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Experimental Investigation on the Composition, Mechanical Strength and Self-Cleaning Ability of Photocatalytic Mortars

Investigação experimental sobre composição, resistência mecânica e capacidade de auto-limpeza de argamassas fotocatalíticas

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Abstract

The self-cleaning ability of photocatalytic cement-based materials has the potential to preserve the esthetic appearance of building facades over time thus reducing cleaning costs. In the present work , the joint effect of several factors on the mechanical strength and self-cleaning ability of photocatalytic mortars was studied. For this purpose, four different mortar mixes containing two binder/sand ratios (1:3 and 1:4) were analyzed. Two mixes containing only Portland cement and the other two possessing 50% Portland cement and 50% aerial lime. For each mix, four different compositions were manufactured, each one with a different titanium dioxide-TiO2 content (0%, 2%, 4% and 6%). The results show that w/b increases with TiO2 which, in turn, leads to lower mechanical strength. Results also show that the mixes with 2% TiO2 had the highest self-cleaning effect.

Resumo

A capacidade de auto-limpeza de materiais cimentícios fotocatalíticos apresenta potencial para preservar a aparência estética das fachadas de edificios ao longo do tempo reduzindo dessa forma os custos de limpeza das mesmas. No presente trabalho estudou-se o efeito conjunto de vários factores na resistência mecânica e na capacidade de auto-limpeza de argamassas fotocatalíticas. Para este objectivo analisaram-se quatro argamassas contendo dois rácios ligante/areia (1:3 e 1:4). Duas composições continham sómente cimento Portland e outras duas continham 50% de cimento Portland e 50% de cal aérea. Para cada uma destas composições produziram-se quatro misturas com uma percentagem variável de dióxido de titânio - TiO2 (0%, 2%, 4% e 6%). Os resultados mostram que o aumento da percentagem de TiO2 implica um aumento da razão água/ligante que se traduz em menor resistência mecânica. Os resultados mostram também que as argamassas com 2% de TiO2 apresentaram a maior capacidade de auto-limpeza.

Keywords

Photocatalytic mortars; Portland cement; aerial lime; self-cleaning ability

Palavras-chave

Argamassas fotocatalíticas, cimento Portland, cal aérea, capacidade de auto-limpeza

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Introduction

The photocatalityc capacity of semiconductor materials has the potential to induce important changes in the field of construction and building materials. Several semiconductors materials such as TiO_2, ZnO, Fe_2O_3, WO_3 and CdSe, possess photocatalytic capacity [1]. However, TiO_2 is the most used of all due to its low toxicity and stability [2]. TiO_2 can crystallize as rutile, anatase and brookite. The first being the most stable form (thermodynamically speaking). It is also the most available form (it is the 9th most abundant element in the Earth crust) and is currently used as an additive in the painting industry. The anatase and brookite forms are meta-stable and can be transformed into rutile by thermal treatment. Being a semiconductor with photocatalytic capacicity, when TiO_2 is submitted to UV rays (320-400nm) and when in the presence of water molecules [3], it leads to the formation of hydroxyl radicals (OH) and superoxide ions (O2-). Those highly oxidative compounds react with dirt and inorganic substances promoting their disintegration. Photocatalys of TiO_2 is also responsible for the reduction of the contact angle between water droplets and a given surface. This leads to super-hydrofobic or super-hydrophilic surfaces thus increasing their self-cleansing capacity. Water repellent surfaces are one of the features of natural systems as it happens in the leaves of the lotus plant whose microstruture allows self-cleansing ability. According to Fujishima et al. [4], the potential of photocatalysis can be perceived by the high number of citations of a related 1972 paper published on *Nature*, as well as by the number of papers concerning photocatalysis investigations, which increased in an exponential pattern. Considering the cost to clean graffiti (in the city of Los Angeles this figure could amount to 100 million euro/year [5]) one can realize the huge potential of the photocatalytic capacity of nanomaterials. Although the self-cleaning properties of photocatalyst materials are known since the 60´s [6], it was only recently that these materials start to be used in a wide manner [7] and that a patent on a concrete block with self-cleaning ability has been issued [8]. The first application of self-cleaning concrete took place in the church “Dives in Misericordia” in Rome. This building was designed by the Architect Richard Meyer and officially opened in 2003. It is composed of 346 prestressed concrete blocks made with white cement and TiO_2 (binder 380 kg/m^3 and w/b=0,38) [9].Visual observations carried out six years after construction revealed only slight differences between the white color of the outside concrete surfaces and that of the inside blocks [10]. Diamanti et al. [11] studied mortars containing TiO_2 having noticed reductions in the contact angle between water and the solid surface of almost 80%. Ruot et al. (2009) [12] mentioned that the photocatalytic activity is dependent on the matrix properties. Increasing TiO_2 content in cement pastes above 1% leads to a proportional increase in photocatalytic activity, as for mortars, a TiO_2 content increase just induces to a very small increase in the photocatalytic activity. Those authors suggest that most TiO_2 particles in mortars are not reached by UV radiation. Several authors [12, 13] used Rhodamine B-based colourimetric test to evaluate the self-cleaning ability of photocatalytic cement-based materials, however, it is important to assess the self-cleaning performance when traditional spray paint is used. Research already carried out on TiO_2 mortars has a strong focus on the photocatalytic reaction but is weak concerning the properties of the same mortars. This means that investigations that relate the composition of mortars traditionally used for external renders with its mechanical strength and self-cleaning capacity are still missing.

EXPERIMENTAL WORK

Materials and mortars preparation

The fine aggregate used was a river sand with a specific gravity of 2.6, a 24 hour water absorption of 1.0% and a finess modulus of 3.24 (Fig.1). An ordinary white Portland cement (CEM II/B-L32,5R) where used. This cement was chosen to avoid the usual white dots of TiO_2 particles when traditional Portland cements is used. Besides, using a white cement mortar could serve as a final render thus avoiding the use of paint. A hydrated commercial lime powder, supplied by Lusical with more than 70% of CaO and a density of 0.46 g/cm^3 was also used (Table 1).

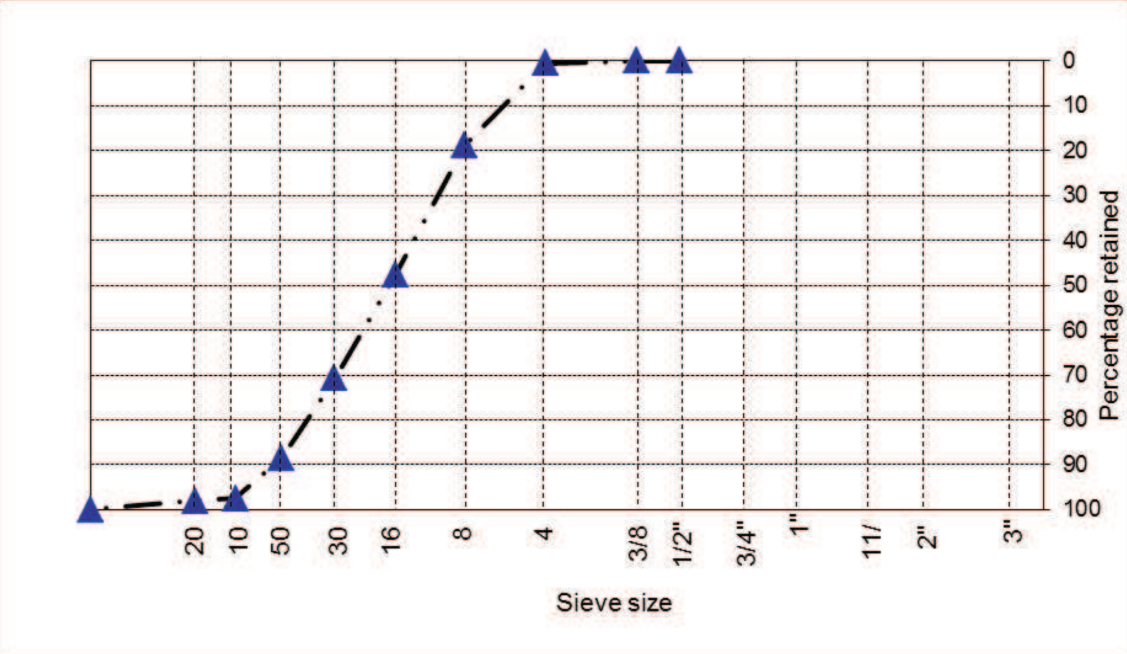

Fig. 1 – Fine aggregate gradation

Table 1- Chemical composition of the aerial lime H100

Elements	Percentage
$Ca(OH)_2$	96.5
$CaCO_3$	1.75
Al_2O_3	0.04
SiO_2	0.09
MgO	0.32
SO_3	0.11
K_2O	0.02
CaO	74.10
Fe_2O_3	0.04

Commercially available nano-TiO_2 powder (P25, Evonik Degussa) was used in all the experiments. The particle size of the TiO_2 is 21 nm, with a specific BET surface area of 50 m^2/g. Although the use of nanoparticles is very recent, it has already raised issues concerning its potential toxicity. Some investigations showed that nanoparticles can cause symptoms like the ones caused by asbestos fibres [14,15]. Therefore, during the mortar mixing masks and gloves were used to avoid contact with the nano-TiO_2 powder. Four different mortar mixes were studied, having two binder/sand ratios (1:3 and 1:4). Two mixes contained only Portland cement and the other two were composed of 50% Portland cement and 50% aerial lime. For each mix, four different compositions were manufactured with a different TiO_2 content (0%, 2%, 4% and 6%), which is, in turn, related to the sand mass. The amount of water used for each mix was calculated in order to keep the mortars with similar consistence [16], (of aprox. 162±2mm) flow (Table 2). The water needs increase with TiO_2 content thus leading to higher porosity mortars.

Table 2 - Water needs to achieve similar flow

Mix	Cement (g)	Lime (g)	Sand (g)	TiO_2 (g)	w (g)	w/b	Flow (mm)
Cement:sand (1:3)	338.8	-	1296.8	-	263.6	0.78	166.0
			1270.9	25.5	299.3	0.88	160.0
			1244.9	51.9	340.2	1.00	160.0
			1219.0	77.8	414.4	1.22	162.0
Cement:sand (1:4)	279.4	-	1426.2	-	271.2	0.97	164.0
			1397.6	28.6	330.8	1.18	162.0
			1369.2	57.7	387.4	1.39	160.0
			1340.6	85.6	456.0	1.63	160.0
Cement: Lime: sand (1:1:6)	170.3	170.3	1303.7	-	327.1	0.96	161.0
			1277.6	26.1	360.0	1.06	162.0
			1251.5	52.1	421.6	1.24	162.0
			1225.5	78.2	482.4	1.42	162.0
Cement:Lime:sand (1:1:8)	140.4	140.4	1432.4	-	329.8	1.17	160.0
			1403.8	28.6	377.0	1.34	161.0
			1375.1	57.3	433.2	1.54	160.0
			1346.5	85.9	494.8	1.76	160.0

Experimental procedures

Compressive and tensile strength

The compressive and tensile strength tests were performed under EN 1015-11 [17]. The mortar specimens were conditioned at a temperature equal to 21 ± 2 ºC and cured in a moist chamber until they have reached the testing ages. Tests were performed on 40x40x160 mm^3 specimens. Compressive strength for each mixture was obtained from an average of 3 specimens determined at the age of 28 days of curing.

Self-cleaning effect

For self-cleaning evaluation, 200×200×10 mm^3 specimens were used. The reason for this option lies on the fact that some authors suggest that in order to avoid an excessive TiO_2 consumption the mortar thickness should not exceed 10mm [9]. These specimens were marked with current red spray paint and submitted for 30 days to UV radiation provided by fluorescent lamps (TL-D 18W black light blue-BLB SLV, Philips, Holland). The wavelength of the lamps ranged from 300 to 400 nm with a maximum intensity at 365 nm. The distance between the lamps and the mortar surface was 19cm. The color changes of the spray paint were measured by a portable sphere spectrophotometer.

4. Results and discussion

4.1 Compressive and tensile strength

Figure 2 shows the compressive strength of the mortars. The results show that the use of TiO_2 is associated with a severe compressive strength loss. Other authors [18] report an increase in compressive strength when TiO_2 is used, however, they forget to mention that comparisons between different mixes must be made for similar workability. The addition of TiO_2 has a filler effect, but at the same time, it increases the water requirements. For the mortars with lime, the compressive strength loss is lower. Table 3 presents the mortar mix category according to compressive strength [19]. Figure 3 shows the tensile strength of the mortars.

Similar considerations can be made about the reduction in strength with TiO_2 content. None of the lime-cement mixes was able to fulfil minimum tensile strength requirements (0.7 MPa) for external renders conservation purposes [20]. This means that new investigations are needed to find optimum TiO_2 content in mortars they can be able to fulfil standard mechanical requirements.

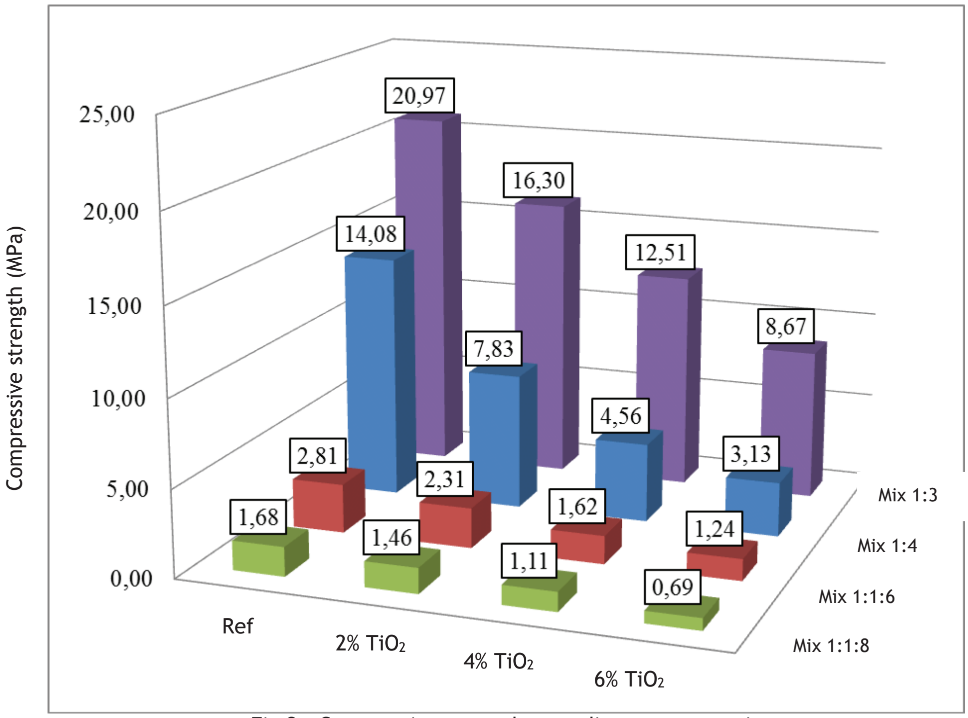

Fig.2 - Compressive strength according to mortar mix

Table 3: Mortar mix category according to compressive strength

Mix	TiO_2 (%)	Category
Cement:sand (1:3)	-	IV
	2	IV
	4	IV
	6	IV
Cement:sand (1:4)	-	IV
	2	IV
	4	II and III
	6	II
Cement: Lime: sand (1:1:6)	-	II
	2	I and II
	4	I
	6	I
Cement: Lime: sand (1:1:8)	-	I
	2	I
	4	I
	6	I

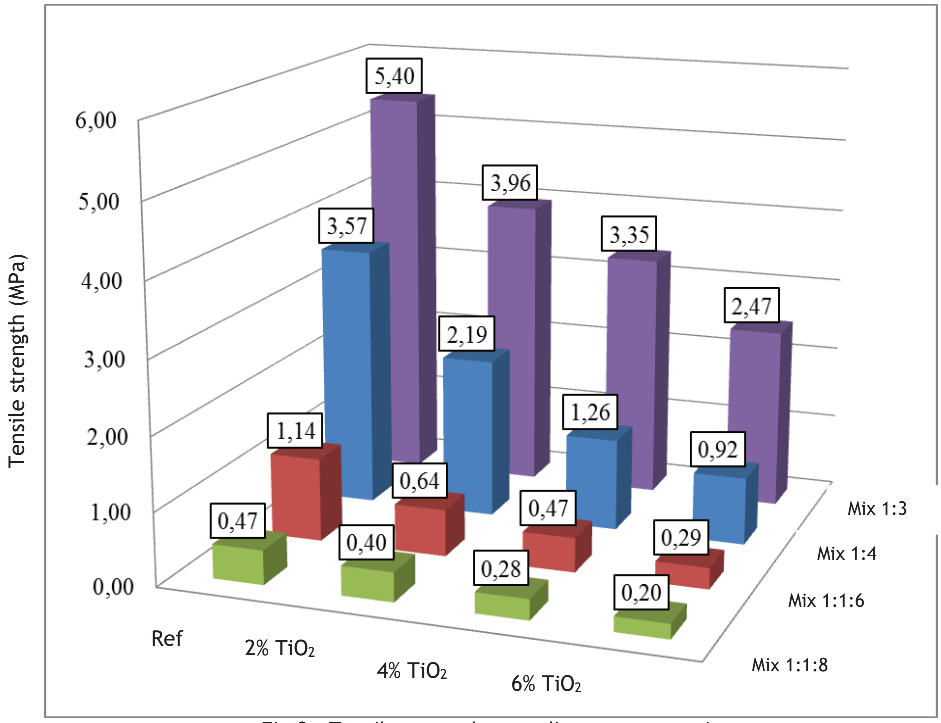

Fig.3 – Tensile strength according to mortar mix

Self-cleaning effect

The color variation is presented in Table 4. Results show that all the mixes with 2% TiO_2 had the highest self-cleaning results. This confirms results obtained by other authors [21]. The lime-cement mix with 2% TiO_2 has the highest self-cleaning effect. Increasing the sand content improves self-cleaning effect which may be due to the higher w/b used in this mixes, and therefore, due to a higher porosity. However, this is in contradiction with the fact that increasing TiO_2 decreases the self-cleaning effect.

Table 4: Color variation according to TiO_2 content and w/b

Mix	TiO_2 (%)	w/b	(%)
Cement:sand (1:3)	-	0.78	0
	2	0.88	2.09
	4	1.00	1.40
	6	1.22	0.25
Cement:sand (1:4)	-	0.97	0
	2	1.18	3.22
	4	1.39	2.28
	6	1.63	0.47
Binder:sand (1:3)	-	0.96	0.46
	2	1.06	4.32
	4	1.24	2.86
	6	1.42	2.30
Binder:sand (1:4)	-	1.17	0.27
	2	1.34	1.45
	4	1.54	0
	6	1.76	0.72

Conclusions

From the information presented in this paper, the following conclusions can be drawn:

1. The use of TiO_2 is associated with a severe compressive strength loss;
2. Lime-cement mixes with TiO_2 do not satisfy minimum tensile strength requirements;
3. Mixes with 2% TiO_2 had the highest self-cleaning results;
4. The lime-cement mix with 2% TiO_2 has the highest self-cleaning effect of all;
5. Future investigations must address optimum TiO_2 content in mortars so they can be able to comply with full external renders requirements

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