



# Photocatalyst efficiencies in concrete technology: The effect of photocatalyst placement



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## ABSTRACT

The application of photocatalysts in concrete technology is by now a well-established concept. However, despite the great opportunities for air quality improvements to be derived from the considerable concrete surfaces exposed to the atmosphere, particularly in cities where air quality is greatly affected by vehicle exhaust and industrial emissions, photocatalytic concretes are still not in mainstream application. With current levels of NO<sub>x</sub> pollution considerably exceeding EU legislative guidelines in urban centres throughout the industrialised world, it is important to consider what the issues are. The likely barriers to more widespread implementation are likely to include cost effectiveness, which needs to be related to photocatalyst impact, but the challenges in measuring impact on air quality directly are complex. This paper seeks to place photocatalytic efficiencies into context, comparing performances of the conventional photocatalyst dispersion in surface mortar coatings with that of photocatalysts supported on surface exposed aggregates. The nature and impact of catalyst binding to the aggregate is also discussed.

## 1. Introduction

There has been significant media attention in recent years on deteriorating air quality in urban environments. The negative health implications from airborne particulates and oxides of nitrogen (commonly expressed as NO<sub>x</sub> but mainly NO and NO<sub>2</sub>), primarily from vehicle emissions, have become a global issue [1]; European Directives define the atmospheric concentration of NO<sub>x</sub> in ambient air to be at maximum of 40 µg/m<sup>3</sup> [2], while the actual concentration of NO<sub>x</sub> in almost all main European cities far exceeds this value, e.g., an hourly average of ca. 300 µg/m<sup>3</sup> (160 ppb) was reported in London (July 2017) [3]. The situation in China is even more extreme with NO<sub>x</sub> concentrations in large cities in the North China Plain (Beijing, Tianjin, most of Hebei, Henan, and Shandong provinces and the northern parts of Anhui and Jiangsu provinces) exceeding 450 ppb in July 2013 [4]. As an example of recent trends, NO<sub>x</sub> pollution in key UK populations centres (London and Edinburgh) are highlighted in Table 1 [3,5].

Photocatalysis has been associated in the scientific literature with NO<sub>x</sub> abatement for more than 20 years and photocatalytic concrete, as a photocatalyst support [6–18], has more recently been the subject of several significant research programmes [19,20] and the basis for commercial photocatalytic cements. However, despite the current and increasing air quality issues, photocatalytic concretes are still rarely

utilised in mainstream construction, their application being limited only to several site demonstrations in Italy [21], France [22], Japan [13,14], Belgium [23], United Kingdom [24], Netherlands [12], and China [25], etc.

A number of significant factors which limit photocatalytic efficiencies in cement-based systems have been previously summarised, e.g. [26], and some have been addressed, such as the use of surface treatments in improving photocatalyst dispersion [27,28]. In the present application, further significant efficiency advantages are derived from the separation of the photocatalyst chemistry from the interfering effects of cement chemistry [26,29] by supporting the photocatalyst onto a surface mounted aggregate (Fig. 1). Supported catalysis is a well-developed concept in offering improved exposure of the catalysts to reactants and is common in industrial catalytic technologies. In such a configuration however, the nature of the photocatalyst-support interactions is important. For durable performance, a strong chemical bond is necessary but the influence of bonding on photocatalytic mechanisms must be considered. This paper addresses these influences, specifically the efficiency of the photocatalytic process.

The barriers to more widespread implementation of photocatalytic concretes are likely to include cost and perhaps even a measure of scepticism as to their general effectiveness. The definition of photocatalyst efficiencies can represent a source of confusion; this is normally

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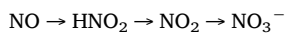
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**Table 1**  
General trends towards NO<sub>x</sub> pollution in key populations centres of London and Edinburgh [3,5]

place	Parameter	NO <sub>x</sub> concentration (µg/m <sup>3</sup> )							
		2010	2011	2012	2013	2014	2015	2016	
London mean roadside	Average	135.9	136.6	150.6	148.3	147.3	140.2	155.3	
	Maximum	241.1	268.1	280.0	265.3	298.2	275.7	335.8	
Edinburgh St Leonard- s	Average	96.9	73.6	76.1	68.8	59.4	N/A	73.4	
	Maximum	531	361	541	365	250	N/A	742	

defined as the photonic efficiency and values of 0.01–1% are often quoted [30,31]. Since these numbers are normalised to the number of photons impinging on the photocatalyst, they do not readily convey the impact of the photocatalyst on moderating NO<sub>x</sub> concentrations. This paper places photocatalytic efficiencies into the context of the application by illustrating how photonic efficiencies translate into impacts on air quality, utilising comparisons between performances of photocatalysts, (i) conventionally placed, i.e. by incorporation into a surface mortar layer, and (ii) supported on surface exposed aggregates.

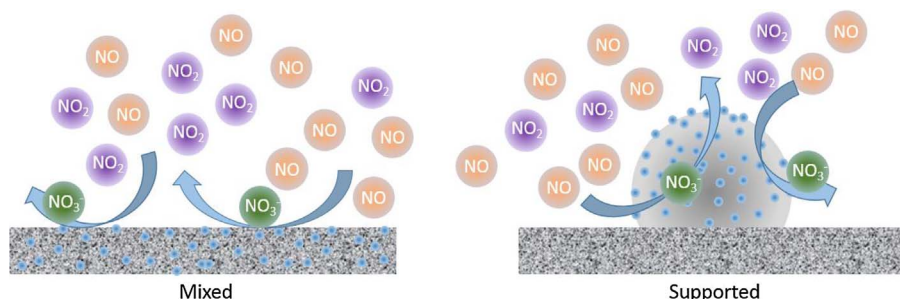
The photocatalytic treatment of NO<sub>x</sub> has been typically described as a sequential oxidation process. The higher the degree of NO and NO<sub>2</sub> conversion, the greater the catalyst activity.



However, the photogenerated charge carriers on the catalyst can stimulate reduction as well as oxidation mechanisms so in practice, the reactions above may lead to intermediates in the above sequence being released to the atmosphere. This is problematic as the toxicity of NO<sub>2</sub> is considerably greater (by conservatively a factor of 3) than that of NO, the primary pollutant, and it can be a precursor for even more toxic atmospheric constituents, e.g. ozone and PAN (Peroxyacyl nitrates) [1,32,33]. Consequently, oxidation through to nitrate (NO<sub>3</sub><sup>-</sup>) is the preferred reaction with respect to air quality.

The accumulation of NO<sub>3</sub><sup>-</sup> on catalytic surfaces must however be managed; adsorbed NO<sub>3</sub><sup>-</sup> blocks catalytic sites from further NO/NO<sub>2</sub> adsorption (and catalytic activity) and catalytic reduction back to NO<sub>2</sub> is likely, reducing nitrate selectivity. Therefore, NO<sub>3</sub><sup>-</sup> must be removed regularly by washing. In conventional photocatalytic concretes, nitrate washings *via* condensed atmospheric moisture represents a mild risk from acidification of the cement (carbonated at the near surface) which may influence leaching induced damage over time. In the present configuration, the photocatalyst adsorbing and converting NO<sub>x</sub> to nitrate is supported on a quartz substrate mounted externally to the concrete and surface penetration of the concrete by acidified washings is less likely.

A measure of the effectiveness of the photocatalytic process in driving oxidation through to NO<sub>3</sub><sup>-</sup> is given by the nitrate selectivity [31]. This property of TiO<sub>2</sub> is also addressed in the paper, particularly in the context of catalyst-support binding.



**Fig. 1.** Conventional (mixed) and aggregate-supported configurations for photocatalyst (blue) applications in concrete technology. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## 2. Experimental procedure

### 2.1. Materials

The aggregate used as a support in this study is ISO standard sand (ISO 679: 2009, quartz sand (LEUCATE, France), 1–2 mm diameter). Titanium tetra-isopropoxide (TTIP, 99.9%), acetic acid (CH<sub>3</sub>COOH, 99.6%), Calcium hydroxide (Ca(OH)<sub>2</sub>, 98%), absolute ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99.9%), NaOH (sodium hydroxide, 0.1 M), were purchased from Sigma-Aldrich. Deionized water (18.2 MΩ.cm) was used throughout the preparation process.

### 2.2. Methods

#### 2.2.1. TiO<sub>2</sub> hydrosol preparation

A low temperature precipitation-peptization method was employed to prepare anatase TiO<sub>2</sub> hydrosols as follows: 2.5 ml of TTIP was dissolved in 7.5 ml of absolute ethanol, with stirring for about 30 min at 50 °C. Then, the obtained solution was added dropwise into a mixture containing 2 ml of acetic acid and 40 ml of deionized water (1–2 drop/s). After that, the suspension was continually stirred for 48 h at 50 °C, and then aged for at least 72 h at room temperature to produce a translucent sol.

#### 2.2.2. TiO<sub>2</sub>/quartz sand aggregate preparation

A cyclic coating regime was employed to produce different loading levels of TiO<sub>2</sub> on the quartz sand surface. Specially, to maximize the surface hydroxide groups, the quartz sand aggregates were treated with 0.1 M NaOH for 24 h followed by washing with deionized water 3 times prior to immersion in the anatase TiO<sub>2</sub> hydrosols suspension; 1–2 mm alkaline treated quartz sands were immersed in anatase TiO<sub>2</sub> hydrosol suspensions for 5 min at room temperature. The resulting composites were then separated by filtration and dried at 105 °C for 30 min. This process was repeated for the required number of coating cycles. In the final step, all samples were dried at 105 °C for 24 h, then washed three times using deionized water before final drying at 105 °C for 24 h. These samples are labelled QST-X, where X is the number of coatings (X = 0, 1, 2, 3, 4, 5, 6).

#### 2.2.3. Durability of coatings – evaluation methods

**2.2.3.1. Mechanical.** The mechanical durability of the QST aggregates (TiO<sub>2</sub>-loaded quartz composites) was evaluated using two methods [34]. Method 1: 15 g QST aggregates were immersed in 30 ml deionized water and gently shaken manually for ca.15 s. The water was replaced and the process repeated for up to 30 cycles. Method 2: QST aggregates were immersed in deionized water, and then sonicated for 10 min, using a Branson ultrasonic bath (B300, 34 kHz, 50 W), after which it was washed with deionized water several times until a clear solution was observed.

**2.2.3.2. Chemical.** The influences of cement chemistry were tested on the aggregate-supported catalyst system as follows:

- (1) QST-X aggregates were immersed in saturated aqueous Ca(OH)<sub>2</sub> solution for 1, 5, 10 and 30 min. The wet sample was then placed in a vacuum oven (105 °C; 4 h at 0.1 MPa), after which it was placed in a sample bottle and stored in a desiccator to await testing and designated (QST-X-Ci, Ci (i = 1, 5, 10, 30) represents Ca(OH)<sub>2</sub> attacking time). A QST-X was alternatively immersed in 0.1 M NaOH for 24 h, and then washed to neutral condition (denoted as QST-X-N);
- (2) Carbonation – the above QST-X-Ci aggregates were placed in a flowing atmosphere containing 100% CO<sub>2</sub> (BOC U1013) at a relative humidity of 70% 1 h (flow rate: 5 ml/min), before being placed in a sample bottle and stored in a desiccator to await testing and designated QST-X-CiC (CiC represents QST-X-Ci being carbonated).

### 2.3. Characterization

The phase compositions of TiO<sub>2</sub> and QST were determined by comparing X-ray diffraction (XRD) patterns, obtained on a PHILIPS P W 3040/60X<sup>\*</sup> PertPRO diffractometer in the range 20–70° 2θ under Cu Kα radiation at a scanning speed of 6° min<sup>-1</sup>, against reference XRD data.

Fourier transform infrared (FT-IR) spectra were obtained using a Perkin-Elmer Spectrum 2 spectrometer with 48 scans per sample collected from 400 to 4000 cm<sup>-1</sup> at 2 cm<sup>-1</sup> resolution. The obtained FT-IR spectra were deconvoluted using Peakfit V. 4.1.2 software [35], and the concentrations of the chemical linkage Si-O-Ti, relative to SiO<sub>2</sub> and TiO<sub>2</sub> were calculated by the following formula [36]:

$$D_{(\text{Si-O-Ti})} = \frac{S_{(\text{Si-O-Ti})}}{S_{(\text{Si-O-Si})}} \times \frac{X_{\text{Si}}}{X_{\text{Ti}}} \quad (1)$$

where  $D_{(\text{Si-O-Ti})}$  represents the concentration of Si-O-Ti bonds relative to Si-O-Si, normalized to the TiO<sub>2</sub>/SiO<sub>2</sub> molar ratio;  $S_{(\text{Si-O-Ti})}$  and  $S_{(\text{Si-O-Si})}$  represent the background-corrected areas associated with the Si-O-Ti (ca. 940 cm<sup>-1</sup>) and Si-O-Si (ca. 1170 cm<sup>-1</sup>) absorption frequencies, respectively;  $x_{\text{Si}}/x_{\text{Ti}}$  represents the SiO<sub>2</sub>/TiO<sub>2</sub> molar ratio, obtained by quantitative X-ray fluorescence (XRF, Rigaku NEXQC<sup>+</sup>) calibrated using TiO<sub>2</sub>-quartz sands mixtures in the range 0.1–50 wt.% TiO<sub>2</sub>. The estimated error in  $D_{(\text{Si-O-Ti})}$  is around ± 6% [35].

Morphologies of samples were observed by scanning electron microscope (SEM, Zeiss EVO MA10) equipped with an energy dispersive x-ray spectrometry (EDS, Oxford INCA) for elemental composition analyses.

The theoretical loading thickness of TiO<sub>2</sub> film on quartz sand aggregate surface was calculated based on the model illustrated in Fig. 2 [34,37] and Eqs. (2) and (3):

$$\omega\% = \frac{\left(\frac{D_{\text{st}}}{D_s}\right)^3 - 1}{\frac{6 \times \rho_s}{\pi \times \rho_t} + \left(\frac{D_{\text{st}}}{D_s}\right)^3 - 1} \times 100 \quad (2)$$

$$d = \frac{D_{\text{st}} - D_s}{2} \quad (3)$$

Where  $\rho_s$  is the density of support, 2.4 g/cm<sup>3</sup>;  $\rho_t$  is the density of TiO<sub>2</sub>,

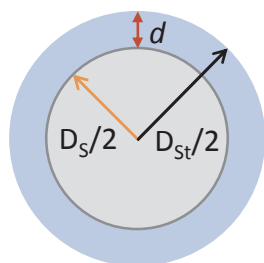


Fig. 2. Geometric model for evaluating loading thickness of TiO<sub>2</sub> on aggregates and definition of parameters.

3.8 g/cm<sup>3</sup>;  $D_s$  is the average diameter of support, nm;  $D_{\text{st}}$  is the average diameter of TiO<sub>2</sub> loaded support, nm;  $\omega\%$  is the mass fraction of TiO<sub>2</sub> measured by XRF;  $d$  is the thickness of loaded TiO<sub>2</sub> film, nm. The model assumes that the coating layer consists of two dimensional closed packed spherical particles fully covering the smooth aggregate surface, with successive layers contributing to the thickness,  $d$ .

### 2.4. Photocatalytic performance

The photocatalytic performance of prepared samples were identified in a flow-through reactor (ISO 22197-1: 2007) schematically illustrated in Fig. 3.

10 g of QST aggregates were uniformly distributed in a rectangular recess (monolayer distribution, area  $5 \times 10^{-3}$  m<sup>2</sup>) inside the reactor so the NO gas had to flow over the sample surface. The sample was irradiated by a 500W Xe-lamp solar illuminator (Sciencetech, Inc, Canada) light source; the resulting photon flux at the position of the sample was measured to be  $3.05 \times 10^{-6}$  mol s<sup>-1</sup> m<sup>-2</sup> using a broadband thermopile detector (Gentec-EO-XLP12-3S-H2-D0). 1 ppm of NO gas in synthetic air, conditioned at a constant 40% relative humidity, measured using a HygroPalm 1 detector (Rotronic) at 25 °C, was passed at a volumetric flow rate of  $5 \times 10^{-5}$  m<sup>3</sup> s<sup>-1</sup> through the reactor. The concentrations of NO, NO<sub>2</sub> and NO<sub>x</sub> were detected by a Thermo Scientific Model 42i-HL High Level NO-NO<sub>2</sub>-NO<sub>x</sub> Analyzer (Air Monitors Ltd., United Kingdom). Each sample was measured in the dark until equilibrium concentrations were reached and afterwards, under illumination, until steady state concentrations were observed. For comparison, the photocatalytic performance of pure TiO<sub>2</sub> (0.1 g), obtained by drying the TiO<sub>2</sub> hydrosol at 105 °C for 24 h, was measured under identical conditions. Kisch and Bahnemann [38] showed extended NO<sub>x</sub> experiments on a commercial TiO<sub>2</sub> photocatalyst which indicated that steady state conditions were reached 2 h after illumination. Consequently all concentrations for subsequent calculations of photonic efficiency and selectivity were extracted 2 h after illumination. The photocatalytic efficiency ( $\xi$ ) was calculated according to Eq. (4). The catalyst selectivity for nitrate ( $S\%$ ) was calculated according to Eq. (5).

$$\xi = \frac{(c_d - c_i)VP}{\Phi ART} \quad (4)$$

$$S\% = \frac{\xi_{\text{NO}_x}}{\xi_{\text{NO}}} \times 100 \quad (5)$$

Where  $c_d$  is the concentration in dark,  $c_i$  the concentration under illumination,  $V$  the volumetric flow rate,  $p$  the pressure,  $A$  the irradiated sample area,  $R$  the gas constant,  $T$  the absolute temperature and  $\Phi$  the photon flux impinging the photocatalyst surface. The photocatalytic efficiency was determined separately for NO, NO<sub>2</sub> and total NO<sub>x</sub>.

## 3. Results and discussion

### 3.1. Physical and chemical properties

The XRD pattern of the prepared TiO<sub>2</sub> shows the sample was well-crystallised anatase (Fig. 4). TiO<sub>2</sub> loaded onto quartz in the QST composites was of insufficient quantity to appear in the composite powder patterns but XRF results, shown in Table 2, confirm that the TiO<sub>2</sub> loading increases with the number of coating cycles as expected. This translates to loading thicknesses ( $d$ ) of up to 1850 nm at a TiO<sub>2</sub>/SiO<sub>2</sub> mass fraction (MF) of 0.61%. It can be concluded that the coating method produces TiO<sub>2</sub> multilayers. These represent agglomerates derived from individual TiO<sub>2</sub> nanoparticles; these represent agglomerates derived from individual TiO<sub>2</sub> nanoparticles; XRD data (peaks corresponding to (101) and (200)) and the Scherrer equation give a mean crystallite size of  $10.3 \pm 0.2$  nm.

As shown in Fig. 5, the semi-quantitative FT-IR technique with peak deconvolution was used to characterise the TiO<sub>2</sub>-SiO<sub>2</sub> binding in the

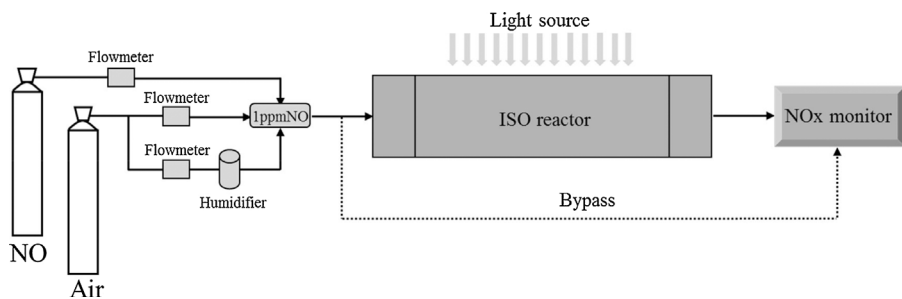


Fig. 3. Schematic showing testing configuration for photocatalytic NO<sub>x</sub> degradation.

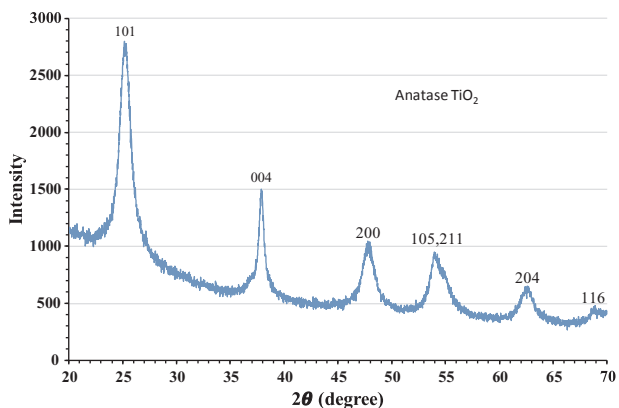


Fig. 4. Indexed XRD pattern of prepared TiO<sub>2</sub> hydrosols dried at 105 °C.

Table 2

TiO<sub>2</sub> loading average mass fraction (%) and average thickness (nm) on quartz sand aggregates surface with different coating times.

Sample	QST-0	QST-1	QST-2	QST-3	QST-4	QST-5	QST-6
MF <sup>a</sup> /%	–	0.16%	0.20%	0.31%	0.37%	0.46%	0.61%
d <sup>b</sup> /nm	–	480	620	940	1140	1400	1850

<sup>a</sup> Mass fraction, obtained by XRF measurement with calibration.

<sup>b</sup> Thickness, calculated by formulae (2) and (3) using measured mass fraction; QST-X represents X cycle coating times (X = 0, 1, 2, 3, 4, 5, 6).

QST-X composites. Fig. 5(a) presents a typical FT-IR spectrum (in this case, QST-2 (0.2% TiO<sub>2</sub> mass fraction)) in the range of 650–1350 cm<sup>-1</sup>. The equivalent spectrum for quartz is also shown. The absorption bands at 695, 778, 797, 1062, 1085, and 1165 cm<sup>-1</sup> are associated with Si–O–Si bonds [39–42]. The broad absorption in the range of 850–1000 cm<sup>-1</sup> is attributed to Ti–O–Si chemical linkages between the support and TiO<sub>2</sub> particles [30]. It is reported that the broad peak in the range of 800–1350 cm<sup>-1</sup> can be deconvoluted into five peaks [36,43,44] as shown in Fig. 5(b). The deconvoluted peaks at ca. 1066, 1088, 1117, and 1171 cm<sup>-1</sup> are associated with the symmetric and asymmetric vibrations of Si–O–Si bonds, and the deconvoluted peak at ca. 940 cm<sup>-1</sup> is attributed to Si–O–Ti bonds. The best separation of Si–O–Si peaks from the Si–O–Ti peak is achieved with the Si-O-Si absorbance at 1170 cm<sup>-1</sup> so this peak was subsequently used in calculation of (Ti–O–Si)/(Si–O–Si) concentration ratios. When plotted against the mass fraction of TiO<sub>2</sub> in each composite, Ti-O-Si/Si-O-Si area ratios present similar values (Fig. 6), indicating similar levels of Ti–O–Si bonding on quartz surfaces in all samples irrespective of TiO<sub>2</sub> loading. This is consistent with a TiO<sub>2</sub>-saturated aggregate surface across the TiO<sub>2</sub>-loading range. As TiO<sub>2</sub> loading increases, multi-layer (agglomerated) TiO<sub>2</sub> increases (Ti–O–Ti) but does not affect the level of interfacial bonding. Nevertheless, this effect dilutes the effects of Ti–O–Si linkages (decreasing D<sub>(Ti–O–Si)</sub>).

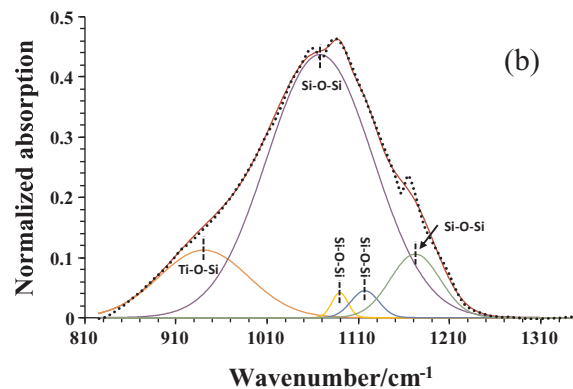
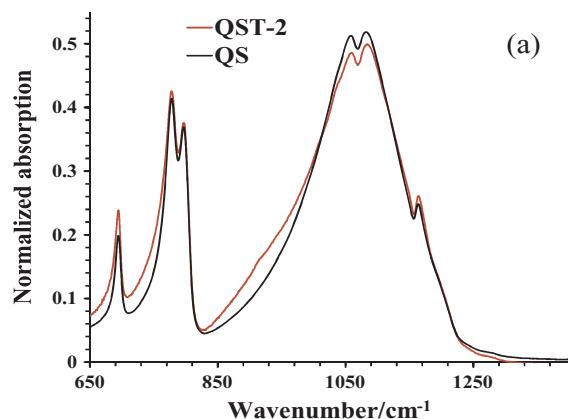


Fig. 5. Representative FT-IR spectra of (a) QS (aggregate) and TiO<sub>2</sub>-loaded aggregate (QST-2; 0.20% TiO<sub>2</sub> mass fraction), and (b) QST-2 with component peaks identified by deconvolution in the wavenumber range 825–1350 cm<sup>-1</sup>.

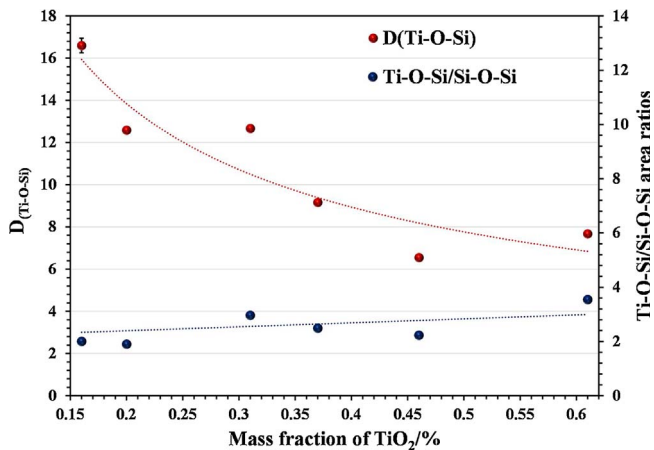


Fig. 6. Variation in Ti–O–Si/Si–O–Si area ratios and D<sub>(Ti–O–Si)</sub> with TiO<sub>2</sub> loading on QST–X composites.



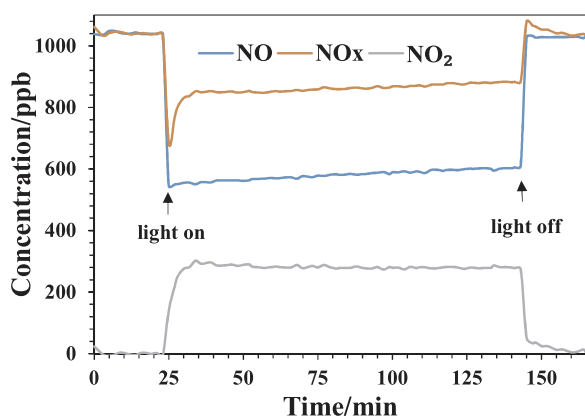


Fig. 7. Concentration profiles for NO, NO<sub>2</sub> and NO<sub>x</sub> (NO + NO<sub>2</sub>) during the photocatalytic oxidation of NO on TiO<sub>2</sub> hydrosol (0.1 g) photocatalysts.

### 3.2. Utilization efficiencies of supported TiO<sub>2</sub>

A typical concentration profile observed for the prepared TiO<sub>2</sub> sample during the photocatalytic oxidation of NO<sub>x</sub> on TiO<sub>2</sub> photocatalysts is shown in Fig. 7. Three stages can be identified: 1) NO<sub>x</sub> concentrations stabilization without light illumination, 2) NO<sub>x</sub> photocatalytic reaction with light on, 3) NO<sub>x</sub> concentrations recovery after turning off the light. NO concentration decreases rapidly upon sample illumination, and remains almost constant, while NO<sub>2</sub> concentration increases significantly at the same time. When the light is switched off, NO<sub>2</sub> concentrations decrease to zero. The photonic efficiency ( $\xi$ ) of NO, NO<sub>x</sub> removal and NO<sub>2</sub> intermediate production, as well as the nitrate selectivity (S%) for all QST samples with different TiO<sub>2</sub> mass fractions are shown in Fig. 8. It can be noted that  $\xi$  (NO) increased initially with increasing TiO<sub>2</sub> mass fractions but became steady around 0.76%. At the same time, the  $\xi$  (NO<sub>x</sub>) and S% also increase with increasing the mass fraction of TiO<sub>2</sub> which drives a corresponding decrease of NO<sub>2</sub> production rate. Compared with the NO<sub>x</sub> removal results for pure TiO<sub>2</sub> (Fig. 7), the calculated values according to Eqs. (4) and (5) are ca. 0.6% for  $\xi$  (NO) and ca. 40% for nitrate selectivity, whilst the supported TiO<sub>2</sub> particles present higher photonic efficiency for NO removal, but lower nitrate selectivity (due to reduced NO<sub>2</sub> removal efficiency).

The detrimental influence of the Ti–O–Si linkage on selectivity has already been reported [45] but in this case, an increase in S% with TiO<sub>2</sub> loading fraction can be observed. This is still consistent with our earlier findings [30,45]. Where TiO<sub>2</sub> loading on SiO<sub>2</sub> is increased, the concentration of Ti–O–Si, which is located only at the catalyst-support interface, with respect to Ti–O–Ti, is diluted by the multi-layer TiO<sub>2</sub> ‘coating’, thus reducing the negative impact of the TiO<sub>2</sub>-SiO<sub>2</sub> bonded interface and enabling S% to increase as is shown in Fig. 9. Further, the

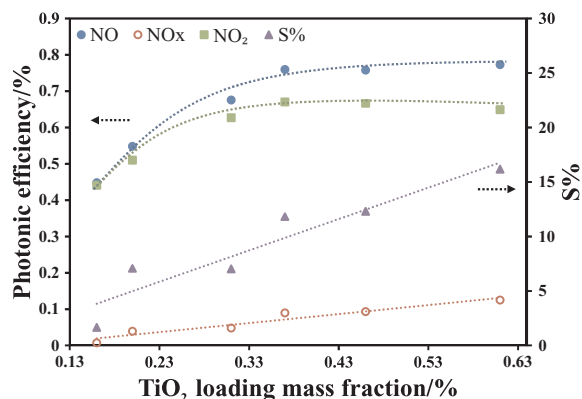


Fig. 8. The dependence of NO<sub>x</sub> photonic efficiency and nitrate selectivity of QST-X samples on TiO<sub>2</sub> loading mass fraction.

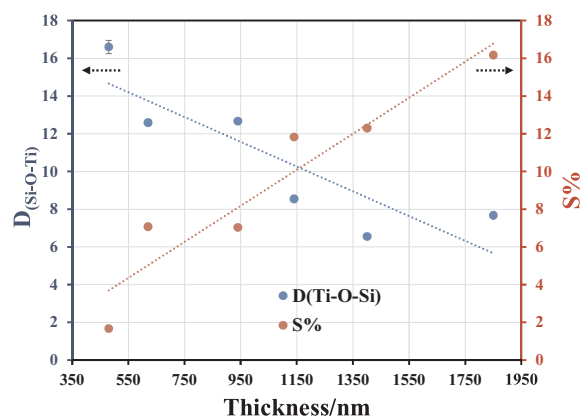


Fig. 9. The dependence of nitrate selectivity and  $D_{(Si-O-Ti)}$  on TiO<sub>2</sub> loading thickness for QST-X samples.

general shape of the  $\xi$  (NO) vs TiO<sub>2</sub> loading mass fraction profile in Fig. 8 is consistent with that observed earlier utilising smaller aggregate sizes [27]. In this case, the variation in  $\xi$  (NO) as TiO<sub>2</sub> loading increases was correlated almost perfectly with the trend in BET surface area (see Fig. S1), suggesting the importance of an effective surface area of TiO<sub>2</sub>, probably influenced by particle packing in the multi-layer agglomerated structures.

### 3.3. Durability of supported TiO<sub>2</sub>

#### 3.3.1. Mechanical

The stability of TiO<sub>2</sub>-aggregates composites is very important to the real engineering applications for long-term degradation of pollutants. Fig. 10 presents durability data for QST subjected to water washing. With gentle agitation, 30% of TiO<sub>2</sub> was removed after 10 cycles, however, only a further ca. 6% was lost after between 10 and 30 cycles. By comparison, after 10 mins sonication (SW10), ca. 56% of the TiO<sub>2</sub> loading remained. In both cases, a strong adhesion is indicated in the inner part of the composite, with weaker (outer) attachments being broken at higher loadings (greater distances from the bonded interface). Quantitative FT-IR data support this, showing constant Ti-O-Si/Si-O-Si area ratios throughout the durability test (See Fig. 10).

Coating TiO<sub>2</sub> onto quartz can be observed in Fig. 11 which shows complete TiO<sub>2</sub> coverage (Fig. 11(b)) compared with the uncoated quartz (QS) (Fig. 11(a)). Fig. 11(c) (and spectrum 3) shows that TiO<sub>2</sub> is still associated with the support even after sonication and washing, although at reduced level, as indicated by Spectrum 3 and the FTIR data.

Fig. 12 shows the photonic efficiency and nitrate selectivity of QST-6 and washed QST-6 samples with different washing cycles and regimes. It is noted that the washed QST samples present slightly different De-NO<sub>x</sub> performances (0.65–0.78%  $\xi$  (NO)) and nitrate selectivity

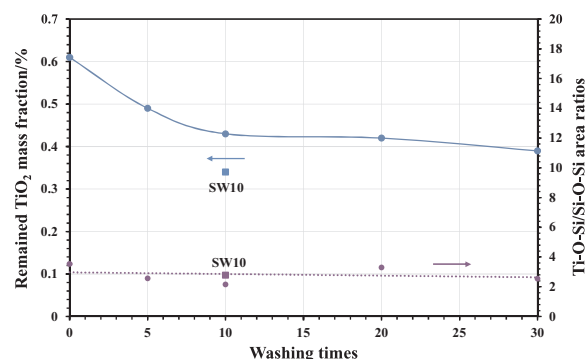


Fig. 10. Adhesion durability of QST-6 (0.61% TiO<sub>2</sub>); SW10 indicates 10 min ultrasonication followed by water washing to clear supernatants.

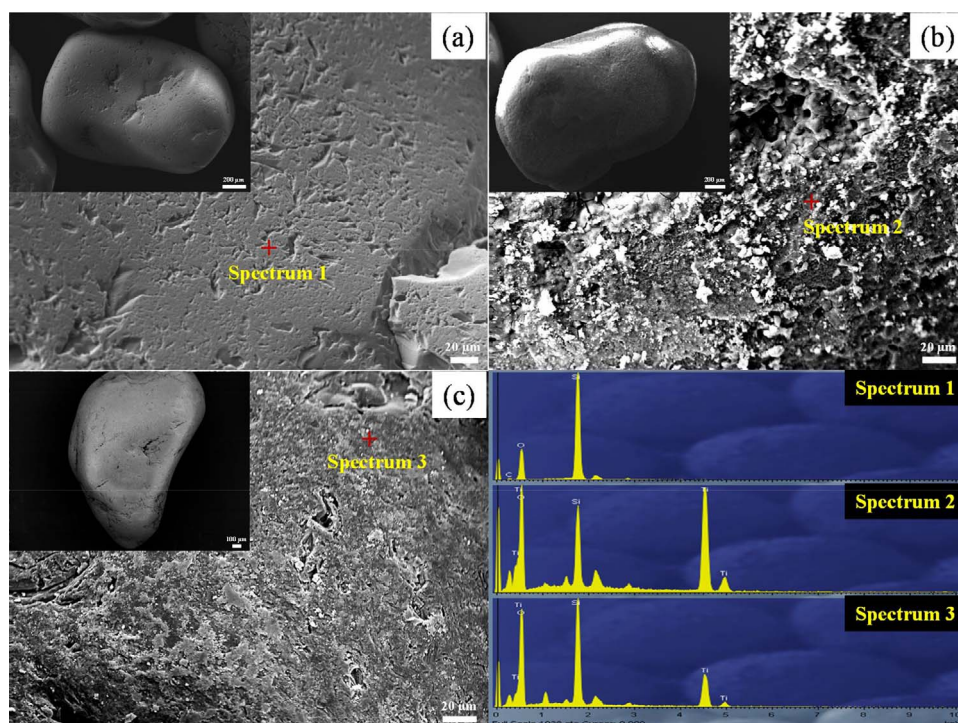


Fig. 11. SEM images and EDS spectra of: (a) pure quartz sand aggregate; (b) QST-6 with 0.61% TiO<sub>2</sub> mass fraction; (c) QST-6 after ultrasonication (0.34% TiO<sub>2</sub> mass fraction).

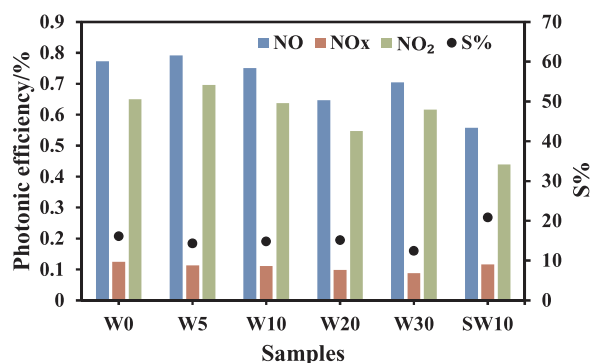


Fig. 12. Photonic efficiency and nitrate selectivity of QST-6 (0.61% TiO<sub>2</sub> mass fraction) and washed QST-6 samples (with reduced TiO<sub>2</sub> mass fraction) as a function of washing cycles and regimes.

(12%–15%). Even after the more aggressive sonication/washing treatment (SW10), the  $\xi$  (NO) photonic efficiency is only reduced by 30% even though almost half of the TiO<sub>2</sub> has been lost (0.34% remaining; Fig. 10). The greater selectivity of SW10 relative to W10 (Fig. 10) presents an apparent contradiction, i.e. the higher nitrate selectivity seems to be associated with a reduced TiO<sub>2</sub> layer thickness, contrary to the trend of Fig. 9. However, *accessible* surface area is believed to be important and it is suggested that the increased agitation from sonication has exposed more TiO<sub>2</sub> surface, increasing the degree of surface water on TiO<sub>2</sub>. This has previously been shown to increase nitrate selectivity on TiO<sub>2</sub> [30]. The reduced  $\xi_{\text{NO}}$  may be attributed to reduce NO adsorption due to competition with water whilst NO<sub>2</sub> oxidation is enhanced in the presence of physi-sorbed water [30].

More significantly, this performance, which is achieved with approximately 34 mg of TiO<sub>2</sub> is similar to that of pure TiO<sub>2</sub> (0.1 g), confirming that supported TiO<sub>2</sub> has greater utilization efficiency, corresponding to a considerably lower cost of use in photocatalytic concrete.

### 3.3.2. Chemical

The influence of the chemical environment in cements (alkali, Ca substances, CO<sub>2</sub>, etc.) must also be considered for real photocatalysis

applications [15,26,46–54]. We have recently reported positive correlations between photocatalytic performance and alkalinity during TiO<sub>2</sub> preparation/conditioning [30] so the QST composites were subjected to immersion in freshly prepared saturated Ca(OH)<sub>2</sub> solution. Fig. 13 shows SEM/EDS data for QST-6 after 30 min immersion (QST-6-C30). Also shown are data for the same material subsequently exposed to 1000 ppm CO<sub>2</sub> at 70% RH for 1 h (QST-6-C30C).

It can be observed that the morphologies of both samples are similar to those shown in Fig. 13 and indicate that there is still a deposited TiO<sub>2</sub> layer on the quartz surface, also confirmed by XRF measurement (0.5% TiO<sub>2</sub> mass fraction). The EDS data of Fig. 13(a) confirm the incorporation of Ca in the layer, presumably due to Ca(OH)<sub>2</sub> deposition, although at the resolution shown there is no specific morphological confirmation. In alkaline conditions, the negative surface charge on TiO<sub>2</sub> may be a factor in encouraging Ca(OH)<sub>2</sub> association, *via* the  $\delta^+$  charge on Ca. A similar interpretation can be offered for the QST-6-C30C sample, where carbonation of the deposited Ca(OH)<sub>2</sub> must be assumed. In either case though, the TiO<sub>2</sub> layer seems to have been sustained and its photocatalytic performance appears to have improved after exposure to Ca(OH)<sub>2</sub> (Fig. 14). This is an interesting observation as the enhancement of nitrate selectivity (S%) is particularly important. It is not clear why such an improvement should be associated with Ca but the earlier mentioned relationship with the effects of alkalinity on activating the TiO<sub>2</sub> surface is likely to be responsible, as supported by the example with NaOH treatment. A further factor is the positive role of surface adsorbed water in conditioning nitrate selectivity of TiO<sub>2</sub> [30], also induced by alkaline hydrolysis of the TiO<sub>2</sub> but which may also be enhanced by the presence of the hydrophilic Ca(OH)<sub>2</sub>.

These effects appear to be slightly inhibited upon carbonation (Figs. 13 and 14). In fact, the reduction in alkalinity arising from carbonation may be a factor but also, it is less hydrophilic than Ca(OH)<sub>2</sub> and therefore less likely to favour an enhancement in water adsorption. The residual enhancements observed in the QST-6-CiC series are therefore likely to be due to uncarbonated Ca(OH)<sub>2</sub>.

The negative effects of Ca additions on supported TiO<sub>2</sub> are mainly associated with activity. A decrease in  $\xi$  (NO) from 0.78% to 0.41% in the first 5 min of Ca(OH)<sub>2</sub> exposure (QST-6-C5) can be noticed in Fig. 14. It then becomes steady, indicating some competing influence

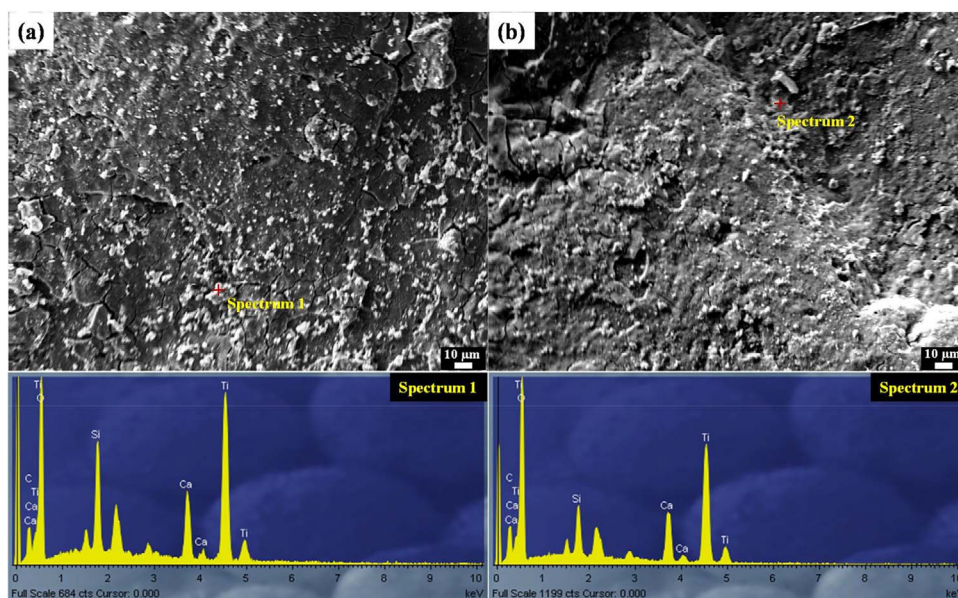


Fig. 13. SEM images and EDS elements spectra of: (a) QST-6-C30; (b) QST-6-C30C.

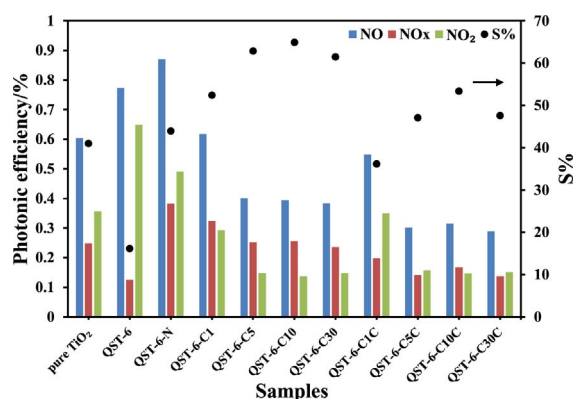


Fig. 14. Photonic efficiency and nitrate selectivity of pure  $\text{TiO}_2$  and QST-6 (0.61%  $\text{TiO}_2$  mass fraction) under different exposure conditions.

but it is unlikely to represent  $\text{TiO}_2$  film saturation which would be expected to reduce  $\xi(\text{NO})$  to zero. A similar trend is observed for the carbonated sample but again, this may be attributed only to the reduced availability of  $\text{Ca}(\text{OH})_2$ .

### 3.4. Opportunities for implementation

A basis for translating the photonic efficiency into quantifiable impacts on air quality in a real-life context may be modelled from data gathered using a photocatalytic reactor consistent with ISO 22197-1:2007. Rearrangement of Eq. (4) enables the photocatalyst-modified concentration,  $C_i$ , to be calculated from the photonic efficiency defined under laboratory conditions (Eq. (5)); NO is chosen for this illustration but NOx and  $\text{NO}_2$  can be similarly treated.

$$C_i = C_d - \frac{\xi(\text{NO})\Phi\text{ART}}{VP} \quad (5)$$

$C_d$  represents the concentration measured over a non-illuminated area, expected to represent the equivalent of the concentration over a non-photocatalytically treated (reference) area;  $\xi(\text{NO})$  represents the laboratory determined photonic efficiency of the photocatalyst. Other terms in Eq. (5) are previously defined, except for  $\Phi$  and  $V$ . The UV irradiation intensity ( $\Phi$ ), is calculated according to Ref. [55] for noon on each day over a 1 year period (see Fig. S2). The model in ref [55] produces  $\Phi$  in units of  $\text{W m}^{-2}$  and conversion to moles of

photons. $\text{m}^{-2} \text{s}^{-1}$ , as required in Eq. (5), is by application of Eq. (6).

$$\Phi(\text{mols. photons}/\text{m}^2. \text{s}) = \Phi(\text{W}/\text{m}^2) \times \frac{\lambda}{N_A \times h \times c} \quad (6)$$

where  $\lambda$  is the wavelength (taken as  $3.65 \times 10^{-7} \text{ m}$ ),  $N_A$  is Avogadro's number,  $h$  is Planck's constant ( $6.63 \times 10^{-34} \text{ J.s}$ ) and  $c$  is the velocity of light ( $2.998 \times 10^8 \text{ m.s}^{-1}$ ).

The volumetric flow rate ( $V$ ,  $\text{m}^3 \text{s}^{-1}$ ), is calculated from ambient wind speed  $v$  ( $\text{m s}^{-1}$ ) corrected according to the height (distance) from the photocatalytic surface. In this case, Eq. (5) utilizes a value for  $\xi(\text{NO})$  derived from measurements in which the air volume above the photocatalyst had a maximum height of 5 mm so recorded wind speeds measured at height  $h$  can be adjusted to that at 5 mm using Eq. (7); the results are shown in Table S1:

$$v_w(h) = v_{10} \times \left(\frac{h}{h_{10}}\right)^a \quad (7)$$

where  $v_w(h)$  is velocity of the wind ( $\text{m s}^{-1}$ ), at height  $h$ ;  $v_{10}$  is velocity of the wind ( $\text{m s}^{-1}$ ), recorded at height  $h_{10} = 10 \text{ m}$ ;  $a$  is Hellmann exponent, which depends on the location and the shape of the ground; for unstable air in cities and villages,  $a = 0.27$  [56]. Volumetric flow rate at 5 mm is then calculated using Eq. (8):

$$V = w \times h \times v_{5\text{mm}} \quad (8)$$

where  $w$  is the width (m) and  $h$  is the height (m) of air volume passing over the photocatalytic area (m). It can be noted that the closed volume of ISO reactor defines a different flow velocity gradient but the distribution calculated using Eq. (7) is considered to provide a close approximation to near surface (5 mm) wind velocities.

When tested against data acquired from a photocatalytic test site of Ref. [55], the model was not able to reproduce the measured effect of photocatalysis with the lab-measured  $\xi(\text{NO})$  value for the photocatalyst (mixed in a cement mortar) of 0.023%. Fitting the measured trend in NO concentrations required an 'effective' photonic efficiency,  $\xi'(\text{NO})$ , of 0.005% (see SI testing model section). The most likely reason for the deviation is that the model predicts the concentration in the air volume up to a height of only 5 mm from the photocatalyst surface whereas the site measurement was obtained at a height of 2 m. Parameters controlled in the laboratory are mostly variable in the environment, i.e., humidity, light intensity (cloud cover), and other environmental parameters such as local airflow characteristics and competition for photocatalyst adsorption sites (e.g. from water, SOx and VOCs). All can be expected to influence measured NO concentrations, both  $C_i$  and  $C_d$ .



Nevertheless, it can be anticipated that these model outputs represent a source term data set which can be implemented in a fluid dynamics model to define the distribution of NO concentrations from the modelled 5 mm volume to more useful volumes of relevance to the public, i.e. up to 2–3 m.

The implications of this analyses underlines the significance of a high photonic efficiency. In the application of the source term model to the Copenhagen site, the effective photonic efficiency,  $\xi(\text{NO})$ , of 0.005% required in an empirical fitting of the measured data is 22% of the laboratory based value. Applying the same factor to the aggregate-supported photocatalyst QST-6-N (i.e. the free-standing composite), with a  $\xi(\text{NO})$  of 0.89%, would give a  $\xi(\text{NO})$ , of 0.2%, a 40 times improvement in NO removal efficiency. However, the diffusion rates of NO into this remediated volume balanced against the production rates (from vehicle emissions and other sources), as well as humidity and competition influences must also be considered in extending the model to more practical air volumes on site.

#### 4. Conclusions

In this study, various quartz-supported  $\text{TiO}_2$  composites were prepared by coating with  $\text{TiO}_2$  loadings varying from  $\text{TiO}_2/\text{SiO}_2$  ratios of 0.16–0.61%. In these, Ti–O–Si chemical linkages were confirmed and  $\text{TiO}_2$  was accumulated on the surface in multiple agglomerated layers. The Ti–O–Si/Si–O–Si linkage ratios, obtained from a quantitative treatment of FTIR spectra, remained constant despite the  $\text{TiO}_2$  loading, indicating that the bonded interface saturated the  $\text{SiO}_2$  surface. Durability assessments of the composites showed significant losses of  $\text{TiO}_2$  (almost half) at the highest loading levels, whereas composites with lower loadings were stable due to the strength and short range influence of the chemical Ti–O–Si binding.

Photocatalytic performance was also dependent on loading; activity increased with  $\text{TiO}_2$  content up to ca. 0.76% and nitrate selectivity increased across the loading range. This is strongly conditioned by the negative influence of the Ti–O–Si bond on selectivity and the effect of dilution as  $\text{TiO}_2$  loading is increased. However, after washing to remove weakly bonded  $\text{TiO}_2$ , photocatalytic activity ( $\xi(\text{NO})$ ) is only reduced by 30% even though almost half of the  $\text{TiO}_2$  has been lost (0.34% remaining) whereas selectivity is not significantly affected (Fig. 12).

The simulated cement environment has indicated an enhancement in nitrate selectivity. This may be associated with alkaline hydrolysis of the  $\text{TiO}_2$  surface and/or to influencing the availability of surface physio/chemisorbed water reported to be important in the photocatalytic oxidation of  $\text{NO}_2$  [35]. The deposition of  $\text{Ca}(\text{OH})_2$ , which also positively influences selectivity, may be important in attracting surface water.  $\text{CaCO}_3$  deposition is at the expense of  $\text{Ca}(\text{OH})_2$  and consequently, its positive effects are diluted.

A model is presented to illustrate the expected seasonal impact of the produced photocatalyst-support composites on near-surface air composition, based on their measured photonic efficiencies. The model is not yet suitable for predicting impacts on air quality but provides a basis for fluid dynamics modelling to provide more accurate predictions of concentration distribution arising from the balance between the remediated surface layer and  $\text{NO}_x$  production in the higher zones. Despite the early stage of development, the model clearly highlights the importance of maximising photonic efficiency. The significant increase in  $\xi(\text{NO})$  highlighted for the  $\text{TiO}_2$ -support composites compared with conventionally dispersed photocatalyst in cements is readily extrapolated to illustrate the impacts on near-surface remediation efficiencies.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.10.013>.

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