

## ECODESIGN IN ADVANCED TECHNICAL CERAMICS

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## 1. AIR POLLUTION IN CITIES

**The atmosphere is a common and essential asset** for life which everyone has a right to use and to enjoy, and is obliged to preserve. Since it is a vital resource, and as a result of the damage its pollution can cause human health, preserving air quality must be a priority of any environmental policy.

However, in spite of the achievements, **air pollution is still a reason for concern in Spain and in the rest of the world**. All the assessments carried out reveal that, despite the implemented measures, both the levels of pollution and the associated adverse effects are still very significant, especially in built-up urban areas. Also, the most recent studies confirm that environmental and health problems will intensify in the future if new and imminent measures are not adopted.

In the specific case of Spain, these assessments demonstrate that, under certain circumstances, the problem may become even worse due to our particular weather and geographic conditions. The **emission of nitrogen oxides (NOx)** – unavoidably formed in fossil fuel combustion – to the atmosphere produces different health problems for the population as well as negative environmental effects on the planet.

In Spain, there exists a public network of air pollution surveillance and control with measuring stations distributed throughout the entire national geography at points that represent the quality of the atmospheric air we breathe.

## 2. ECODESIGN IN ADVANCED TECHNICAL CERAMICS

In this context, **BIONICTILE®** has been developed and patented by CERACASA. This is a new range of ceramic products with photocatalytic properties the main asset of which, once installed on the façades and envelopes of polluted city centres, is that they chemically reduce the NOx (nitrogen oxides) produced by vehicles and industries to innocuous nitrites and nitrites that are soluble in water (or atmospheric humidity), continuously eliminating them from the air. This is an important contribution made by Construction Materials (CMs) to **SUSTAINABILITY IN CONSTRUCTION**.

This product is the result of a determined ECO-INNOVATION and ECODESIGN effort of two companies, **CERACASA** and **FMC FORET**:

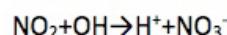
- **FMC FORET:** The company has been in Spain for over 100 years and occupies one of the main positions among the country's manufacturers of chemical products. It does significant work in Research and Development, from which the compound has emerged which, thanks to  $TiO_2$  and the addition of dopants, has a photocatalytic effect.

**Photodegradation of NO<sub>x</sub>, reducing the polluting substances present in the air.**

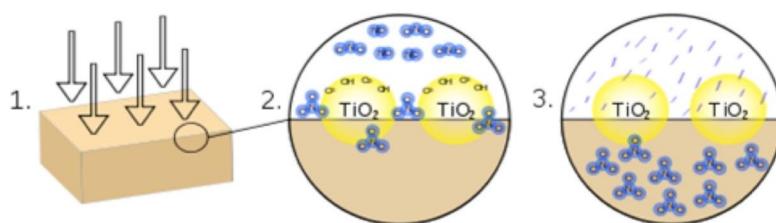
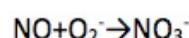
**ACTION MECHANISM. Water photolysis:**



The hydroxyl radical is a powerful oxidising agent and it can oxidise nitrogen dioxide to nitrate ions:



The superoxide ion is in turn capable of transforming the nitrate ions based on nitrogen monoxide:



*Figure 1.*

- **CERACASA:** In its innovation-specialisation strategy, it reached an agreement with FMC FORET for transferring these photocatalytic qualities of the TiO<sub>2</sub> to a glassy-immobilised ceramic tile body which is capable of reducing air pollution throughout the building life cycle once it has been installed on exteriors as façades and envelopes. CERACASA has developed the raw material prepared by FMC FORET in order to make it feasible in ceramic applications.

It has also performed an ecodesign exercise focused on designing and adapting the variables, on a laboratory and industrial scale, of surface design, surface glaze layer formulation, and manufacturing process conditions in order to achieve the maximum photocatalytic activity of the tile in time (the building life cycle).



Figure 2.

The PATENTING process for this product is currently in the application stage of the unified procedure, which allows application in a centralised manner (PCT).

### **3. METHODOLOGY FOR ASSESSING THE REDUCTION OF POLLUTION (NO<sub>x</sub>)**

#### **3.1. Laboratory tests.**

The properties for reducing pollution (NO<sub>x</sub> and other air contaminants) must be quantified through internationally standardised tests: **ISO 22197-1:2007 Fine ceramics (advanced ceramics, advanced technical ceramics) -- Test method for air-purification performance of semi-conducting photocatalytic materials -- Part 1: Removal of nitric oxide.**

- **ITQ CSIC-UPV:** the Institute of Chemical Technology – High Council of Scientific Research (CSIC) – Polytechnic University of Valencia (UPV) is a research centre specialised in the field of catalytic processes for eliminating polluting agents. It has a research team with experience and instrumentation for applying the international regulation **ISO 22197-1:2007** to assess the photocatalytic activity of the experiments carried out by CERACASA during the development of the product.

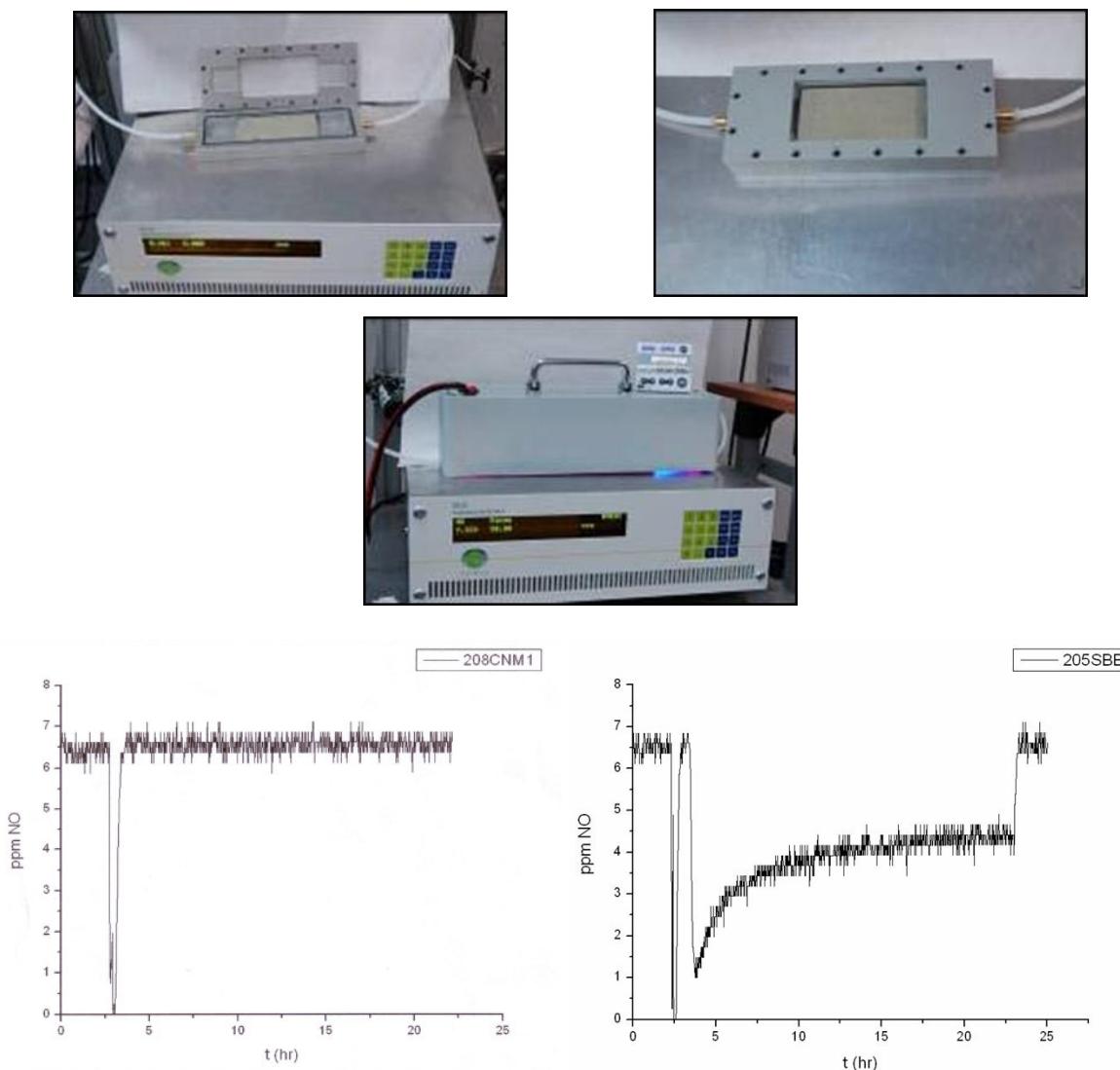


Figure 3.

The testing system consists of a flow meter which will supply the mixture of gases, a motor reactor, a UV lamp and a NOx analyser. The equipment is designed for measuring low concentrations of NOx and is built with materials with low adsorption and resistance to UV radiation. The tested tiles were photocatalytically activated by UV lighting, which caused the NO gas phase to oxidise in nitric acid (or nitrate) on its surface.

The testing conditions were as follows:

- NO = 6 ppm.
- Flow of 200 ml/min.
- Relative humidity: 50%.
- Size of tiles: 50 x 100 mm.
- 480 Wm<sup>2</sup>.

### 3.2. Climate scenarios/pollution and real-scale tests.

The verification of the decontaminating properties of this photocatalytic cladding needed to be justified with the current state of the art and technique, on the one hand simulating geographic and climate representative scenarios of the cities where it could be included on building façades and, on the other hand, the temporal scale of the useful life of reference for the building: 50-80 years.

- **CEAM**: the Mediterranean Environmental Studies Centre. The Mediterranean Environmental Studies Centre Foundation. This was created in 1991 by the Generalitat Valenciana and Bancaja, with the support of the Secretary of State for Universities and Research and of the European Commission (DG XII). It is an Applied Research Centre, recognised as a Technology Innovation Centre by the CICYT, and it operates as an Associate Unit of the CSIC.

**It has a Line II.** An operation with a great European system (EUPHORE simulation chambers), and its accessory equipment with the objective of using the knowledge and experience gained to promote technological development in measuring and controlling instruments in industrial processes.

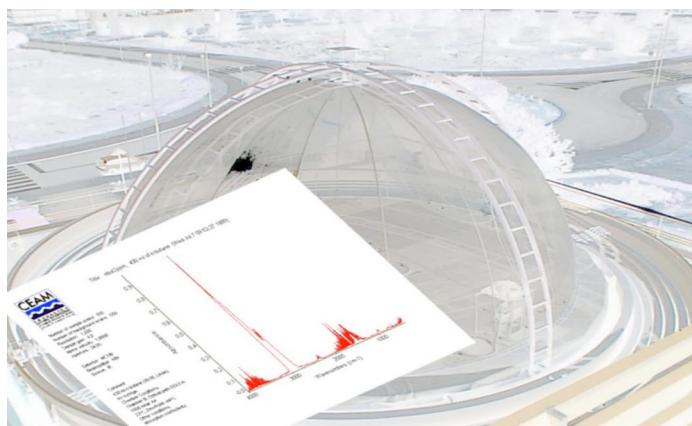


Figure 4.

### 3.3. Life cycle analysis (LCA), environmental product declaration for construction products (EPDc).

Finally, if we consider the positive and negative impacts throughout the entire life cycle of our photocatalytic ceramic cladding: from the extraction of the raw materials to the end of its useful life when the building is demolished, including the manufacturing, transport, installation on the façade while the building is being constructed and the use stage, we shall be providing the interested parties with relevant information for assessing the **SUSTAINABILITY IN CONSTRUCTION**.

It is in this context that the ISO (International Standard Organization) and the CEN (European Committee for Standardization), through mandate 350 of the EC, are completing a set of standards that will allow the "Sustainability of Construction Works" to be assessed.

- **ReMa-MEDIO AMBIENTE, S.L.:** An engineering and environmental consultancy firm with wide experience in Life Cycle Analysis (LCA), Ecodesign and Environmental Product Declaration for Construction Products (EPDc) which assesses the environmental performance of CERACASA's photocatalytic ceramic cladding using the ISO/CEN set of standards in order to quantify its contribution to SUSTAINABILITY IN BUILDING CONSTRUCTION.

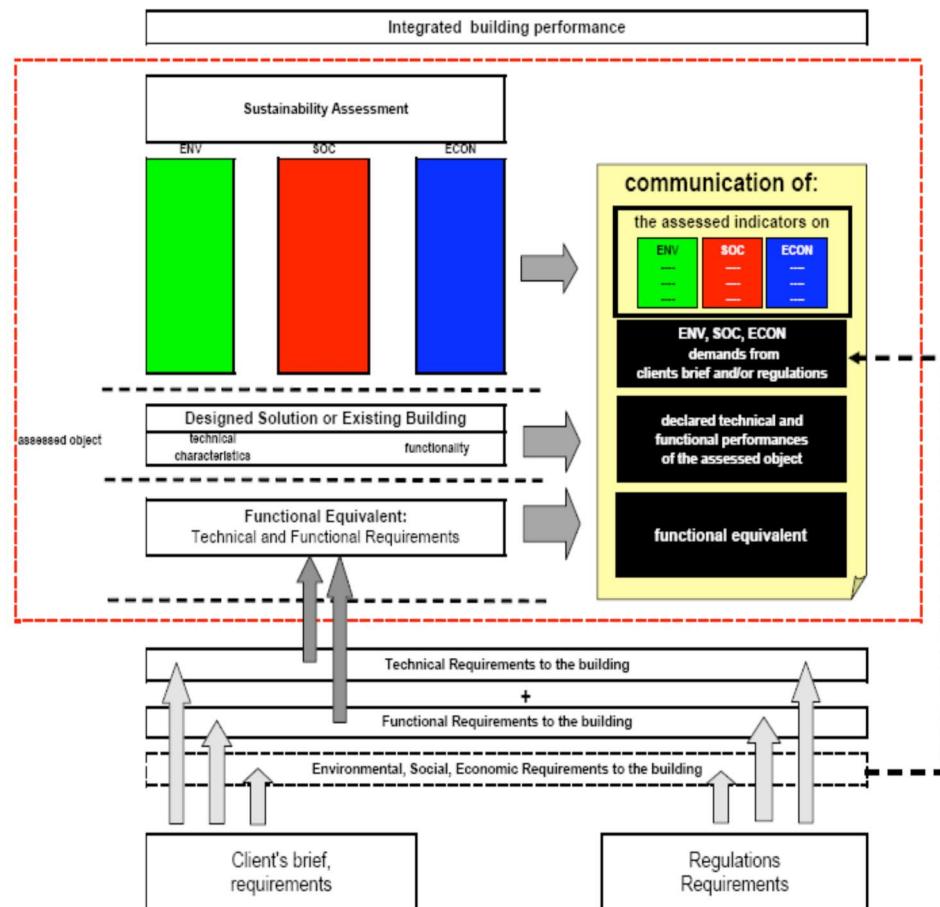


Figure 5.

#### 4. FROM DESIGN TO ECODESIGN

In the last few years, the design of ceramic products has evolved to an optimum level of production, possibilities, technical resources and multiple applications... but, in most cases, without taking the ECODESIGN factor into account.

The product described in this report, since its design, only takes one objective into account: protecting the environment and people's health while the product is being manufactured, during its useful life or the use stage.

The design of the surface of these ceramic tiles was particularly important. For this, we carried out the study and observed nature in order to try to imitate it not only in its shape, but also by studying why it has this shape and which advantages it offers us.

By analysing the macro and microscopic structure of different plant leaves, we reached interesting conclusions on how the final design of the surface of the ceramic tile should be and on the functions that were conditioning factors for it.

- We observed that, in plants, there is a general harmony between the different leaves that make it up.
- We paid attention to the repetition of textures and to the perfect symmetry that their shapes reproduce.
- The surface roughness was an important aspect in the external design of the plant and tree leaves. It is normally a striated surface.
- A surface that produces irregular microscopic shapes that increase the specific surface in contact with the air.
- This aspect is important for the sun's ultraviolet rays to react on most of the plant's surface.



Figure 6.

The product that results from this work imitates the design of the micro-embossments of the textures we see on the leaves to thereby reproduce and increase the specific surface in contact with the air, which favours the photocatalysis process.

The surface design follows some patterns that increase its contact surface. It is uniform but irregular, and finely textured. After many trials, tests and design corrections, we reached a series of conclusions.

The product must meet some thickness requirements and irregularities, but it also has to be a repetitive pattern.

The increased image reproduces the aspects that most favour the interactivity and function of the  $TiO_2$  glaze. It allows us to increase the surface in contact with the  $NO_x$ , the oxygen, moisture, and sunrays.

A larger magnification makes us see sharply that the micro-design is irregular but uniform. The pleasant touch helps, and it is self-cleaning thanks to the humidity

or water, which is a highly important factor for the ultimate purpose of reducing pollution caused by NOx.



Figure 7.

Tiles fired at 1200°C, ready to be installed as a façade. Their function in a city will be similar to that of "tile forests".

## 5. FROM INNOVATION TO ECO-INNOVATION

**ECODESIGN** provides extremely valuable functions and applications. However, if we also do an innovation exercise by providing this design with a function, we manage to increase the product's **ECO-EFFICIENCY**.

The concept of ECO-EFFICIENCY was formulated in 1992 by the companies belonging to the World Business Council for Sustainable Development.

"**ECO-EFFICIENCY** is an attempt to create the **highest value with the least environmental impact**. All in all, it is a management philosophy that allows the environmental performance of companies and other agents to be guided and measured in their economic activity. It consists of new (or modified) processes, techniques, systems, products and services that prevent or reduce damage to the environment."

The design of the photocatalytic ceramic cladding developed by CERACASA has considerable arguments (research in compositions, applications and processes) which make it different from what we can currently find on the market both in conventional ceramics and in other products with photocatalytic properties. A studied composition of the surface layer of the ceramic, which is completely interactive with the environment and which increases photocatalytic properties, along with the suitable design, offers an **extremely valuable feature**. Result: an eco-efficient product that transmits expectation and enthusiasm for it offers specific solutions and a **direct, quantifiable, immediate and continuous** benefit to society.

What novelty are we offering that other similar products do not offer?

- Ecodesign is the **axis for the development of ceramic products** with decontaminating functions.
- The **incorporation of substances that act as TiO<sub>2</sub> enhancers** has also improved the photocatalytic activity which would otherwise decline through time.
- **The enhancing additives reduce the TiO<sub>2</sub> load** by adjusting the ceramic product's eco-efficiency.
- **The high photocatalysing capacity** is combined with the high performance of the ceramic (durability, hardness, resistance and zero absorption).

All developments of this range of ceramic products have been verified according to standard tests, the **ISO-22197-1 2007 (E)** standard, determined by the Institute of Chemical Technology of the Polytechnic University of Valencia (Spain)..

### **Photo-catalyser (TiO<sub>2</sub>)**

- It absorbs light and converts it into chemical energy.
- It is deactivated due to the resulting products.
- The nitrate annuls and deactivates the properties of the TiO<sub>2</sub>.

### **Activator**

- It has no photocatalytic activity.
- It absorbs the resulting products in a priority way.
- It prevents the deactivation of the TiO<sub>2</sub>.
- It is similar to natural minerals.
- It is non-toxic and innocuous.
- It is inert.

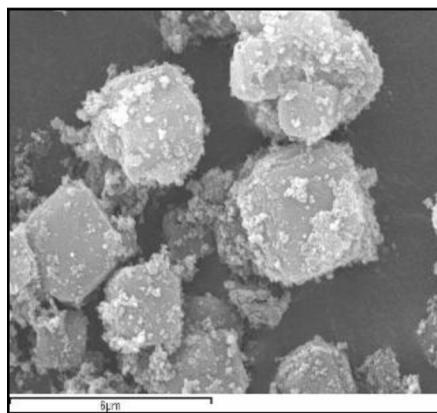


Figure 8.

### **5.1. Products resulting from the photocatalytic reaction.**

- The only products observed by ion chromatography were nitrates (98%) and nitrites (2%).

- We assume that water is also a reaction product.
- The pH of the washing water is 5.2, slightly acid, but much less than vinegar (2.9).

### **Positive effects of Nitrate on the Environment**

- Necessary for plants.
- It helps to fix  $N_2$ .
- The intake of nitrates prevents botulism.
- It increases defences against intestinal pathogens.

### **Negative effects of Nitrate on the Environment**

- Excess eutrophication of water.
- Limit in water for consumption of  $50 \text{ mg/l}^{-1}$ .
- Intoxication  $>3.7 \text{ mg/body kg and day}$ .

**Directive EU 91/676/EEC (Royal Decree 140/2003):** Human consumption distribution network: 50 mg/l nitrates and 0.5 mg/l nitrites.

- The amounts generated are lower than the indicated values, as well as being innocuous for people and the environment.

### **5.2. Durability and permanence in time.**

**Photocatalysers are resistant and do not suffer corrosion.** These metal oxides are easily found in nature.

**The activators are long-lasting and do not suffer corrosion.** These activators are found in nature.

The tests with **concentrations of NOx of 500 ppm are equivalent to a prolonged ageing** of the surface. **No problems are observed.**

**Washing with (rain) water allows** nitrates and nitrites to be detected, and the surface NOx decomposition activity **is partially or totally recovered.**

## **6. SCOPE OF THE DECONTAMINATION RESULTS**

We are faced with an important scientific challenge for assessing and quantifying this porcelain cladding's decontaminating capacity once it has been installed on a building façade. The scientific rigour and the best technical and human resources have been placed at the service of this challenge. The responsibility and credibility of the project depends on this.

## 6.1. Laboratory tests.

The Institute of Chemical Technology of the **Polytechnic University of Valencia-CSIC** carried out the laboratory tests during the product development and final finish stages according to the standard:

- *ISO 22197-1:2007 Fine ceramics (advanced ceramics, advanced technical ceramics) -- Test method for air-purification performance of semiconducting photocatalytic materials -- Part 1: Removal of nitric oxide.*

Result: BIONICTILE® is capable of decomposing the amount of 3,630 µg NOx per m<sup>2</sup> and hour (ISO 22197-1:2007), using a light that is 64 times more powerful than sunlight.

In an ESTIMATE on a city centre with **200 buildings** clad with this range of products (30 m x 40 m x 4 faces = 4,800 m<sup>2</sup> of ceramics per building), in an atmosphere 5 times more polluted than the maximum values allowed and assuming an identical insolation 365 days a year an average of 12 hours/day), **238,491 g NOx a year would be decomposed**, which is the equivalent of an 18.8% reduction in the NOx concentration in the atmosphere.



Figure 9.

## 6.2. Photocatalysis kinetic model.

The photocatalytic reaction kinetics of NOx is influenced by different variables, such as:

- Light intensity.
- Relative humidity.
- Concentration of NOx.

A kinetic model therefore needs to be defined and verified which allows the decontamination potential to be predicted and calculated in time and in the different real conditions we shall find in the cities where it is installed.

The Institute of Chemical Technology of the **Polytechnic University of Valencia-CSIC** has worked in this direction and the kinetic expression corresponding to the **Langmuir-Hinshelwood** model has been obtained.

$$r_{NO} = -\frac{k K_{NO} C_{NO}}{1 + K_{NO} C_{NO} + K_w C_w} \quad k = k' \left( -1 + \sqrt{1 + \alpha E} \right)$$

$$v_{air} \frac{dC_{NO}}{dx} = a_v r_{NO} \quad C_{NO}(x=0) = C_{NO,in}$$

Parameter	Value
$K'$ (mole dm <sup>-2</sup> min <sup>-1</sup> )	$7.24 \times 10^{-10}$
$\alpha$ (dm <sup>2</sup> W <sup>-1</sup> )	$1.40 \times 10^6$
$K_{NO}$ (dm <sup>3</sup> mole <sup>-1</sup> )	$2.50 \times 10^{10}$
$K_w$ (dm <sup>3</sup> mole <sup>-1</sup> )	$7.67 \times 10^5$

Table 2. Non linear parameters optimization (based on 36 experimental results) employing the Excel Solver tool and the numerical solution of the NO differential mass balance performing a forward discretization.

### 6.3. Validation of the predictive model and real-scale tests.

The scope of the pollution reduction results needed to be validated and, in any case, we were obliged to adjust the model through real-scale tests. To do so, a search was made for the expert organization and the facilities capable of carrying out these tests and the result was:

- **Expert organization:** CEAM, the Foundation of Mediterranean Environmental Studies Centre
- **Laboratory facilities with this capacity: (EUPHORE simulation chambers),** one of the three that exist in the world which does basic and applied research in three areas of investigation: Atmospheric Chemistry, R&D on pollutant dynamics and pollutant dynamics applications.



Figure 10.

Experiments have been programmed to be carried out in November, and the results are expected to be available for the dates of QUALICER 2010.

#### Design of the Experiment:

- **City:** Valencia.
- **Climate scenario:** Mediterranean winter period.

- Duration: 4 days.
- Atmospheric conditions: clear day with a high light intensity.
- Atmospheric variables: A concentration of contaminants of a standard Valencia city station.

#### **6.4. Assessment of the impact of the construction solution during the building life cycle.**

The results using the available knowledge, facilities, experiments and experts, certified by independent organizations for a construction material or a construction solution are of no use independently, but they have to be included in the international assessment framework of SUSTAINABILITY IN CONSTRUCTION.

It is in this context that the ISO (International Standard Organization) and the CEN (European Committee for Standardization) are completing a set of standards that will allow "Sustainability of Construction Works" to be assessed.

The assessment of the performance of this range of photocatalytic porcelain claddings as a functional unit within the building life cycle is at an advanced stage, and the following are being completed:

- a) **Life Cycle Analysis (LCA) study** according to the Product Category Rules (PCR).
- b) Preparation of a **Project Report** for verification by the authorised company.
- c) Preparation of an **Environmental Product Declaration for Construction Products (EPDc)** in the framework of a national or international programme.
- d) **Verification of the EPDc** by the authorised verifying company.
- e) Obtaining the **registration and label for BIONICTILE®** which allows it to be used by operators and parties interested in SUSTAINABILITY IN BUILDING CONSTRUCTION. The design of ceramic products has evolved in the last few years to an optimum level of production, possibilities, technical resources and multiple applications..., but, in most cases, the ECODESIGN factor has not been taken into consideration.

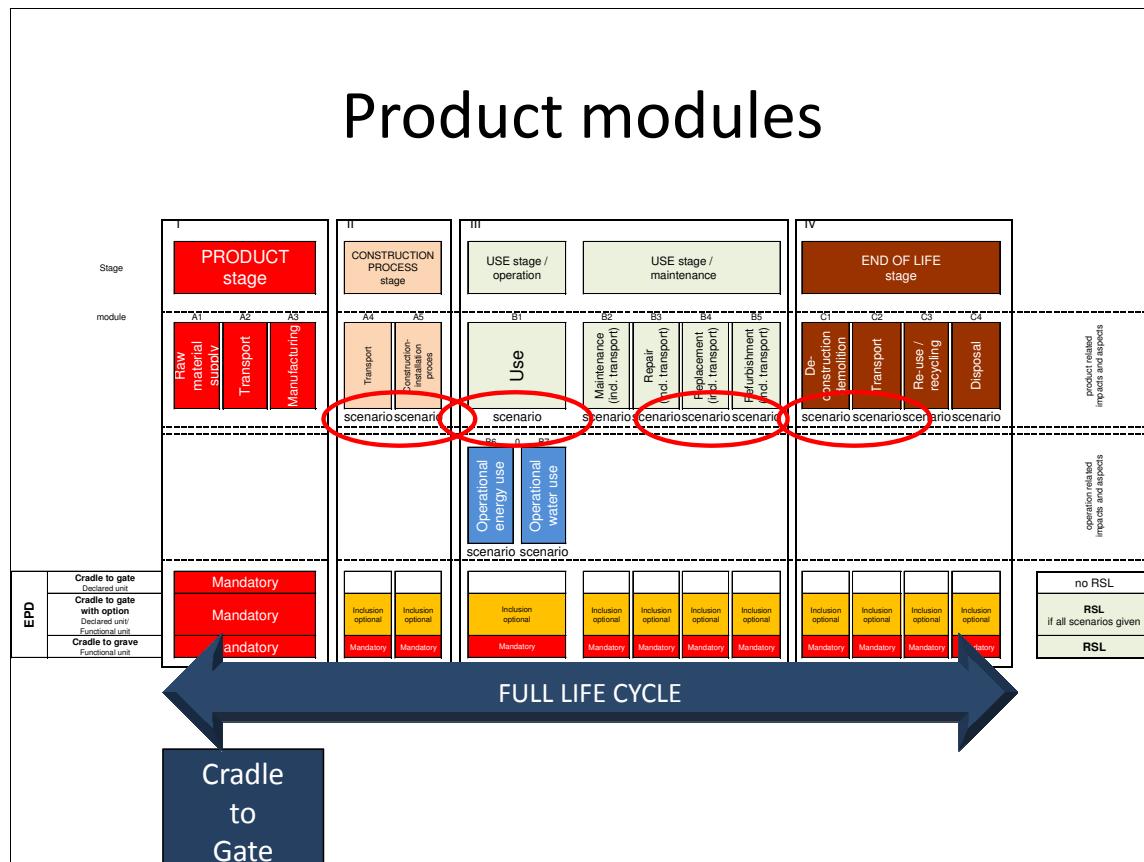


Figure 11.

## 7. PROPERTIES TO BE INVESTIGATED – BENEFITS TO BE QUANTIFIED

The state of the art of the photocatalytic properties of TiO<sub>2</sub> indicates that they go beyond reducing the NOx; in the literature, properties for reducing other contaminants like volatile organic compounds (VOCs), as well as bactericidal and fungicidal properties, are mentioned.

The project team is conducting a follow-up of the work documents of the ISO-TC 206 "Fine ceramics", which is preparing international test methods for:

- **ISO/CD 22197-2:** Test method for air purification performance of semiconducting photocatalytic materials – **Part 2: Removal of acetaldehyde.**
- **ISO/CD 22197-3:** Test method for air purification performance of semiconducting photocatalytic materials – **Part 3: Removal of toluene.**
- **ISO/WD 22197-4:** Test method for air purification performance of semiconducting photocatalytic materials – **Part 4: Removal of formaldehyde.**
- **ISO/WD 22197-5:** Test method for air purification performance

of semiconducting photocatalytic materials - **Part 5: Removal of methylmercaptane.**

- **ISO/FDIS 27447:** Test method for **antibacterial activity** of semiconducting photocatalytic materials.
- **ISO/WD 13125:** Test method for **antifungal activity** of semiconducting photocatalytic materials.

In a city environment, this product is capable of eliminating hydrocarbons that are present in the air.

It also **degrades the volatile organic compounds** contained in paints and plastics used in street furniture.

In interior applications, homes and offices, it can be used for **air treatment and disinfection.**

It has a **bactericidal effect** due to its surface acid pH.

## 8. CONCLUSIONS

Ceramics are still static elements, but let us think of the reflection made previously about being able **to convert buildings into trees and cities into tile forests** that carry out a continuous decontaminating function. This means a change, a revolution in favour of the environment and of the improvement in the quality of life.

The **BIONICTILE®** products by CERACASA open up a new way to design the 21st century's sustainable architecture with the use of **ecodesigned** and **eco-efficient** materials, since our responsibility towards the environment must acquire more importance every day.

**Specialisation, research and innovation are a significant part of our company philosophy, but acquiring a serious commitment to the Environment by designing and developing sustainable materials prevails over everything else.**

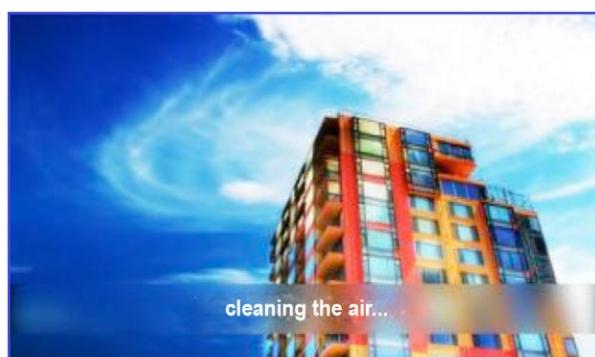


Figure 12.

## 9. CERTIFICATES



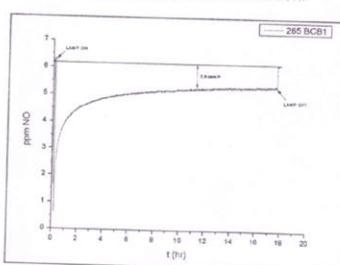
Hermenegildo García Gómez, Spanish ID 20.402.567-A, Full Professor at the Technical University of Valencia and at the University Institute of Chemical Technology (from now named as ITQ), CERTIFIES THAT:

The results presented by CERACASA about the photocatalytic activity of the ceramic sample with reference number 265 SBB1 (a porcelanic piece containing the photocatalytic coating BIONICTILE) have been performed in my laboratory and under my supervisión, following an adapted versión of the ISO 22197-1: 2007 standard that is recommended to determine the photocatalytic activity of surfaces exposed to UV light.

The conditions of the measurements have been the following:

- NO concentration = 6 ppm
- Gas flow 200 mL/min
- Relative humidity : 50%
- Sample size: 50 x 100 mm
- Light intensity 480 W/m<sup>2</sup>

The following plot obtained from the corresponding chemiluminescence NO detector shows the photocatalytic response in the decrease of the NO concentration:



Based on these data and according to the above-mentioned ISO standard, these results show that the ceramic tile exhibits photocatalytic activity for the decomtamination of nitrogen oxides.

Therefore and in order to prove it and upon CERACASA request, I sign the present document in.

Valencia, September eight of two thousand and nine



Fdo. HERMENEGILDO GARCIA GÓMEZ

Figure 13.

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