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Obtaining of self-cleaning repair air lime mortars with photocatalysts

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Abstract: The obtaining of self-cleaning mortars is very interesting to apply them in Built Heritage. Atmospheric pollutants, mainly carbonaceous particles and gases like NO_x and SO_2 can lead to severe aesthetic and functional damages in artworks. In the case of mortars and renders, the use of photocatalysts -usually based on TiO2- can be worthy of consideration. Photocatalysts, after being activated by light, are able to oxidize pollutants avoiding their deposition onto building materials. In this work, different air lime mortars modified upon the addition of TiO2-based photocatalysts were obtained and studied. Photocatalysts can be incorporated in bulk and the changes in fresh state properties were studied as well as the effect of the presence of the photocatalysts on the pore structure and mechanical resistance. Finally, the photocatalytic efficiency of these materials was carried out by means of a NOx abatement test. Results showed that the presence of the photocatalysts had a positive impact on the preservation of the lime mortars characteristics.

Introduction

One of the severe problems of current society is the atmospheric pollution that is caused due to existence of toxic gases in the atmosphere, as for example NO_x [1]. NO_x are thought as damaging gases for environment because they are one of the responsible of ozone depletion and acid rain. In addition, the interaction of NO_x could lead to damages onto building materials and the accumulation of the degradation products and dirt induces detrimental aesthetic consequences. In order to eliminate NO_x, photochemical oxidation (PCO) has been used in the last years and has gained a great attention. One of the most commonly used photocatalytic agents is TiO_2 [2]. This compound is used due to its high stability, low toxicity and exceptional photocatalytic activity under ultraviolet irradiation (UV). However, the UV in total solar radiation is only around 4% of the total spectre, so that in order to enhance the spectral absorption of the TiO_2 this component has to be doped with other metals (Fe, V, Cr…) [3], increasing its sensitivity towards visible light.

The following step aims to introduce these photocatalysts into matrix with the aim of immobilizing them. There are some previous works about successful TiO_2 addition in building materials as Portland Cement [4, 5] with effective results in terms of NO_x abatement as well as of self-cleaning ability of their surfaces. A widespread distribution of the active agent is achieved with the incorporation of photocatalysts into cement materials and, if it is applied to outdoor exposed surfaces large enough, could be helpful in urban environments to reduce the contaminants level. On the other hand, the self-cleaning capacity safeguards the aesthetic characteristics and minimizes the maintenance and cleaning expenses [6].

The interest in the use of repair air lime based mortars for Built Heritage is growing because these materials present good compatibility with ancient building materials [7]. The development of repair mortars with enhanced properties, such as photocatalytic ability and self-cleaning characteristics could be of great interest in order to reduce the problems ascribed to the pollutants deposition. Therefore, the main objective of this work is the obtaining of air lime mortars modified with TiO_2, doped Fe-TiO_2 and V-TiO_2. The PCO efficiency under UV as well as visible light irradiation of these mortars will be determined, in order to assess the sensitivity of these materials towards the light spectrum.

Materials and methods

Air lime (Class CL 90-S, according to the European norm EN 459-1:2011, supplied by CALINSA) was used in order to prepare the mortars. A SiO_2-based aggregate was added [8]. As photocatalysts, TiO_2 (Aeroxide P25, Evonik, average particle size: 21nm; surface area 50 ± 15 m^2 g^{-1}), and two different doped TiO_2 (TiO_2 doped with iron 0.5%; and TiO_2 doped with vanadium 1% obtained by means of a Flame Spray Pyrolysis process) were used (supplied by Lurederra).

Samples were prepared with an air lime:aggregate ratio of 1:3 by weight. As requested, different amounts of photocatalyst were added: 0.5%, 1% and 2.5% with respect to the lime. These samples required different amounts of water in order to yield a suitable consistency, so spread of the mortar after 15 jolts of the flow table was measured giving 175 ± 10 mm, according to the flow table test [9]. To ensure a proper distribution, in bulk additions, air lime and photocatalytic additives were blended for 10 min at low speed in a mixer (Laboratory V-blender model BL-16, Lleal S.A.). Water was then added and mixed for 90 seconds at low speed. After that fresh properties were studied. Next step was moulding the mortars in 36x40 mm cylindrical casts and de-moulded 24 h later. Finally the moulds were cured at lab conditions, 20º C and 60% RH, during 28 days. Three specimens of each mortar were tested with the aim of making results representative.

In the fresh state, consistency (by means of the flow table test [9]) and setting time [10] were studied (setting time, obtained from a specific device provided with a bradawl, which pushed the fresh sample until the strength applied to introduce it into the sample was higher than 15 N). After a curing period of 28 days, compressive strengths were measured in hardened samples at a loading rate of 50 $N \cdot s^{-1}$. Pore size distributions (PSD) were carried out by mercury intrusion porosimetry (Micromeritics-AutoPoreIV-9500; pressure 0.0015 to 207 MPa).

NO_x abatement tests were carried out on mortar samples in a laminar-flow reactor (ISO 22197-1[11]). UV radiation was imposed by a OSRAM Ultravitalux 300 W lamp with an irradiance of 30±1 W·m^2 adjusted by a UV-A radiometer; and visible radiation was imposed by a PHILIPS Master SON-T PIA Plus 150W with an irradiance of 28±1 W·m^2 adjusted by a visible radiometer**.** Conditions were 50±10% RH and 20±2ºC. A NO stream of 500 ppb was introduced into the photoreactor where the samples were placed. NO and NO_2 concentrations were registered every minute by a chemiluminescence detector (Environnement AC32M) at a 0.75 L·min^{-1} flow. Lime mortars samples were discs of 36 ± 3 mm of diameter and 10 ± 3 mm of thickness. Photocatalytic additives in powder were also studied. 500 ± 2 mg of powder were placed inside the reactor under the aforementioned conditions. Experiments have 3 common steps: firstly 10 min of NO concentration stabilisation; secondly 30 min of irradiation (UV o visible) and finally 10 minutes of darkness.

Results and discussion

Influence of the photocatalysts on lime mortar properties

The incorporation of photocatalytic additives increased the water demand of lime mortars due to the small particle size of these additives. In general, it could be said that lime samples with photocatalytic additive incorporated showed higher setting times than control lime samples. Only for 0.5 wt.% V-TiO_2 and 1 wt.% Fe-TiO_2 samples, setting times were slightly lower (103 minutes and 133 minutes respectively) than control samples: for practical applications, these values are perfectly acceptable.

Regarding the mechanical resistance, the incorporation of V-TiO_2 yielded compressive strengths greater than 1MPa for all samples (Fig. 1). It could be seen that upper amounts of V-TiO_2 gets higher compressive values. Nevertheless, the presence of either TiO_2 or Fe-TiO_2 yielded lower values than that of the control lime sample. This reduction does not follow a linear pattern in connection with the additive content. This fact has been noticed in previous works [12]. Despite this decrease in mechanical resistance, the compressive strength of some of the mortars could be large enough for many practical applications [13].

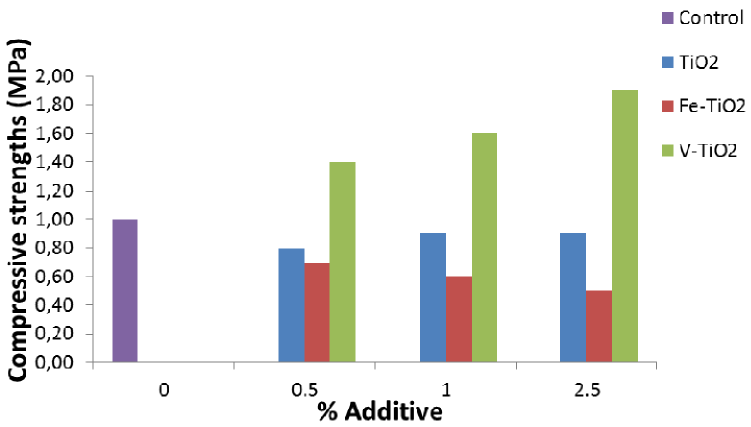

Fig. 1 Compressive strength values of lime mortars doped with TiO_2, Fe-TiO_2 and V-TiO_2. (28 curing days)

Plain lime mortars showed a unimodal pore size distribution with the mean pore size at 0.68 µm. When photocatalytic additives are incorporated, the pore size distribution patterns did not change considerably (Fig. 2). In terms of total porosity there are some modifications: total porosity value for control mortar was 33.32%. Incorporation of V-TiO_2 into a lime mortars gave rise to a slight increase in total porosity: 34.03% for samples with 2.5 wt.%. There is no significant changes in the mean pore size. The incorporation of TiO_2 presents total porosity values analogous to the plain samples and also an average pore size similar than that of the control sample. For Fe-TiO_2 incorporation, total porosity values underwent a significant increase, these samples yielding similar compressive strengths values than those of the plain lime samples.

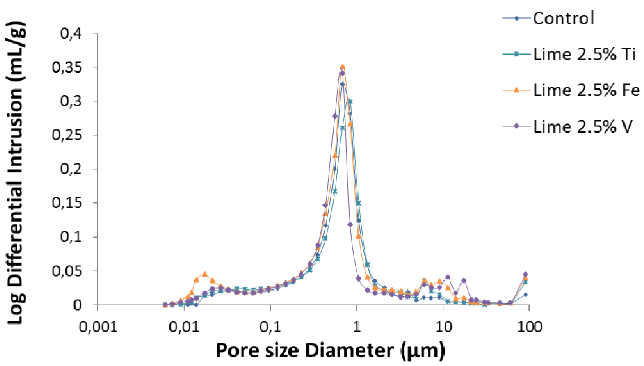

Fig. 2 Pore size distributions of mortars doped with TiO_2, Fe-TiO_2 and V-TiO_2 in a 2.5wt.%

Photocatalytic activity of the lime mortars

Firstly, the NO abatement ability of the powdered photocatalysts was assessed by means of the procedure previously described under UV and visible radiation. NO abatement under UV radiation is similar for the three different photocatalytic additives (Fig. 3). Previous works reported comparable NO abatement results [14] with TiO_2 doped with N and S. The doping of the crystalline network of the titania did not involve a severe reduction of its activity under UV irradiation. Under visible radiation, TiO_2 powders achieved a 20.01% NO abatement, whereas a remarkable increase was determined for Fe-TiO_2 and V-TiO_2 additives, in which the percentages of NO removal were 24.34% and 25.09%, respectively. This finding can be explained due to the presence of iron and vanadium into the TiO_2 structure, which reduced the band gap of the titania, increasing its sensitivity towards visible light spectrum. Taking into account the low doping percentage (0.5% of Fe and 1% of V), the significant increase in the visible light efficiency was noticeable. Moreover, previous works have shown comparatively lower NO abatements (around 12%) for some photocatalytic additives sensitive to visible light [14].

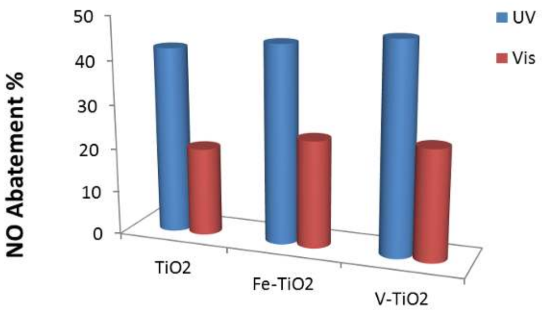

Fig. 3 NO abatement of photocatalytic additives

When the photocatalysts were incorporated to mortars, NO abatement results were also measured (Fig. 4 and Fig. 5). Control lime mortars yielded a 6.28% of NO removal under UV radiation and 2.15% of NO removal under visible radiation. It has to be noticed that these mortars are samples without any photocatalytic additive. Their removal action, therefore, does not include a PCO process. A previous work [5] has reported that mortars with high pH are capable to carry out NO degradations by a direct NO_2^- and NO_3^- formation and the elimination of HONO and HNO_3 intermediates. It is due to the disproportionation of the NO as a result of the own action of OH^- which are accessible on mortar surface due to alkaline media. Under UV radiation (Fig 4), all the mortars including photocatalysts presented better results in NO removal than those of the control samples. In general, an increase in the additive content allowed the samples to show better photocatalytic results. Samples doped with 0.5 wt.% and 1 wt.% of additive showed results similar between the three photocatalytic additives but for 2.5 wt. % of additive, TiO_2 yielded the best NO abatement with a 26.70% of NO removal. This finding is in line with the initial hypothesis of the excellent photocatalytic activity of TiO_2 under UV radiation owing to its 3.2 eV band gap.

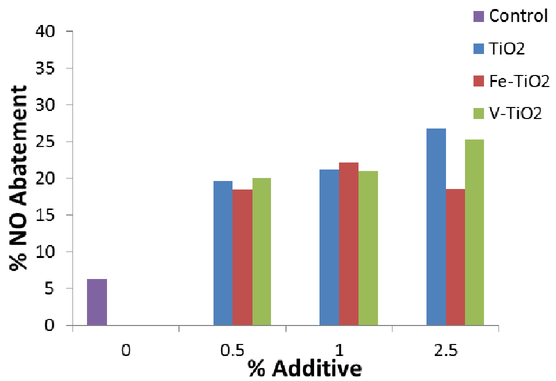

Fig. 4 NO abatement of lime mortars under UV radiation

Lime mortars were also tested under visible radiation (Fig. 5). Samples with TiO_2 and V-TiO_2 displayed satisfactory results, and it could be said that lime mortars modified upon the presence of Fe-TiO_2 exhibited the most efficient NO abatement in all proportions. This fact is due to the reduction in the photocatalyst band gap and consequently the enhancing of the photocatalytic activity under visible radiation. In the case of the samples with the V-TiO_2, the low doping percentage could explain the results as compared with the Fe-TiO_2 samples. For these mortars, the absence of a direct dosage-response pattern (especially with respect to 1% mortar) could be explained by the coupling between gaps and electrons resulting in an efficiency drop.

Previous research has shown a relationship between the mortars pore size distribution and photocatalytic activity [12]. It has been established that the most favourable conditions combine a mortar with good pore size distribution and an appropriate amount of catalyst in order to favour the pollutant access into the structure of the material, for bulk additions of the photocatalysts. In the tested samples, the high total porosity values for lime samples doped with Fe could explain the excellent NO abatements of these samples (Table 1). Total NO removal values under visible radiation can be considered as good results, since it has to be considered that pure additives powder yielded maximum NO removal values of ca. 25% but when they are incorporated in the bulk mass of the mortars, the highest percentage was 2.5 wt.%. Therefore, the NO abatements close to 10% can be considered as good NO removal rates for these bulk additions. This point shows how interesting would be to use doped photocatalysts under visible radiation: further research should be devoted to study the effect of higher additions to air lime mortars.

Table 1. Total porosity (%) and main pore size diameters (µm)

	TiO_2		Fe-TiO_2		V-TiO_2	
	Total porosity (%)	Main Diameter (µm)	Total porosity (%)	Main Diameter (µm)	Total porosity (%)	Main Diameter (µm)

0%	33.32	0.68	-	-	-	-
0.5%	28.05	0.83	29.58	0.68	41.84	0.83
1%	34.43	0.83	35.30	1.05	32.11	0.68
2.5%	33.06	0.83	36.02	0.68	34.03	0.68

In this sense, the quantum efficiency should be also taken into account. Previous studies have evaluated the apparent photonic efficiency in order to know all available photons instead of the fraction absorbed by the photocatalyst [15, 16, 17]. Results showed that, in all cases [18], reactions efficiencies and quantum efficiencies are higher for UV radiation than for visible radiation. The lower, but, at the same time, promising NO abatements under visible radiation than under UV abatements could be partially ascribed to this fact.

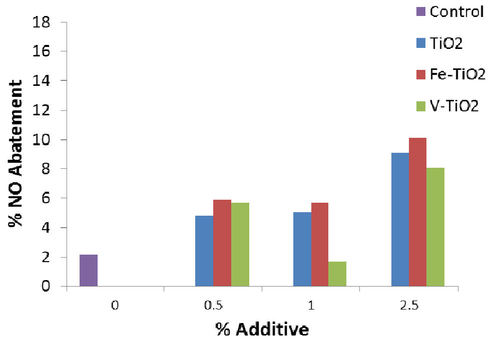

Fig. 5 NO abatement of lime samples under visible radiation

Conclusions

Air lime mortars including three types of photocatalytic have been successfully obtained and tested as NO depolluting agents. The incorporation of the three additives in three different proportions did not involve substantial changes in their physical properties, within a range of acceptable values, so that a first conclusion is that the tested photocatalysts were perfectly compatible with the air lime to be included as bulk addition in mortars.

The three photocatalytic additives powder were active under both types of radiations. The percentages of NO removal rates were comparable to previous works, even better in some cases. Lime mortars without additive exhibited a certain ability for NO abatement, because of the alkaline pH of the material and the disproportionation of the nitrogen compound. The presence of photocatalytic additives yielded much better NO abatements than control lime samples. It has been also confirmed that there was a clear relationship between photocatalytic activity and porosity of the material. Future prospect is to optimize an efficient coating with these photocatalytic additives to cover lime surface with the aims of improving NO abatements and decreasing economic costs.

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