* [11] that refers to the color of the sample. The parameter "a" was recorded at 0h, 4h and 26h of exposure to sunlight, taking 5 reference points in each sample to obtain an arithmetic mean, which gave us the final parameters that are presented in Table 1 and will be used in equations 1 and 2.

*Equation 1* Value R4

$$R_4 = \frac{a(0h) - a(4h)}{a(0h)} * 100 \qquad (1)$$

*Equation 2* Value R26

$$R_{26} = \frac{a(0h) - a(26h)}{a(0h)} * 100 \qquad (2)$$

TABLE 1
Values of parameter "a"

| Samples \ Time | 0h | 4h | 26h |
|---|---|---|---|
| M-0 | 41.6 | 34.2 | 21.7 |
| M-4 | 52.4 | 28.2 | 12.6 |
| M-7 | 61.6 | 36 | 13.8 |
| M-9.5 | 57.2 | 32.8 | 17.6 |

*Source: self-made*

These values are the "a" coordinate of each sample, which refers to the red color that it approximates since they are positive values, and in order to better understand them, Figures 3, 4, 5 and 6 can be seen where we observe this color variation over time.

*Fig. 3* Rhodamine B test - sample 0 (M-0), 0h, 4h and 26hr. Source: self-made

*Fig. 4* Rhodamine B test - sample 4 (M-4), 0h, 4h and 26hr. Source: self-made

*Fig. 5* Rhodamine B test - sample 7 (M-7), 0h, 4h and 26hr. Source: self-made

*Fig. 6* Rhodamine B test - shows 9.5 (M-9.5), 0h, 4h and 26hr. Source: self-made

Having the parameters, we proceed to use the formulas to find the R4 and R26 values that will indicate the photocatalytic activity that exists in the samples, having to comply that R4 must be greater than 20% and R26 greater than 50% to determine if the samples are photocatalytic or if they are not. In table 2 we can see the comparison of the R4 and R6 values of all the samples and thus determine what percentage has a more appropriate photocatalytic activity.

TABLE 2
R4 and R26 values of the mortar samples

| Parameters \ Samples | M-0 | M-4 | M-7 | M-9.5 |
|---|---|---|---|---|
| R4 | 17.788% | 46.183% | 41.558% | 42.657% |
| R26 | 47.837% | 75.954% | 77.597% | 69.231% |

*Source: self-made*

Observing these results, we can affirm that Zinc oxide does contribute photocatalytic properties to the concrete, since it meets the aforementioned conditions, unlike the standard concrete that is below the given values.

### *B. Phenolphthalein Test*

When the samples were left exposed to the elements for 1 month, the sample is cut in half and phenolphthalein is sprayed on it. When it comes into contact with the mortar, it will begin to stain fuchsia, indicating that has an alkaline PH greater than 9, on the other hand, the parts that do not stain will be those that have a more acidic PH, which means that carbonation has occurred in that area of the sample. We can see in figure 7 what were the reactions that occurred in each sample, and in Table 3 what was the depth that carbonation reached in each of these.

*Figure 7* Reaction of mortar samples to phenolphthalein. Source: self-made

Table 3
Depth of carbonation in samples in mm

| | M-0 | M-4 | M-7 | M-9.5 |
|---|---|---|---|---|
| Depth(mm) | 1.4 | 2.2 | 4.6 | 5.8 |

*Source: self-made*

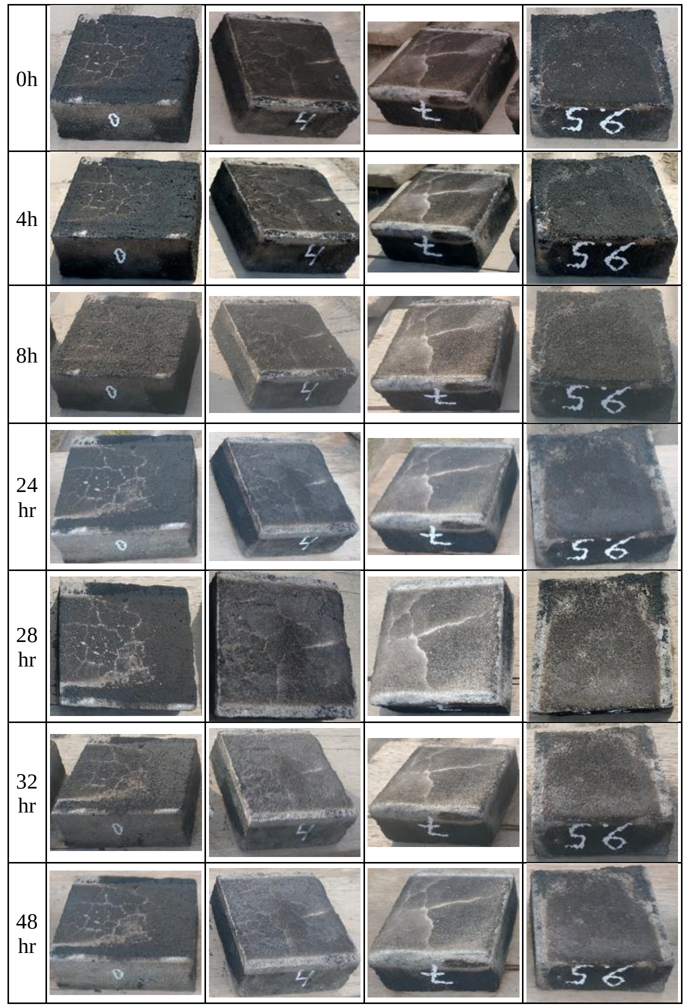
We can see that the more zinc oxide aggregate the sample has, the carbonation depth increases, this being much more significant when the aggregate exceeds 4% of the sample, so a comparison of the speed of carbonation between these 2 samples could be made to determine if it really implies a significant depth difference, which with further study could be determined with the existing equations more accurately or by longer exposure tests.

### *C. Exposure test for polluting gases*

The samples were placed as close as possible to the site where the burning of fuels, rubber, and plastics took place. After 20 minutes of exposure, the evidence was recorded and the samples were placed in sunlight to start the photocatalytic process that will oxidize the contaminants to make them harmless to the environment, thus recording how the samples reacted at 0h, 4h, 8h, 24hr, 28h, 32hr and 48hr of exposure to sunlight, as can be seen in Table 4.

Table 4
Progress of samples according to time of exposure to sunlight

| | M-0 | M-4 | M-7 | M-9.5 |
|---|---|---|---|---|




*Source: self-made*

As can be seen, the higher the percentage of zinc oxide in the sample, the greater the self-cleaning property, the better the results are appreciated after 24 hours of exposure to sunlight. Finally, water was sprayed on the samples to simulate the effect of rain and thus conclude the photocatalytic process in order to appreciate the final results of self-cleaning as shown in Figure 8 and Table 5.

*Fig. 8* Simulation of rain on samples subjected to exposure to polluting gases. Source: self-made

Table 5
Final results of the self-cleaning capacity of the samples

| | M-0 | M-4 | M-7 | M-9.5 |
|---|---|---|---|---|
| Self-cleaning ability |  |  |  |  |

*Source: self-made*

*Compressive strength test*

3 specimens of each concrete sample were tested at the age of 28 days, in order to obtain an average of the resistance in $kg/cm^2$ whose values are shown in Table 6.

Table 6
Results of compression tests of concrete samples

| Test tube \ Sample | M-0 | M-4 | M-7 | M-9.5 |
|---|---|---|---|---|
| 1 | 209.504 | 111.601 | 40.621 | 27.713 |
| 2 | 209.851 | 112.035 | 40.508 | 28.427 |
| 3 | 208.302 | 111.839 | 41.374 | 27.614 |
| Average resistance($kg/cm^2$) | 209.219 | 111.825 | 40.834 | 27.918 |

*Source: self-made*

It is observed that there is a decrease in the resistance to compression as the percentage of zinc oxide increases, so it would not be recommended for structural elements since these require that the required concrete resistance be maintained, but to better appreciate how much this difference is with respect to the compressive strength of the concrete for which the samples were designed, we have Table 7.

Table 7
Percentage Representing Expected Strength Results

| Expected resistance (210 $kg/cm^2$) | M-0 | M-4 | M-7 | M-9.5 |
|---|---|---|---|---|
| 100% | 99.63% | 53.25% | 19.44% | 13.29% |

*Source: self-made*

The 7% and 9.5% zinc oxide aggregate samples show more than 80% loss of compressive strength, while the sample of 4% aggregate shows a decrease of 46.75% of the expected resistance, therefore, despite being lower, it would no longer be suitable to be used in structural elements because it would greatly weaken the structure.

## IV. CONCLUSIONS

The investigation was able to demonstrate that by actually adding zinc oxide to a concrete mix, it manages to act by granting a self-cleaning property due to the photocatalysis that it produces, and through the tests carried out, it was possible to determine in what aspects and at what level in general it would be possible to counteract the deterioration of concrete constructions according to each of the properties that were evaluated.

In the Rhodamine B test, it was confirmed that zinc oxide acts as a photocatalytic material in concrete, its effectiveness being greater as the percentage of zinc oxide increases, but at the same time without a very significant difference between the evaluated percentages of the samples with zinc oxide, the difference between their effectiveness percentages being less than 5%.

In the Phenolphthalein test, it was found that with the percentages of zinc oxide aggregate greater than 4%, the concrete began to present a greater depth of carbonation, increasing considerably the higher the percentage of aggregate, but in the case of the comparison between the standard concrete sample and the sample with 4% zinc oxide, there is no significant difference, so with that percentage it would be possible to reduce the possibility of greater carbonation and also reduce the deterioration of buildings due to chemical attack of acids, since these two pathologies together, what they do to the standard concrete is that, as the contamination remains impregnated on the surface of the concrete, it causes it to deteriorate and at the same time accelerates the carbonation process because these contaminants are absorbed by the concrete, making it more acidic, while with the addition of zinc oxide, this contamination, which normally permeates the surface, would be decomposed and become non-contaminating particles that, with humidity or rain, would come off more easily from the surface, thus preventing further deterioration of the concrete layer by layer. To confirm this behavior in concrete, it is suggested to carry out a deeper study about this property focused on the problem of carbonation.

In the polluting gas test, it was observed that zinc oxide manages to break down the impregnated pollutants and thus facilitate their cleaning of the concrete surface, being effective with all the percentages of zinc oxide in the mixture, being more noticeable the higher the percentage of the aggregate.

In the compressive strength test, it was concluded that since there is a decrease in the normal compressive strength of the concrete while a higher percentage of zinc oxide is added, reaching a 46.75% decrease in the sample of 4% aggregate, it would not be recommended that it be used in large percentages for the construction of structural elements, since this could weaken the structure, which is always to be avoided when building a building. In this sense, it would be better to be used as a mortar.

Finally, we can say that concrete with zinc oxide aggregate is an effective photocatalytic concrete that gives conventional concrete the self-cleaning property and that this can help to counteract the deterioration of concrete constructions in different ways.

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