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Citation: Nuño, Manuel, Pesce, Giovanni, Bowen, Chris, Xenophontos, Panayiotis and Ball, Richard (2015) Environmental performance of nano-structured Ca(OH)₂/TiO₂ photocatalytic coatings for buildings. Building and Environment, 92. pp. 734-742. ISSN 0360-1323

Published by: Elsevier

URL: <http://dx.doi.org/10.1016/j.buildenv.2015.05.028>
<<http://dx.doi.org/10.1016/j.buildenv.2015.05.028>>

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Environmental performance of nano-structured $\text{Ca}(\text{OH})_2/\text{TiO}_2$ photocatalytic coatings for buildings



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ARTICLE INFO

Article history:

Received 17 March 2015

Received in revised form

5 May 2015

Accepted 18 May 2015

Available online 27 May 2015

Keywords:

Stone decay

Photocatalysis

Pollutant

Sulphur dioxide

Nitrogen dioxide

Calcium hydroxide

Limestone

ABSTRACT

This paper describes the environmental performance of a mixed phase coating (photocatalytic nanolime) manufactured from a colloidal nano-structured calcium hydroxide in alcohol (nanolime) combined with titanium dioxide. While nanolime is used as a consolidant in the field of cultural heritage and titanium dioxide is used as a photocatalytic material for self-cleaning coatings and environmental pollution control within the construction industry both materials are often used separately. We report in this paper an approach to combine both materials for the development of a photocatalytic nanolime coating. The photocatalytic effect of titanium dioxide on the carbonation of nanolime and its influence on the degradation processes in polluted environments is assessed. A suspension of 25 g/l of nanolime in ethanol and 7.4% wt/vol titanium dioxide was applied to specimens of Bath stone. For comparison, additional specimens were treated only with the nanolime. The specimens were exposed to oxides of nitrogen and sulphur under 30% relative humidity (RH) for 120 h. Exposure was carried out under both, UV and daylight. After exposure, the effect of titanium dioxide on the carbonation of nanolime and on the degradation processes was investigated using scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDS) and X-ray photo electron spectroscopy (XPS). Results were evaluated considering the dissolution processes of the two oxides in water and modelled using PHREEQC. Nanolime and the photocatalytic nanolime coatings were shown to promote the reaction of SO_2 . Results from the photocatalytic nanolime formulation suggest they could be used to reduce atmospheric pollutant levels through creation of a sacrificial layer. Such coatings have the potential to prevent further damage to limestone façades and could be applied in cities where pollution is detrimental to historic buildings.

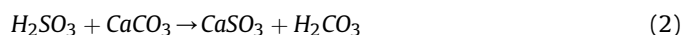
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1. Introduction

Since the industrial revolution, concentrations of the acid forming pollutants sulphur dioxide (SO_2) and nitrogen oxides (NO_x) have increased. This has resulted in the accelerated degradation of new and historic buildings in city centres and industrial areas. The introduction of more resistant materials and coatings to reduce these undesirable effects represent a challenge for the modern construction industry.

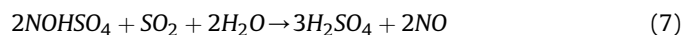
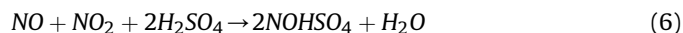
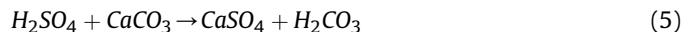
The processes of chemical decay of calcium carbonate (CaCO_3), which is one of the main constituents of limestone, has been the focus of numerous studies. The most aggressive chemical attack is

mainly attributed to the oxides of sulphur and nitrogen. When SO_2 dissolves in water sulphurous acid (H_2SO_3) is formed whereas dissolution of SO_3 in water generates sulphuric acid (H_2SO_4). Both acids are strong enough to dissolve CaCO_3 contained in the stones or renders that are used as outer skins of buildings. Equations (1)–(7) show the proposed mechanism for sulfonation and the role of NO_2 in the oxidation of SO_2 [1,2]:

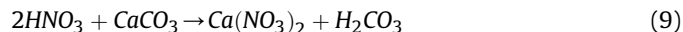


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Sulfonation, however, is not the only process that can lead to chemical degradation of $CaCO_3$. This, in fact, can also be degraded by the products formed by the dissolution of NO_2 in water, as shown in Equations (8) and (9) [3,4]:



1.1. Nanolime

In this work nanolime is examined as the calcium hydroxide based material. Nanolime is a colloidal suspension of nano-sized particles of calcium hydroxide ($Ca(OH)_2$) in an alcohol such as ethanol or isopropanol. It is commonly used as a consolidant in the field of cultural heritage [5]. The material acts as a binding agent of degraded surfaces because after application the $Ca(OH)_2$ reacts with the atmospheric carbon dioxide (CO_2) to produce $CaCO_3$. In contrast to building lime, which is formed by burning a source of calcium carbonate, nanolime is produced by precipitation. Nano-sized $Ca(OH)_2$ crystals are precipitated following mixing of super-saturated aqueous solutions of calcium chloride ($CaCl_2$) and sodium hydroxide ($NaOH$) under carefully controlled conditions. Following precipitation, water is substituted with alcohol to extend the long term stability of the nano-sized $Ca(OH)_2$ crystals [6]. Precipitated crystals are plate-like with hexagonal shape and an aspect ratio of approximately 10:1. The average particle size is 150 nm (IBZ-Freiberg n.d.) although crystals can range from tens to several hundred nanometres [7]. The product was developed at the beginning of the new millennium as a consolidant for frescos [8,9] and as de-acidification treatment for paper and canvas [10]. Later, however, its use extended to stone consolidation [6,11] and as a nano-coating. When mixed with other materials such as titanium dioxide (TiO_2) the nanolime acts as a binding agent.

1.2. Titanium dioxide and photocatalysis

Titanium dioxide is the natural oxide of Ti^{+IV} which is a semiconductor with three main crystallographic structures. Anatase is one of the polymorphs and is widely studied for its photocatalytic properties when exposed to UV radiation. Previous researchers have investigated the use of titanium dioxide and its photocatalytic reactions in a wide range of applications such as water treatment [12–14], air purification [15–19] self-cleaning surfaces [20–26] or for the development of new super hydrophilic surfaces [21].

Photocatalysis is a chemical phenomenon observed in certain compounds that are able to absorb UV photons which in turn promote the migration of electrons from the valence to the conduction band, creating a charge separation. This separation produces a reactive hole (h_{vb}^+) and electron (e_{cb}^-) that can migrate to the surface of the material. At the surface the holes and electrons are able to participate in a photocatalytic process by adsorbing and reacting with molecules such as H_2O and O_2 . This leads to the formation of free radicals as described by Equations (10)–(15) [27–30].



This paper investigates the effect of a TiO_2 on the carbonation and sulphation of nanolime in SO_2 and NO_2 rich environments to produce nano-structured $Ca(OH)_2/TiO_2$ photocatalytic coatings for buildings. Surfaces consisting of nano-particles of anatase mixed with nanolime were applied to specimens of Bath stone: a porous building limestone that has been used for centuries in the South West of the United Kingdom.

2. Experimental method

All specimens used in this test were cut from a single piece of newly quarried Bath stone extracted from the Combe Down mines in Bath and North East Somerset, UK. The stone was cut into test specimens $5 \times 10 \times 10$ mm where all surfaces were freshly cut (un-weathered). Each piece was individually cleaned with acetone and distilled water to remove impurities prior to being dried in an oven at $60^\circ C$ for 12 h.

Three different specimens were used in each test: 1) a control specimen made of uncoated sound stone; 2) a specimen coated with nanolime and 3) a specimen coated with a mixture of nanolime and TiO_2 .

Nanolime suspension was supplied by IBZ-Salzchemie GmbH & Co. KG (Germany) under the trade name $CaLoSil^{\text{®}}$. A product with a concentration of 25 g/l in ethanol was used in all cases. Anatase in the form of $Aeroxide^{\text{®}}$ P25 was supplied by Sigma Aldrich ($\geq 99.5\%$ trace metals basis, average particle size 21 nm, surface area from $35 \text{ m}^2/\text{g}$ to $65 \text{ m}^2/\text{g}$). In order to obtain a stable colloidal suspension, 7.4% wt/vol anatase was dispersed in $CaLoSil^{\text{®}}$ just before the application and then sonicated for approximately 20 s.

The coating was applied by immersing the specimens in the suspensions for approximately 10 s. This allowed five sides of each specimen (main face of 10×10 mm and four sides of 5×10 mm) to be evenly covered. After immersion, the specimens remained in air at room temperature for several seconds to allow evaporation of the ethanol before being placed in the reactor at $25^\circ C$.

Photocatalytic activity was evaluated for the specimens exposed to SO_2 under both UV and daylight radiation. UV radiation was obtained from a 4x4 array of 16 individual GaN UV-LEDs with a wavelength range of 376–387 nm and total intensity of $8 \text{ W}/\text{m}^2$. All other specimens were only exposed to daylight simulating external environmental conditions. The power of the light in the UVA range was $3 \text{ mW}/\text{m}^2$.

All specimens were exposed for 120 h to atmospheres produced with: 1) artificial air containing 7 ppm SO_2 ; 2) artificial air containing 7 ppm NO_2 ; 3) artificial air containing 3.5 ppm SO_2 and 3.5 ppm NO_2 . The concentration of pollutants was set to 7 ppm in all the experiments since previous research showed optimum results after exposing to 5–10 ppm pollutants [2,31], and the RH remained constant at 7 ppm exposure and 30% respectively. Table 1 shows details of the experimental conditions.

The cylindrical 3 mm thick soda glass reactor with a diameter of 78 mm used in the tests is shown in Fig. 1. The reactor contained two gas inlets, a gas outlet and a lid to facilitate introduction and

Table 1
Experimental conditions showing the gas flow and the RH of each experiment. Pollutant concentrations (in ppm) are calculated considering the initial concentration and the mixed volumes of gas. All the experiments were carried for five days, under the constant conditions.

Experiment number	Exposed pollutant	SO ₂ flow (ml/min)	NO ₂ flow (ml/min)	100% Humid air (ml/min)	Light irradiation
1	7 ppm SO ₂	22	–	10	Daylight cycles
2	7 ppm NO ₂	–	22	10	Daylight cycles
3	3.5 ppm SO ₂ and 3.5 ppm NO ₂	10	10	10	Daylight cycles
4	7 ppm SO ₂ under UV	22	–	10	Constant 8 W/m ²

removal of the specimens. The gas system that allowed production of specific atmospheres was designed in order to be able to introduce all three gases at the same time. The desired gas compositions for the experiments were produced by introducing the following gases into the cell: 1) zero air grade (composition: 0.5 ppm H₂, 2 ppm He, 1 ppm CH₄, <5 ppm H₂O, 5 ppm Ne, ~20.95% O₂, 9300 ppm Ar, 385 ppm CO₂, 0.8 ppm N₂O, N₂ balance); 2) zero air grade containing 10.7 ppm of NO₂; 3) zero air grade containing 10.4 ppm of SO₂ in the appropriate proportions. All gases were supplied by BOC Gases Ltd. Each gas cylinder was connected to a gas flow meter capable of measuring gas flows from 5 cm³/min to 100 cm³/min with an accuracy of ±0.5 ml/min (Platon Gap meter Type NGX supplied by Roxspur Measurement & Control Ltd). The gas from the zero air grade cylinders was humidified by passing it through a glass bubbler containing deaerated water before being passed into the cell. The other gas inlet of the cell was used to introduce the dry gas from the other two cylinders that were mixed using a three-way valve.

3. PHREEQC modelling

To evaluate the experimental results, dissolution of SO₂, NO₂ and CO₂ in water was modelled using PHREEQC [32]. The program is based on equilibrium chemistry of aqueous solutions interacting with several phases, including gases. PHREEQC is routinely used in

disciplines such as geochemistry, hydrology, environmental pollution, water treatment and the construction industry. PHREEQC has been used to simulate the ion–ion and the ion–solid interactions in the multi-ionic transport in concrete [33,34], chemical degradation of concrete [35–37], dissolution processes of calcium-silicate-hydrate [38,39], and phase and morphology evolution of CaCO₃ precipitated by carbonation of hydrated lime [40,41].

Simulations applied in this work were based on previously reported PHREEQC protocols [32]. Initial conditions consisted of 1 kg of pure water at 25 °C with pH = 7 (this was set to be as an adjustable parameter to achieve charge balance). The equilibrium phases included two species: gas and solid. CO₂, SO₂ and NO₂ were considered as gas with the respective concentrations calculated according to Table 1 and the log of *p*CO₂ (in bar) was set to simulate the different partial pressures. The number of moles considered was set to 100 to model the equilibrium with infinite reservoirs. Solid phases considered were modelled using an infinite number of moles and a saturation index (SI) of 0 so that these had to be in equilibrium with the solution at the end of the simulation. Simulations were performed with the thermodynamic data from the Lawrence Livermore National Laboratory database of Berkeley (the LLNL database built in PHREEQC). The PHREEQC input file used is shown in Algorithm 1.

4. Chemical and physical characterisation

Micro-morphologies of the Bath stone and coatings used in the tests were evaluated using a JEOL JSM64802V scanning electron microscope (SEM) with a working distance of 10 mm, an accelerating voltage of 15 kV and a spot size of 30 nm. Specimens were coated with a 20 nm thick layer of gold using an Edward Sputter S150B Coater to prevent surface charging. Energy Dispersive X-ray Spectroscopy (EDS) was performed on uncoated specimens using a working distance of 10 mm, accelerating Voltage of 25 kV and a spot size of 51 nm in high vacuum (25 MPa). Due to its penetration depth (1–2 μm), this technique was used to evaluate the degradation processes carried within the bulk of the coating.

The surface layers (within 1–10 nm) were characterized using X-ray Photoelectron Spectroscopy (XPS) using a Thermo Scientific Theta Probe with an AlK_α (1486 eV) X-ray source, operated at 100 W (Thermo Fisher Scientific Inc., Waltham, MA.) using a flood gun in an operating vacuum of 10^{−8} mbar. The adventitious hydrocarbon C1s peak at 284.8 eV was used to correct the spectra for specimen charging. The software CASAXPS 2.3.16 RP 1.6 (Casa Software Ltd., Teignmouth, Devon, UK) was used for the peak fitting. The atomic percentage of each element detected was calculated from the peak areas, assuming a Shirley background and fitted using a Gaussian/Lorentzian ratio and asymmetry factors to give the best fit to the peaks. All the fitted peaks were normalized excluding the area of the adventitious carbon peak.

Wide scan survey spectra were obtained between 0 and 1400 eV binding energy (BE) with pass energy of 200 eV and dwell time of 50 ms. In addition, scans of higher resolution were taken at different BE ranges with pass energy of 40 eV and dwell time of 100 ms for C1s, N1s, O1s, S2p, Ca2p and Ti2p regions.



Fig. 1. Image of the glass reactor. Reactor diameter 78 mm for scale.

5. Results

5.1. PHREEQC simulation

Table 2 reports the activity of CO_3^{2-} , SO_4^{2-} and NO_2^- ions in pure water (i.e. no solid phase was introduced as the initial condition) as calculated by PHREEQC using different gas mixes and the model shown in Algorithm 1 (the simulation number is equivalent to the experiment number in Table 1). The data show that in pure water, the activity of SO_4^{2-} ion is many orders of magnitude higher than the activity of NO_2^- and CO_3^{2-} ions in all conditions.

Table 3 shows the activity of CO_3^{2-} , SO_4^{2-} and NO_2^- ions when calcite is introduced as the main solid phase in contact with the solution. Calcite used in this model since it simulates the presence of CaCO_3 formed during the carbonation of nanolime. Results show that, as in pure water, the activity of the SO_4^{2-} ion is several order magnitudes higher than the activity of NO_2^- and CO_3^{2-} ions and that under these conditions Anhydrite (CaSO_4), Bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) can be formed as solid phases.

Table 4 shows the activity of CO_3^{2-} , SO_4^{2-} and NO_2^- ions when both, calcite and Portlandite are included in the simulation. Portlandite used in this model simulates the presence of uncarbonated nanolime particles during the tests. The results show that, as well as in pure water, and in presence of calcite, the activity of SO_4^{2-} ion is several orders of magnitude higher than the activity of NO_2^- and CO_3^{2-} ions. Furthermore, the results suggest that Anhydrite (CaSO_4), Bassanite ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) are the only solid phases that could be formed at the end of the test.

5.2. SEM imaging

Fig. 2 shows the surfaces of the control specimen (a), the specimen coated with nanolime (b) and the specimen coated with the nanolime-titania coating (c) after exposure to SO_2 . Fig. 2a shows the structure of Bath stone with a distributed set of clusters composed by Oolites that makes the stone's structure very porous. Bath stone was previously characterized by mercury intrusion porosimetry (MIP) using a Micrometrics AutoPore III [42]. The majority of the pores were around 10 and 0.1 μm in diameter, and the macro pores were over 100 μm and micropores (between Oolites) which are between 10 and 1 μm in diameter. Fig. 2b illustrates the even distribution of nanolime on the surface and within the surface pores of the stone, thereby covering the Oolites. Fig. 2c shows Bath stone covered with a photocatalytic mixed phase nanolime coating. The presence of TiO_2 in the photocatalytic nanolime coating is not visible in the SEM images due to their fine particle size. Fig. 2b and c shows a coating with a high surface area. By comparing the coated (Fig. 2b and c) and uncoated (Fig. 2a) stone images the macropores are not blocked allowing gas and liquid vapour to diffuse into and out of the stone.

5.3. Energy dispersive X-ray spectroscopy (EDS)

Following exposure to the conditions in Table 1, quantitative analysis of the specimens was carried out using EDS, the results of which are shown in Table 5. The data in the table is an average calculated from the results of five individual analyses, each carried out at a randomly selected representative location of the specimen surface.

EDS analysis did not detect the presence of nitrogen based molecules in the surface of specimens exposed to 7 ppm of NO_2 . Between 4.4 and 7.12 atomic % titanium was identified on the specimens coated with TiO_2 whereas no appreciable amount was detected on the other specimens. However in comparison to the specimen exposed to 7 ppm SO_2 , results indicated the presence of sulphur, with higher values in the specimens coated with nanolime and photocatalytic nanolime. Exposure to the 3.5 ppm NO_2 and 3.5 ppm SO_2 gas mixture showed a reduction in the amount of sulphur detected on the nanolime coated specimen (0.34 atomic %), compared with the 7 ppm SO_2 exposure, which was within the range of sulphur detected in the untreated specimens (0.37 and 0.56 atomic %). The photocatalytic nanolime coating showed 1.68 atomic % of sulphur which was comparable to the value of 1.77 atomic % obtained for the 7 ppm of SO_2 .

5.4. X-ray photoelectron spectroscopy (XPS) results

The nature of the surface layer of the specimens after five days exposure was evaluated using XPS analysis, a survey spectra is shown in Fig. 3. Binding energies and elemental ratios for carbon, nitrogen, oxygen, sulphur, calcium and titanium, calculated from higher resolution spectra in specific regions, are shown in Table 6.

The adventitious carbon contamination peak at 284.8 eV was identified on all the specimens examined and used to calibrate the spectra for surface charging, however an additional peak corresponding to CaCO_3 was also identified. The binding energy of this peak ranged between 288.6 and 289.2 eV which is in agreement with studies by Kang [43] and Demri [44] who report CaCO_3 binding energies of 288.6 and 289.2 eV. The binding energy for the Ca 2p peak ranged between 346.3 and 347.5 eV which is in accordance with previous studies by Ming [45] and Stipp [46] who reported CaCO_3 binding energies of 346.5 and 347.7 eV.

The specimens exposed to 7 ppm NO_2 diluted in air did not show the presence of sulphur, indicating that no significant amount of sulphur was present in the specimen stone before testing, and that any sulphur detected on the surface of the specimens exposed to SO_2 originated from a surface reaction. Peaks corresponding to N 1s were identified between binding energies of 399.1–400.6 eV, related to the presence of a carbon–nitrogen bond within an organic matrix [47]. In the spectral region corresponding to nitrate (N 1s 407.5 eV) [48] no signal was detected suggesting that $\text{Ca}(\text{NO}_3)_2$ was not formed.

Table 2
Activity of CO_3^{2-} , SO_4^{2-} and NO_2^- ions in pure water as calculated by the PHREEQC.

Simulation number	Gas phases	Ion activity as calculated by PHREEQC		
		CO_3^{2-}	SO_4^{2-}	NO_2^-
1	385 ppm CO_2 7 ppm SO_2	1.047×10^{-24}	4.089×10^{-3}	–
2	385 ppm CO_2 7 ppm NO_2	2.700×10^{-24}	–	2.160×10^{-14}
3	385 ppm CO_2 3.5 ppm SO_2 3.5 ppm NO_2	8.872×10^{-26}	6.028×10^{-3}	8.203×10^{-15}

Table 3
Activity of CO_3^{2-} , SO_4^{2-} and NO_2^- ions in pure water in equilibrium with calcite and solid phases formed at the end of the simulation.

Simulation set up			Ion activity			Solid phases formed
N.	Gas phases	Solid phases	CO_3^{2-}	SO_4^{2-}	NO_2^-	
1	CO_2 (385 ppm) SO_2 (7 ppm)	Calcite	8.031×10^{-9}	1.721×10^{-1}	–	CaSO_4 $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
2	CO_2 (385 ppm) NO_2 (7 ppm)	Calcite	1.808×10^{-8}	–	2.463×10^{-11}	–
3	CO_2 (385 ppm) SO_2 (3.5 ppm) NO_2 (3.5 ppm)	Calcite	9.270×10^{-9}	1.822×10^{-1}	1.594×10^{-11}	CaSO_4 $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Table 4
Activity of CO_3^{2-} , SO_4^{2-} and NO_2^- ions in pure water in equilibrium with calcite and portlandite, and solid phases that could be produced at the end of the tests.

Simulation set up			Ion activity			Solid phases formed
N.	Gas phases	Solid phases	CO_3^{2-}	SO_4^{2-}	NO_2^-	
1	CO_2 (385 ppm) SO_2 (7 ppm)	Calcite Portlandite	6.775×10^{-9}	7.822×10^{-2}	–	CaSO_4 $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
2	CO_2 (385 ppm) NO_2 (7 ppm)	Calcite Portlandite	1.968×10^{-8}	–	1.672×10^{-9}	–
3	CO_2 (385 ppm) SO_2 (7 ppm) NO_2 (7 ppm)	Calcite Portlandite	1.063×10^{-8}	1.451×10^{-1}	1.032×10^{-9}	CaSO_4 $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

Binding energies for Ti 2p_{3/2} peaks varied between 458.1 and 459.0 eV, and for O 1s the observed peaks are within the range of 528.8–529.5 eV. These results agreed with studies carried by Dementjev [49] and Bedri [50], which identified Ti 2p_{3/2} binding energies from 458.0 to 459.4 eV and for O 1s from 529.4 to 530.6 eV. These were attributed to the TiO₂ in the coatings.

The XPS spectra of specimens exposed to 3.5 ppm NO₂ and 3.5 ppm SO₂ also showed S 2p_{3/2} peaks at binding energies between 167.8 and 168.3 eV which corresponded to CaSO₃. Calculated atomic percentages of 0.5, 0.3 and 0.1 for the untreated, nanolime coating, and photocatalytic nanolimes were less than that observed on the specimens exposed to 7 ppm SO₂. These smaller concentrations may be attributed to the lower concentration of SO₂.

The XPS spectra from specimens exposed to 7 ppm SO₂ diluted in air at a relative humidity of 33% with daylight cycles all showed peaks corresponding to sulphur. The binding energies between 166.6 and 168.6 eV are in agreement with studies by Siriwardane and Hong [51,52], and characteristic of calcium sulphite (SO₃²⁻). Compositions of 1.0, 3.2 and 4.6 atomic % for the untreated (stone surface), nanolime coating, and photocatalytic nanolime indicated that the nanolime is more reactive when compared to the stone substrate. This may be attributed to the higher solubility of Ca(OH)₂ compared to CaCO₃ and the higher surface area of the nanolime compared to stone.

The XPS spectra from specimens exposed to 7 ppm SO₂ diluted in air at 33% RH under UV light also showed peaks corresponding to sulphur. The binding energies between 168.4 and 168.6 eV observed for the nanolime and untreated stone are in agreement with studies by Siriwardane and Hong [51,52], and characteristic of calcium sulphite (SO₃²⁻). The atomic percentages of 2.2 and 4.0 are slightly higher, but still comparable with the equivalent specimens exposed to daylight cycles.

The specimen containing photocatalytic nanolime exposed to UVA had a Ca 2p_{3/2} binding energy of 348.2 eV which was higher than values between 346.3 and 347.5 eV which was detected for all the other specimens. This is comparable to a Ca 2p_{3/2} binding energy of 348 eV observed by Siriwardane [51] for calcium sulphate. A higher binding energy for S 2p_{3/2} of 169.9 eV, compared to values ranging between 167.8 and 168.6 eV, is also in agreement with

previous research by Moulder et al. [47] who observed a binding energy of 169.4 eV for sulphate. The difference in behaviour of the photocatalytic nanolime under UV irradiation is illustrated in Fig. 4 which shows the spectra over the S 2p range for the nanolime coated specimen and photocatalytic nanolime. A shift of approximately 2 eV is observed between the S 2p peaks of nanolime coating and photocatalytic coating. On nanolime CaSO₃ was observed whereas for the photocatalytic coating CaSO₄ was generated.

6. Discussion

The combined results given by EDS and XPS reveal a difference in the elemental concentration between the bulk of the coating (1–2 μm) and the surface layer (maximum 10 nm). The concentration of CO₂ in the gas mixture was approximately 55 times higher than that of the NO₂ and SO₂, however the concentration of sulphur compounds detected on the surface was similar to that of the CaCO₃ detected. Simulations using PHREEQ suggest that, because of the very low activity of the NO₂ ion in aqueous solution only the solid phases produced by the interaction of SO₂ with the system should be detected at the end of the experiments.

For the experiment that exposed specimens to 7 ppm of NO₂, the exposure did not affect the composition within the bulk; it is possible that the gas concentration or the activity of nitrogen ions was too low to produce phases detectable by EDS. In addition, XPS showed a small amount of organic matrix in the outermost layer.

The formation of CaSO₄ on the surface of carbonate containing materials historically used in construction, such as limestone, is widely accepted. However previous research, under atmospheric conditions, by Chin [53] describes the formation of CaSO₄ as a two stage process involving the initial formation of CaSO₃ (IV) which is followed by further oxidation to sulphate (VI) [53]. The rate of these two reactions is dependent on the local water and oxygen concentrations.

Analysis of the S 2p_{3/2} binding energies obtained for the XPS spectra from the specimens indicated the presence of SO₃²⁻ in the form of calcium sulphite. This phase was identified on the uncoated limestone surface in addition to nanolime and photocatalytic

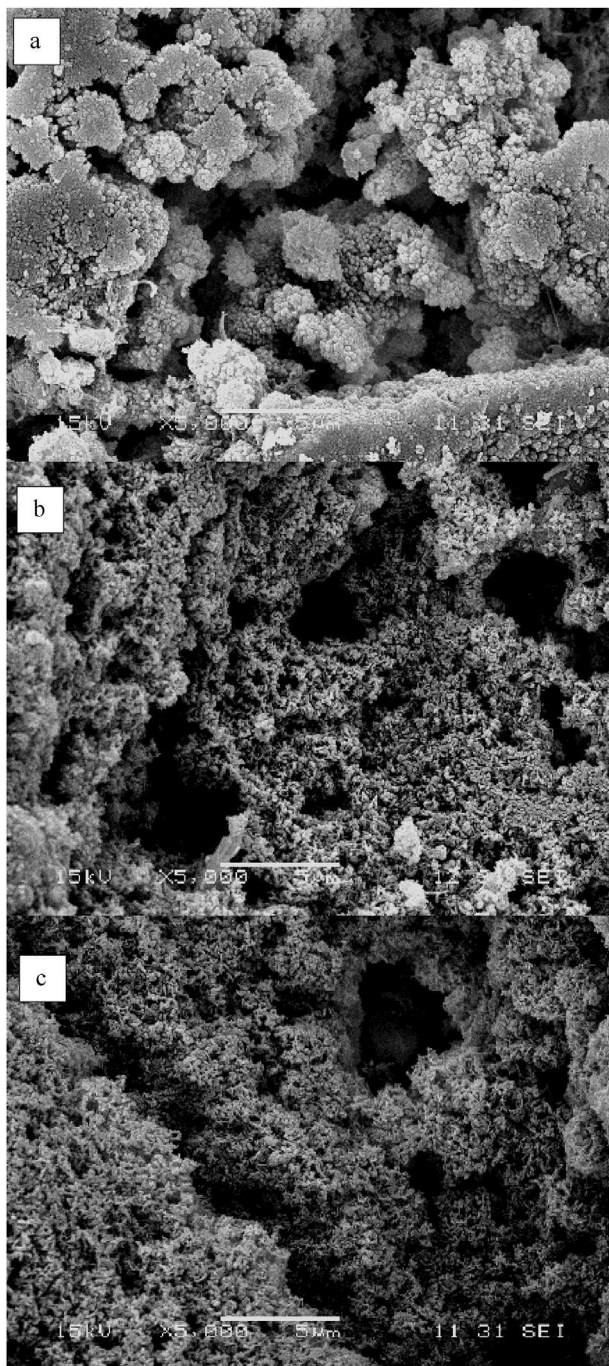


Fig. 2. SEM images of: a) Uncoated Bath stone after SO_2 exposure; b) Nanolime coated Bath stone specimen after SO_2 exposure; c) Bath stone treated with the photocatalytic nanolime coating after SO_2 exposure.

nanolime surfaces. The concentration of sulphur on surfaces coated with nanolime and photocatalytic nanolime was three times higher than that on the stone surface due to the presence of more reactive $\text{Ca}(\text{OH})_2$ and the associated higher surface area. EDS indicated a six-fold increase, the higher value compared to XPS, was attributed to the greater penetration depth of the analysis into the specimen surface.

The addition of anatase to the nanolime, increased the surface area and the absorption of SO_2 and NO_x onto the outermost layer of material. When the photocatalytic nanolime coating was exposed to UV irradiation, XPS revealed the presence of SO_4^{2-} as calcium

Table 5

Specimen composition determined by EDS spectroscopy on specimens following experimental conditioning exposure.

	Specimen	S (at. %)	Ti (at. %)
7 ppm NO_2 33%RH Daylight cycles	Untreated	–	–
	Nanolime coating	–	–
	Photocatalytic nanolime	–	4.4
7 ppm SO_2 33%RH Daylight cycles	Untreated	0.37	–
	Nanolime coating	2.36	–
	Photocatalytic nanolime	1.77	7.12
3.5 ppm NO_2 +3.5 ppm SO_2 33% RH Daylight cycles	Untreated	0.56	–
	Nanolime coating	0.34	–
	Photocatalytic nanolime	1.68	4.4
7 ppm SO_2 33% RH UV-light	Untreated	0.72	–
	Nanolime coating	2.38	–
	Photocatalytic Nanolime	4.45	6.6

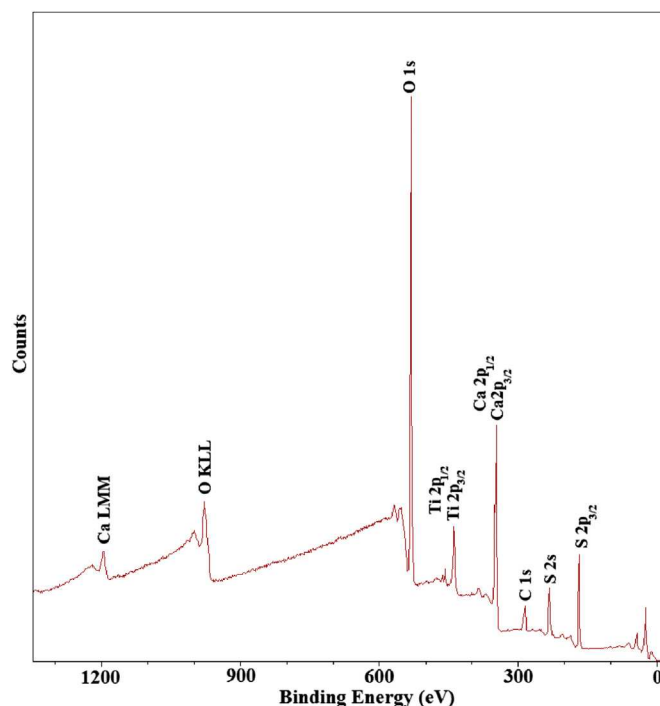


Fig. 3. Typical wide scan survey XPS spectrum for photocatalytic nanolime coated Bath stone after five days exposure to 7 ppm SO_2 under UV irradiation.

sulphate. Compared to all the other specimens examined the amount of CaCO_3 detected was considerably lower.

The presence of calcium sulphate suggests reaction with sulphuric acid opposed to sulphurous acid. Margitan [54] demonstrated that a hydroxyl radical can initiate the oxidation of SO_2 into SO_3 as described by Equations (14)–(16). This radical is known to readily form on the surface of photocatalysts such as anatase under illumination with UV light [28–30].



Sulphuric acid can form by the reaction of SO_3 with water as shown in Equation (16), however reaction with the hydroxyl radical has also been shown to lead to the formation of sulphuric acid as in Equation (17).

Table 6
Binding energies and relative concentration in atomic percent of carbon, nitrogen, oxygen, sulphur, calcium and titanium obtained from XPS analysis.

Experimental conditions	Specimen ID	Binding energy, eV/Relative concentration in atomic %									
		C 1s		N 1s		O 1s		S 2p _{3/2}		Ca 2p _{3/2}	Ti 2p _{3/2}
		CO ₃ ²⁻	Organic matrix	CO ₃ ²⁻	TiO ₂	CO ₃ ²⁻	TiO ₂	SO ₃ ²⁻	SO ₄ ²⁻	Ca 2p _{3/2}	Ti 2p _{3/2}
7 ppm NO ₂	Untreated	288.6/3.3	399.5/0.9	531.5/78.8	—	—	—	—	346.4/17.0	—	
33% RH	Nanolime coating	289.1/4.3	399.2/0.2	531.3/59.9	—	—	—	—	346.8/35.6	—	
Daylight cycles	Photocatalytic nanolime	288.8/3.5	399.3/0.4	530.9/54.5	528.8/1.7	—	—	—	346.6/28.4	458.1/11.5	
7 ppm SO ₂	Untreated	288.9/5.0	399.3/0.6	531.0/65.0	—	167.9/1.0	—	—	346.3/28.4	—	
33% RH	Nanolime coating	288.7/4.4	399.1/0.2	530.9/56.4	—	166.6/3.2	—	—	346.4/35.8	—	
Daylight cycles	Photocatalytic nanolime	288.8/1.0	399.1/0.2	532.0/62.4	—	168.6/4.6	—	—	347.3/27.1	459.0/4.6	
3.5 ppm NO ₂ + 3.5 ppm SO ₂	Untreated	288.8/3.1	399.7/1.0	531.7/77.9	—	167.9/0.5	—	—	346.7/17.5	—	
33% RH	Nanolime coating	289.0/5.0	399.8/0.4	530.8/58.7	—	167.8/0.3	—	—	346.3/35.6	—	
Daylight cycles	Photocatalytic nanolime	289.1/3.4	399.2/0.1	531.0/53.3	528.9/3.1	168.3/0.1	—	—	346.7/27.0	458.9/13.0	
7 ppm SO ₂	Untreated	288.8/3.3	399.7/0.9	531.7/69.4	—	168.6/2.2	—	—	346.9/24.2	—	
33% RH	Nanolime coating	289.0/2.1	400.6/0.1	532.2/66.1	—	168.4/4.0	—	—	347.5/27.7	—	
UV exposure	Photocatalytic nanolime	287.8/0.7	400.2/0.1	532.4/50.9	529.5/6.9	—	169.4/8.2	—	348.2/24.1	459.0/9.1	

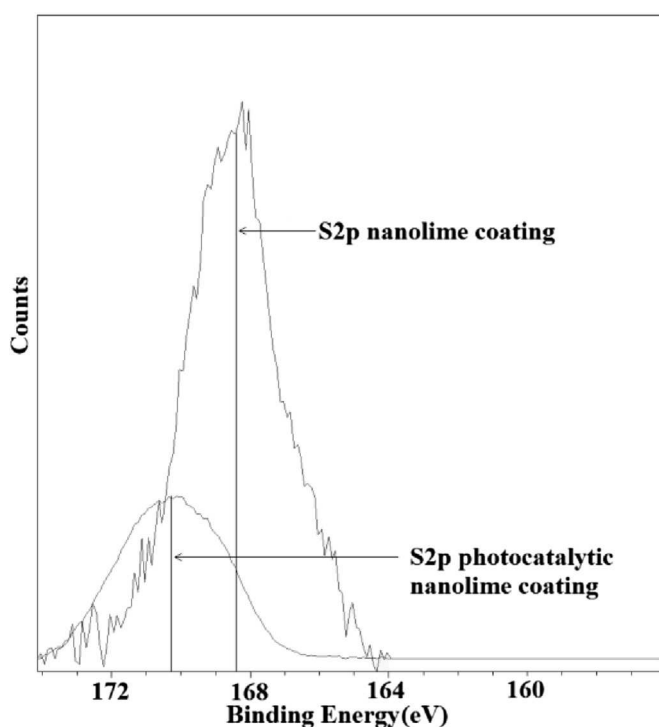
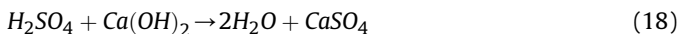


Fig. 4. XPS spectra of sulphur 2p_{3/2} region for nanolime and photocatalytic nanolime coated Bath stone after five days exposure to 7 ppm SO₂ under UV irradiation.



When the sulphuric acid is formed, it reacts with Ca(OH)₂ and CaCO₃ as shown in Equations (18) and (19) to form calcium sulphate.



7. Conclusions

This study provides an insight into the effect of the addition of photocatalytic titanium dioxide on the carbonation process of nanolime and in its degradation process when exposed to SO₂.

There was no evidence of nitration under exposure to 7 ppm NO₂ for all the materials evaluated in this study. XPS data indicated the binding energies of the N 1s peak were characteristic of N–C bonds in an organic matrix. The concentration of nitrogen deposited was increased when the gas composition consisted of 3.5 ppm of SO₂ and 3.5 ppm of NO₂.

In the case of the specimens coated with nanolime the results show a preferential reaction of Ca(OH)₂ with SO₂ relative to CO₂, which is further enhanced in presence of anatase and UV light. Under these conditions the majority of the Ca(OH)₂ reacts with SO₂ to form calcium sulphate, and only a small amount reacted with CO₃²⁻ to form CaCO₃. Results show the presence of anatase increased the deposition of sulphur and nitrogen when the specimens were exposed to 7 ppm of SO₂ and UV light, and the CaSO₄ generated reduced carbonation. This was attributed to the oxidation of SO₂ to SO₃ by hydroxyl radicals generated on the surface of nano-anatase thus forming sulphuric acid opposed to sulphurous acid. Results from the photocatalytic nanolime formulation suggest they could be used to reduce atmospheric pollutant levels through creation of a sacrificial layer. Such coatings have the potential to prevent further damage to limestone façades and could be applied in cities where pollution is detrimental to historic buildings.

Acknowledgement

The authors acknowledge research funding from a University of Bath Research Studentship and the Engineering and Physical Sciences Research Council (EPSRC) through project EP/K025597/1. Thanks are also due to the National EPSRC XPS Users' Service, hosted by nanoLAB at the University of Newcastle, UK, in particular Dr Anders Barlow. The authors are grateful to Professor W. N. Wang for specifying the UV-LED source and to Dr John Mitchels and Ursula Potter for assistance with EDS spectroscopy and SEM imaging.

SEM and EDX data supporting this paper are provided in full in the results section. XPS data is openly available from the University of Bath Data Archive at <http://dx.doi.org/10.15125/BATH-00097>. PHREEQC results were obtained using PHREEQC Interactive version 3.1.7-9213 and using the algorithm described in algorithm 1 and the details specified within the Materials and Methods section.

Appendix

Algorithm 1. PHREEQC model used to simulate the dissolution of CO₂, NO₂ and SO₂ and water with and without solid phases. The code shows the model used to simulate the dissolution of 7 ppm of SO₂ and 385 ppm of CO₂ in pure water and in absence of solid

phases as initial conditions (hashtags inform the software to ignore the code lines where these are located). For each condition described in Table 1, the gas phases, the gas concentrations and the solid phases were modified by commenting or un-commenting the code with a hashtag.

```
SOLUTION 1
temp 25
pH 7 charge
pe 4
redox pe
units mol/kgw
density 1
Alkalinity 0
-water 1 # kg

EQUILIBRIUM_PHASES 1
# Calcite 0 1000
# Portlandite 0 1000
CO2(g) -3.408822658 100
# NO2(g) -5.149185348 100
SO2(g) -5.149185349 100
END
```

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