

Photocatalytic self-cleaning of fiber reinforced cement materials modified by neutral hydrosol coatings

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Abstract

Environmental pollution has an evidently adverse impact on the buildings that was constructed by the glass fiber reinforced cement (GRC) materials. In the presented work, the stable, neutral and N-doped hydrosols were prepared by using the $\text{Ti}(\text{O})_2$ as titanium source, as peptizing agent under the solvothermal condition. In the synthetic hydrosol, lots of nanopartilces with several diameters can be observed. The hydrosol can be coated on the GRC surface and exhibited high photocatalytic activity and stability in the degradation of Rhodamine B.

Keywords: Self-cleaning, Fiber reinforced cement materials, Photocatalytic,

INTRODUCTION

With the sustainable development of economy and society, the environment contaminate has become into a major public concern. Meanwhile, nano-photocatalytic technology has been becoming one of the more promising technologies to treat pollution control due to its high degradation efficiency, mild reaction condition, low energy consumption and less secondary pollution^[1, 2]. The glass fiber reinforced cement (GRC) is a very attractive material and widely applied for the building, but the building image was often suffering the increasing serous of damage, leading to a large cost on cleaning^[3, 4]. Therefore, the development of self-cleaning treatments technology could be very necessary.

The TiO_2 , as the most widely used photocatalytic materials, has been coated on the based materials to form the thin films and produce photo-induced self-cleaning effect by many preparation technologies^[5-7]. To date, many methods have been developed to due to prepare the photocatalytic materials. Among that, the liquid phase method like liquid phase deposition^[8] or sol-gel method^[9] gets more extensive research due to the advantages in cost and operability. The sol-gel method is simple and inexpensive, and enables the coating of large surfaces with good thermal and mechanical stabilities, which make it become the most natural way to prepare films. However, the sol-gel method is usually require a high temperature treatment ($>300\text{ }^\circ\text{C}$) to produce thin films with the defined crystallographic phase, which limits the possibility of achieving well-crystallized films, to supports with reasonable thermal stability of cement^[10]. Therefore, it is necessary to prepare nanocrystalline solution in advance for covering it into the GRC at room temperature. Meanwhile, the TiO_2 has a relative big band gap, about 3.2 eV, and only can absorb the ultraviolet light, which greatly limits its further application. Doping nitrogen into the lattice can make it absorb the visible light, and the main synthetic methods contain the In-stiu calcination mixtures of ammonia and TiO_2 , hydrothermal process and chemical vapor deposition, etc^[11-13].

In the present work, the neutral hydrosol and N-doped hydrosol with good stability were first synthesized by using the assisted precipitation-peptization processes following with

hydrothermal crystallization. Then the acrylic emulsion coating as the GRC waterproof layer was first coated on the GRC surface, after the neutral sol as inorganic insulation was coated on the GRC surface by the dip-coating method. The and N-doped hydrosol were finally coated on the top of GRC surface as photocatalytic layer. The self-cleaning discoloration kinetics on the GRC supported photocatalyst was evaluated during the photodegradation of Rhodamine B and tested during repeated cleaning cycles to demonstrate the stable photocatalytic nature of the coating.

MATERIAL AND METHODS

Materials.

All reagents used were of analytical grade purity without further treatment. SiO_2 sol (30 wt %) was provided from Hengsheng Reagent Co. Ltd. $\text{Ti}(\text{SO}_4)_2$, $\text{NH}_3 \cdot \text{H}_2\text{O}$, HNO_3 , NaOH were obtained from Shanghai Reagent Ltd. The GRC sample was prepared as follows:

Firstly, the fiber reinforced cement (GRC) decorative layer mortar was prepared by mixing the raw materials as according to the following formula: cement 25 kg, sand 35 kg, glass particles 13 kg, PVA fibers 1 kg, PP fibers 1 kg, pigments 5 kg, dispersible emulsion powder 6 kg, metakaolin 4 kg, and water 11 kg. Then this mortar was injected into the prepared mould as the decorative layers with 3 cm thickness. The fiber reinforced cement (GRC) structural layer mortar was prepared by mixing the raw materials according to the following formula: cement 25 kg, sand 46 kg, alkali-resistant glass fiber 3 kg, basalt fiber 2 kg, dispersible emulsion powder 6 kg, metakaolin 4 kg, and water 14 kg. And then this mortar was injected into the mould which is previously filled with the GRC decorative layers materials, slicked by using the scraper blade and finally compacted by the compression roller as the GRC structural layer. After the demoulding, the obtained GRC product was incised in to small samples with length 5 cm, width 3 cm and height 1cm.

Synthesis of the N-doped hydrosol by -assisted method and the formation film on the GRC surface

The hydrosol was prepared by followed process: Firstly, 100 mL 0.2 M $\text{Ti}(\text{SO}_4)_2$ aqueous solution was hydrolyzed by dilute solution, adjusting the pH value to 7.0. The resulting slurry was filtered and washed until the electric conductivity of the filtrate was below 100 $\mu\text{s}/\text{cm}$. Secondly, 20 mL (40 wt %) was added to the washed cake to adjust the pH value of the slurry to 7. Finally the orange transparent peroxy titanate acid (PTA) sol was obtained. 0.05g melamine () was dripped into the PTA sol as nitrogen sources to get the intermediate suspension. After that, the PTA sol with and without melamine were hydrothermally treated at 110 for 6 h in an autoclave with the internal volume of 100 mL. Finally, the and N-doped photocatalytic hydrosols were prepared successfully.

Before the film on the GRC surface was formed by dipping method, the organic protective layer (acrylic emulsion coating) and inorganic insulation layer (neutral sol) was coated on the GRC surface by dipping method and dried for 24 h in air. The acrylic emulsion can form the film on the GRC surface and prohibit the water molecules into the GRC materials. Then the GRC sample into the hydrosol and lifting once at a rate of 1500 $\mu\text{m}/\text{s}$, and then dried at the room temperature.

Photocatalytic self-cleaning test

The self-cleaning properties were characterized by the ultraviolet (UV, 300 W Hg lamp) or visible light (300 W Xe lamp) irradiation. In a typical experiment a drop of Rhodamine B was dispersed on the hydrosol coated GRC samples. The discoloration was followed quantitative as a function of time. The durability of coatings on GRC was evaluated by comparing the decomposition activity of the-coated GRC to Rhodamine B, before and after 10 launderings.

RESULTS AND CONCLUSIONS

The structure of and N-doped hydrosol

Figure 1(a) shows the photos of the prepared and N-doped hydrosol. Freshly prepared hydrosol was white and N-doped was yellowish. These hydrosols were stable without any precipitation for more than one month. The crystal phases of and N-doped hydrosol were studied by XRD. Figure 1(b) shows the XRD patterns of pure and N-doped powders. It can be seen that the hydrosol samples exhibit the anatase phase with peaks at about 22.7°, 37.8°, and 48.1° and no traces of rutile or brookite were observed, indicating that single phase anatase nanocrystals are formed. After doping the nitrogen into , the peak position has no obvious change, only the intensity was weakened, which may be caused by the slight distortion of network caused by nitrogen doping.

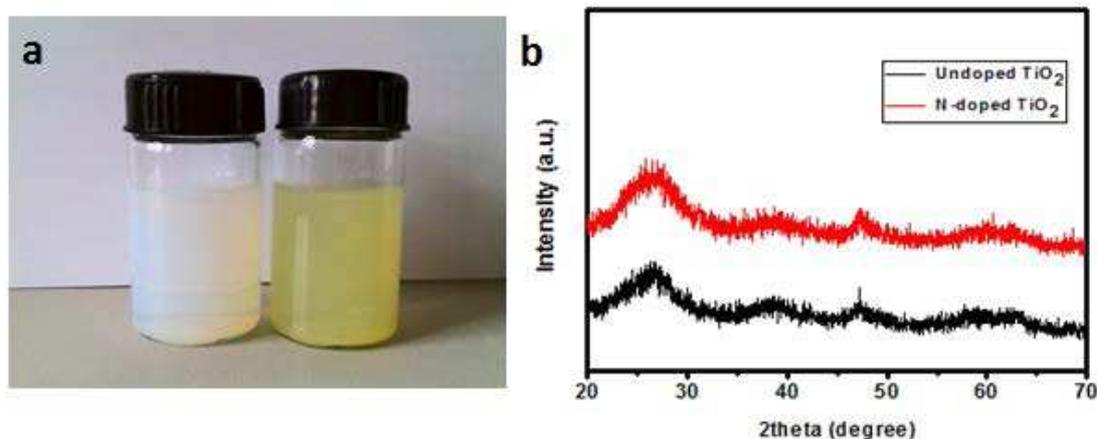


Figure 1. (a) the photograph and (b) the XRD patterns of the synthetic acidic sol (left) and / hydrosol (right)

Figure 2(a) shows the HRTEM images of sol. nanoparticles were well dispersed with narrow size distribution and had a diameter about several nanometers. Figure 2(b) shows the selected area electron diffraction (SAED). Measurements of lattice spacing from the corresponding SAED pattern show the anatase . The HRTEM of hydrosol was shown in the Figure 2(c), the interplanar spacing was 0.34 nm, which was corresponding to the (101) diffraction of anatase . However, Figure 2(d) shown that the N-doped has a cross-linked two dimensional film structure.

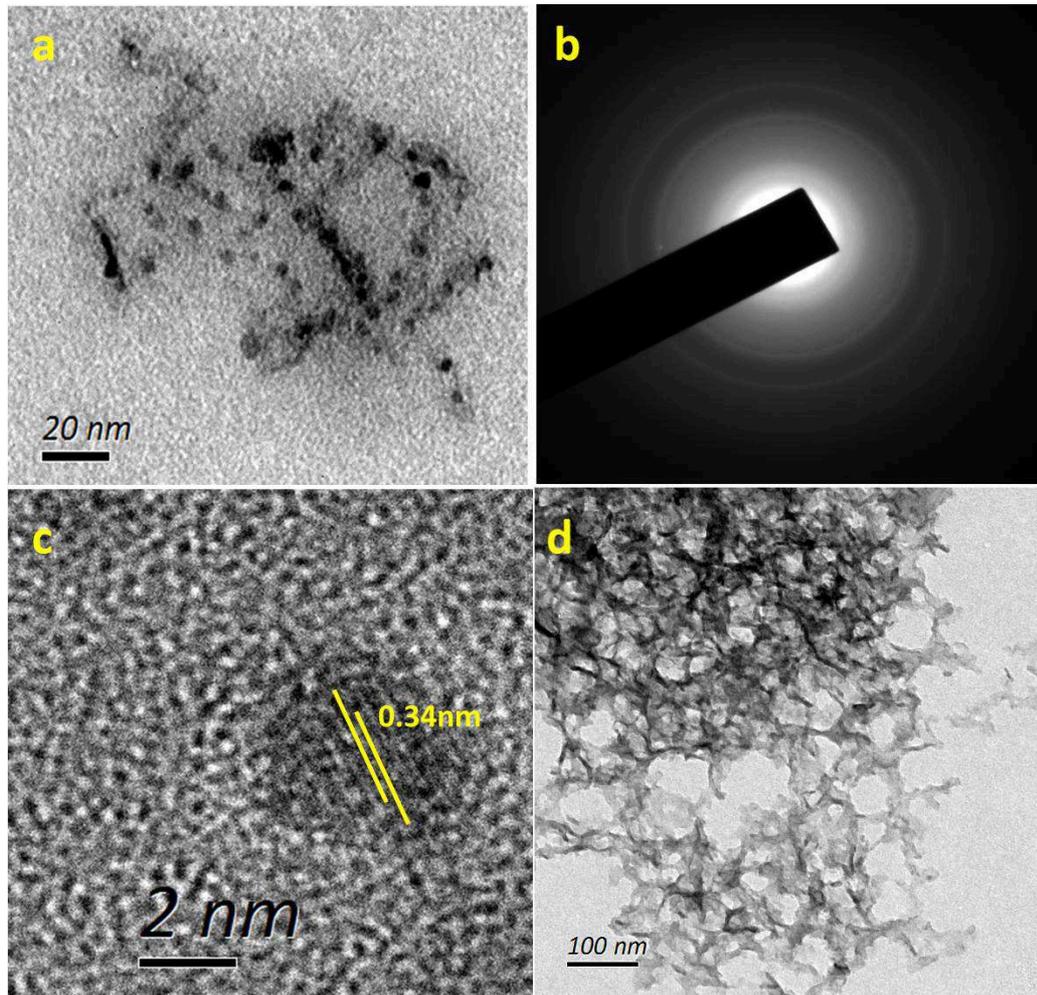


Figure 2. The TEM (a), SAED (b) and HRTEM (c) of hydrosol and TEM (d) of N-doped hydrosol.

Since the cement as porous materials was easy to absorb water, the organic protective layer which plays a part in waterproof layer and inorganic isolate layer which is to avoid the photocatalytic oxidation of organic protective layer by the photocatalytic layers were covered on the GRC surface in advance. To further prove the / hydrosol has been covered on the GRC surface by the dip-coating method. The UV transmissions spectrum of pure GRC and GRC coated by photocatalytic hydrosol was completely implemented. As shown in Figure 3, in the UV spectral region (250-500 nm), UV transmissions of -coated GRC were relatively much lower than that of the pure GRC, especially the absorption band from the 370 nm, suggesting the stronger UV-absorption. From the UV-absorption results, it is certain that coatings on the GRC and expected to have good photocatalytic activity. Moreover, the GRC coated by the N-doped hydrosol show the absorption band from 450 nm, suggesting the visible light absorption for N-doped hydrosol.

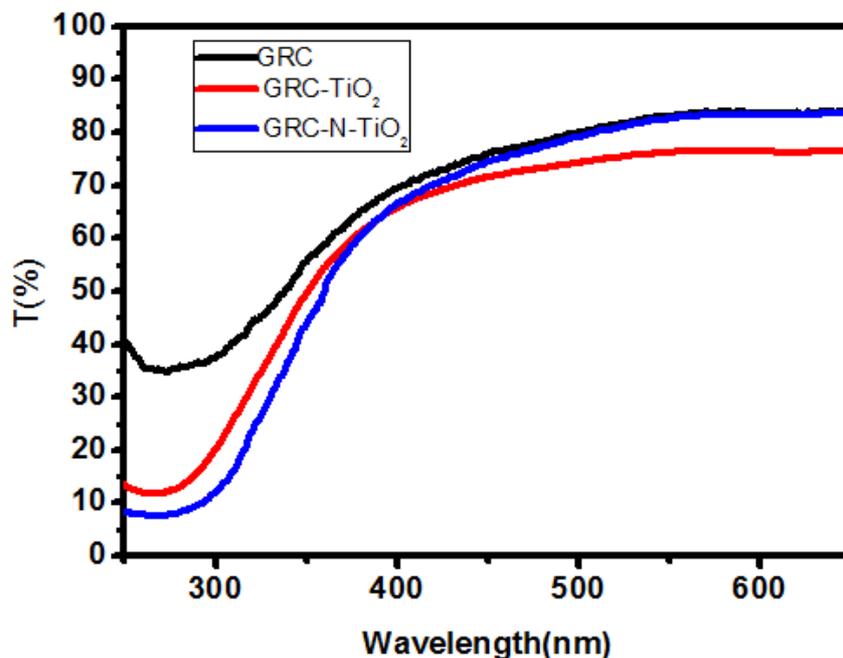


Figure 3. The UV transmissions spectrum of pure GRC, coated GRC and N-doped coated GRC

The self-cleaning performance on the and N-doped coated GRC materials

We have further investigated the self-cleaning properties of the products on the GRC tested by carrying out a photodegradation test of stains previously deposited on the GRC surface. Rhodamine B was used as the staining agent, and the top of GRC sample has no any treatment, but the bottom of GRC which was previously loaded by acrylic emulsion and sol was coated hydrosol. Figure 4 shows the photocatalytic performance of -coated GRC and uncoated GRC before and after 10 launderings.

It can be seen from the Figure 4 (a), (b) and (c) that the colorant concentration of Rhodamine B under UV irradiation was reduced individually by -coated GRC (right) before laundering with the increase of irradiation time, which suggests that / has the colorant decomposition activity. Generally, when the photocatalyst is subject to irradiation with UV light, the photon energy generates electron-hole pairs on the surface. The generated electron-hole pairs can induce the formation of reactive oxygen species, such as $\text{OH}\cdot$ and $\cdot\text{O}_2$. The reactive oxygen species generated on the surface of photocatalyst decomposed the colorant under UV irradiation by participating in a series of oxidation reactions resulting in carbon dioxide. However, the colorant concentration in contact with pure GRC substrates (left) without coatings remained almost at the same level during UV irradiation (Figure 4), which means that this type of cotton substrates has no colorant decomposition ability and the dye itself would not be decomposed by UV radiation.

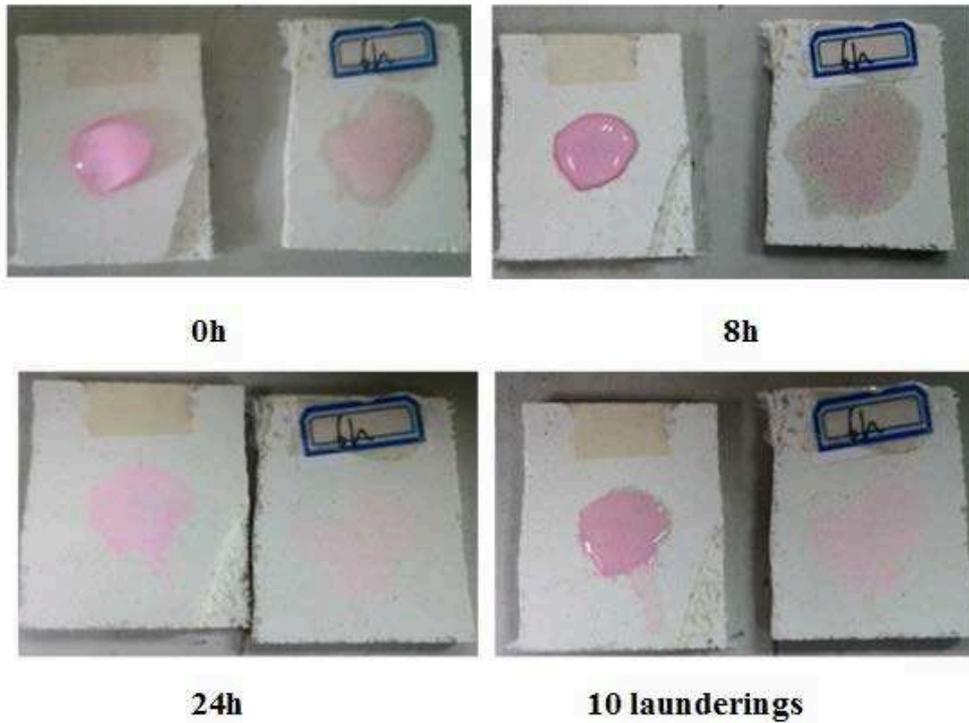


Figure 4 The Rhodamine B decomposition test. The images shown the exposed side of pure GRC (left) and coated GRC (right) before laundering subjected to 0 h, 8 and 24 h of light irradiation, and the / coated GRC after 10, 20 launderings subjected to 24 h of UV light irradiation

The durability of coatings on GRC was investigated by comparing the Rhodamine B decomposition activities of -coated GRC before and after 10 launderings, as shown in Figure 4 (d). Although the rates of colorant decomposition of -coated GRC samples were decreased after 10 launderings (Figure 4d) compared to that before laundering, they still possess some significant photocatalytic power compared to that of pure GRC, which suggests that the durability might be maintained or is very slowly reduced after 10 launderings. Figure 5 shown the photocatalytic degradation Rhodamine B performance of pure GRC (left) and GRC coated N-doped TiO₂ hydrosol (right) under visible-light irradiation.

It can be seen that the Rhodamine B on the GRC coated N-doped hydrosol was decomposed after illuminating for 24 h, but it still remains on the pure GRC surface. Moreover, the GRC coated hydrosol still possesses some photocatalytic ability after 10 launderings, which suggests that the durability might be maintained.

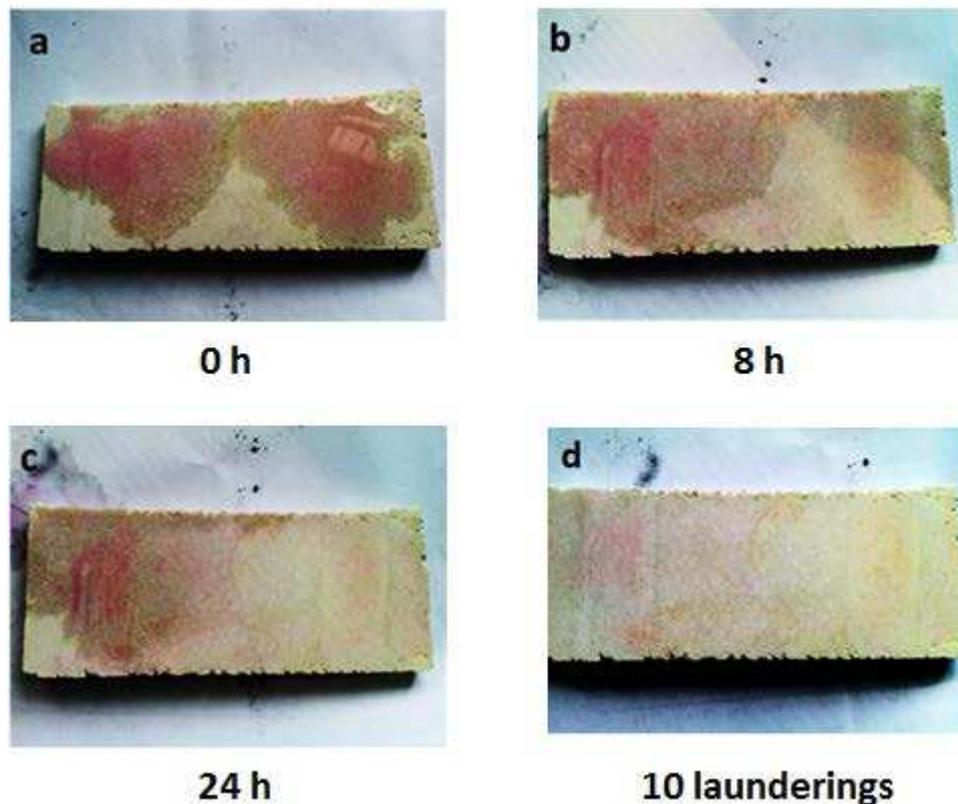


Figure 5 The photocatalytic degradation Rhodamine B performance of pure GRC (left) and GRC coated hydrosol (right) before laundering subjected to 0 h, 8 and 24 h of light irradiation and the coated GRC after 10 launderings subjected to 24 h of visible light irradiation

CONCLUSION

The and N-doped hydrosol were prepared by a simple liquid process, which shown good stability and dispersity. The and N-doped hydrosol on the GRC surface show significant photocatalytic self-cleaning performance as demonstrated by the degradation of the Rhodamine B under the UV and visible light irradiation, respectively. This photocatalytic self-cleaning ability still remains after 10 launderings. The method of preparing neutral hydrosol in this study not only eliminates the need for high temperature conditions, but also extends their applications to poor acid-resistant cement-based materials.

ACKNOWLEDGMENTS

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REFERENCES

- [1] LINSEBIGLER A L, LU G, YATES JR J T. Photocatalysis on surfaces: principles, mechanisms, and selected results [J]. Chemical Reviews, 1995, 95(3): 735-58.
- [2] LEGRINI O, OLIVEROS E, BRAUN A. Photochemical processes for water treatment [J]. Chemical Reviews, 1993, 93(2): 671-98.
- [3] FERREIRA J, BRANCO F. Structural application of GRC in telecommunication towers [J]. Construction and Building Materials, 2007, 21(1): 19-28.
- [4] ENFEDAQUE A, PARADELA L S, S NCHEZ-G LVEZ V. An alternative methodology to predict aging effects on the mechanical properties of glass fiber reinforced cements (GRC) [J]. Construction and Building Materials, 2012, 27(1): 425-31.
- [5] YU J, ZHAO X, ZHAO Q, et al. Preparation and characterization of super-hydrophilic porous coating films [J]. Materials Chemistry and Physics, 2001, 68(1): 253-9.
- [6] NAKAJIMA A, HASHIMOTO K, WATANABE T, et al. Transparent superhydrophobic thin films with self-cleaning properties [J]. Langmuir, 2000, 16(17): 7044-7.
- [7] YURANOVA T, SARRIA V, JARDIM W, et al. Photocatalytic discoloration of organic compounds on outdoor building cement panels modified by photoactive coatings [J]. Journal of Photochemistry and Photobiology A: Chemistry, 2007, 188(2): 334-41.
- [8] YU J-G, YU H-G, CHENG B, et al. The effect of calcination temperature on the surface microstructure and photocatalytic activity of thin films prepared by liquid phase deposition [J]. The Journal of Physical Chemistry B, 2003, 107(50): 13871-9.
- [9] DJAOUED Y, BADILESCU S, ASHRIT P, et al. Low temperature sol-gel preparation of nanocrystalline thin films [J]. Journal of sol-gel science and technology, 2002, 24(3): 247-54.
- [10] LANGLET M, KIM A, AUDIER M, et al. Transparent photocatalytic films deposited on polymer substrates from sol-gel processed titania sols [J]. Thin Solid Films, 2003, 429(1): 13-21.
- [11] ASAH I R, MORIKAWA T, OHWAKI T, et al. Visible-light photocatalysis in nitrogen-doped titanium oxides [J]. Science, 2001, 293(5528): 269-71.
- [12] GHICOV A, MACAK J M, TSUCHIYA H, et al. Ion implantation and annealing for an efficient N-doping of nanotubes [J]. Nano Letters, 2006, 6(5): 1080-2.
- [13] SATO S, NAKAMURA R, ABE S. Visible-light sensitization of photocatalysts by wet-method N doping [J]. Applied Catalysis a-General, 2005, 284(1-2): 131-7.

Heat insulated fabrication GRC panel

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Abstract

This study is about Desostone facade exterior cladding GFRC panel. This panel gives opportunity to obtain light weight cast concrete panel and heat insulation layer at the same time with the same color and texture variety of GFRC. First of all, the scope of the invention has explained and physical and also heat insulation properties installation process and finished project with the product are included to the study.

INTRODUCTION

For all kind of building facade claddings for aesthetic purpose and heat insulation is a very import need. For obtaining regular temperature inside the building the heat conductivity can only be obtained with heat, sound design and also correct heat insulation sound isolation materials.

DESOSTONE is designed to change these disadvantages to an advantage. Desostone is a lightweight heat insulated GRC panel, cladding including both insulation and decorative layers. It can be used in every kind of projects such as shopping malls, schools, hospitals, office buildings and residences. Because of having a lightweight structure, it also provides statically advantage to the construction. This is the main purpose for the design process of the product. The installation process provides a fast and practical way for the exterior facade cladding. Two layers (heat insulation, decorative cladding) has been obtained with one installation process.

Desostone is obtained with 8 -10 mm GFRC shell 50 mm rock wool, aluminium frame and aluminium anchorages and it is installed with aluminum fixing units mechanically.

SCOPE

After the heat insulation layer cladding, the decorative cladding comes as a second layer on facade and increases the thickness of the facade claddings total thickness. The decorative cladding also increases the facade load and the building gains extra static loads by this way. Cladding the heat insulation layer and the decorative cladding layer separately increases the initial costs and time plan for the facade. By this way desostone is designed:

- a. To create a facade covering both supplies heat, sound and humidity insulation and used for decorative purpose.
- b. To create a façade covering that gives opportunity to insulate decorative look and also water sound and vapor insulation.
- c. To decrease the facade covering system thickness between the wall and the facade shell.
- d. To prevent the internal usage of the steel construction in facade coverings.
- e. To prevent usage of vertical steel tubes on facade on application process.
- f. To decrease the static loads coming from extra steel structure.
- g. To prevent extra workmanship costs for heat insulation.

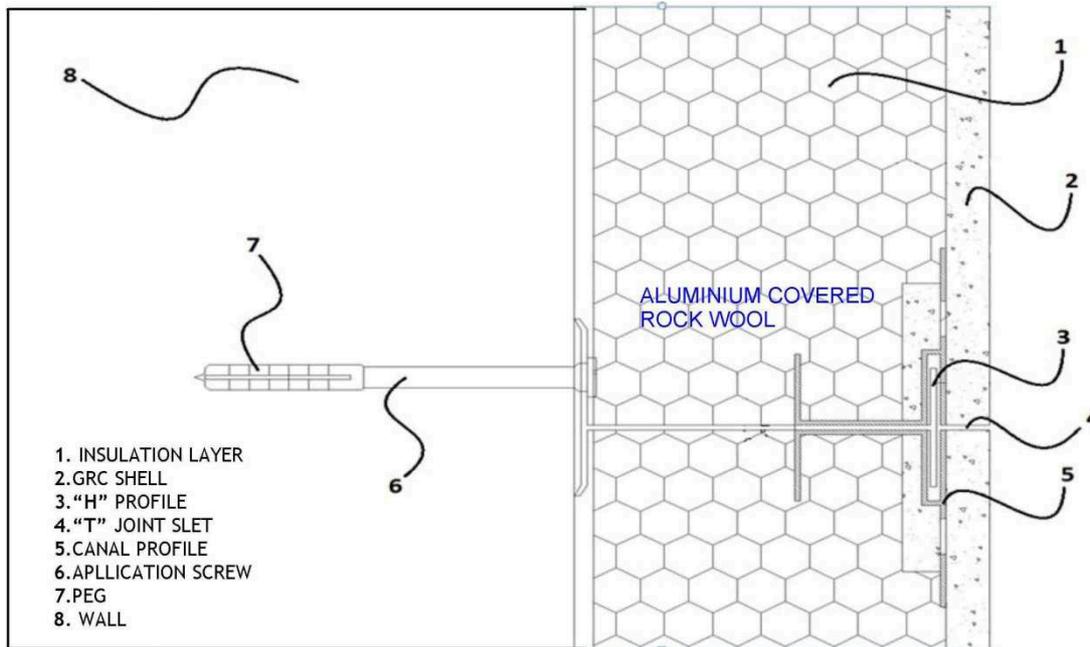


Figure1. Panel section

PHYSICAL PROPERTIES

Test	GRC - GFRC
Compressive Strength	f_c : 30-55 N/mm ²
Tensile Strength	f_{ct} : 4-10 N/mm ²
Modulus of Rupture	LOP: 7-9 N/mm ²
Flexural Strength	MOR: 10-20 N/mm ²
Expansion Limit	eu: 0,5-4 %
Modulus of Elasticity	E: 10-13 kN/mm ²
Density	1,8 - 2 kg/dm ³
Expansion	T: 1.0 - 15 X 10 ⁻⁵
Heat Conductivity	0,8 - 1,2 W/mk
Fire Resistance	(DIN 4102) A1
Shrinkage Value	ϵ_{cs} : 1.0 – 2.0mm/m
Water Absorption	3-15 %
Vapor Diffusion	μ : 50 – 200

CHARACTERISTIC PROPERTIES

Fire Standard	A1
Horizontal Surface	$\pm 1 - 1.5$ mm
Vertical Surface	± 1.5 mm
Thickness	10mm ± 1 mm
Length	20-120mm ± 1 mm