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

Manuel Nuño a, Giovanni L. Pesce a, Chris R. Bowen b, Panayiotis Xenophontos a, Richard J. Ball a, *

a BRE Centre for Innovative Construction Materials, Department of Architecture and Civil Engineering, University of Bath, Claverton Down, BA2 7AY, UK
b Department of Mechanical Engineering, University of Bath, Claverton Down, BA2 7AY, UK

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A B S T R A C T

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 resilient 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$_2$SO$_3$) is formed whereas dissolution of SO$_3$ in water generates sulphuric acid (H$_2$SO$_4$). 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]:

\[
\text{SO}_2 + H_2O \rightarrow H_2SO_3
\]

(1)

\[
H_2SO_3 + CaCO_3 \rightarrow CaSO_3 + H_2CO_3
\]

(2)

\[
SO_2 + NO_2 \rightarrow SO_3 + NO
\]

(3)

\[
SO_3 + H_2O \rightarrow H_2SO_4
\]

(4)
\[ H_2SO_4 + CaCO_3 \rightarrow CaSO_4 + H_2CO_3 \]  
\[ NO + NO_2 + 2H_2SO_4 \rightarrow 2NOHSSO_4 + H_2O \]  
\[ 2NOHSSO_4 + SO_2 + 2H_2O \rightarrow 3H_2SO_4 + 2NO \]  
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]:

\[ NO_2 + H_2O \rightarrow HNO_3 \]  
\[ 2HNO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + H_2CO_3 \]  

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].

Photocatalytic activity was 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].

\[ TiO_2 \rightarrow h^+_vb + e^{cb} \]  
\[ h^+_vb + H_2O \rightarrow \cdot OH + H^+ \]  
\[ e^{cb} + H^+ \rightarrow \cdot H \]  
\[ e^{cb} + O_2 \rightarrow O_2^- \]  
\[ h^+_vb + O_2^- \rightarrow O_2 \]  
\[ H^+ + O_2^- \rightarrow HO_2 \]  

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 × 10 × 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 °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®. A product with a concentration of 25 g/l in ethanol was used in all cases. Anatase in the form of Aerioxide® P25 was supplied by Sigma Aldrich (>99.5% trace metals basis, average particle size 21 nm, surface area from 35 m²/g to 65 m²/g). In order to obtain a stable colloidal suspension, 7.4% wt/vol anatase was dispersed in CaloSIL® 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 °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 W/m². All other specimens were only exposed to daylight simulating external environmental conditions. The power of the light in the UVA range was 3 mW/m².

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 [23,31], 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...
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 7.3 ppm SO₂ and 3.5 ppm NO₂. 3) zero air grade containing 7 ppm NO₂; 4) zero air grade containing 7 ppm SO₂ under UV.

### 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 pCO₂ (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 nm, 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 AlKα (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.

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**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.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Exposed pollutant</th>
<th>SO₂ flow (ml/min)</th>
<th>NO₂ flow (ml/min)</th>
<th>100% Humid air (ml/min)</th>
<th>Light irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7 ppm SO₂</td>
<td>22</td>
<td>–</td>
<td>10</td>
<td>Daylight cycles</td>
</tr>
<tr>
<td>2</td>
<td>7 ppm NO₂</td>
<td>–</td>
<td>22</td>
<td>10</td>
<td>Daylight cycles</td>
</tr>
<tr>
<td>3</td>
<td>3.5 ppm SO₂ and 3.5 ppm NO₂</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>Daylight cycles</td>
</tr>
<tr>
<td>4</td>
<td>7 ppm SO₂ under UV</td>
<td>22</td>
<td>–</td>
<td>10</td>
<td>Constant 8 W/m²</td>
</tr>
</tbody>
</table>

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**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 \( \text{CO}_3^{2-} \), \( \text{SO}_4^{2-} \), and \( \text{NO}_2^- \) 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 \( \text{SO}_4^{2-} \) ion is many orders of magnitude higher than the activity of \( \text{NO}_2^- \) and \( \text{CO}_3^{2-} \) ions in all conditions.

Table 3 shows the activity of \( \text{CO}_3^{2-} \), \( \text{SO}_4^{2-} \) and \( \text{NO}_2^- \) 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 \( \text{CaCO}_3 \) formed during the carbonation of nanolime. Results show that, as in pure water, the activity of the \( \text{SO}_4^{2-} \) ion is several order magnitudes higher than the activity of \( \text{NO}_2^- \) and \( \text{CO}_3^{2-} \) ions and that under these conditions Anhydrite (\( \text{CaSO}_4 \)), Bassanite (\( \text{CaSO}_4\cdot0.5\text{H}_2\text{O} \)) and Gypsum (\( \text{CaSO}_4\cdot2\text{H}_2\text{O} \)) can be formed as solid phases.

Table 4 shows the activity of \( \text{CO}_3^{2-} \), \( \text{SO}_4^{2-} \) and \( \text{NO}_2^- \) 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 \( \text{SO}_4^{2-} \) ion is several orders of magnitude higher than the activity of \( \text{NO}_2^- \) and \( \text{CO}_3^{2-} \) ions. Furthermore, the results suggest that Anhydrite (\( \text{CaSO}_4 \)), Bassanite (\( \text{CaSO}_4\cdot0.5\text{H}_2\text{O} \)) and Gypsum (\( \text{CaSO}_4\cdot2\text{H}_2\text{O} \)) are the only solid phases that could be formed at the end of the test.

5.2. SEM imagining

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 \( \mu \text{m} \) in diameter, and the macro pores were over 100 \( \mu \text{m} \) and micropores (between Oolites) which are between 10 and 1 \( \mu \text{m} \) 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 Ca(NO\(_3\))\(_2\) was not formed.

---

### Table 2

<table>
<thead>
<tr>
<th>Simulation number</th>
<th>Gas phases</th>
<th>Ion activity as calculated by PHREEQC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{CO}_3^{2-} )</td>
<td>( \text{SO}_4^{2-} )</td>
</tr>
<tr>
<td>1</td>
<td>385 ppm ( \text{CO}_2 )</td>
<td>7 ppm ( \text{SO}_2 )</td>
</tr>
<tr>
<td>2</td>
<td>385 ppm ( \text{CO}_2 )</td>
<td>7 ppm ( \text{NO}_2 )</td>
</tr>
<tr>
<td>3</td>
<td>385 ppm ( \text{CO}_2 )</td>
<td>3.5 ppm ( \text{SO}_2 )</td>
</tr>
</tbody>
</table>
Binding energies for Ti 2p3/2 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 2p3/2 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 2p3/2 peaks at binding energies between 168.4 and 168.6 eV which corresponded to CaSO3. Calculated atomic percentages of 0.5, 0.3 and 0.1 for the untreated, nanolime coating, and photocatalytic nanolime indicated that the nanolime was 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 NO2 and 3.5 ppm SO2 also showed S 2p3/2 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 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.

Table 3 Activity of CO2−3, SO42− and NO2− ions in pure water in equilibrium with calcite and solid phases formed at the end of the simulation.

<table>
<thead>
<tr>
<th>Simulation set up</th>
<th>Ion activity</th>
<th>Solid phases formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>N.</td>
<td>CO2−3</td>
<td>SO42−</td>
</tr>
<tr>
<td>1</td>
<td>CO2 (385 ppm)</td>
<td>SO4 (7 ppm)</td>
</tr>
<tr>
<td>2</td>
<td>CO2 (385 ppm)</td>
<td>NO2 (7 ppm)</td>
</tr>
<tr>
<td>3</td>
<td>CO2 (385 ppm)</td>
<td>SO4 (7 ppm)</td>
</tr>
</tbody>
</table>

Table 4 Activity of CO2−3, SO42− and NO2− ions in pure water in equilibrium with calcite and portlandite, and solid phases that could be produced at the end of the tests.

<table>
<thead>
<tr>
<th>Simulation set up</th>
<th>Ion activity</th>
<th>Solid phases formed</th>
</tr>
</thead>
<tbody>
<tr>
<td>N.</td>
<td>CO2−3</td>
<td>SO42−</td>
</tr>
<tr>
<td>1</td>
<td>CO2 (385 ppm)</td>
<td>SO4 (7 ppm)</td>
</tr>
<tr>
<td>2</td>
<td>CO2 (385 ppm)</td>
<td>NO2 (7 ppm)</td>
</tr>
<tr>
<td>3</td>
<td>CO2 (385 ppm)</td>
<td>SO4 (7 ppm)</td>
</tr>
</tbody>
</table>

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 2p3/2 binding energies obtained for the XPS spectra from the specimens indicated the presence of SO42− in the form of calcium sulphite. This phase was identified on the uncoated limestone surface in addition to nanolime and photocatalytic
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
Ca(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
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 sul-
phuric acid opposed to sulphurous acid. Margitan [54] demon-
strated 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].

SO$_2$ + •OH → HOSO$_2$•                          \hspace{1cm} (14)

HOSO$_2$• + •OH → H$_2$O + SO$_3$                  \hspace{1cm} (15)

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).
CaCO₃ as shown in Equations (18) and (19) to form calcium hydroxide coating Bath stone after Fig. 4. XPS spectra of sulphur 2p₃/2 region for nanolime and photocatalytic nanolime.

Table 6

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Specimen ID</th>
<th>Binding energy, eV/Relative concentration in atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO₂⁻, N 1s, O 1s, S 2p₃/2, Ti 2p₃/2, Ca 2p₃/2, Ti 2p₃/2</td>
</tr>
<tr>
<td>7 ppm NO₂</td>
<td>Untreated</td>
<td>288.6/3.3, 399.5/0.9, 531.5/78.8, 528.8/1.7, 458.4/11.5</td>
</tr>
<tr>
<td>33% RH</td>
<td>Nanolime</td>
<td>289.1/4.3, 399.3/0.2, 531.3/59.9, 167.9/1.0, 459.0/4.6</td>
</tr>
<tr>
<td>Daylight cycles</td>
<td>Photocatalytic nanolime</td>
<td>288.8/3.5, 399.3/0.4, 530.9/54.5, 166.6/3.2, 457.3/27.1</td>
</tr>
<tr>
<td>7 ppm SO₂</td>
<td>Untreated</td>
<td>288.9/3.0, 399.3/0.6, 531.0/65.0, 166.6/3.2, 457.3/27.1</td>
</tr>
<tr>
<td>33% RH</td>
<td>Nanolime</td>
<td>287.1/4.4, 399.1/0.2, 530.9/56.4, 166.6/3.2, 457.3/27.1</td>
</tr>
<tr>
<td>Daylight cycles</td>
<td>Photocatalytic nanolime</td>
<td>288.8/1.0, 399.1/0.2, 532.0/62.4, 168.6/4.6, 169.3/7.5</td>
</tr>
<tr>
<td>3.5 ppm NO₂ + 3.5 ppm SO₂</td>
<td>Untreated</td>
<td>288.3/3.1, 399.7/1.0, 531.7/77.9, 169.3/7.5, 167.9/1.0</td>
</tr>
<tr>
<td>33% RH</td>
<td>Nanolime</td>
<td>289.0/5.0, 399.8/0.4, 530.8/58.7, 167.8/0.3, 168.6/4.0</td>
</tr>
<tr>
<td>Daylight cycles</td>
<td>Photocatalytic nanolime</td>
<td>289.1/3.4, 399.2/0.1, 531.0/53.3, 168.3/0.1, 167.9/1.0</td>
</tr>
<tr>
<td>7 ppm SO₂</td>
<td>Untreated</td>
<td>288.8/3.3, 399.7/0.9, 531.7/69.4, 168.6/2.2, 168.6/4.0</td>
</tr>
<tr>
<td>33% RH</td>
<td>Nanolime</td>
<td>289.0/2.1, 400.6/0.1, 532.2/66.1, 168.4/4.0, 167.9/7.7</td>
</tr>
<tr>
<td>UV exposure</td>
<td>Photocatalytic nanolime</td>
<td>287.8/0.7, 400.2/0.1, 532.4/50.9, 169.4/8.2, 167.9/7.7</td>
</tr>
</tbody>
</table>

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 CO₂ 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

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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) -3.40882658 100
NO2(g) -5.149185348 100
SO2(g) -5.149185349 100
END

References