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Removal of black carbon using photocatalytic silicate-based coating: Laboratory and field studies

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ABSTRACT

This study investigates how two photocatalytic titanium dioxide (TiO_2) contents (1.6% and 2.5% by volume) in liquid silicates remove black carbon (BC) (8 and 24 $\mu g\,cm^{-2}$) on mortars to recover surface chromaticity (black to white color, L^*) and solar reflectance (*SR*). A new method linking non-intrusive measurements of L^* with *SR* is developed to rapidly diagnose soiling susceptibility and self-cleaning effectiveness of opaque building surfaces. The higher TiO_2 content of 2.5% restores soiled surfaces faster than the 1.6% TiO_2 in silicates by at least 20 h, although the latter can fully recover appearance from a lower BC loading (8 $\mu g\,cm^{-2}$). Tripled BC loading signifies the need and superior self-cleaning capability of the higher TiO_2 content. Laboratory studies characterize the temporal trend in organic bleaching and evidence its delay of BC degradation. A 3.5-year field study validates the applicability of the L^*-*SR* assessment and demonstrates the reduction of a total heat burden of >790 kWh m^{-2}, as well as removal BC-equivalent pollutants of 16 g m^{-2} by the photocatalytic coatings. Taking together pollutant deposition flux, TiO_2 content, solar insolation, appropriate references and sufficient monitoring duration, performance of photocatalytic building coatings can be evaluated for other locations with varied air quality and environmental conditions.

1. Introduction

Soiling of surfaces due to dark-colored deposits of particulate matter (PM), for example, can significantly degrade aesthetic appearance of buildings (Grossi et al., 2003; Newby et al., 1991). Soot, a type of dark PM, can strongly absorb incident light, decrease solar reflectance (*SR*), enhance heat load, and increase surface temperature of building envelope (Berdahl et al., 2002, 2008; Cheng et al., 2012; Dornelles et al., 2015; Kültür and Türkeri, 2012; Levinson et al., 2005). Systematic studies of appearance of Cathedral of St. John of Norwich and the Tower of London in England, United Kingdom, as well as discoloration of Taj Mahal have reported how soot, emitting from combustion, reduced the surface whiteness (L^*) (Bonazza et al., 2007; Bergin et al., 2015). A more recent study also showed that *SR* of a white acrylic elastomeric coating with ceramic microspheres decreased by more than 20% after exposure to the urban environment of São Paulo, Brazil, for 18 months (Dornelles et al., 2015). Considering the local annual solar insolation (1690 kWh m^{-2}, Surface meteorology and Solar Energy, 2017), the decreased *SR* can increase a heat burden on building surfaces by ~500 kWh m^{-2}. Such “aged *SR*” undermines the use of “cool” materials for reducing heat burden on building surfaces, and yet is little complemented by various labor intensive effort including wiping, rinsing, detergent washing and anti-algal cleaning (Akbari et al., 2005). Hence, maintaining *SR* for prolonged duration is of demand to retain desirable appearance and minimize heat load on opaque building envelopes.

Incorporating photocatalysts (such as photocatalytic titanium dioxide, TiO_2) in building coatings is emerging as a promising approach to enable surfaces with prolonged self-clean and well-maintained *SR*. Photocatalytic coatings, which advantageously maximize reactive surfaces, also resolve the issue of less-than-effective removal of pollutants on mortar containing TiO_2 mixed therein (Krishnan et al., 2013a; Pozo-Antonio and Dionísio, 2017). However, more systematic characterization is needed to ascertain their applicability. For example, impacts of photocatalytic TiO_2 coatings on lightfastness (or bleaching) based on changes in L^* and *SR* remain to be quantified although whitening of paints and fabrics caused by TiO_2 were qualitatively reported back in 1929 (Hashimoto et al., 2005; Diamanti et al., 2013; Khataee et al., 2016).

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Nomenclature

aed	aerodynamic equivalent diameter	PM	Particulate matter
BC	Black carbon	s/c	sand/cement ratio
BC_{equv}	Black carbon equivalent	SM	Self-maintenance
CO_2	Carbon dioxide	SO_2	Sulfur dioxide
$CO_{2\text{-}equv}$	Carbon dioxide equivalent	SPM	Spectrophotometer
EC	Elemental carbon	*SR*	Solar reflectance
NIR	Near infrared	SSR	Solar spectrum reflectometer
NO_x	Nitrogen oxides	TiO_2	Titanium dioxide
OC	Organic carbon	UV	Ultraviolet
PDI	Polydispersity index	Vis	Visible
		w/c	water/cement ratio

While photocatalytic building materials effectively remove gaseous pollutants (e.g. NO_x and SO_2), volatile organic compounds, and organic particulates (Ballari et al., 2010; Chen et al., 2011; Chen and Chu, 2011; Hunger et al., 2010; Krishnan et al., 2013b; Martinez et al., 2014; Shen et al., 2015; Spiesz et al., 2016), one of the unresolved questions is whether the material can remove stubborn particulate pollutants, such as soot or black carbon (BC). BC is ubiquitous in urban environment for they are typically in exhausts of incomplete combustion of fuels, for example, from on-road vehicles. BC is also reported as the second most important warming pollutant in the atmosphere after CO_2 with a total climate forcing effects of up to $+1.1$ W m^{-2} (Bond et al., 2013). Hence, removing BC using photocatalytic building envelopes can lower carbon footprints for urban environments.

Evaluating sustainable appearance of opaque building envelopes mainly relies on measurements of colorimetric black-white (or grey) scheme (L^*) and *SR*. Even though both L^* and *SR* change concurrently with compromised building envelopes, separate efforts have been given to measure either L^* for evaluating self-cleaning and de-pollutant capabilities (e.g. Guo et al., 2016; Smits et al., 2013, 2014), or *SR* for estimating heat burden on surfaces (e.g. Sleiman et al., 2011; Synnefa et al., 2007). If a method integrating both L^* and *SR* properties is available, all three self-maintenance (SM) capabilities of self-cleaning, de-pollutants, and heat-load reduction of building envelopes can be evaluated more efficiently by measuring one property alone. In fact, unlike the two SM functions of self-clean and heat-load reduction, which can be assessed based on L^* and *SR* measurements, evaluating de-pollutant capability is most challenging because of the infeasibility of quantifying airborne pollutants reduced by photocatalytic coatings in an open atmosphere. This restrains the de-pollutant capability as a conceptual contribution for actual applications.

To address the needs and intended applications mentioned above, this study establishes an approach to rapidly diagnose soiling susceptibility and self-clean effectiveness of opaque surfaces. In addition to investigating how photocatalyst contents in silicates affect recovery of surfaces soiled by BC, our laboratory studies elucidate removal processes of carbonaceous components through photocatalysis with corresponding changes in surface heat load and appearance. By linking accelerated laboratory findings with 3.5-year field monitoring, the established method and a proposed quantitative index are applied to approximate the heat burden reduced and pollutants removed by photocatalytic coatings under a warm and humid urban environment. Various details of new methods established in this study are provided in the Supplementary Material.

2. Material and methods

2.1. Materials, specimens, and coatings

Normal Portland cement and natural sand were used for mortar specimens with a water/cement ratio (w/c) of 0.5 and a sand/cement ratio (s/c) of 2.5 by mass. The sand was sieved and the fineness modulus of the sand was calculated as 2.96. Prism specimens with a dimension of 160 mm × 40 mm × 40 mm were cast and moist cured at 28–30 °C for 7 days followed by exposure to laboratory air for 21 days. Various properties of the specimens prepared for individual analyses are specified in Table 1.

One out of three evaluated commercial silicate coatings showed the best stability and homogeneity when mixed with TiO_2, and thus was employed to evaluate the efficiencies of photocatalytic degradation of BC in this work. Preliminary experiments indicated that the solid content of the silicate was 13.5%. According to the manufacturer, silicate shows a pH of approximately 11, and comprises potassium silicate, silica sol, and organic additives. A commercially available TiO_2 (Degussa P-25, EVONIK Industries AG, Germany) employed in this study comprises 80% anatase and 20% rutile with a primary size of 21 nm. The X-ray diffraction (XRD)

Table 1
Measurement and specimens studied.

Measurement	Instrument	Specimen material and surface dimension (mm)	No. of measurement
Color reading (L^*, b^*)	Spectrophotometer	Mortar 80 × 40	72[a]
Solar reflectance (*SR*)	Solar spectrum reflectometer	Mortar 80 × 40	9[b]
UV–Vis–NIR reflectance	UV–Vis–NIR spectrophotometer	Mortar 40 × 40	3[c]
Organic carbon (OC) and elemental carbon (EC) concentration	OC-EC thermal optical analyzer	Quartz slides 10 × 10	3[d]

[a] Two readings at each point, 12 points per specimen, and three specimens for individual nine types of surfaces.
[b] Three readings per specimen, three specimens for individual nine types of surfaces.
[c] Three readings per specimen, one specimen for individual nine types of surfaces.
[d] Three slides throughout each irradiation experiment.