"Effect of Climate Change on Built Heritage",
WTA-Colloquium, March 11-12, 2010, Eindhoven, The Netherlands,
WTA-Schriftenreihe, Heft 34, 45–58 (2010)

Developments in the Field of Cementitious Mortars for the Restauration of Monuments

G. Hüsken and H.J.H. Brouwers
Eindhoven University of Technology, The Netherlands

Abstract

A major part of CO_2 is emitted by the cement clinker production. This produced cement is used as a binder in mortars and concrete. In this paper it is shown that the cement content of mortars can be reduced by employing by-products in cement, such as stone waste materials. Furthermore, the cement content as such in mortars can be reduced, e.g. by including inert fines and a smart mix design concept. It will be seen that mortars with superior mechanical (e.g. strength) and physical (e.g. durability) properties can be produced that are low-cost and environmental friendly. An additional feature can be obtained by adding TiO_2 to the mortar. In this way, the mortar and surrounding stones will, due to the photocatalytic activity (self-cleaning effect), remain free of soiling. Besides this, the mortar contributes in removing NO_x from the air, the so-called air-purifying effect.

Götz Hüsken
Dipl.-Ing. Götz Hüsken studied Civil Engineering at the Bauhaus-University Weimar, Germany, with a specialization in the area of structural engineering. He did his graduation work to the nonlinear load bearing behavior of wood under longitudinal load. After finishing his master thesis he started as Ph.D. student at the University of Twente (Enschede, The Netherlands) in 2005. As from 2009 he is working as researcher at Eindhoven University of Technology. His research project comprises concrete technology with focus on Earth-Moist Concrete and innovate concrete mass products.

H.J.H. Brouwers
Prof. dr. ir. H.J.H. Brouwers studied Mechanical Engineering at Eindhoven University of Technology (The Netherlands) and did his graduation work in the field of Nonlinear Dynamics. After his graduation in 1986, he worked at Akzo Nobel Central Research in Arnhem on plastic production processes and products. In 1990, he completed his PhD thesis on the heat and mass transfer in plastic heat exchangers and condensers. From 1992 till 2009 he was appointed by the University of Twente, with as fields of interest: Sustainable Building and Construction Materials. As from 2009 he is working as full professor for building materials at Eindhoven University of Technology.

1 Introduction

The application of eco mortars for the restauration of monuments requires the integration of new materials that are characterized by multifunctional properties. In the considered case, mortars that have low cement contents combined with the addition of photocatalytic acting materials seem to be a promising development in that field. Lowering the cement content in cementitious mortars and concrete is as such an ecological benefit since it contributes to a decrease in the CO_2 emission produced during the production of cement clinker which is as such a major part of the annual CO_2 emission around the world. The financial crisis of the year 2008/2009 resulted in a stagnation of the cement production while an increase, especially in the developing countries, is predicted for the coming years.
However, not only the emission of CO_2 forms a major problem in our modern society, but also the air quality in inner-city areas with high traffic loads is a serious issue. Limiting values can be easily exceeded during rush hour times. Here, the application of photocatalytic materials, such as titanium dioxide, results in a beneficial contribution to the overall reduction of nitrogen oxides (NO_x). The air-purifying property of these new building materials containing materials having photocatalytic properties is not the only interesting point, but also the preservation of a clean aspect offers different fields of new applications in façade systems. As these systems keep the original appearance over a longer period of time than classical systems, cleaning costs are reduced and less deleterious detergent are used. This self-cleaning effect offers a beneficial contribution to the overall aspect of eco mortars.

2 Development of eco mortars with low cement contents

The optimization of particle packing allows the design of cementitious mortars or concrete mixes that are characterized by a denser granular structure. Such a structure results in improved mechanical properties such as compressive strength or flexural strength. Not only the mechanical properties are affected, but also the durability of the designed mortar is improved due to the denser granular structure and the lower porosity of the cement paste.
The idea of optimized particle packing and its beneficial influence on the concrete properties forms the basis of a new mix design concept that is explained in detail in /1/. This new mix design concept can also be applied for the design of eco mortars. Here, two main aspects have to be pointed out. First, eco mortars can be designed that are characterized by lower cement contents. This can be realized due to the denser granular structure that results in improved mechanical properties such as higher compressive strength values. The higher compressive strength of the designed mortar allows a cement reduction. The second aspect deals with the replacement of cement by other materials such as by-products or stone waste powders generated by the natural stone industry. During the production of washed rock aggregates, high amounts of fine stone waste powders in slurry form are gener-

ated throughout the washing process. Also the production of ornamental natural stone slabs generates high amounts of fines as a by-product of sawing, polishing, etc.

Depending on the origin and the generation, two different options are possible for the application of the fine stone waste materials from rock production in cementitious mortars. The first option is based on the use of the generated filter cake, for instance as a re-dispersion of the remaining filter cake, in slurry form. This approach is suitable if the material is already generated or the generation of fine stone waste materials cannot be avoided (e.g. through cutting and polishing processes) The second option considers the direct use of the broken rock materials, hence including the fine fraction (< 125 m). In this case, the stone waste material will not be generated as the original product allows a direct use of the material in special types of concrete. This method involves a higher financial and environment-friendly aspect as an intermediate step in the production of broken rock aggregates is eliminated. Therefore, the direct use of this untreated product, its sand fraction here named Premix 0-4, is of major interest.

By characterizing this material and its properties (particle size distribution (PSD) and particle shape), Premix 0-4 can replace primary raw materials like limestone powder or clinker. The last results in a second benefit, as the clinker production requires a lot of energy and contributes to the emission of high quantities of greenhouse gases such as carbon dioxide. Also the production of limestone powders requires energy. Therefore, from an environmental and economical point of view, the use of these primary raw materials should be optimally deployed to meet the mechanical and durability requirements of cementitious mortars, and the application of the appropriate industrial by-products should be favored.

As discussed before, particle packing plays an important role in the mix design. Using the new mix design tool, mixes can be developed in which cement is partly replaced by the fines of the Premix 0-4 (see Figure 1).

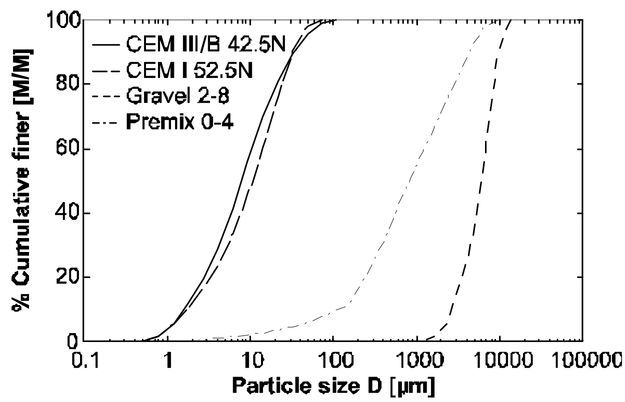

Figure 1: PSDs of aggregates and fines used (cumulative finer mass fraction).

Table 1: Composition of the tested mortars

Mix	CEM III/B 42.5 N	CEM I 52.5N	Premix 0-4	Granite 2-4	Water	SP [(a)]	w/c	w/p
	[kg/m³]	[kg/m³]	[kg/m³]	[kg/m³]	[kg/m³]	[kg/m³]		
Premix C402	262.8	139.5	1462.3	178.9	173.0	2.00	0.43	0.33
Premix C363	254.3	109.0	1503.2	163.3	176.7	2.05	0.49	0.33
Premix C289	202.5	86.8	1649.7	133.0	157.9	1.86	0.55	0.33
Premix C252	176.4	75.6	1702.9	117.5	156.5	1.75	0.62	0.35
Premix C289	202.5	86.8	1649.7	133.0	157.9	1.86	0.55	0.33

(a) : SP: Superplasticizer

Four different mortar mixes have been selected based on the ideas of the new mix design concept. The designed mortars consist of premixed sand (Premix 0-4), containing both fine aggregate fraction and inert stone powder, in combination with varying cement contents. The cement content ranges from 252 to 402 kg consisting of a blend of 65% slag cement (CEM III/B 42.5 N LH/HS) and 35% Portland cement (CEM I 52.5 N). The cement reduction is compensated by increasing the amount of Premix 0-4 and granite as well. Owing to the high content of fines and low cement content in the mortar mixtures, the amount of water is maintained as low as possible in order to achieve w/c ratios around 0.50. This low w/c ratio requires the use of a plasticizer to allow a sufficient workability and compaction of the produced mortar samples under laboratory conditions. The detailed mortar composition is presented in Table 1.

The designed mortars are submitted to a compressive strength as well as a flexural strength. For testing the compressive strength, cubes of 50 × 50 × 50 mm have been produced and tested after 3, 7 and 28 days. The mean values of the compressive strength tests are depicted in Figure 2.

The compressive strength after 28 days of the samples having a cement content of 402 kg and 363 kg is not influenced by the cement content of the designed mix. Here, the mortar having a cement content of 363 kg achieves the same compressive strength after 28 days as the mix containing 402 kg cement. The optimum cement content for obtaining the densest possible packing seems 340 kg in this case.

It appears that a reduction in the cement content is not influencing the compressive strength when the original cement content is already higher than actually needed. In this case the additional cement acts as a kind of filling instead of a binding material. A reduction of the cement content highly influences the compressive strength in case the cement content is already below the necessary amount needed for optimum packing. A further reduction in the cement content is influencing the packing fraction of the granular structure in a negative way.

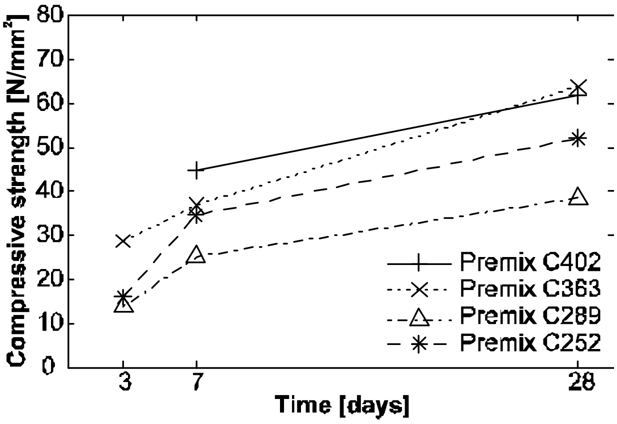

Figure 2: Development of the compressive strength for tested mortar samples.

Considering the mix proportioning as given in Table 1, the w/p ratio and the workability is constant for mixes having a cement content of 402, 363 and 289 kg. However, the w/p ratio was increased from 0.33 to 0.35 for the mix having a cement content of 252 kg. This slight increase in the water content improved the workability properties of the mortar and resulted in a denser granular structure of the hardened mortar. Therefore, the mix containing 252 kg cement achieved higher compressive strength values than the mix using 289 kg cement. The present results show clearly that cement can be used in a more efficient way when the packing of the granular materials is optimized.

The development of the flexural strength of the mortar samples was determined after 3, 7 and 28 days on prisms 40 × 40 × 160 mm . The results are presented in Figure 3.

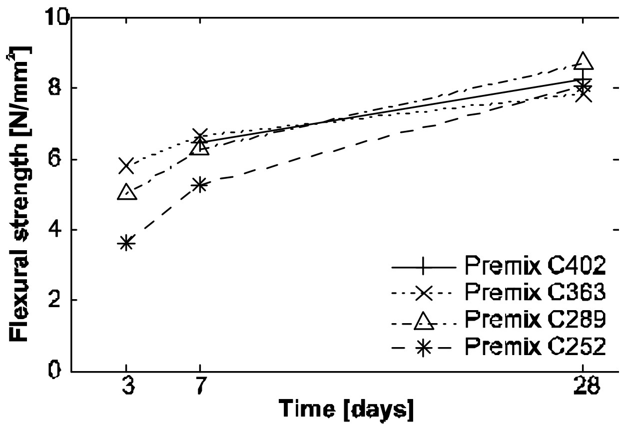

Figure 3: Development of the flexural strength for tested mortar samples.

Significant variations in the development of the flexural strength with respect to the mortar composition are noticed up to 7 days. To describe the effect of cement reduction on the results of the flexural strength after 28 days is hardly possible due to the high standard deviation. All tested series using Premix 0-4 showed after 28 days flexural strength values in the range between 7.9 and 8.1 N/mm^2.

3 Application of TiO_2 in cementitious mortar systems

3.1 Introduction

The application of photocatalytic active materials, such as titanium dioxide (TiO_2), in cementitious based construction materials allows the development of multi-functional building materials. The photocatalytic reaction at the material's surface provides the possibility to degrade inorganic and/or organic pollutants that are deposited on the surface. This allows for i) the degradation of air pollutants such as nitrogen oxides (NO_x) and ii) the prevention of surface soiling due to algae growth or other staining substances.
Another interesting application of photocatalytic active materials is related to their hydrophilic surface properties. Water droplets are not formed since the photo-induced super-hydrophilicity of the photocatalytic surface induces the formation of a uniform thin water layer. This thin water layer can easily flow under pollutants that adhere to the surface or can prevent the fogging of glasses. Due to the higher roughness of concrete surfaces compared to glass, the self-cleaning effect is of minor interest since a free flowing of the formed water layer is hampered. Therefore, the self-cleaning abilities of photocatalytic surfaces are mainly applied to glass and ceramic due to their denser surface texture.

3.2 General aspects

The photocatalytic effect of TiO_2 is known since the beginning of the 20th century. The fading of paint materials containing titanium white was reported by /2/ and /3/. However, the extensive research on photocatalytic materials was initiated many years later by the photoelectrochemical cell for water splitting developed by Fujishima and Honda /4/.
After the discovery of the so called Honda-Fujishima effect, a lot of research was conducted on photocatalytic reactions due to an increasing demand for artificial systems capable to convert solar energy to chemical or electrical energy. Later the research focused mainly on the treatment of waste water. The photocatalytic oxidation (PCO) gained considerable attention regarding the removal of air pollutants during the last years. Since the middle of the 1990s efforts have been made, first in Japan, in large scale applications of this photocatalytic property for air-purifying purposes and self-cleaning applications. The construction industry provides several products containing photocatalytic materials on commercial basis. These products are, for example, window glass and ceramic tiles providing self-cleaning features. The utilization of the self-cleaning abilities of modified blends of cement was

Figure 4: Church "Dio Padre Misericordioso", Rome, Italy (Source: Richard Meier & Partners, http://www.richardmeier.com).

used for the first time in 1998 for the construction of the church "Dio Padre Misericordioso" in Rome, designed by Richard Meier (see Figure 4).

The basic working principle of the PCO of TiO_2 is based on the optoelectronic properties of the crystalline form anatase. This crystalline form shows a band gap of 3.2 eV and a high oxidizing potential of the valence band that amounts to 3.1 eV (at pH = 0). The PCO is induced by the transfer of electrons from the valence band to the conduction band by photons in the UV-A range. The UV-A absorption creates electron holes that are responsible for the formation of radicals and charged species such as $OH^{\bullet}$, $O_2^{\bullet -}$, $HO_2^{\bullet}$.

The generation of hydroxyl radicals results from the presence of water at the surface of the photocatalyst. For this purpose, a certain amount of water molecules, supplied by the humidity of the atmosphere, and electromagnetic radiation are required to initiate the degradation process. The electromagnetic radiation *E* is expressed by the product of Planck's constant *h* and the frequency *f* /5/:

$$TiO_2 \xrightarrow{hf} TiO_2 + e^- + h^+ \quad (1)$$

$$H_2O \leftrightarrow OH^- + h^+ \quad (2)$$

$$OH^- + h^+ \rightarrow OH^{\bullet} \quad (3)$$

The formed hydroxyl radicals act as a strong oxidant for organic and inorganic compounds in further reactions. According to Herrmann /5/, the most reactive species are hydroxyl radicals after fluorine ones. Further reactions follow the heterogeneous photocatalysis and are characterized by the adsorption of the precursor and the desorption of the reaction products. A test setup including a suitable measuring procedure was developed allowing the evaluation of photocatalytic concrete products under equal test conditions (ISO standard ISO 22197-1:2007). The methodology is described in detail in /6/.

3.3 Air-purification of cementitious mortars containing TiO_2

Air quality in inner-city areas remains a major problem for the future. Promising solutions are given by the use of air-purifying concrete products since available filters to reduce the emission of NO_X are not effective. According to the literature (e.g. /7/ and /8/) the degradation of nitric oxide (NO), or more generally of nitrogen oxides (NO_X), also referred to as the DeNOx-process (denitrogenization), is as such necessary to purify the air in inner-city areas. This denitrogenization process can roughly be described as a two-stage reaction on the surface of the photocatalyst:

$$NO + OH^{\bullet} \rightarrow NO_2 + H^{+} \tag{4}$$

$$NO_2 + OH^{\bullet} \rightarrow NO_3^{-} \tag{5}$$

The formed nitrogen dioxide (NO_2) is a key precursor for the further reaction and is oxidized to nitrate ions (NO_3^-) that can either be bound by alkalis dissolved in the pore solution or will, most probably, be washed from the concrete surface as weak nitric acid.
A comparative study on selected concrete products of the European market was carried out in 2007 to show the efficiency of air-purifying concrete products under laboratory conditions /9/. This study was followed by the development of specific cementitious mortars containing TiO_2 dioxide. The composition of the mortars differed with respect to the amount and the type of TiO_2 powders and the addition of pigments. The properties of the tested TiO_2 are given in Table 2. The composition of the designed mortars is given in Table 3.

Table 2: Properties of the tested TiO_2.

	TiO_2 A	TiO_2 B	TiO_2 C	TiO_2 D	TiO_2 E‡
Specific density [g/cm^3]	3.9*	3.94	3.9	3.9*	3.9*
Characteristic particle sizes [m]					
$d_{0.1}$	0.65#	1.193	0.641#	0.593#	0.574#
$d_{0.5}$	1.245#	2.72	2.104#	2.014#	2.075#
$d_{0.9}$	2.487#	6.535	7.123#	4.349#	4.92#
Surface area (computed)					
Specific surface [cm^2/g]	15 847#	7 916	11 910#	13 139#	13 113#
Specific surface [m^2/cm^3]	6 181#	3 115	4 645#	5 195#	5 114#

‡ carbon-doped TiO_2
* taken from data sheet
# based on measured agglomerates

Table 3: Mortar composition.

	Reference mortar		3% TiO_2	5% TiO_2	10% TiO_2
	dm³/m³	**kg/m³**	**kg/m³**	**kg/m³**	**kg/m³**
CEM I 52.5N	195.8	600.0	600.0	600.0	600.0
Sand 0-2	490.6	1 300.0	1 300.0	1 300.0	1 300.0
TiO_2	-	-	18.0	30.0	60.0
Water	250.0	250.0	250.0	250.0	250.0

Slabs of 100 x 200 x 20 mm were produced and tested with respect to their degradation properties according to the procedure described in /9/.
In Figure 5 the results obtained for different types of TiO_2 are shown. The experimental data show a clear dependence of the fineness of the powder on the degradation properties (see Figure 5 and Table 2).

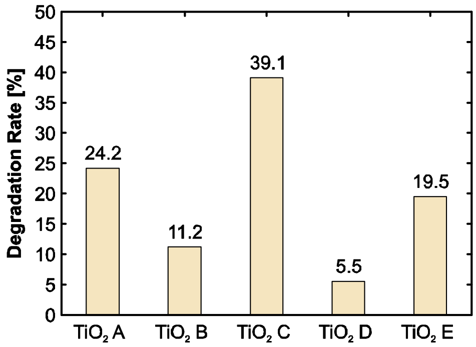

Figure 5: Degradation rate of tested TiO_2-powders.

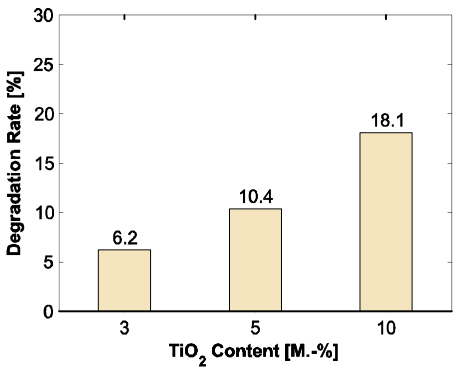

Figure 6: Influence of the TiO_2 content on the degradation rate.

This is in accordance to the expectations based on the higher specific surface area of e. g. TiO_2 C, which is about 30% higher than the surface area of TiO_2 B. Furthermore, the effectiveness of the degradation of NOx could be increased for the doped TiO_2 E as this modified powder uses UV-A radiation as well as bigger parts of the visible light.

In Figure 6 the degradation rate of TiO_2 B for varying powder contents is shown. The test results show clearly that the degradation rate increases for increasing powder content.

The influence of a red pigment on the degradation of NO_x is shown in Figure 7. The results shows that the degradation rate of the mix containing 3% TiO_2 is not influenced by the addition of pigments 1 (P1) or 2 (P2) for contents up to 2%. The values of the degradation rates are deviating in the same order of magnitude as expected for the scattering of the measuring data. Higher contents of TiO_2 (5% and 10%) associated with higher pigment contents (5% P1) are not reducing the degradation rates verifiably and the obtained degradation values are increasing, as expected from Figure 6, with increasing TiO_2 content. Solely the workability of the fresh mortar was reduced significantly as the content of fine particles (TiO2 and red pigment) increased.

3.4 Prevention of soiling processes by means of TiO_2

The staining of building materials due to black soot precipitation and by the growth of green algae poses a problem in case of conditioning in a shady and permanently humid environment. This biological staining is typical for roof tiles and façades facing north especially in a rural environment. Paved areas without direct sunlight are also affected by this phenomenon.

Besides the oxidative degradation of a wide range of organic and inorganic compounds, biological species (bacteria, algae and molds) can also be decomposed by means of UV-A in the presence of TiO_2. The decomposition of green algae

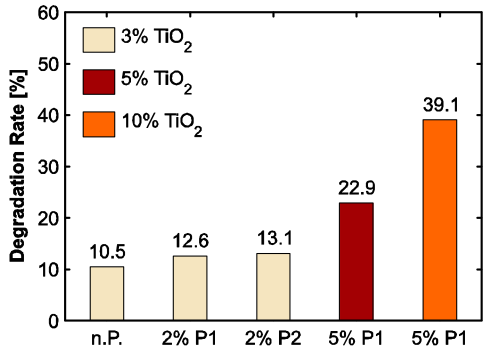

Figure 7: Influence of red pigments on the NO_x degradation rate: no pigment (n.P.); 2% pigment type 1 (2% P1); 2% pigment type 2 (2% P2); 5% pigment type 1 (5% P1).

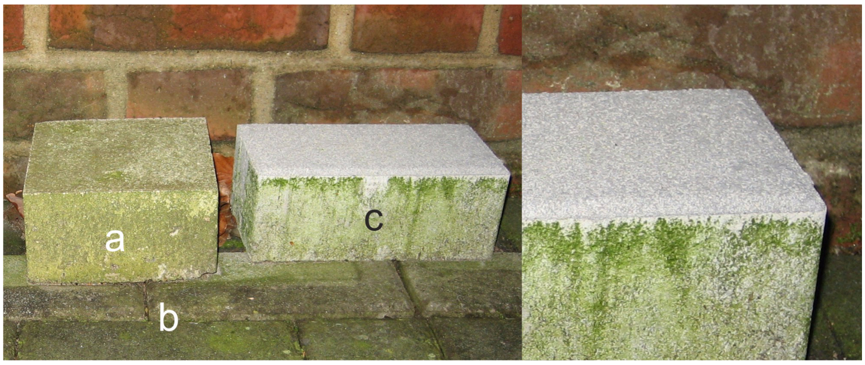

Figure 8: Staining of concrete paving blocks due to algae growth: untreated sample (a); paving of untreated paving blocks (b); paving block containing TiO2 in the functional top layer (c).

(Cladophora) was successfully shown on TiO_2 coated glass beads /10/. Therefore, the decomposing mechanism of TiO_2 in its anatase form is also expected for cementitious mortars. To investigate the inhibitive effect of TiO_2 on the growth of green algae, a concrete paving block with a cementitious mortar containing TiO_2 in its functional top-layer (sample c) and a blank sample (sample a) were placed in humid conditions and exposed to low direct sunlight where the staining of an already existing paving (sample b) by algae is a typical problem (see Figure 8). After a short period of time, the reference sample (sample a) of Figure 8 was covered with algae on its lateral side as well as on its top side. This process also occurred on the lateral side of the concrete paving block containing TiO_2, (sample c) but here only up to the level of the core mix which did not contain photocatalytic active TiO_2. The remaining lateral side of the functional top-layer as well as the top side of the paving block are not covered by any algae as here the photocatalytic material prevents soiling by algae. This exposition of concrete paving blocks at a location that is not suitable for the degradation of NO caused by high humidity and low natural light showed another potential of photocatalytic products regarding the prevention of undesirable staining due to algae growth.

4 Conclusions

This paper presents innovative developments in the field of cementitious mortars. These mortars are characterized by their multifunctional properties such as low cement contents and photocatalytic activity. Low cement contents are obtained by a denser granular structure of the designed mortars due to optimized particle packing. The lowered cement contents cause an economical and environmental benefit in comparison to classical systems.

Furthermore, the application of photocatalytic materials, such as titanium dioxide, gives the designed mortars multifunctional properties. Here, the degradation of air pollutants as well as the prevention of soiling is possible. The air-purifying abilities of these mortar systems are a valuable contribution to improve the inner-city climate. Moreover, the original appearance of buildings is preserved.

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