The evaluation of the thermal behaviour of a mortar based brick masonry wall coated with TiO₂ nanoparticles: An experimental assessment towards energy efficient buildings

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ABSTRACT

The transfer of energy (in the form of heat) between the building and its surroundings affects its thermal performance. When a given building system is thermally inefficient it will require that the HVAC equipment will be in permanent activity, increasing the underlying energy costs. This work evaluates the influence of using a TiO₂-coated plastering mortar in the thermal performance of a building wall model. The TiO₂ aqueous solution was sprayed onto the mortar surface, in its fresh state, by using an atmospheric air compressor at a distance of about 20 cm, during 30 s and the speed of the aqueous solution jet set at 100 mL/min, thus leading to a coverage rate of about 12 mg/cm². For the first time, as far as the authors' knowledge, this research work allowed to test the previously speculated hypothesis and verify its feasibility in the building industry context. It has been observed that the application of a TiO₂-coated mortar worsens the thermal behaviour of the wall model, in 10% and 13% for the conduction thermal resistance and for thermal transmission coefficient, respectively. Furthermore, the deposition of TiO₂ nanoparticles on the exterior wall surface enhances the water evaporation rate in 136%.

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1. Introduction

Energy is the main source of all human-related activities and its consumption must be reduced in every step of the value chain of industrial activities that lead to technological and societal development. Natural resources are fundamental for the economy and to the maintenance of life quality as the current consumption patterns are no longer a viable option. In fact, it is now critical to enhance energy efficiency in order to ensure the economic growth. A more efficient use of energy will create significant economic opportunities, improve productivity, reduce costs and foster the competitiveness of countries.

Accordingly to the International Energy Outlook 2013 report [1], the energy that is consumed in the building sector (combining residential and commercial end-users) is the responsible for about one quarter of the total energy consumed worldwide and is still

rising every year [2]. In this sense, some efforts have been made to enhance the thermal comfort of buildings. As an example, Sage-Lauckand and Sailor [3] have studied the influence of adding phase change materials (PCM) in indoor environmental quality and building energy use. The authors have concluded that the incorporation of 0.9 kg/m² floor area of PCM could reduce the zone hours overheated by ~50%. Veira et al. [4] reported the data related with the functionalization of mortars by using TiO₂ nanoparticles, superabsorbent polymer (SA) and PCM towards the control of the indoor ambient of buildings. They stated that mortars containing PCM were able to delay the temperature variation while the use of SA particles conducted to a higher hygroscopic capacity.

The current concern in the construction industry is the development and design of smart innovative systems and materials for space cooling in buildings. It should be pointed out that the transfer of energy between the building and its surroundings substantially affects the thermal performance of a building. In fact, when a certain building system is thermally inefficient it will require that the heating, ventilation and air-conditioning (HVAC) equipment will be in permanent activity, thereby increasing the

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Fig. 1. Energy-saving system applied on buildings facades coated with a TiO₂ photocatalyst irradiated by solar light.

underlying energy costs. Moreover, the level of energy consumption in high-density urban environments causes an expected temperature increase, the so-called heat island phenomenon.

1.1. TiO₂ coated surfaces as efficient energy-saving technology

Titanium dioxide (TiO₂) based powders are known to be used as white pigments from ancient times [5]. TiO₂ has been highlighted as an ideal candidate for industrial applications due to its intrinsic characteristics such as high chemical stability, availability, low cost and low toxicity. TiO₂ materials have been used to produce surfaces with photocatalytic, self-cleaning, anti-bacterial and anti-fogging properties based on its photo-induced hydrophilicity/hydrophobicity and decomposition photo-reactions. While the construction industry has been identified as an important market for the incorporation of photocatalytic products (due to the high surface area of the structures, thus leading to the scalability of the processes that may make this approach a real scale economy), the large-scale application of TiO₂ materials is still limited by the needed external excitation sources [6]. In this sense, the research works have been focusing on the development and incorporation of nanosized TiO₂ to enhance the light absorption due to the high surface-to-volume ratio of nanograins [7]. In accordance with Zheng and co-workers [8], the increased surface area of nanoparticles can provide surface states within the band-gap and, thus, effectively reducing the energy required to promote an electron from the valence band to the conduction band.

Although the photo-induced redox reactions on the surface of TiO₂ materials has been described elsewhere [9–11], it is important to emphasize that the aforementioned properties do not occur in the presence of additional chemical compounds: the material is environment friendly in the sense that only the presence of sunlight and rainwater are required [12].

Hashimoto et al. [5] have proposed a system (shown in Fig. 1) that involves sprinkling water continuously on building facades previously coated with a TiO₂ photocatalyst.

According to the authors, under the action of light irradiation the TiO₂ coated building surface becomes super-hydrophilic. This surface state means that even a small amount of water sprinkled on the building would be enough to form a water thin film that could cover the building facade. In this sense, those researchers suggested that the hot surfaces of buildings might be cooled via a thermodynamic process, by releasing a certain amount of latent heat flux when water evaporates. This smart process for cooling down the buildings may contribute to reduce the amount of electricity consumed by conventional air conditioning.

In order to contribute to the scientific knowledge in this field, an experimental campaign has been performed to examine the

Table 1
Mortar composition.

Mix (cement:lime:sand)	(w/b) Ratio	Flow table (mm)
1:1:6	0.50	160

influence of using a TiO₂-coated plastering mortar in the thermal performance of a building wall model. For the first time, as far the authors knowledge, this research work allowed to test the hypothesis previously speculated by Hashimoto et al. and verify its feasibility in the building industry context—which is the potential of using TiO₂ coated facades, as being an alternative and a smart process to implement strategies for energy savings in buildings.

2. Experimental details

2.1. Preparation of standard mortar

The preparation of the standard mortar was carried out according to NP EN 196-1 (2006). A typical mortar composition was considered in this experimental study, namely 1:1:6 (cement:lime:sand) in volume. The cement (density of 3210 kg/m³) used in the mortar composition was CEM II/B-L 32.5N, according to European standard EN 197-1. The lime that was used consists of a hydrated lime (density of 2240 kg/m³), according to European standard EN 459-1. Finally, the aggregate was a sand (density of 2518 kg/m³), which resulted from the combination of two sands available in the market, namely medium sand (M) (60%) and fine sand (F) (40%). The idea was to obtain more extensive sand, which should improve the workability properties of the mortar.

According to the results obtained by Haach et al. [13], it is possible to improve the workability of the mortars, by increasing the amount of water, even if it means a reduction of its flexural and compressive strength. In order to guarantee suitable mortar workability, a water/binder ratio (w/b) was defined based on a flow table, obtained by following the procedure described in the European Standard EN 1015-3 (2004). Thus, for the mortar mix 1:1:6, a (w/b) ratio of 0.5 was defined, corresponding to a flow table of 160 mm. The mortar composition used in this research work is presented in Table 1.

2.2. Preparation of modified mortar through the addition of TiO₂ nanoparticles

In this research work, commercial TiO₂ nanoparticles (Aeroxide TiO₂ P25 from Quimidroga) were used to modify the standard mortar. The semiconductor material was applied by spraying an aqueous solution of TiO₂ nanoparticles onto the mortar surface. The aqueous solution was prepared by using 1.0 wt% of TiO₂ nanoparticles and 1.0 wt% of an acrylic binder on the weight of solution. In a common experiment, 1 g of TiO₂ nanoparticles were sonicated for 30 min with 97.5 g of distilled water, 0.5% of a non-ionic surfactant (TRIDAC ISO 8) and 1 g of an acrylic binder. The mixture was then stirred at 4000 rpm for 1 h. The pH of the aqueous solution was then adjusted at pH 8 by using a 0.3 M NaOH solution to obtain a suitable zeta potential value [14]. Using an atmospheric air compressor, the surface of the standard mortar was sprayed at a distance of about 20 cm, during 30 s and the speed of the aqueous solution jet set at 100 mL/min, thus leading to a coverage rate of about 12 mg/cm². The TiO₂ aqueous solution was sprayed onto the mortar surface in its fresh state. This approach helps to enhance the surface adhesion of TiO₂ nanoparticles (by an entrapment mechanism) during the hardening process of the mortar.

It is important to emphasize that the option for using the spraying process is related to three main points: (1) since TiO₂ is a

semiconductor material, sunlight is mainly absorbed by particles that rests on the substrate surface; (2) since the semiconductor material is deposited as a thin surface layer, it is not expected that any significant changes would occurs in the physical and mechanical properties of the mortar; (3) the spraying process avoids the waste of the semiconductor material (thereby reducing the modification costs) that may arise from the volume addition of TiO_2 nanoparticles, according to procedures followed by different authors [14,15].

2.3. Material's characterization methods

The crystal structure of the TiO_2 particles was determined from powder X-ray diffraction (XRD) measurements using a $\text{CuK}\alpha$ radiation source from a Philips PW 1710 X-ray diffractometer, with the conventional Bragg–Brentano geometry. Specific software was used to measure the precise 2θ positions and the full-width at half-maxima (FWHM) of the diffraction peaks. The average crystallite size of TiO_2 particles was calculated from the XRD pattern by applying the Scherrer's equation [16]. Scanning Electron Microscopy (SEM) and Energy Dispersive spectroscopy (EDS) were used to study the surface morphology of the standard and the TiO_2 -coated mortar. The samples preparation consisted of using $2.5\text{ cm} \times 2.5\text{ cm}$ specimens (standard mortar and TiO_2 -coated mortar), which were coated with a thin layer of gold in order to ensure electric conduction. Microscopy analysis was conducted by using a FEI Nova 200 (FEG/SEM) microscope, which also integrates a X-ray micro-analysis system (EDS—energy dispersive spectrometer) that is used for the elemental analysis or chemical characterization of the samples.

2.4. Experimental setup and applied strategy

In order to implement this research study, two test wall models were built with the same overall dimensions. The dimensions of the test wall are $44\text{ cm} \times 38\text{ cm} \times 16.5\text{ cm}$ (width $\times$ height $\times$ thickness). Two layers compose the standard wall model that are, from the interior to the exterior: a 15 cm ceramic brick masonry wall filled by a 1.5 cm plastering mortar previously designed. The brick is horizontally perforated and is characteristic of non-loadbearing enclosure masonry walls in Portugal and various European countries [17]. The second wall model (Fig. 2) is essentially the same as the previous one being the only difference the

Fig. 2. Schematic representation of a TiO_2 coated masonry wall model under UV irradiation.

plastering mortar coated with a TiO_2 nanoparticles based thin surface layer with a thickness of about $0.8\text{ }\mu\text{m}$ (irradiated with UV lamps). By using several layers of extruded polystyrene (XPS), in which each layer is composed by two XPS plates (each have a thickness of 3 cm), all sides of the test wall (except the front and the back side) were carefully thermally insulated in order to ensure a unidirectional heat transfer.

In order to obtain the thermal characteristics of both test wall models, the experimental setup includes one heat flowmetre (from Hukseflux HFP01), which is fixed in the wall back face (Fig. 3a), a heat source (a 120 W heating vent), surface temperature sensors (seven per face wall), two ambient temperature sensors (one located near the heat source and the other placed in a region close to the back surface wall), a data logger (dataTaker DT 800) and a computer. For the wall model having the external surface modified by the superficial addition of TiO_2 nanoparticles, the experimental setup also includes two UV lamps (PHILIPS TL-D 18 W BLB SLV). In order to activate the semiconductor material, the light source was fixed on a support structure placed at a distance of about 30 cm from the TiO_2 coated surface wall (Fig. 3b). At this distance, the UV light power intensity is about 8 W/m^2 (measured with a Quantum Photo Radiometer HD9021 Delta Padova).

Essentially, the experimental analysis consisted on monitoring over time the thermal behaviour of the test wall models, namely the TiO_2 -coated mortar and the uncoated ones (i.e. the standard model), that from now on will be designated by TiO_2 -CSurf and UncSurf, respectively.

In this work, the used thermodynamic model refers to one-dimensional (1D) heat flow across the wall model. Under a

Fig. 3. Photographic image of the experimental setup: (a) detail regarding the position and fixing of the heat flowmeter and surface temperature sensors and (b) overall view of the experimental setup; the inset shows the two UV lamps as well as the surface temperature sensors.

Fig. 4. 1D heat transfer across the standard wall model and electric analogy.

steady-state condition, the model includes both convective and conductive heat transfer (Fig. 4). If bear in mind that the deposited TiO_2 layer is a thin layer of about $0.8 \mu\text{m}$ and that its deposition on a mortar wall did not conduct significant changes in the optical (colour) and surface properties of the mortar wall, it is not plausible to expect a variation in the sample's surface emissivity (i.e. the surface maintains its dark colour, thus its lower emissivity). Due to this fact, the radiative component of heat flux was not taken into account in the thermodynamic model.

By using the electric analogy, the thermal transmission coefficient, U for the test wall models were computed according to the following equation

$$U = \frac{1}{R_{\text{conv},1} + R_{\text{cond}} + R_{\text{conv},2}} \quad (1)$$

where $R_{\text{conv},1}$ and $R_{\text{conv},2}$ are the convective thermal resistances, respectively, corresponding to exterior and interior surfaces of the test wall model, and R_{cond} is the conduction thermal resistance of the wall model. Furthermore, the thermal resistances of a building system, such as the wall model considered herein, can be quantified by applying the following equations:

$$R_{\text{cond}} = \frac{T_2 - T_3}{\varphi} \quad (2)$$

$$R_{\text{conv},1} = \frac{T_1 - T_2}{\varphi} \quad (3)$$

$$R_{\text{conv},2} = \frac{T_3 - T_4}{\varphi} \quad (4)$$

in which φ (W/m^2) is the average value of heat flow across the test wall model, experimentally recorded by the flowmeter; T_1 and T_4 are, respectively, the average values of the exterior (hot air) and interior (cold air) temperatures recorded by the ambient temperature sensors and T_2 and T_3 correspond, respectively, to the temperature average values (recorded by the surface temperature sensors) of exterior and interior surfaces of the wall model.

For both wall models considered in this work, the thermal tests took about 15 h. The temperatures (T_1 to T_4) and the heat flow across the wall models were measured continuously (in between 1 min intervals). In order to apply Eqs. (1)–(4) the steady-state condition was considered as being roughly comprised within the first 5 h of the test experiments.

As previously referred, one of the main objective of this research work was to evaluate the thermal performance of a TiO_2 -coated plastering mortar after subjecting its surface to the sprinkling of a small amount of water. To achieve this goal, the exterior surfaces of both wall models were sprayed with some 50 mL of water. In this way, the water spraying took place after an elapsed time of

Fig. 5. XRD pattern of the commercial Aeroxide TiO_2 P25.

about 5.5 h from the starting of the thermal tests. Because of water spraying, the energy from the hot air (heated by the heating vent) is absorbed by the thin water surface layer. The absorbed heat can be diffused downward, or otherwise lost again through the water surface. It will be assumed that the dominant process of heat loss is the latent heat flow by water evaporation, q_L (W/m^2). The latent heat corresponds to the heat flow variation, which is recorded by the flowmeter during the interval of time in which the water spraying took place, namely:

$$q_L = \varphi - \varphi(t) \quad (5)$$

where φ is the average heat flow under the steady-state condition and $\varphi(t)$ corresponds to the heat flow measured at a particular instant of time, t during the water spraying. The latent heat flow by water evaporation is related to the water evaporation rate by the following equation [18]:

$$q_L = L\rho \frac{d\eta}{dt} \quad (6)$$

where L (J/kg) is the latent heat of evaporation, ρ (kg/m^3) is the water density and $d\eta$ is the thickness of the layer evaporated during the time dt .

3. Experimental results and discussion

The results obtained and their discussions are as follows.

3.1. Crystallographic structure of TiO_2 powders

Fig. 5 shows the XRD spectrum of the TiO_2 particles used in this work. The crystalline phases can be confirmed by the presence of (1 0 1), (0 0 4) and (2 0 0) diffraction peaks, for the case of anatase phase and (1 1 0), (1 1 1), (2 1 1) and (0 0 2) for the rutile crystalline phase.

Using the Scherrer equation, it was observed that the mean crystallite grain size of the TiO_2 nanoparticles was around 23 nm and 28 nm for anatase and rutile phases, respectively. These values were calculated from the full-width at half-maxima intensity of the (1 0 1) anatase diffraction peak (corresponding to $2\theta = 25.3^\circ$) and rutile diffraction peak (corresponding to $2\theta = 54.1^\circ$). A mixture of anatase and rutile phases in TiO_2 particles was found, being possible to calculate the weight percentage of the anatase phase, W_A , using the following equation [19]:

$$W_A = \frac{1}{1 + 1.26 (I_R/I_A)} \quad (7)$$

Fig. 6. Surface SEM micrograph and EDS spectrum of the standard mortar mix.

where I_A denotes the intensity of the strongest anatase reflection and I_R is the intensity of the strongest rutile reflection. In our case, the TiO_2 particles have a percentage of the anatase phase equal to 78.4% as calculated by Eq. (7).

3.2. Surface characterization

Fig. 6 shows the SEM micrograph of the standard plastering mortar. Along with the SEM micrograph, the corresponding results from EDS analysis is also presented.

It can be observed that the sample's surface appears to be moderately uniform and regular, although in some surface regions the formation of pores is observed. Results of the EDS spectrum provide the elemental analysis of the standard mortar mix, showing the chemical elements that are characteristic of cement and lime based mortar. Multiple regions in the surface were analyzed and revealed comparable concentrations of the chemical elements at the specimen's surface.

Similarly, Fig. 7 refers to the SEM micrograph and results of EDS analysis for the TiO_2 -coated mortar.

Observing the SEM micrograph for the TiO_2 -coated mortar, it is possible to verify that its surface morphology is quite different from the one corresponding to the original standard mortar. In fact, it is possible to observe the formation of numerous aggregates, which are organized in a lamellar type structure and that partially cover the surface of the original mortar. From the EDS spectrum of the TiO_2 -coated mortar, it is possible to identify that the major chemical element that is detected at the surface of this specimen

Fig. 7. Surface SEM micrograph and EDS spectrum of the TiO_2 -coated mortar.

Fig. 8. Temperatures and heat flow for the wall model with the standard mortar.

is titanium, as was already expected. The presence of the Ti chemical element on the mortar surface is desirable in order to study the influence of using TiO_2 coated surfaces, as being an alternative for energy savings in buildings. Once again, some different surface regions of this specimen were analyzed, and revealed comparable concentrations of the Ti chemical element.

3.3. Thermal performance of wall models

The obtained experimental data is presented graphically in Figs. 8 and 9, respectively, for the standard and TiO_2 -coated mortar wall models.

By analysing the graphs of Figs. 8 and 9, the first clear evidence refers to a strong variation on the values of the temperature T_2 and in the heat flow ϕ . These high variations occur around a time interval comprised between 5.5 h and 6 h after the starting of thermal tests, and arise from the effect of the water spraying on the front surface of the test wall models.

Moreover, for time intervals up to and after water spraying, it is possible to verify that the temperature's values of the front and back wall surfaces, respectively, T_2 and T_3 , and the back ambient temperature, T_4 are in general stable over time. However, for both wall models, the temperature values recorded by the exterior ambient temperature sensor, T_1 provides noticeable fluctuations of about 5°C and 4°C , respectively, for the standard and TiO_2 -coated mortar wall models. This was due to the type of heat source that has been used (a heating vent). In order to avoid this situation, the choice of an infrared light as heating source should be implemented in future

Fig. 9. Temperatures and heat flow for the wall model with a TiO_2 -coated mortar.

Table 2
Summarized results of temperatures and heat flow for both wall models. The values were measured in the interval of time considered as the steady-state condition.

Thermal variables	UncSurf av. value (steady-state)	TiO ₂ -CSurf av. value (steady-state)
T ₁ (°C)	51.16	51.22
T ₂ (°C)	47.23	46.35
T ₃ (°C)	30.53	29.40
T ₄ (°C)	24.92	25.04
φ (W/m ²)	33.29	37.38

Table 3
Calculated thermal transmission coefficients and thermal resistances.

Specimens	U (W/m ² °C)	R _{cond} (m ² °C/W)	R _{conv,1} (m ² °C/W)	R _{conv,2} (m ² °C/W)
UncSurf	1.266	0.504	0.118	0.168
TiO ₂ -CSurf	1.427	0.454	0.130	0.117

works since it enables a continuous heating and it is also easy to apply and remove without disturbing the heat flow (presenting also a relatively low cost).

In Table 2 are presented the average (*A_v*) values, in the time interval taken as the steady-state condition, for the thermal variables *T_i* (*i* = 1 to 4) and φ for the two wall models considered in this research work.

The thermal gradient between exterior and interior ambient temperatures (Δ*T* = *T*₁–*T*₄) attained during the tests is suitable to apply the 1D heat transfer model already presented. These thermal conditions, enables the existence of a required heat flow across the wall models, always from the outside to the inside, which is necessary to evaluate its thermal performance.

Considering the steady-state condition, the data obtained through the experimental test and registered by the heat flowmeter and temperature sensors, were introduced in Eqs. (2)–(4) in order to obtain the thermal resistances *R*_{cond}, *R*_{conv,1} and *R*_{conv,2} for both walls models. Using these values and applying Eq. (1) the values of the thermal transmission coefficient *U* for the standard and for the TiO₂-coated mortar wall models were determined, as shown in Table 3.

Comparing the steady-state values of *R*_{cond} and *U* it is possible to conclude that the application of a TiO₂-coated mortar worsens the thermal behaviour of the wall model, in 10% and 13%, respectively, for the conduction thermal resistance, and for thermal transmission coefficient. Moreover, the obtained differences in the internal convection heat resistance *R*_{conv,2}, (comparing the coated and uncoated wall) may also result from the contribution of water evaporation, which occurs in the outer surface of the wall that changes both the heat flow and the temperature of the wall (*T*₃) and the interior temperature (*T*₄); this circumstance should have an impact on *R*_{conv,2}. In addition, constructive differences and/or standard material heterogeneities may also influence the obtained values for internal *R*_{conv} parameters.

The obtained results show that TiO₂-coated mortar has a worse thermal insulation capacity than the standard mortar. These results are probably related to the differences between the thermal diffusivities (α = λ/ρ*C_p*) of both materials, where λ (W/m°C) is the material thermal conductivity, ρ (kg/m³) is the material density and *C_p* (J/kg°C) is the material's specific heat. The higher the value of α, more rapidly heat will diffuse through the material. By examining the variables that compose α, it is possible to check this dissimilar behaviour. A high value of α can be due to a high value of thermal conductivity, or otherwise, can result from a low thermal capacity, ρ*C_p*.

The thermal characteristics of the different materials, namely for a standard mortar and for the TiO₂ nanoparticles (anatase phase

Table 4
Thermal behaviour of the standard mortars and TiO₂ nanoparticles [18,19].

	Standard mortar	TiO ₂ nanoparticles
Density (g/cm ³)	2.04	4.25
Specific heat (J/kg °C)	642	680
Thermal conductivity (W/m °C)	0.58	11.7
Thermal diffusivity (mm ² /s)	0.44	4.1

and size of about 25 nm), are presented in Table 4, according the works performed by different research teams [20,21].

By examining Table 4, it is possible to verify that the thermal diffusivity of TiO₂ nanoparticles is much higher than that of standard mortar. This difference mainly results from the effect of the material's thermal conductivity. Actually, the thermal conductivity of the TiO₂ nanoparticles is about 20 times higher than that of the standard mortar, and therefore, overlaps the effect of heat capacity. In fact, the thermal capacity of TiO₂ nanoparticles is only 2 times higher than that of the standard mortar. Additionally, another reason for the occurrence of the decrease in the conduction thermal resistance may be due to slight constructive differences and/or standard material heterogeneities that could have occurred during the manufacture of the tested walls.

Additionally, it was also analyzed thermal behaviour of the wall models in the transient condition (i.e. due to water spraying). Fig. 10(a) and (b) shows the heat flow variation (i.e. the latent heat flow by water evaporation) for the TiO₂-coated and standard mortar wall models, respectively.

By examining the graphs of Fig. 10(a) and (b), it is possible to verify that during the interval of time in which the water spraying took place, the heat flow variation increases over time. This is not unexpected since, during this interval of time, the surface temperatures of the exterior wall models (*T*₂) also decreases rapidly due to the effect of water spraying, and therefore enabling the redirect of heat flow from the wall's exterior surface to the water surface layer that is already deposited.

By using the OriginPro 8 software, it was performed a non-linear fit to the experimental data (scatter points) shown in Fig. 10(a) and (b) in order to express *q_L* as a function of time, according the following expression:

$$q_L = A \left(1 - e^{-t/m} \right) \tag{8}$$

where the fitting parameters are shown in Table 5.

As can be checked out, for the TiO₂-coated wall model (TiO₂ CSurf), the value of the fit parameter *m* (the so called time decay constant) is less than the one obtained for the standard mortar wall (UncSurf), being only about 43% of the value obtained for the uncoated specimen. Fig. 11(a) and (b) shows the rate of heat flow variation (i.e. the time derivative of the expression (8)) for the TiO₂-coated and standard mortar wall models, respectively.

From the graphs plotted in Fig. 11(a) and (b) it can be observed that in the initial instants of time (corresponding to the start of water spraying), the rate of heat flow variation (loss of latent heat) is very high, and tends to decrease rapidly over time.

However, the loss of latent heat is much higher for the TiO₂-coated wall model. For example, at *t* = 0 the loss of latent heat for the TiO₂-coated wall model is about 5 times higher than the one obtained for the standard mortar. Once again, this behaviour is probably related to the differences between the thermal diffusivities of the used materials, and could be explained by the same reasons that were previously invoked.

Therefore, it is anticipated that for the TiO₂-coated mortar its water evaporation rate (dη/d*t*) should be also higher. In fact, by using Eqs. (6) and (8) it is possible to express the water evaporation

Fig. 10. Heat flow variation during water spraying: (a) TiO_2 -coated wall model and (b) standard wall model.

rate as a function of the heat flow variation (loss of latent heat), according the following expression:

$$\frac{d\eta}{dt} = RA(1 - e^{-t/m}) \quad (9)$$

where t is the elapsed time from the starting of water spraying, A is the maximum heat flow variation (presented in Table 5 and obtained from the non-linear fit to the experimental data) and $R = 1/L\rho = 4 \times 10^{-10} \text{ m}^3/\text{J}$.

In order to compare the water evaporation rate for the both wall models, this parameter was evaluated for $t = m$ that corresponds to the instant of time in which the evaporation rate reaches about 63% ($1 - e^{-1}$) of its maximum value.

Table 5

Non-linear fitting parameters of the experimental data.

Specimens	$A \text{ (W/m}^2\text{)}$	$m \text{ (s}^{-1}\text{)}$
$\text{TiO}_2\text{-CSurf}$	12.39 ± 0.222	168.63 ± 1.07
UncSurf	5.22 ± 0.009	392.70 ± 2.81

Thus, by introducing in Eq. (9) the values presented in Table 5 the obtained results for the water evaporation rate are about 1.32 nm/s and 3.12 nm/s, respectively, for the standard mortar and TiO_2 -coated wall models. In this sense, it is possible to conclude that the deposition of TiO_2 nanoparticles on the exterior wall surface improves the water evaporation rate in 136%.

Fig. 11. Rate of heat flow variation during water spraying: (a) TiO_2 -coated wall model and (b) standard wall model.

4. Conclusions

This research work was focused on the analysis of the thermal performance of a standard building wall and its comparison with a brick masonry wall coated with a TiO_2 plastering mortar in its exterior side. The experimental work showed that the application of a TiO_2 -coated mortar worsens the steady-state thermal behaviour of the wall model, in 10% and 13%, respectively, for the conduction thermal resistance, and for thermal transmission coefficient, when compared to the standard wall model.

This thermal behaviour can be due to high thermal diffusivity of the TiO_2 nanoparticles. The thermal conductivity of the TiO_2 nanoparticles is about 20 times higher than that of the standard mortar, and therefore, overlaps the effect of heat capacity.

From the SEM micrographs presented, it was possible to verify that the surface morphology of the TiO_2 -coated mortar is quite different from the one corresponding to the original standard mortar. It was observed the formation of numerous aggregates organized in a lamellar type structure that partially covers the surface of the original mortar. From the EDS spectrum of the TiO_2 -coated mortar, it was identified that the major chemical element detected at the surface of this specimen was titanium. The presence of the Ti chemical element on the mortar surface is a desirable feature in order to study the influence of using TiO_2 nanocoated surfaces.

It was also possible to conclude that the deposition of TiO_2 nanoparticles on the exterior wall surface enhances the water evaporation rate in 136%. In a future experimental campaign, aiming the real context application, the evaluation of the thermal behaviour should be achieved by taking longer time intervals. During these time intervals, the frequency of the water sprinkling should also be increased. Under this condition, it will be expected a more pronounced temperature decrease of the exterior wall surface, thereby increasing the thermal service performance of the building system since the latent heat flux should be higher.

As final remark, it should be emphasized that the thermal performance of TiO_2 -coated masonry brick wall may be influenced by the concentration of aqueous solution containing TiO_2 nanoparticles and also by the applied UV irradiation power. In this sense, it will be useful in future experiments to investigate the influence of these features in the overall performance of these systems.

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References

- [1] M. Leahy, J.L. Barden, B.T. Murphy, N. Slater-Thompson, D. Peterson, International Energy Outlook 2013, U.S. Energy Information Administration (EIA), Office of Energy Analysis, U.S. Department of Energy, Washington, DC, 2013.
- [2] R. Parameshwaran, S. Kalaiselvam, Energy efficient hybrid nanocomposite-based cool thermal storage air conditioning system for sustainable buildings, *Energy* 59 (2013) 194–214.
- [3] J.S. Sage-Lauck, D.J. Sailor, Evaluation of phase change materials for improving thermal comfort in a super-insulated residential building, *Energy and Buildings* 79 (2014) 32–40.
- [4] J. Vieira, L. Senff, H. Gonçalves, L. Silva, V.M. Ferreira, J.A. Labrincha, Functionalization of mortars for controlling the indoor ambient of buildings, *Energy and Buildings* 70 (2014) 224–236.
- [5] K. Hashimoto, H. Irie, A. Fujishima, TiO_2 photocatalysis: a historical overview and future prospects, *Japanese Journal of Applied Physics* 44 (2005) 8269–8285.
- [6] J.O. Carneiro, V. Teixeira, A. Portinha, A. Magalhães, P. Coutinho, C.J. Tavares, et al., Iron-doped photocatalytic TiO_2 sputtered coatings on plastics for self-cleaning applications, *Materials Science and Engineering B* 138 (2007) 144–150.
- [7] B.Y.R.D. Shannon, M.H.N.H. Baur, O.H. Gibbs, M. Eu, V. Cu, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallographica A* 32 (1976) 751–767.
- [8] S.K. Zheng, G. Xiang, T.M. Wang, F. Pan, C. Wang, W.C. Hao, Photocatalytic activity studies of TiO_2 thin films prepared by r.f. magnetron reactive sputtering, *Vacuum* 72 (2003) 79–84.
- [9] U. Diebold, The surface science of titanium dioxide, *Surface Science Reports* 48 (2003) 53–229.
- [10] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 1 (2000) 1–21.
- [11] K. Hashimoto, H. Irie, A. Fujishima, A historical overview and future prospects, *AAPPS Bulletin* 17 (2007) 12–28.
- [12] J.O. Carneiro, V. Teixeira, S. Azevedo, F. Fernandes, J. Neves, Development of photocatalytic ceramic materials through the deposition of TiO_2 nanoparticles layers, *Journal of Nano Research* 18–19 (2012) 165–176.
- [13] V.G. Haach, G. Vasconcelos, P.B. Lourenço, Influence of aggregates grading and water/cement ratio in workability and hardened properties of mortars, *Construction and Building Materials* 25 (2011) 2980–2987.
- [14] J.O. Carneiro, S. Azevedo, V. Teixeira, F. Fernandes, E. Freitas, H. Silva, et al., Development of photocatalytic asphalt mixtures by the deposition and volumetric incorporation of TiO_2 nanoparticles, *Construction and Building Materials* 38 (2013) 594–601.
- [15] S.S. Lucas, V.M. Ferreira, J.L.B. de Aguiar, Incorporation of titanium dioxide nanoparticles in mortars—influence of microstructure in the hardened state properties and photocatalytic activity, *Cement and Concrete Research* 43 (2013) 112–120.
- [16] R.H. Jenkins, R.L. Snyder, Introduction to X-ray powder diffractometry, Wiley-Interscience, New York, 1996.
- [17] P.B. Lourenço, G. Vasconcelos, P. Medeiros, J. Gouveia, Vertically perforated clay brick masonry for loadbearing and non-loadbearing masonry walls, *Construction and Building Materials* 24 (2010) 2317–2330.
- [18] A.K. Wählin, A.M. Johansson, E. Aas, G. Broström, J.E.H. Weber, J. Grue, Horizontal convection in water heated by infrared radiation and cooled by evaporation: scaling analysis and experimental results, *Tellus, Series A: Dynamic Meteorology and Oceanography* 62 (2010) 154–169.
- [19] R.A. Spurr, H. Myers, Quantitative analysis of anatase–rutile mixtures with an X-ray diffractometer, *Analytical Chemistry* 29 (1957) 760–762.
- [20] Y. Xu, D.D.L. Chung, Effect of sand addition on the specific heat and thermal conductivity of cement, *Cement and Concrete Research* 30 (2000) 59–61.
- [21] M. Saeedian, M. Mahjour-Shafiei, E. Shojaei, M.R. Mohammadzadeh, Specific heat capacity of TiO_2 nanoparticles, *Journal of Computational and Theoretical Nanoscience* 9 (2012) 616–620.