

#### UNIVERSITY OF POLYTECHNIC DELLE MARCHE

(Department of Materials, Environmental Sciences and Urban Planning (SIMAU)Engineering Faculty)

Innovative multifunctional finiture for the comfort and health of indoor environments

Student

Rao Muhammad Aftab Mehboob

Supervisor

Prof. Francesca Tittarelli

Co- Supervisor

Eng. Chiara Giosuè

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## **1** Chapter 1 Introduction

#### 1.1 Indoor air quality

Indoor air quality (IAQ) is a term which refers to the air quality within and around the area of the building and structures, especially more focused on health and resident building. Indoor air quality does not only focus on improving residential buildings like a house an apartment but also on nonresidential structures for example schools, factories, and hospitals. The level of indoor air quality within a building can be affected by conditions such as odors, humidity, or chemicals. More specially, factors such as lead based paints, secondhand smoke, and high level of CO<sub>2</sub> can create unhealthy and even dangerous living environment. European people are spending 90% of their time in indoor environment, much more than a year ago. These environments correspond to e.g., buildings offices, schools, and public transport. Researchers and expert policymakers have discussed the role of indoor air quality in several documents, and they stressed the determinant role of IAQ on population health. The harmful risk of the indoor environment due to a high concentration of pollutants is significant. The pollutant is classified into different categories: physical, chemical, and biological for some examples are volatile organic compounds (VOC).

The relationships between the volume of air contained in the indoor space, the rate of production or release of the pollutant, the rate of removal of the pollutant from the air via reaction or settling, the rate of air exchange with the outside atmosphere, and the outdoor pollutant concentration determines the concentration of a pollutant indoors. Actual human exposure, on the other hand, is notoriously difficult to quantify. This is due to the fact that an individual's behavior and activity patterns can have a significant impact on their exposure levels. The results of the US Environmental Protection Agency's (EPA) TEAM (Total Exposure Assessment Methodology) tests conducted in the 1980s repeatedly reveal that personal exposure to numerous contaminants can far exceed those expected from concentrations [1].

#### 1.2 Nature and Types of VOCs

VOC are wide range type of chemicals that are found in many products used to construct and decorate homes. Once used, they release "off gas" into the indoor air which may be detected by smell. For example, VOCs which may be present in the air are: methylene chloride, formaldehyde, benzene, ethylene glycol.

VOCs are sometimes categorized by the ease of how they will be emitted. For example, the World Health Organization (WHO) categorizes indoor organic pollutants. There are three types of volatile organic compounds (VOCs) based on the boiling point of each chemical; including.

- 1. Very volatile organic compounds (VVOCs)
- 2. Volatile organic compounds (VOCs)
- 3. Semi-volatile organic compounds (SVOCs)

For example, acetaldehyde and formaldehyde fit for VVOC grouping, whilst chemical including toluene, xylenes, and benzene are categorized into VOCs. The most common indoor air pollutants are defined as heaving a boiling point between 50°C and 260°C. The low boiling point allows evaporation of VOCs from the solid phase into the air. The total number of VOCs detected in the indoor air is usually higher than in outdoor air. In 1981, over 250 VOCs were identified, in 1986 the amount of VOC s increased up to more than three hundred, and in 1989 the United States Environmental Protection Agency identified over 900 VOCs [2].

Description	Abbreviation	Boiling Point Ranges (C)	Example Compounds
Very volatile (gaseous) compounds	vvoc	<0 to 50-100	Propane ,butane
Volatile organic compounds	VOCs	50-100 to 240-260	Formaldehyde, d- Limonene,toluene, acetone,
Semi-volatile organic compounds	SVOCs	240-260 to 380-400	Pesticides, (DDT, chlordane, plasticizers )

#### **Table 1.Analysis of Volatile Organic Compounds**

Volatile organics are a group of substances with boiling points ranging from below 0°C to around 400°C. WHO divided them into four categories, Compound volatility was used to classify the stocks. This overview is focused on volatile organic compounds (VOCs), which have boiling points ranging from 50°C to 260°C. The molecular weight ranges from 50-70 Dalton to around 300. In the temperature and humidity ranges

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seen inside, VOCs reside mostly in the gas phase. Except for boiling point and vapor pressure, there is no evident distinction between SVOCs and VOCs. Aldehydes in general are also taken into account in this review. In the interior environment, hundreds of organic compounds have been discovered. depicts the primary classifications. Their indoor/outdoor concentration ratios are also used to classify them. The ratio is more than one for common indoor VOCs. Furthermore, VOC concentrations exhibit significant change in time and place, because of source dynamics and building features. The latter is exemplified by the wide range of building styles and ventilation methods used. Indoors, concentrations are typically below threshold limit value (TLV) and below airway irritation thresholds. Indoor concentrations are typically below TLV levels and below airway irritation limits, but they may exceed odor thresholds. With the exception of formaldehyde and acrolein, VOCs measured indoors are generally considered "non-reactive" as single compounds. Because of the multifactorial etiology of sick building syndrome (SBS), a direct link between VOC concentrations and increasing SBS prevalence is difficult to establish. Particles, particularly floor dust, can act as transporters of VOCs and SVOCs, making skin resuspension an option to inhalation. In addition to surfactants, dust can also carry water soluble VOCs such formaldehyde.

#### **1.3 Human Health Effect**

Indoor air pollution is now realized as an important public health issue. The role of indoor air pollution in producing bad effect on human is more complex and less well understood than the role of outdoor air pollution. Adverse health effect from a particular substance will result from a broad range of responses and reactions that in the body. The biological mechanisms of poor health effects are largely dependent on the chemical structure and reactivity of the substances. The air quality can have a serious impact on health and sense of well-being. The public point of view, air pollution and its potential health effects is invariable linked to the emission from industrial stacks and motor vehicles. The main concern is the potential for VOCs to adversely impact the health of people that are exposed. As VOCs have a different chemical classis the severity of results at the same concentration level may differ by order of magnitude. Moreover, many pollutants are present at low concentrations, there may be possibility of combined human health effects can be very different to predict. The health effect of VOCs in the non-industrial indoor environment ranges from sensory irritation at low levels of exposure to toxic effects at high exposure levels. Some of the sudden effects include an irritated eye, runny nose, or headaches. It is necessary to remember that VOCs belong to different group of chemicals, each chemicals have its own toxicity and potential for causing different health effects.

It is apparent that burning biomass (particularly for cooking) produces a lethal cocktail of pollutants in developing regions of the world. Every year, over 2,000,000 individuals, mostly women and children, die as a result. It is one of the world's most pressing environmental and health challenges, but it has received little attention so far. In general, little is known about indoor air quality and ailments, such as allergies. Multidisciplinary reviews of the whole scientific literature have been done in the Nordic nations (NORDWORKS) and in Europe to highlight the state-of-the-art in scientific knowledge about exposures in non-industrial indoor settings and health (EUROWORKS). Over the last 30 years, the prevalence of asthma and allergies has risen across the developed world. Because of the brief time span in which this increase occurred, it is more likely to be related to changes in environmental exposures than to genetic alterations. Because interior air is the most common exposure route, changes in indoor environments require specific attention. Increased exposure to allergens and/or adjuvants (enhancing substances) could each be a contributing cause. Several multidisciplinary assessments of the scientific literature on the relationship between indoor exposure and health/asthma/allergies have been undertaken. There is now scientific evidence that single VOC concentrations, or the total mass of such (measured) compounds TVOC, are not a viable assessment of health concerns, and that new meaningful risk indicators for exposure to organic compounds in indoor air in non-industrial settings are needed. In comparison to particle exposures in ambient air, there is minimal scientific evidence about the impact of particles in indoor air from a health standpoint. This could be due to a lack of studies and challenges in determining the health effects of particles (so far, mainly mass or number).

#### **1.4** Conventional strategies for Indoor Air Quality:

There are three well-known strategies which target dilution of indoor air pollutants The primary technique to dilute indoor-emitted contaminants is by ventilation. During this technique outdoor air (OA) is introduces into a building, Odor, and pollutants, emitted by unavoidable sources, are removed, and displaced by ventilation [3]. To enhance this method gas adsorption and chemical gas filters are used along with dilution and ventilation. This ventilation air must be controlled to take care of temperatures and relative humidity in an appropriate range to match the indoor environment which is named as active engineered control systems (in Heating, Ventilation, and Air-Conditioning, HVAC). It needs majority of energy consumption especially in commercial buildings [4]. The energy cost of increased ventilation could also be reduced by systematic heat recovery. The second technique is source control which has also been used with great success outdoors and it is the reason why the outdoor air quality in many cities within the

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advanced world is even better in the recent time as compared to 20 or 50 years ago. In the new European guidelines for the indoor environment [5]. there is brawny uplifting to design low-polluting buildings and direction on low-polluting building materials are given. The method of source control limits dangerous discharge by locking the source. This method bases its effectiveness on the limitation, as an example, of furniture or forbidding smoking in indoor environments. Source control is the most effective thanks to reduced indoor pollution, but sources usually cannot be avoided because pollutants come from occupancies activities. The most origin of airborne bacteria is in enclosed spaces is animal organisms and human. Additionally, microbiological indoor air pollutants may develop in heating or ventilation systems, monitoring of microbial IAQ is therefore necessary. For several years now, occupants of polluted cities have frequently used air purificators (Aps) which is one amongst the techniques to extend their wellbeing by decreasing their exposure to air pollutant [6].

#### 1.5 New perspective for Indoor Air Quality: passive systems

Buildings account for about 40% of the global energy consumption and contribute over 30% of the CO2 emissions. A large proportion of this energy is used for thermal comfort in buildings [7]. Thus, energy efficiency for maintaining the indoor environment healthier is the global challenge.

The previous study states [8] that conventional indoor air cleaning methods are usually ineffective since they merely replace the contaminated air with new polluted air (ventilation systems) or change the pollutant to a different phase without neutralizing it (air purifiers). Building's materials (e.g., mortars, internal plasters, and finishes) can positively interact with indoor environment, as reactive building materials can help active systems to be effective using less amount of energy [9]. It has been demonstrated that indoor materials can act as buffers for VOCs, and it has been highlighted that polar compound were more strongly adsorbed by highly porous materials [10]. Depolluting process in passive building materials can be promoted by two different processes: adsorption and Photocatalytic Oxidation (PCO). Adsorption could be a process where fluid phase components (adsorbates), which might be gaseous or liquid, are transferred on the solid surface (adsorbent). This is often a passive removal system of substance. Forces of attraction are established among the compounds of fluid phase: the adsorbate covers the surface of the adsorbent with a molecular layer.

The methods want to capture are differences in polarity (force of electrostatic nature), difference in relative molecular mass (components with higher mass will have a next boiling temperature, so it will

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deposit preferentially on the surface of the solid) difference in size (geometry of the particle size is that the base for a mechanism, the solid has the function of molecular sieve). A fundamental requirement for the adsorption process is that the high specific surface of the solid adsorbent because the adsorption process is concentrated on the surface of the solid (the process needs a high contact area soil-fluid). Very porous particles are needed to realize the method (surface area of 300 – 3000 m2/g). A large extend of adsorptive materials is required for cleaner air to get high removable efficiency of pollutants [9].

PCO may also represent an optimum option choice to provide a healthier indoor environment. The appliance of nanotechnology with engineering science related industry can play a vital role within the quality of building materials [11]. One amongst the foremost famous nano-catalyst is TiO2: nowadays there is an increasing interest in using this catalyst is in cementitious materials [12], [13]. PCO could be is a superficial phenomenon [14] well researched for the decomposition of pollutants in less harmfully compounds. PCO degradation of pollutants implies different steps, indicated to previous authors [15], [16]. The reaction mechanism needs UVA light wavelength (320 - 400 nm) to be activated, so it is possible the generation of hole/pair. This step is then followed by the adsorption phase of the pollutants onto the TiO2. Fundamental requirements for indoor materials are that the high transpire ability, to avoid the storage of humidity and therefore the ability to be a hygroscopic buffer able to absorb and desorb moisture [17], [18]. A promising strategy during this sense is expounded to the employment of hygroscopic materials to dampen indoor humidity variations [19]. Daily changes in room humidity (RH) can be modulated by the indoor porous materials. Water vapor is absorbed during exposure at high levels of RH and then released during the desorption phase. This capacity can be expressed in terms of Moisture Buffering Value (MBV) [20]. Against the expansion of molds, TiO2 is tested. If activated, TiO2 gives a high photocatalytic activity, and increases not only the efficiency of NO removal but also a complete inactivation of molds [21]. Furthermore, the overall high alkalinity of cement-based mortars could inhibit itself the biological war [20].

## 2 Chapter 2. Material and Method

## 2.1 Material

An analysis of the finishes and subfloor mortars available on the market was carried out to select both the reference finish to be compared with the patented formulation and 2 different substrates to be tested in combination with the patented formulation.

From the results obtained, 2 commercial premixes were selected as substrates (Figure 1.1) produced by Diasen srl (Sassoferrato, AN):

- 1. Historical Lime C: one-component mortar based on natural hydraulic lime NHL 5, characterized by excellent mechanical resistance and high adhesion to the support.
- Diathonite Deumix D: fiber-reinforced dehumidifying product with cork, clay, natural hydraulic lime NHL5, diatomical powders, highly breathable, ideal for carrying out dehumidification interventions.



Figure 1.Tested commercial substrates: CALCE STORICA (left) and DIATHONITE deumix (right)

- Lime paint L: water paint currently used as a finish for the background Calce Storica and Diathonite Deumix, highly opaque and breathable, lime-based, to be used as a finish for walls and ceilings indoors. Its high breathability helps to regulate the hygrometric balance of the rooms, preventing the formation of mold and contributing to indoor well-being.
- Argacem HP A: Powder finishing shaving based on hydrated lime, natural fillers, and pure mineral aggregates of calcareous origin that give the product antibacterial and vapor permeability properties currently used with Lime paint L as a finishing package for the Diathonite Deumix D substrate.

The application of Lime paint requires the preliminary application on the substrate of a Primer based on acrylic resin to water **(D20)** to improve the adhesion and durability of the finish.



Figure 2.Tested commercial finishes: LIME PAINT (left), ARGACEM HP (center) and Primer D20

## 2.2 Choosing the Substrate on Which to apply the Finish

Multifunctional MORTAR is a finish for indoor applications based on:

- 1. biomass ash
- 2. light adsorbent aggregates
- 3. photocatalyst, capable of mineralizing adsorbed pollutants
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To confirm its effectiveness in improving energy saving, comfort and healthiness of environments even on a real scale, the activities developed in the period 15-03-2021/15-09-2021 (SAL 1) concerned the:

#### 2.2.1 Choice of biomass ASH:

to package the patented finish on a large scale among those easy to find

#### 2.2.2 Synthesis and characterization of an innovative photocatalytic agent:

from industrial by-products to be included in the patented finish to replace commercial  $TiO_{2}$ , for an improvement in sustainability and, possibly, photocatalytic performance

## 2.2.3 Characterization of the finishing specimens

(at laboratory scale)

#### Choice of Biomass ASH

The patented finish is packaged with light (Fly Ash) and heavy (Bottom Ash) biomass ash which, being industrial by-products of the combustion of cellulosic wood biomass to produce electricity, give the finish sustainability, low cost, but also lightness (Bottom Ash) and mechanical performance thanks to the pozzolanic action (Fly Ash).

Packaging the patented finish on a large scale requires the choice of biomass ash that is easy to find. As industrial by-products, biomass ash from different plants has different properties. Even with the same plant, given the variability of incoming biomass, the relative by-product may have different characteristics.

Among the easily available biomass ash, 3 different light and heavy ash were selected from a:

- 1. **Ravenna** https://www.powercrop.it plant
- 2. **Rieti** https://www.epicoholding.it/ plant
- 3. Trento https://www.ledroenergia.it/ plant



Figure 3.Bottom and Fly Ashes analyzed

which have been tested in terms of:

- 1. Chemical Characterization of Ashes by X-Ray Diffraction and Thermogravimetry
- 2. Finish obtained with ashes: Porosity, Mechanical Properties, Aesthetic Appearance

## 2.3 Prepare Green Synthesized TiO<sub>2</sub> (Anatase) Nanoparticles

 Wash Olive leaves waste thoroughly with tap water to get rid of soil/sand impurities etc. (you can do synthesis this with Autumn fall leave waste as well, but now in this season, they are not available) and put them at room temperature for drying (it is important to dry at room temperature to avoid photodissociation of secondary metabolites).

- 2. Completely dried leaves (usually it will take 2-3 days at room temperature) will be grinded using electric grinder to get very fine powder.
- 3. Next step is preparing water extract: Take 5g of as prepared leave powder into 100mL of  $dH_2O$ . with this ratio you can proceed (probably you need in liters, so take 50g/L).
- 4. Leave powder will be soaked in dH<sub>2</sub>O for 24 hours, then heated at 85C using hot water bath for 3 hours. Allow the extract mix to cool down at room temperature and put for filtration (Whatman filter paper). Collect the filtrate (water extract) from the bottom and store at room temperature for further usage (we have to use it within 48 hours). Residue powder left over the filter paper will be discarded. It is good to store the extract in flask washed with methanol, otherwise we will have fugus in the extract after 24 hours.
- 5. Now your extract is ready, next step is setting up the reaction mixture Take 0.1 M Titanium sulphate salt by weight (it is Sulphuric acid hydrate salt in water extract.

You need to check the molecular weight of the salt first and then take 0.1 M into 1 liter of the extract. Prepare 3M solution of NaOH in 200mL because you going to need this later. Before you put titanium salt into extract it is important to set the reaction flask with extract on the hot plate magnetic stirrer and set the reaction temperature to 85 C and stirring 300rpm. When the extract temperature reaches 85 C (you can check the temperature using temperature probe, temperature should be between 85-90 C, not less or more), slowly add the calculated weight of the salt.

First allow the reaction to continue for 20 minutes, then start adding NaOH through dropper to slowly increase the pH of the reaction to 4 in 1.5 hours (pH can be check using pH strips). Please note that before adding NaOH, the pH is almost 0-1. Once the pH reaches to 4, stop the reaction, remove the reaction flask, and put at room temperature of cooling.

After cooling, shake the flask, start pouring/filling reaction mixture in centrifuge tubes, and centrifuge at 9000 rpm for 15 minutes. Remove the supernatant after centrifugation and recover the product from the bottom. Recovered product will be washed again two times with water through centrifugation at 9000 rpm for 15 minutes (this step is important to get rid of uncoordinated secondary metabolites).

6. All the collected products will be first dried at 85 C in heating oven for 24 hours then calcined in furnace at 370 C for 5 hours (when your stich off the furnace, please don't remove the product immediately, allow the temperature to fall down at least 90 C). After calcination and cooling the product at room temperature (in dissector) please thoroughly grind (manually using mortar/pistil) the product to achieve the homogenous size distribution!

## 3 CHAPTER 3. Result and Discussion

## 3.1 Characterization of ash

Chemical analysis by X-ray diffraction (XRD) that all biomass ash tested contain calcium carbonate  $(CaCO_{3})$ and calcium oxide/hydroxide (CaO, Ca(OH)2). However, Ravenna ash is also very rich in sodium and potassium sulfate (Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub>) and potassium chloride (KCl), all soluble salts that could give efflorescence problems to the finishes during their life in service.



Figure 4. Chemical characterization by XRD of the ashes of the Ravenna, Rieti and Trento plants

In addition, the visual examination showed a markedly darker color for the ashes of Ravenna which would inevitably give a darker color even to the finish in which they are added, affecting the possibility of coloring the same by means of pigments, a characteristic that is very important for the marketing of the final product. So the ashes of Ravenna were immediately excluded from the subsequent experimentation. The thermogravimetric (TG) analysis was therefore conducted only on the ashes of Trento and Rieti at v = 10 ° C / min, in the air. The weight loss by endothermic process up to about 150 ° C is due to the loss of H<sub>2</sub>O, the exothermic one from about 120 ° to 450 ° C to the combustion of organic material, around 500 ° C there is an endothermic weight loss due to the decomposition of Ca (OH)<sub>2</sub> and the last endothermic weight loss up to about 800 ° C is due to the decomposition of CaCO<sub>3</sub>.



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 Figure 5.Chemical characterization by TG of the ashes of the Rieti and Trento plants

From TG analyses it was possible to quantify the Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> content of the ashes

	Fly Ash Trento	Bottom Ash Trento	Fly Ash Rieti	Bottom Ash Rieti
Ca(OH) <sub>2</sub>	1.3	0.6	0.8	8.2
CaCO <sub>3</sub>	25.4	17.5	25.4	30.0

Table . Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> content of Trento and Rieti ash (% by weight)

While the 2-light ash have a comparable  $CaCO_3$  content, the heavy ash of Rieti has a  $CaCO_3$  content almost twice that of Trento, justifying their slightly lighter coloration. On the other hand, the content of Ca  $(OH)_2$ , which could contribute to the activity of the binder used to package the finish, is significantly higher in the heavy ashes of Rieti.

#### 3.2 Finish obtained with ashes: Porosity, Mechanical Properties, Aesthetic

#### Appearance

To evaluate the effect of the 2 ashes of Rieti and Trento on the porosity, the mechanical performance, and the aesthetic appearance of the finish in which they are inserted, with each biomass the finish was packaged, following the patented formulation, without considering the addition of the photocatalytic agent. In particular, a silica gel in granules with =  $1.31 \text{ g/cm}\rho^3$  was used under SSA (Saturated Dry Surface) conditions, with absorption at = 86%, previously ground and sieved at a d<sub>max</sub> = 300 µm by means of a marble mill .To ensure the clear color of the formulation, ITALCEMENTI's PRO CALIX WHITE NHL 3.5 natural hydraulic lime was chosen as the binder





Figure 6.Silica Gel (left) and Natural Hydraulic Lime (right) used to package finishes

The 2 Bottom Ash, already characterized in terms of particle size distribution and cleaned of the coarsest impurities , were ground by means of a marble mill for a total of 45 minutes (30 min + 15 min) and sieved at  $ad_{max} = 500 \text{ um}$ .



Figure 7.Particle size analysis of heavy ash from Rieti (left) and Trento (right)



Figure 8. Marble mill (left) and coarse impurities separated from heavy ash (right)

Bottom ash, fly ash and dry silica gel were mixed first; then, the lime was inserted and finally the amount of water needed



Figure 9.Aggregates + Lime (left) and final dough UNIVPM (right)

The workability, measured by means of the slump test (UNI EN 1015-3:2007) was rigid (UNI EN 1015-6:2007; d < 140 mm), optimal as a finish to be applied in vertical walls



Figure 10.Slump UNIVPM finish test

After 7 days of curing at UR = 95% and T = 23 ° C and 21 days of curing in air, the mercury porosimetric test showed a greater open porosity (to the advantage of the breathability of the finish) and, despite this, a greater mechanical compressive strength, for the mortar packaged with Rieti ash (Probably the higher content of Ca(OH)<sub>2</sub> in the heavy ash of Rieti compared to that of Trento, contributes to the development of the mechanical performance of the finish.



Figure 11.Comparison of the porosimetric distribution of finishes packaged with the ash of Rieti and Trento

Table 2.Total porosity, average pore diameter and mechanical strength of finishes packaged with Rieti and Trento ash

	Porosity (%)	average diameter (μm)	Rcm 28dd
UNI Rieti 2021	51	0.0418	8.7
UNI Trento 2021	46	0.0501	3.5

In addition, visual observation showed a slightly lighter coloration of the finish packaged with the ashes of Rieti than that packaged with the ashes of Trento



Figure 12. Aesthetic appearance of the finishes made with the ashes of Trento (above) and Rieti(below).

Since among the ashes tested, those of Rieti were those that give the finish:

- 1. the lightest color
- 1. a low content of soluble salts responsible for possible efflorescence
- 2. greater porosity to the advantage of lightness and breathability
- 3. better mechanical performance

#### 3.3 Synthesis and Characterization of an Innovative Photocatalytic Agent

#### 3.3.1 Summary of the old TiO<sub>2</sub>

The application of nanotechnology can play an important role in the quality of building materials. Different commercially available titanium dioxides (TiO2) are tested and compared in this thesis. The photocatalytic products are: P-25 Aeroxide by Evonik and two different products by KRONOS International, Inc., activated by visible light (according to the technical datasheet).

P-25 is probably the most used photocatalytic agents UVA sensible in commerce. The properties are taken by the data sheet. This TiO2 is a mixture of anatase-rutile amorphous phases, 78 – 14 - 8% in weight, respectively. Particles have nano-size of about 20 - 50 nm. The specific surface, measured by BET, is 35 -65 m2/g. The pH value in 4% dispersion is 3.5 - 4.5. Density is evaluated as 3.1 g/cm3. KRONO Clean<sup>®</sup> is a TiO2-photocatalysis that degrades pollutants with visible light and with UV radiation, as reported in the data sheet. TiO2 content is higher than 97.5%, with a prevalence of anatase phase. Crystallite size is approximately 15 nm. The specific surface area measured by BET is declared higher than 225 m2/g. pH values is 4-9, density is 3.9 g/cm3. KRONOS produces also a TiO2 photocatalyst in slurry form to be added in water during the preparation of mortars. The slurry is the commercial product KRONO Clean 7404, a carbon-dopes titanium dispersed in water (40% of TiO2 and 60% of water) with a pH of 7 - 8 and a density at 20 °C of about 1.4 g/cm3.

#### 3.3.2 Introduction of the new TIO<sub>2</sub>

The synthesis of the innovative photocatalytic agent (TiO<sub>2</sub>) from vegetable waste (fallen autumn leaves) and industrial (Metallic waste Ti)



Figure 13. Methodological diagram of the synthesis of the new TiO2 step 1-3

Figures obtained by XRD show the polycrystalline nature of the new  $TiO_2$  while observations at SEM and TEM reveal that the new  $TiO_2$  is formed by nanoparticles of ~ 34-80 nm.



Figure 14.Crystallographic parameters of the new TiO2



Figure 15. Observations by SEM and TEM of new synthesis TiO2

#### 3.3.3 Photocatalytic characterization of the new TiO<sub>2</sub>

The photocatalytic properties of the new TiO 2 were compared with those of 2 different commercial TiO<sub>2:</sub>

- 1. Titanium Aeroxide TiO<sub>2</sub> P25: TiO<sub>2</sub> in white powder (d ~ = 21 nm), specific surface (50 m<sup>2</sup>/g), Anatase (80%) and Rutile (20%), =  $3.1 \text{ g/cm}\rho^3$ .
- 2. KRONO Clean 7404: TiO<sub>2</sub> dispersed in water (40% in TiO<sub>2</sub>),pH ~ 7-8, =  $1.4 \text{ g/cm}\rho^3$ .



Figure 16.Comparison of the diffractogrammi of the two commercial TiO2 (P-25 and KRONOS) and thenewly synthesized TiO2 (UNIVPM-Ti-NPs). The peaks indicated by the blue squares correspond to the anatase

With regard to photocatalytic characterization, the apparatus and test conditions are those suggested by the UNI 11247 standard, which uses a continuous flow for the determination of the degradation of nitrogen oxides in the air by inorganic photocatalytic materials. The NOx flow inside the reactor, supplied by a tank (499 ppb NO) (SAPIO Srl, Monza, Italy), is kept constant by a dilution system (Calibrator 8188, Rancon Instruments spa, Milan, Italy) that uses atmospheric air at  $T = 27 \pm 2^{\circ}C$ ) and UR = 45  $\pm$  5%. The specimens under examination are placed internally in the center of a reactor, consisting of a 3L Pyrex glass cylinder. For photocatalytic characterization in UV, the specimen was irradiated from the outside with a 400W halogen UV lamp, with an irradiance measured on the specimen surface of 20 W/m<sup>2.</sup> For photocatalytic characterization in visible the specimen was irradiated from the outside with a 42 W Philips halogen lamp .



Figure 17. Apparatus for photocatalytic characterization





Figure 18.Results of the tests of the photocatalytic activity of the 3 TiO2 under UV radiation (above) and VISIBLE (below).

The new  $TiO_2$  is the one with the best photocatalytic activity in UV, with a no removal rate of 30%. In visible, the % of removal of NO is instead equal to 7%, and comparable with that of commercial  $TiO_2$  P25. The commercial  $TiO_2$  KRONO Clean 7404, on the other hand, did not show any photocatalytic activity in the visible.



Figure 19. Comparison of the % of NO removal under UV and VISIBLE radiation of the different TiO2 Therefore, from the results obtained, newly synthesized TiO<sub>2</sub> (Ti-NPs) and commercial TiO<sub>2</sub> Aeroxide P25

were selected as photocatalytic agents to be included in the finish in subsequent experimental tests.

#### 3.4 Characterization of Finishing Specimens: at laboratory scale

Activity 1 has selected 2 premixes as commercial substrates on which to apply the patented formulation:

- 3. Historical Lime C
- 4. Diathonite Deumix D

and 2 commercial reference finishes to compare with the patented finish:

- 5. Lime paint L, water paint currently used as a finish for the background Calce Storica
- Argacem HP A (smoothing) + Lime paint L (water paint) currently used as a finishing package for the Diathonite Deumix D substrate

In addition, we selected the commercial  $TiO_2$  (AEREOXIDE P25 – T1) to be included in the mixtures in comparison with the innovative  $TiO_2$  (T-NPs – T2) synthesized from industrial by-products.

Therefore, to evaluate by laboratory scale tests the effect of the 2 different commercial substrates C and D on the performance of the finish on which it is applied, and the performance of the patented finish compared to the commercial reference ones, different specimens were manufactured, obtained with different combinations of substrates and finishes

Auditions	ACRONYM
Historical Lime	С
Historical Lime + Limepaint	C+L
Historical Lime + UNIVPM finish	C+UNI
Historical Lime + UNIVPM + $TiO_2$ 1 finish	C+UNI T1
Historical Lime + UNIVPM + TiO <sub>2</sub> 2 finish	C+UNI T2
Diathonite Deumix	D
Diathonite Deumix + Argacem HP + Limepaint	D +A+L
Diathonite Deumix + Univpm finish	D + UNI
Diathonite Deumix + Univpm finish + TiO <sub>2</sub> 1	D + UNI T1
Diathonite Deumix + Finish Univpm + $TiO_2$ 2	D + UNI T2

C	D
C	D
UNI C	D Calce Storica
UNI T1 C	Diathonite Deumix D Argacem UNI UNI
UNI T2 C	UNI T2 UNI T1 D UNI T2

Figure 20.Laboratory scale tested specimens

to be characterized in terms of:

Physical characterization

- 1. Permeability to water vapor
- 2. Moisture Buffering Value (MBV)
- 3. Thermal conductivity

Tests of "Depollution"

- 1. Photocatalytic Tests
- 2. MEK Adsorption Test

#### 3.5 Preparation of specimens

The different mixtures were disposed of in formworks of different geometries depending on the specifications of each test:

- 1. prisms 4x4x16 cm for mechanical tests
- 29

- 2. PVC cylinders (d = 20 cm, h = 3 cm) for Water Vapor Permeability tests
- 3. PVC cylinders (d = 10 cm and h = 3 cm) for MBV tests
- 4. wooden prisms, with galvanized steel sheet bottom, 30x30x3 cm for thermal conductivity tests cylinders 8x0.8 cm for "Depollution" tests



Figure 21.Formwork for mechanical, vapor permeability, MBV, thermal conductivity, and "depollution" tests (from left to right)

The substrates C and D were prepared first, adding water to the pre-mixed as suggested by the technical sheet and mixing with a whisk drill until a homogeneous dough with a yogurt-like consistency for C and foamy (shaving foam, ice cream cream) for D was obtained. Workability was assessed by slump test.



Figure 22.Slump test: background C (left) and D (right)

The mix was then inserted into the formworks in 2 successive layers, slightly vibrating the formwork by hand to facilitate the filling and escape of the incorporated air, and the surface smoothed with a stage. All specimens were covered with film and left to mature for 8 days at ambient T. After 8 days from the casting the film was removed.



Figure 23.Background specimens C (left) and D (right).

After 28 days of curing the specimens C and D were characterized in terms of density in the hardened state, and mechanical compressive strength Rc obtaining the results reported, 5 specimens were tested for each type and the average value reported.



Figure 24.Specimens for the mechanical characterization of Historical Lime C (left) and Diatonite D (right).

Table 3.Density and Rc of substrates C and D after 28 days of curing

	С	D
Density (gr/cm <sup>3</sup> )	1.76	0.68
Rc (MPa)	16.3	4.3

## 3.6 Preparation of specimens of the finishes

After 15 days from the casting, on the substrate D, previously wet with a brush, the ARGACEM A finish was applied in:

- 1. n° 3 cylindrical specimens for Water Vapor Permeability
- 2. n° 3 cylindrical specimens for MBV
- 3. n° 1 specimen for Thermal Conductivity
- 4. n° 8 auditions for Depollution

According to the technical sheet, A was applied in two layers at a distance of 1 day: the first (2.5 mm) to homogenize the surface of the support, the second (2.5 mm) to reach the desired thickness. The data sheet indicates to mix 6.5 - 7 l of water per 25 kg of Argacem. The mixing was carried out with a mixer for

5 minutes until a homogeneous mortar with a yogurt-like consistency was obtained. Workability was assessed by slump test.



Figure 25.Slump test: Argacem

Then the first finishing layer A was applied using a spatula; specimens were sealed with film for 24 hours and then the second layer applied. Acetate rails helped the application of an exact and homogeneous thickness of finish. The surface was then sponged with a moistened sponge, to highlight the grain making and making the appearance of the product homogeneous. After 7 days of curing in the air, small cracks appeared that were closed with a small mixture of A through a spatula and subsequent sponging.





Figure 26.Specimens with finish A

The LIMEPAINT L finish has been applied both on the Calce Storica C substrate and on the Diathonite D+ Argacem A system on:

- 1. n° 3 cylindrical specimens for Water Vapour Permeability test
- 2. n° 3 cylindrical specimens for MBV test
- 3. n° 1 prismatic specimen for Thermal Conductivity test
- 4. n° 8 disk specimens for "Depollution" test

Before applying Lime paint it was necessary to apply the D20 primer, in order to improve adhesion between surfaces. The technical data sheet indicates a yield of  $0.15 - 0.20 \text{ I/m}^2$  by application with a short-haired roller, making the product penetrate well into the support and perfectly covering the entire surface.



Figure 27.Specimens C (left) and D+A (right) + D20

The specimens with the D20 were dried for 24 hours in the air, then L was applied in 2 layers perpendicular to each other, according to the technical sheet, at a distance of at least 6 hours. The data sheet indicates a yield of 0.35 kg/m<sup>2</sup> per liter suggesting diluting L with 30-40% of water and application by short-haired roller. The specimens were air-dried.



Figure 28.Specimens C+L (left) and D+A+L (right)

The UNI FINISH has been applied on:

- 5. n. 6 cylindrical specimens for MBV tests (C and D+A)
- 6. n. 2 prismatic specimens for Thermal Conductivity tests (C and D+A)
- 7. n. 16 cylindrical specimens for "Depollution" tests (C and D+A)

Since the photocatalytic agent does not influence the thermo-hygrometric properties of the finish but only those of "Depollution", the **UNI+T1 and UNI+T2 FINISHES**, have been applied instead only on:

n. 16 cylindrical specimens 8x0.8 cm for Depollution tests (8 specimens with substrate C and 8 specimens with substrate D);



Figure 29.Specimens on which to apply the UNI finish

The innovative finish was prepared with the same mixture already tested in Activity 2.1.2, adding commercial  $TiO_2$  P25 Aereoxide (T1) and innovative  $TiO_2$  T-NPs (T2), as selected in Activity 2.2., to the dosage of 2.4% on the weight of dry solids for UNI T1 and UNI T2 specimens respectively,  $TiO_2$  added as the last ingredient was previously sonicated with a certain amount of water that was removed from the mix design water. Even with the addition of T1 and T2, rigid workability has been achieved.

BLEND	WATER	LIME (g/l)	SILICA (g/l)	воттом	FLY	TiO2 P25	T-NPs (g/l)
	(g/I)			(g/I)	(g/I)	(g/I)	
UNI	478	437	204	234	204		
UNI T1	478	437	204	234	204	26	
UNI T2	478	437	204	234	204		26

Table 4.Uni finish design mix



Figure 30.Slump test mortar UNI T1 (left) and UNIT2 (right)

The finish was applied by brush up to 5 mm thick, previously wetting the substrate with water. Subsequently, the specimens were covered with film. After 7 days from the casting, removed the film, we noticed numerous cracks in the UNIVPM finish with even detachments from the background C.



Figure 31.Specimens with cracked UNI finish

We tried to grout the cracks with a new UNI mix by wetting the surface in advance and homogenizing the surface with a moistened sponge .



Figure 32.Specimens with stuccoed slots

Despite the grouting, after 7 days new cracks appeared on the surface of the specimens



Figure 33.Cracked specimens after 7 days from grouting

Therefore, to counteract the cracking of the finish once applied in a thin layer on the substrate, it was decided to compare the effectiveness of 2 different modes:

## 3.6.1 Application of the UNI finish in 2 layers:

change the method of application of the UNI finish by replacing the application of a single layer of about 5 mm of mortar with the application of 2 layers of 2.5 mm each, at a distance of 24 hours

#### 3.6.2 Counteract cracking: application of uni finish in 2 layers

On a C substrate panel (35x35 cm), previously moistened by sponge, a 1st layer of UNI finishing 2.5 mm thick was applied to a spatula, left to mature for 24 hours, and then the 2nd layer was applied after wetting the surface by sponge. The thickness of the applied layers was checked by means of balsa rails. The specimen was wrapped with film for 5 days.



Figure 34.Application of the 1st layer of FINISH UNI



Figure 35. Humidification of the 1st layer of casting by means of trowel (left), 2nd finishing layer completed (center), covering of the mix with film (right)

After 5 days of curing, the film was removed, and the specimen still showed no signs of cracking. However, after 24 hours of curing in the air, the first cracks appeared on the surface of the mix that were further accentuated after 7 days of curing in the air.



Figure 36. Finishing after 5 days of curing in film (left), after a subsequent 24 hours of air-conditioned curing (center) and after 7 days of air curing (right).

The change in the mode of application of the UNI finish has therefore reduced the cracking by shrinkage but not significantly.

Therefore, it was decided to modify the UNI formulation by inserting commercial additives that could limit cracking.

#### 3.6.3 Counteract cracking: addition of additives in the UNI finish

In order to avoid the formation of cracks in the UNI finish, the cracking behavior of new UNI mixtures was compared when the following admixtures were added:

- 1. Anti-shrinkage METOLAT<sup>®</sup> P 872 MUNZING (A)
- 1. Cellulose HIDROXYPROPYL METHYL CELLULOSE 75HD60.000 SM QUIMIALMEL (C).
- 2. Resin RESIN REDISPERDIBILE QUIMIBOND 313 QUIMIBOND (R)
- 3. Fluidifier MELMENTF10 NEUCHEM (F)
- 4. Aerante SILIPON<sup>®</sup> RN HERCULES (AIR)

In particular, 5 different UNI formulations have been created by adding in the patented mixture:

- 1. all additives: ALL
- 2. anti-shrinkage: A
- 3. anti-shrinkage + cellulose + resin: A-C-R
- 40

- 4. anti-shrinkage + cellulose + fluidifier: A-C-F
- 5. anti-shrinkage + resin + fluidifier: A-R-F

The additive UNIVPM formulations were applied in 2 layers of 2.5 mm each (since the 2-layer application had reduced cracking), at a distance of 24 h, on half the panel of substrate C, which was the one in which the cracking of the finish was worse. On 0.22 l of cast, 1.043 g of A, 1.460 g of C, 1.460 g of R, 0.042 g of F, 0.042 g of AIR were added. The addition of the different additives made it necessary to increase the amount of water to meet the workability requirement as reported in the last column of table.

	H <sub>2</sub> O	BOTTOM ASH	FLY ASH	SILICA GEL	LIME	H <sub>2</sub> O addition (1st layer)	H <sub>2</sub> O addition (2nd layer)
ALL	119	44	39	39	83	27	29
A	119	45	39	39	84	16	16
A-C-R	119	44	39	39	83	23	27
A-C-F	119	45	39	39	83	28	30
A-R-F	119	45	39	39	83	17	18

Table 5.Mix design in g of the UNI additive finishes (V = 0.22 I)

All ingredients have been mixed via mixer, until the desired consistency was reached. The finishes were then applied by means of a spatula and American trowel, moistened by sponge, and then seasoned in the air, not covered with film, to simulate the worst conditions for any cracks, also given the high summer temperatures (mix 5 August 2021). Comparing the applicability and cracking behavior of the different doughs, the ALL mix shows good workability, applicability, and absence of cracks after 24 h from the cast



Figure 37.ALL mix: Consistency, application, after sponging and after 24 h of air curing

In mix A, the mere presence of the anti-shrinkage additive does not improve the workability of the dough. To ensure the support, it was necessary to insist several times with the spatula and the American trowel on the surface to avoid removal of material. In addition, after 2 h from the cast the first signs of cracking were already evident, worsened after 24 h



Figure 38.Mix A: Consistency, application, cast after sponging and after 24 h of curing in the air

In the A-C-R cast, the absence of the fluidifying additive does not guarantee the perfect workability of the mix that tends to agglomerate, making it difficult to spread the mix. However, the surface remains free of cracks after curing



Figure 39.Mix A-C-R: Consistency, application, cast after sponging and after 24 h

In the A-C-F mix, the combination of anti-shrinkage, cellulose and fluidifier gives a good workability, which facilitates the application while remaining free of cracks after 24 hours of curing .



Figure 40.A-C-F mix: Consistency, application, cast after sponging and after 24 h of curing

After 24 hours of curing, the 2nd layer of finishing was applied, after prior wetting of the substrate. Already after 24 h the first cracks are visible in the A and ARF specimens that after 5 days of air curing have become more accentuated



Figure 41.Finishes UNI ALL, A, ACR, ACF, ARF after 5 days from the casting: the cracks are accentuated in specimens A and ARF

Excluding a priori the A and ARF formulations cracked after a few days of air curing, and the ACR formulation due to the poor workability and difficulty of application, between the ALL and ACF formulation with a good behavior both in the fresh and hardened state, it was decided to continue the experimentation with the UNI ACF formulation representing the best compromise between the probability of cracking and the cost of the additives.

#### 3.7 Characterization of the Specimens: Permeability to Water Vapor

Water vapor permeability ( $\delta p$ ) measures the amount of water vapor that passes through, per unit of time, a unit of surface area of the material, for a specimen of unit thickness, when there is a difference in unit vapor pressure. A good water vapor permeability of plasters and finishes for indoor applications is desirable in order to allow the disposal of moisture, the main source of mold growth, to guarantee a more comfortable healthy environment. The Water Vapor Resistance Factor  $\mu = \delta$  air (air water vapor permeability)/ $\delta$  product (water vapor permeability of the product) is dimensionless and indicates how many times the resistance to water vapor diffusion of a product is greater than a volume of air of equal thickness (for air  $\mu = 1$ ).

The UNI EN 1015 – 19: 2008 standard "Test methods for mortars for masonry works – Determination of the water vapor permeability of hardened plaster mortars" specifies a method for the determination of permeability in steady flow conditions for conditions of high humidity. The data were processed using the

UNI EN 12572: 2006 standard "Hygrothermal performance of building materials and products – Determination of the transmission properties of water vapor" with which the hygroscopic permeation of building products in isothermal conditions is determined.



Figure 42.Potassium nitrate in spheres

The cylindrical specimens h = 3 cm and d = 20 cm were placed on top of circular containers, inside which a saturated solution of potassium nitrate (KNO<sub>3</sub>) was inserted, which guarantees a controlled water vapor voltage in the container equal to 93% at T = 20°C. The specimen, positioned in such a way as to guarantee an air gap of (10±5) mm between the specimen and the surface of the solution, has been sealed, along the entire thickness by means of waterproof silicone to avoid external steam leakage to the lower surface of the same and thus ensuring only a one-way flow through the specimen. The specimen-container system was then placed inside an air-conditioned chamber at T = 20±2 °C and UR = 50±5%



Figure 43.Specimen-container scheme and specimens inside the air-conditioned chamber

At daily intervals the specimen-container system was weighed until the stationary conditions were reached, i.e. until constant mass variations over time were achieved (Figure 2.43). In fact, due to the different partial pressure of the steam between the inside of the vessel and the air-conditioned chamber, a transport of steam occurs through the specimens.

For each pair of successive weighings of the specimens, the rate of mass change  $\Delta$ m12 was calculated from the following formula:

$$\Delta m_{12} = \frac{m_2 - m_1}{t_2 - t_1}$$

Where:

 $\Delta m_{12}$  is the change in mass over time for a single determination, measured in kg/s.

 $m_1$  is the mass of the system at time  $t_1$ , measured in kg.

 $m_2$  is the mass of the system at time  $t_2$ , measured in kg.

 $t_1 \, \text{and} \, t_2$  are the next measurement times, measured in s.



Figure 44.Experimental data of the water vapor permeability test with the different specimens

Then the regression line between mass and time was calculated considering the last 4 measurements. The slope of this line is the vapour flow rate G, in kg/s.

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Using G, the density of the flow rate of the water vapour flow, in kg/( $m^2$ ·s), was calculated as:

$$g = \frac{G}{A}$$

where:

A is the area of the test surface of the specimen being detected, given by the arithmetic mean of the upper (specimen area exposed to the chamber) and lower (container area) free surfaces, measured in m<sup>2</sup>.

Subsequently, the permeance of the water vapor Wp was determined, in kg/(m<sup>2</sup>·s·Pa), given by the ratio between the density of the water vapor flow and the difference in partial pressure of the vapor between the two faces of the specimen:

$$W_p = \frac{g}{\Delta_{pv}}$$

where:

Δpv is the difference in water vapour pressure through the specimen, calculated from the average of the measured values of T and RU throughout the test, measured in Pa:

$$\Delta_{pv} = p_{sat} \cdot (UR_1) - p_{sat} \cdot (UR_2)$$

where:

p<sub>sat</sub> (UR<sub>1</sub>) is the vapour pressure inside the test vessel, measured in Pa;

p<sub>sat</sub> (UR<sub>2</sub>) is the vapour pressure inside the air-conditioned chamber, measured in Pa.

With:

$$p_{sat} = exp \left[ 65,81 - \frac{7066,27}{T + 273,15} - 5,976 \cdot ln(T + 273,15) \right]$$

where:

T is the temperature, measured in °C.

From the permeance of the water vapor Wp the permeability to water vapor  $\delta p$  was calculated as:

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$$\delta_p = W_p \cdot h$$

where:

h is the average height of the specimen, measured in m.

In this way the resistance factor to the diffusion of water vapor was calculated from the following formula:

$$\mu = \frac{\delta_a}{\delta_p}$$

where:

 $\delta a$  is the permeability calculated using Schirmer's formula, using the average barometric pressure p throughout the test, measured in kg/(m·s·Pa):

$$\delta_a = 0,0000231 \cdot \left(\frac{p_0}{p \cdot R \cdot T}\right) \cdot \left(\frac{T}{273K}\right)^{1,81}$$

where

Saturated air vapour pressure p <sub>sat</sub>	2339.30 Pa
Vapour pressure inside the vessel	2180.23 Pa
Vapour pressure outside the vessel	1169.65 Pa
Difference in water vapour pressure through the specimen $\Delta p_{\nu}$	1010.58 Pa
Standard barometric pressure p <sub>0</sub>	1013.25 hPa
Barometric pressure p	1013.25 hPa
Temperature T	293.15 °K
Water vapor-specific constant R	462 Nm/(kg·K)
Water vapor permeability of air $\delta_{\text{to}}$	1.94E-10 kg/(m·s·Pa)

Figure 45.shows the averages calculated for the different specimens.



Figure 46. Comparison of hygroscopic resistance factors between the different specimens

It can be noted that while the L and A+L finishes increase the resistivity to the water vapor of the system, the UNI ACF finish does not penalize its breathability. However, when the UNI finish also adds R resin as an additive (C+UNI ALL specimen), the permeability is significantly reduced. Therefore, the results obtained confirm that:

- 1. the patented finish is more breathable than commercial finishes
- the selected additive package ACF, to reduce the probability of cracking, is to be preferred over the more expensive ALL package, also from a point of view of the breathability of the system.

#### 3.8 Characterization of the Specimen: Moisture Buffery Value (MBV)

Indoor humidity greatly affects the air quality of a confined environment, as values that are too high or too low can cause harm to human health, such as asthma and allergies. Indoor humidity may vary daily or seasonally. The hygroscopic buffering capacity of a material allows to moderate the oscillations of relative humidity in an indoor space helping to reduce the phenomenon of condensation in the building envelope and to maintain the healthiness of the air. In addition, the hygroscopic buffering capacity of mortars and application finishes can reduce the energy consumption of buildings. The NORDTEST project defined a method for determining the Moisture Buffering Value (MBV) of materials in indoor environments. MBV defines the moisture absorbed and desorbed by the material on units of surface when it is in an environment characterized by a relative humidity of 75% for 8 hours and 33% for 16 hours.

The evaluation of the MBV of the packaged specimens was carried out following the NORDTEST method. Cylindrical specimens of d = 10 cm and h = 3 cm were used in advance brought to equilibrium up to constant weight at T =  $20\pm2$  °C and UR =  $50\pm5$  %. Then the specimens were placed in a chamber (Figure 2.45) at T =  $20\pm2$  °C and controlled UR where they underwent cycles at RU = 33% for 16 h and UR = 75% for 8 h.



Figure 47.Specimens inside the controlled T and UR cell

During the cycles, mass changes during adsorption  $m_{to}$  (g) of the specimen are calculated:

$$m_a = m_8 - m_0$$

where:

50

 $m_8$  is the mass measured after 8 h with RU=75%, measured in g.

m<sub>0</sub> is the mass measured in the previous weighing, measured in g.

and mass changes during desorption md (g) by the formula:

$$m_d = m_{24} - m_8$$

where:

m<sub>24</sub> is the mass measured after 16 h with RU=33%, measured in g;

m<sub>8</sub> is the mass measured in the previous weighing, after 8 h with UR =75%, measured in g.

The variations m a and  $m_d$  were then normalized with respect<sub>to</sub> the exposed surface of the specimen obtaining:

$$\Delta_a = \frac{m_a}{S}$$
$$\Delta_d = \frac{m_d}{S}$$

where:

 $\Delta a$  is the mass change for one unit of area during the adsorption phase, measured in g/m<sup>2</sup>;

 $\Delta d$  is the mass change for one unit of area during the desorption phase, measured in g/m<sup>2</sup>;

S is the total area of the specimen, measured in<sup>m 2</sup>.

From these results, the change in mass compared to the surface was calculated as the average of the variations in the adsorption and desorption phase:

$$|\Delta_{ciclo}| = \frac{\Delta_a + |\Delta_d|}{2}$$

The MBV value was then calculated as a mass change compared to the  $\Delta$ cycle surface with respect to the RU difference used during the test:

$$MBV = \frac{\Delta_{ciclo}}{UR_{75} - UR_{33}}$$

where:

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 $\Delta$  cycle is the change in mass compared to the surface of the cycle, measured in g/m<sup>2</sup>;

UR<sub>75</sub> is the relative humidity of 75%;

 $UR_{33}$  is the relative humidity of 33%.

For each type of specimen 3 specimens of the same type were tested and the average value of MBV calculated, considering for each specimen the average of the MBV calculated over 3 cycles. the mass changes per unit area of all specimens tested. From which the average MBVs were calculated



Figure 48.Adsorption-desorption cycle of the various specimens



Figure 49.Calculated average MBV of the different specimens

From the results it is observed that substrate D has a slightly greater hygrometric buffer capacity than C but both the application of the L on C finish and A+L on D significantly penalize the MBV of both substrates. On the other hand, the UNI finish not only does not reduce the hygrometric buffer capacity of both substrates but even increases it. The D+UNI system is the one with the best performance.

## 3.9 Characterization of the Specimens : Depollution Test

As a result of regulations on the energy efficiency of buildings, which lead to increasingly sealed structures with reduced air changes, indoor air pollution is growing more and more. Volatile organic compounds (VOCs), due to their direct impact on human health, are the most dangerous pollutants. Therefore, it is of fundamental importance to be able to reduce pollution from these compounds also thanks to passive systems such as building materials that have a high ability to adsorb them (MEK adsorption test) and to mineralize them (photocatalytic tests).

#### 3.9.1 Photocatalytic tests

For the photocatalytic characterization of the finishes, the same procedure already described for the characterization of pure photocatalytic agents. (Figure 50) gives some examples of the photocatalytic results of some specimens in both UV and VISIBLE.









Figure 50. Results of the tests of the photocatalytic activity of the 4 specimens with the UNI finish and the photocatalytic agent.

As can also be seen from the graph of the % of removal of NO, while pure TiO<sub>2</sub> of new synthesis had shown the best photocatalytic performance in both VIS and UV, when it is added in the finish the performance in the VIS is almost canceled. On the other hand, a certain photocatalytic activity in UV remains, although less than that obtained with the commercial T1 P25. The reason for this behavior can be explained by the too low dosage of T2 in the finish or by an incompatibility with the alkaline environment of the matrix in which it is immersed. However, in the VIS field, the commercial photocatalytic agent T1 (P25) when immersed in the finish also completely loses its effectiveness.

Therefore, in the future trial, the photocatalytic activity of the commercial photocatalytic agent KRONOS, excluded in will be evaluated to assess whether the change in the matrix in which it is immersed can vary its behavior



Figure 51. Comparison of the % of NO removal under UV and VISIBLE radiation of the different specimens

#### 3.9.2 MEK Adsorption tests

The depolluting activity by adsorption was evaluated through Gas Chromatography (CG), monitoring over time the concentrations of a volatile organic compound Methyl Ethyl Ketone (MEK) within a closed system, first in the absence and then in the presence of the specimens.



Figure 52.Gas chromatograph Carlo Erba Gas 8000 Top, Hermetic glass container closed with lid, Supports inside the container (from left to right)

The closed system is an airtight glass container shielded from light (Figur) of V = 16.65 l, inside which is inserted a support of non-adsorbent material (aluminum foil) where the specimen is housed and a glass saucer where the MEK is deposited (by injection through a perforated silicone septum placed on the lid). A fan is inserted at the bottom of the container to allow continuous air recirculation. On the lid there is a circular slot in the center that can be closed by means of a perforated silicone septum, through which sampling is carried out using a micro-syringe.

For each volume of tracer injected (50  $\mu$ l) a test of about 90 minutes is carried out, taking 10  $\mu$ l of air from the chamber and injecting them into the chromatograph with a micro syringe every 8 minutes. At the end of this analysis, 11 peaks are detected with the relative areas from which to derive the concentration at the relative retention time, replacing the measured peak area in the calibration curve equation. Subsequently, the percentage concentration C at each moment of detection is calculated using the formula:

$$C = \frac{C_i}{C_0} \cdot 100$$

where:

 $C_i$  is the concentration of MEK relative to each peak, measured in mg/m<sup>3</sup>;

 $C_0$  is the concentration of MEK inserted at the beginning of the test, the maximum theoretical value, measured in mg/m<sup>3</sup>.

These data are graphed as a function of retention time and interpolated with a logarithmic trend line.



Figure 53.MEK depolluting capacity of the different specimens

The graphs show that all specimens with the UNIVPM finish have a significantly higher MEK removal capacity (+30%) than those with the commercial finishes C+L and D+A+L (Figure). The presence of

photocatalytic agents, as expected since the deprivation is conducted in the dark, have no influence on the processes of depollution by adsorption.



Figure 54. Comparison of concentrations (%) at 90 min of the different specimens

## 3.10 Sensor installation Diagram, Application of the Subfloor System and Finishes

## Installation of the Monitoring System

It began with the preparation of the site and the mockups that will be used in the experimentation envisaged by the project.

The area identified for the experimentation is in Ancona, in the Baraccola area. This area is in use at the Marche Polytechnic University and managed by the Department of Industrial Engineering of the Faculty of Engineering.

The site is in an industrial area and covers an area of about 5000 m<sup>2</sup>, where a number of buildings used in previous research of the University are located.

8 boxes of size 3x3x3 m are clearly evident in the area: 1 of them will be used for experimentation. The area had been abandoned for 10 years and therefore it was necessary to restore its operation. Two

dilapidated buildings have been eliminated and the entire area has been cleaned up. A fence has been created for the artificial lake and the water and electricity systems have been arranged.



Figure 55. Area for the project

The patented finish will be tested on a wall of 1 box equipped with air conditioning for the control of T and UR.



Figure 56.North Wall of the Box



Figure 57. South Wall of the Box

On half wall of the box the patented finish will be applied whereas the other half will be covered with the reference finish. The two half will be separated by a plasterboard wall.

Two acquisition systems consisting of data taker instruments were set up, where the temperature probes were connected. Probes are resistance thermometers for measuring surface temperatures and thermocouples for measuring air temperature.

In Figures X, the position in section and in plan of the first sensors that will be inserted for monitoring can be seen. All data converges in a PC that is connected remotely via modem installed inside the boxes.



Figure Box Section



Figure Box plan with the first sensors to be installed

## **4** References

[1]: https://123dok.org/document/9yngojlz-innovative-multifunctional-materials-environmentalimpact-energy-comfort-environment.html

[2]: https://www.epa.gov/indoor-air-quality-iaq/volatile-organic-compounds-impact-indoor-airquality

[3]: Rackes, Adams, and Michael S. Waring. "Using multiobjective optimizations to discover dynamic building ventilation strategies that can improve indoor air quality and reduce energy use." *Energy and Buildings* 75 (2014): 272-280.

[4]: \ Annual Energy Review, US Energy Information Administration September 27 (2012),
 http://www.eia.gov/totalenergy/data/annual/showtext.cfm?t= ptb0211. Accessed May 16, 2013

[5]: Bluyssen, P. M., et al. "European indoor air quality audit project in 56 office buildings." *Indoor Air* 6.4 (1996): 221-238.

[6]: Brągoszewska, Ewa, Magdalena Bogacka, and Krzysztof Pikoń. "Efficiency and eco-costs of air purifiers in terms of improving microbiological indoor air quality in dwellings—A case study." *Atmosphere* 10.12 (2019): 742.

[7]: Yang, Liu, Haiyan Yan, and Joseph C. Lam. "Thermal comfort and building energy consumption implications-a review." *Applied energy* 115 (2014): 164-173.

[8]: J. Vieira, L. Senff, H. Gonçalves, L. Silva, V. M. Ferreira, and J. A. Labrincha, "Functionalization of mortars for controlling the indoor ambient of buildings," *Energy Build.*, vol. 70, pp. 224–236, 2014. [7]:
R. Meininghaus, L. Gunnarsen, and H. N. Knudsen, "Diffusion and Sorption of Volatile Organic Compounds in Building Materials–Impact on Indoor Air Quality," *Environ. Sci. Technol.*, vol. 34, no. 15, pp. 3101–3108, 2000.

[9]: Kunkel D., E. Gall, J. A. Siegel, A. Novoselac, G. C. Morrison, and R. L.Corsi, "Passive reduction of human exposure to indoor ozone," *Build. Environ.*, vol. 45, no. 2, pp. 445–452, 2010.

[10]: R. Meininghaus, L. Gunnarsen, and H. N. Knudsen, "Diffusion and Sorption of Volatile Organic Compounds in Building Materials–Impact on Indoor Air Quality," *Environ. Sci. Technol.*, vol. 34, no. 15, pp. 3101–3108, 2000.

[11]: H. Matsumoto, M. Shimizu, and H. Sato, "The contaminant removal efficiency of an air cleaner using the adsorption/desorption effect," *Build. Environ.*, vol. 44, no. 7, pp. 1371–1377, 2009.

[12]: L. Senff, D. M. Tobaldi, S. Lucas, D. Hotza, V. M. Ferreira, and J. A. Labrincha, "Formulation of mortars with nano-SiO2 and nano-TiO2 for degradation of pollutants in buildings," *Compos. Part B*, vol. 44, pp. 40–

[13]: A. Folli, C. Pade, T. B. Hansen, T. De Marco, and D. E. MacPhee, "TiO2 photocatalysis in cementitious systems: Insights into self-cleaning and depollution chemistry," *Cem. Concr. Res.*, vol. 42, no. 3, pp. 539–548, 2012.

[14]: M. M. Ballari, Q. L. Yu, and H. J. H. Brouwers, "Experimental study of the NO and NO2 degradation by photocatalytically active concrete," *Catal. Today*, vol. 161, no. 1, pp. 175–180, 2011.

[15]: A. Fujishima, X. Zhang, and D. A. Tryk, "TiO2 photocatalysis and related surface phenomena," *Surf. Sci. Rep.*, vol. 63, no. 12, pp. 515–582, 2008.

[16]: Q. L. Yu, M. M. Ballari, and H. J. H. Brouwers, "Indoor air purification using heterogeneous photocatalytic oxidation. Part II: Kinetic study," *Appl. Catal. B Environ.*, vol. 99, no. 1–2, pp. 58–65, 2010.

[17]: S. Lorencik, Q. L. Yu, and H. J. H. Brouwers, "Design and performance evaluation of the functional coating for air purification under indoor conditions," *Appl. Catal. B Environ.*, vol. 168–169, pp. 77–86, 2015.

[18]: H. J. Kim, S. S. Kim, Y. G. Lee, and K. D. Song, "The hygric performances ofmoisture adsorbing/desorbing building materials," *Aerosol Air Qual. Res.*, vol.10, no. 6, pp. 625–634, 2010.
64

[19]: S. Cerolini, M. D'Orazio, C. Di Perna, and A. Stazi, "Moisture buffering capacity of highly absorbing materials," *Energy Build.*, vol. 41, no. 2, pp. 164–168, 2009.

[20]: C. Rode, R. Peuhkuri, B. Time, K. Svennberg, T. Ojanen, P. Mukhopadhyaya, M. Kumaran, and S.W. Dean, "Moisture Buffer Value of Materials in Building," *J. ASTM Int.*, vol. 4, no. 5, pp. 1–12, 2007.

[21]: M. Z. Guo, T. C. Ling, and C. S. Poon, "Nano-TiO2-based architectural mortar for NO removal and bacteria inactivation: Influence of coating and weathering conditions," *Cem. Concr. Compos.*, vol. 36, no. 1, pp. 101–108, 2 013.

[22]: S. Wei, Z. Jiang, H. Liu, D. Zhou, and M. Sanchez-Silva, "Microbiologically induced deterioration of concrete - A review," *Brazilian J. Microbiol.*, vol. 44, no. 4, pp. 1001–1007, 2013.