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RESEARCH PAPER

Airborne reactive oxygen species (ROS) is associated with nano TiO_2 concentrations in aerosolized cement particles during simulated work activities

Kiattisak Batsungnoen · Michael Riediker · Nancy B. Hopf · Guillaume Suárez

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Abstract Photocatalytic cement is self-cleaning due to the addition of titanium dioxide (TiO_2) nanoparticles, which react with sunlight (UV) and produce reactive oxygen species (ROS). Construction workers using photocatalytic cement are exposed not only to cement particles that are irritants but also to nano TiO_2 and UV, both carcinogens, as well as the generated ROS. Quantifying ROS generated from added nano TiO_2 in photocatalytic cement is necessary to efficiently assess combined health risks. We designed and built an experimental setup to generate, under controlled environmental conditions (i.e., temperature, relative humidity, UV irradiance), both regular and photocatalytic cement aerosols. In addition, cement working activities—namely bag emptying and concrete cutting—were simulated in an exposure chamber while continuously measuring particle size distribution/concentration with a scanning mobility particle sizer (SMPS). ROS production was measured with a newly developed photonic sensing system based on a colorimetric assay. ROS production generated from the photocatalytic cement aerosol exposed to UV ($3.3{\cdot}10^{-9}$ nmol/pt) was significantly higher than for regular cement aerosol, either UV-exposed ($0.5{\cdot}10^{-9}$ nmol/pt) or not ($1.1{\cdot}10^{-9}$ nmol/pt). Quantitatively, the level of photocatalytic activity measured for nano TiO_2-containing cement aerosol was in good agreement with the one obtained with only nano TiO_2 aerosol at similar experimental conditions of temperature and relative humidity (around 60%). As a consequence, we recommend that exposure reduction strategies, in addition to cement particle exposures, also consider nano TiO_2 and in situ–generated ROS, in particular if the work is done in sunny environments.

Keywords Photocatalytic cement · Nano cement · Nano TiO_2 exposure · Reactive oxygen species (ROS) · ROS exposure · Health effects

K. Batsungnoen · N. B. Hopf · G. Suárez (✉)
Center for Primary Care and Public Health (Unisanté), University of Lausanne, Lausanne, Switzerland
e-mail: Guillaume.Suarez@unisante.ch
e-mail: Kiattisak.Batsungnoen@unisante.ch

K. Batsungnoen

K. Batsungnoen
e-mail: kiattisak@sut.ac.th

N. B. Hopf
e-mail: Nancy.Hopf@unisante.ch

K. Batsungnoen
Institute of Public Health, Suranaree University of Technology, Nakhon Ratchasima, Thailand

M. Riediker
Swiss Centre for Occupational and Environmental Health (SCOEH), Winterthur, Switzerland
e-mail: michael.riediker@alumni.ethz.ch

Introduction

Nanotechnology—the study of matter in nano range from 1 to 100 nm—is widely used to improve materials' properties especially strength, weight, and insulation. In the construction sector, photocatalytic cement has been introduced for its self-cleaning properties (Lan et al. 2013; Carp et al. 2004; Banerjee et al. 2015) related to the photocatalytic activity of titanium dioxide nanoparticles (nano TiO_2) (Hernández-Rodríguez et al. 2019; Feng et al. 2013; Folli et al. 2010). This cement is composed of regular cement made up of fine inorganic particles such as CaO, SiO_2, Fe_2O_3, and MgO (Meo 2004; Batsungnoen et al. 2019) and nano TiO_2.

It is well-known that inhalation of particulate matter (PM) is associated with pulmonary and cardiovascular diseases (e.g., COPD, asthma, lung cancer) (Risom et al. 2005; Aust et al. 2002; Schins et al. 2004; Ghio and Devlin 2001; Knaapen et al. 2004; Upadhyay et al. 2003; Upadhyay et al. 2003; Park et al. 2018). In addition, IARC has PM as a group 1 carcinogen (IARC 2017) and TiO_2 as possibly carcinogenic to humans (2B) (IARC 2015). Numerous studies have shown that nano TiO_2 is genotoxic and cytotoxic (NIOSH 2009; Sayes et al. 2006), especially for the lung bronchial epithelial cells (Sha et al. 2015; Lee et al. 2010) but can also translocate to other organs via the blood circulation (Wang et al. 2008; Kreyling et al. 2010; Geiser and Kreyling 2010; Shi et al. 2013).

Cell toxicity associated with nano TiO_2 exposure is related to reactive oxygen species (ROS) generation, which may lead to oxidative stress, lipid peroxidation, and nucleic acid alteration (Wang and Fan 2014; Shi et al. 2013; Panieri and Santoro 2016; Liou and Storz 2010). ROS such as hydroxyl radical, superoxide anion radical, hydrogen peroxide (H_2O_2), and singlet oxygen play a mechanistic role in many human diseases, including cancer (Waris and Ahsan 2006; Brieger et al. 2012), especially in the initiation and progression of multistage carcinogenesis (Waris and Ahsan 2006). Elevated ROS levels have also been associated with various inflammation-related human diseases (Alfadda and Sallam 2012).

ROS are also generated outside of the body, and has to be considered together with the endogenous ROS exposure generated through the metabolic response. Environmental ROS generation is especially relevant when airborne nano TiO_2 particulates are exposed to UV (Vernez et al. 2017). Due to its electronic energy band gap, nano TiO_2 behaves as a semi-conductor: UV-excited electrons ($\bar{e}$) reach the conductance band while a hole (h^+) forms at the valence energy level. The resulting $\bar{e}/h^+$ pair reacts with molecular oxygen (O_2) and water giving rise to a series of ROS formation. They react readily with organic materials (e.g., bacteria and mold), giving them a particularly efficient biocide property (Li et al. 2014; Lan et al. 2013; Li 2004; Chen and Poon 2009; Lee et al. 2010).

Photocatalytic cement exposure among outdoor construction workers may thus have direct exposures to ROS as secondary airborne toxicant (exogenous ROS) from UV activation of nano TiO_2. Concentrations of exogenous ROS have not yet been assessed for these workers; consequently, potential health risks associated to this exposure are currently unknown.

Airborne ROS can be quantified using a photonic detection device that was developed at our laboratory and which relies on the formation of a colorimetric complex (Fe (III)-orange xylenol) due to the oxidation of the probe solution containing reduced iron form (Fe (II)) by ROS (Laulagnet et al. 2015). The use of multiscattering absorbance enhancement (MAE) strategy as photonic core principle for the device enabled sensitive ROS determination (Suárez et al. 2013, 2014).

The main objective of the present study was to quantify amount of ROS generated from airborne cement and photocatalytic particles at constant relative humidity of about 60% under controlled conditions:

i) Laboratory aerosolization with photocatalytic and regular cements equipped with a UV lamp;
ii) Exposure chamber setup where two construction activities (cement bag emptying and concrete cutting) were simulated with both cement types separately.

Material and methods

Materials Photocatalytic cement was obtained from ESSROC (TX-Active®, Italcementi group, Nazareth, US), while regular cement defined as Portland cement CEM I (CE number 266–043-4) was purchased from Jura cement (Wildegg, Switzerland). The ROS-detection reagent—so-called FOX solution—was freshly prepared by mixing ammonium iron (Fe (II)) sulfate (260 μM), xylenol orange (130 μM), and D-sorbitol

(100 mM) into sulfuric acid (25 mM). The solution was kept in a fumed glass flask (100 mL). UV exposure was achieved using a solar light simulator (LS-1000 Solar Simulator Solar Light Co., Glenside, PA, USA). Jet-nebulizer system (1-jet Collison Mesa Labs, Butler, NJ; USA) was used to maintain controlled aerosol humidity to 60%. The Ecolog TH1 device enabled monitoring of both temperature and humidity during the aerosol generation (ELPRO-BUCHS AG, Buchs, Switzerland). System airflows were monitored using digital mass flow meters (Vögtlin Instruments AG, flow technology, Aesch BL, Switzerland). Concrete was made by mixing cement and water (2:1). Concrete cutting was operated with a circular saw (diameter 230 mm) and at maximum rated speed (6600 RPM) (PWS 20-230 J, BOSCH, Leinfelden-Echterdingen, Germany).

Methods

Generation of cement aerosols Airborne particles of both photocatalytic and regular cements were generated using an aerosolization system previously described by Ding and Riediker 2015, 2016. Two grams of cement were loaded into a glass funnel and dry air blown upwards through the funnel with 2 L/min. The experimental setup is shown in Fig. 1.

Control of environmental conditions The airborne particles produced in the funnel were transported directly into a mixing chamber by shear force and mixed with humid air originated from a nebulizer. The nebulizer flow rate was 1.5 L/min, which maintained the relative humidity at 60%. Downstream, the aerosol was driven into the exposure cylinder where they were exposed to UV radiation for 2.7 min (average residence time in the cylinder). The UV radiation light source was equipped with solar UV filters to reproduce the UV-A and UV-B spectrum. The lamp produced an irradiance intensity of 785 W/m^2 in the cylinder, corresponding to 12 folds the terrestrial irradiance. The airborne particles exiting the cylinder were captured in an impinger (25 mL) filled with FOX solution (5 mL). Temperature and relative humidity were monitored continuously during the run.

Working activities Two construction activities, cement bag emptying and concrete cutting, were simulated in an exposure chamber (10 m^3) with either photocatalytic or regular cement. Prior to the simulation activities, the ventilation system (80 m^3/h) was running for 2 h in order to reduce background particles, and during simulation, the ventilation system was off. The operator simulating the construction activity wore a respirator (N100, P3, or FFP3), a chemical suit, nitrile gloves, goggles, safety shoes, and hearing protection. The bag emptying activity was performed by turning an open cement bag (25 kg) upside-down, pouring it into a plastic container (diameter × height, 60 × 40 cm), and shaking until the cement bag was empty. The concrete cutting activity was performed by using a circular saw for 10 s cutting a prepared concrete block (size 25 × 36 × 6 cm). The aerosolized cement particles were sampled in the operator's breathing zone with an impinger (25 mL) containing FOX solution (5 mL) and operating at a flow rate of 0.5 L/min. Each experimental construction activity was repeated in triplicate by a single operator, as shown in Fig. 2.

ROS analysis ROS concentration—also defined as oxidative potential—was determined using a photonic system developed by our laboratory and based on multiscattering-enhanced absorbance strategy (Laulagnet et al. 2015; Vernez et al. 2017). In brief, air samples are bubbled through an impinger filled FOX solution (5 mL), which is the reaction medium. In the presence of ROS, the Fe (II) undergoes oxidized into Fe (III) that forms a complex with orange xylenol absorbing light at 580 nm. The color change is measured via the use of a narrow emission led (580 nm) coupled to a photodetector both driven through a microcontroller board (Arduino Uno) The multiscattering regime occurring in the photonic cell due to the combination of rough aluminum cavity and inner Teflon housing enables dramatic lengthening of the optical path and improved analytical sensitivity. The ROS sensor response was calibrated with H_2O_2 and ROS values expressed as H_2O_2 equivalents.

Particles measurements The size distribution and number concentration of airborne nanoparticles in the size range between 11 and 1083 nm were measured by a scanning mobility particle sizer (SMPS) (model SMPS+C model 5400, Grimm Aerosol Technik GmbH & Co. KG, Ainring, Germany). For morphology determination, the particles were collected onto Transmission Electron Microscopy (TEM) grids (Quantifoil R1/4, Quantifoil Micro Tools GmbH, Germany) using a mini particle sampler (MPS) (Ecomesure, Sacly, France)

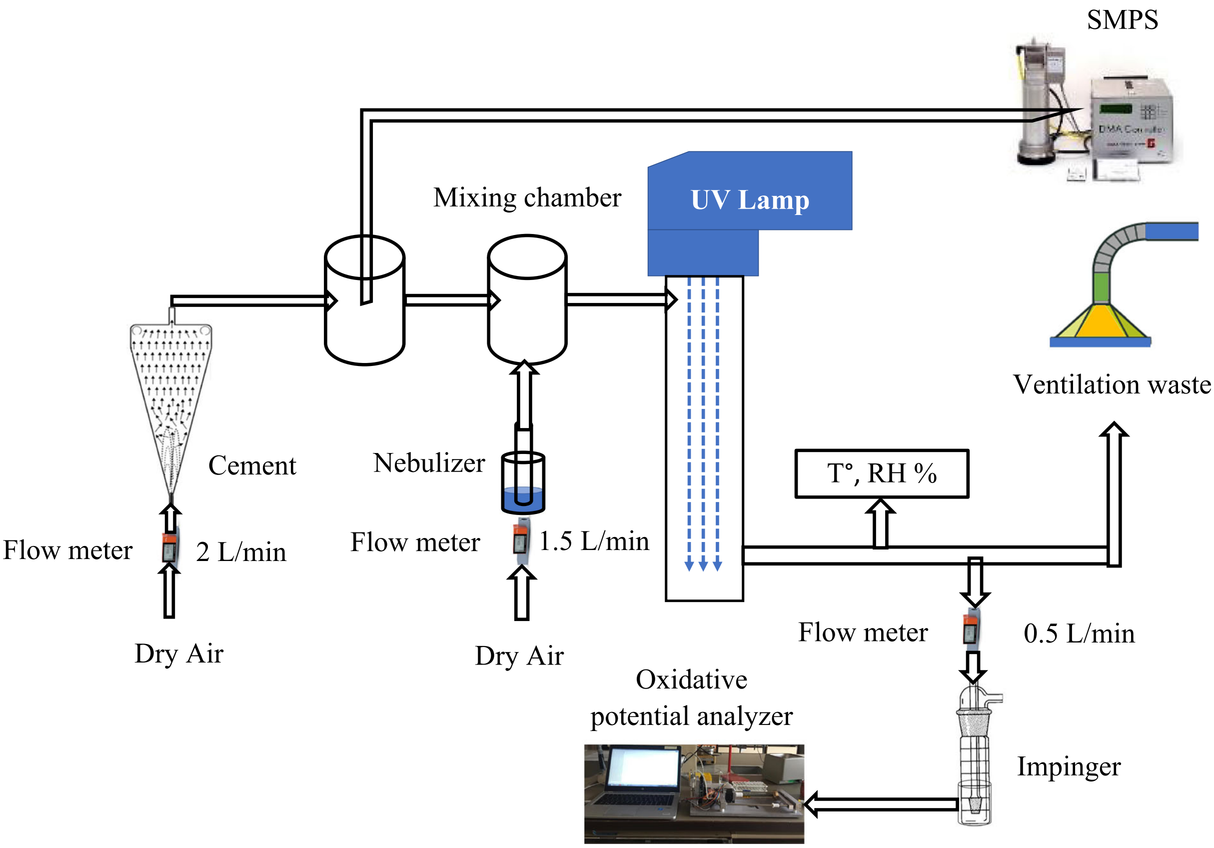

Fig. 1 Setup of cement powder experiment. Cement powder gets aerosolized in the glass funnel (2 L/min) by a gentile airstream (Ding and Riediker 2015, 2016). The main air stream was split into one leading to the SMPS for measuring particle number concentration (11–1083 nm), and a second driving the aerosol to the mixing chamber. The particles were mixed with humid air and transported into the UV-exposure cylinder (solar simulator lamp). Temperature and humidity were monitored after the air passed through the UV-cylinder. The airborne particles were captured in an impinger filled with FOX solution and the associated ROS production analyzed with the oxidative potential analyzer system (Laulagnet et al. 2015, Vernez et al. 2017)

operating at a sampling flow rate of 0.3 L/min. The TEM grids were transferred to a transmission electron microscope (TEM) (TEM CM-100 (JEOL, USA) at 80 kV).

Statistical analysis Means and standard deviations for nanoparticle size and distribution as well as ROS concentrations were compared by two-sample *t* test using STATA version 15.

Results

The ROS detection system developed by our group enabled us to quantify hydrogen peroxide (H_2O_2) and hydroxyl radicals ($OH^{\bullet}$). Quantitative determination of the aerosol reactivity expressed—once normalized by total particle number concentration—in nanomoles of H_2O_2 equivalents per particle (nmol/pt) was possible by combining accurate aerosol generation and sensitive ROS detection.

The average size distribution from aerosolized photocatalytic cement in the experimental setup was around $2{\cdot}10^5$ pt/cm^3, with a geometric mean diameter (GMD) of 285 nm and a geometric standard deviation (GSD) of 1.65 nm. Regular cement aerosol had a particle number concentration of $1{\cdot}10^5$ pt/cm^3 with GMD and GSD of 376 and 1.74 nm, respectively (Fig. 3a). The TEM images confirmed that photocatalytic cement aerosols contained agglomerates from pristine nanoparticles with primary size around 50 nm (Fig. 3b).

In complement, the aerosol ROS generation calculated in the present study indicates that the aerosolized

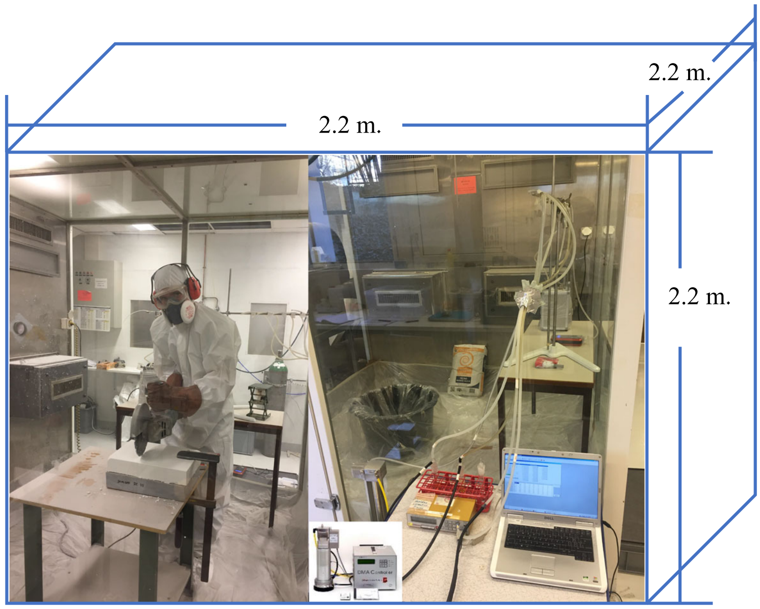

Fig. 2 Experimental setup to characterize work-generated particle emissions. Two activities, bag emptying and concrete cutting, were reproduced experimentally in the exposure cabin. Workers were wearing whole body protection with personal protective equipment (PPE): dust protection cloth, rubber gloves, goggles, safety shoes, ears muff, and respirator

photocatalytic cement exposed to UV irradiance ($3.3 \cdot 10^{-9}$ nmol/pt) is significantly more reactive in terms of produced H_2O_2 equivalents than regular cement exposed to UV ($0.5 \cdot 10^{-9}$ nmol/pt) or not ($1.1 \cdot 10^{-9}$ nmol/pt). ROS generation for non-UV-exposed cement aerosols were $1.6 \cdot 10^{-9}$ nmol/pt and $1.1 \cdot 10^{-9}$ nmol/pt for photocatalytic and regular cement, respectively (Table 1). In good agreement with a prior study (Vernez et al. 2017), the results herein obtained clearly indicate that the presence of nano TiO_2 in the photocatalytic cement do increase its chemical reactivity in terms of ROS generation prompt to act as secondary toxicants.

The effect of UV irradiance on nano TiO_2 is manifest in the fact that ROS generation from photocatalytic cement doubled in the presence of UV irradiance. As expected, ROS production from photocatalytic cement exposed to UV was significantly higher than regular cement with or without UV (Fig. 4). There was no significant difference in ROS generation between regular cement exposed and not to UV light.

Simulated construction work activities performed in exposure chamber to evaluate airborne ROS levels show that for bag emptying activity, the measured ROS production was significantly greater (p value = 0.04) for photocatalytic ($4.6 \cdot 10^{-10}$ nmol/pt) than for regular cement ($1.5 \cdot 10^{-10}$ nmol/pt) during bag emptying (Fig. 5). In the case of concrete cutting, no significant difference was observed between photocatalytic and regular cement, with ROS reactivities of $1.1 \cdot 10^{-10}$ and $1.1 \cdot 10^{-10}$ nmol/pt, respectively (Table 2).

Discussion

Airborne photocatalytic cement particles are a potential source of ROS that is further enhanced in the presence of UV irradiance, and is mainly attributed to the presence of nano TiO_2 on the airborne particles (Batsungnoen et al. 2019). The photo-induced mechanism that triggers the production of ROS—mainly in the form of H_2O_2—at the surface of TiO_2 is well-established (Kakinoki et al. 2004, Ghadiry et al. 2016) and has recently been demonstrated for nano TiO_2 airborne particles in our prior study (Vernez et al. 2017). The results obtained herein clearly indicate that the presence of nano TiO_2 in the photocatalytic cement increase its chemical reactivity in terms of ROS generation, which is in good agreement with this prior study (Vernez et al. 2017).

In the absence of UV irradiance, the ROS generation associated to photocatalytic cement aerosol is not significantly different than the one obtained with regular cement, exposed or not. However, the large interval observed in the ROS production by photocatalytic aerosol without UV exposure might be attributed to the activation of nano TiO_2 by visible light during experimental measurements (Etacheri et al. 2015). Consequently, indoor construction workers using photocatalytic cement under artificial light might have greater exposures to ROS compared with workers using regular cement, although to a far lesser extent than outdoor workers.

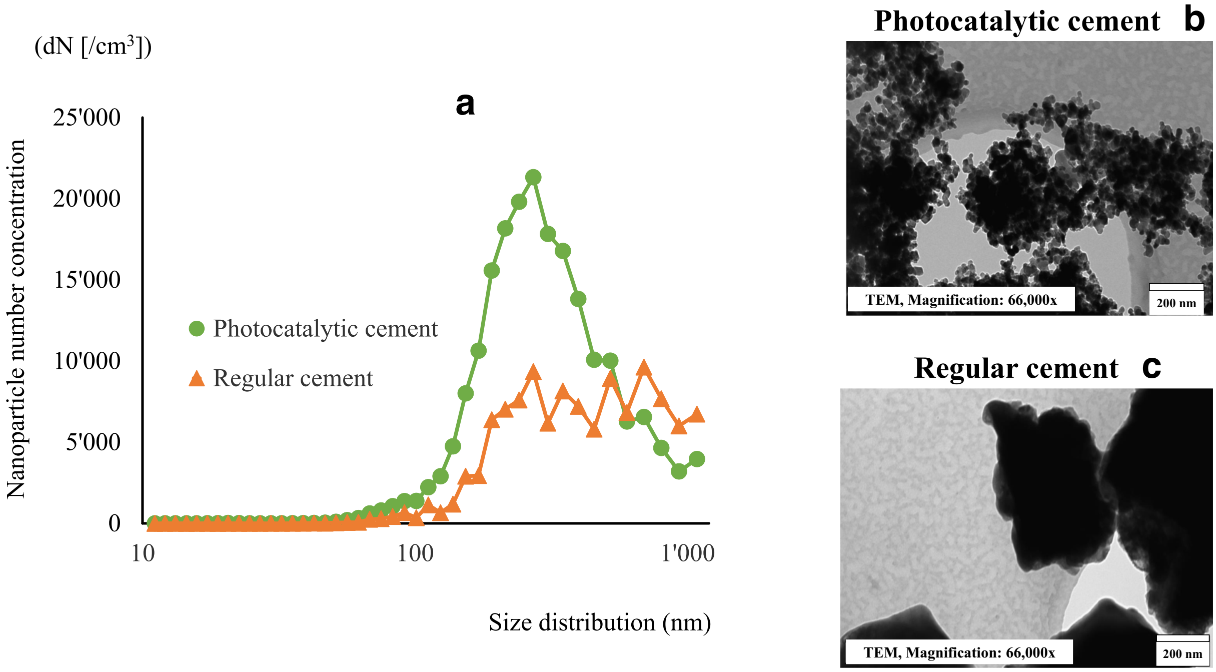

Fig. 3 (**a**) Airborne nanoparticle size distribution expressed in number concentration (dN (/cm3)) obtained by SMPS for photocatalytic cement (solid circles) and regular cement (solid triangles) in the range size between 11 and 1083 nm. TEM images of (**b**) photocatalytic cement and (**c**) regular cement; (magnification, × 66,000)

The low reactivity observed with regular cement particles could potentially be originated from redox reactions in which transition metal in its composition—namely iron oxide (2% Fe_2O_3)—are prone to take part (Batsungnoen et al. 2019). While many studies have demonstrated the ability of iron oxides particles—such as Fe_2O_3 and to a greater extent Fe_3O_4—to activate H_2O_2 into highly reactive hydroxyl radical via their so-called peroxidase-like behavior (Gao et al. 2017; Pham et al. 2012), to our knowledge, the contribution of iron oxide in the generation of exogenous ROS by Portland cement particles was not yet reported.

In the case of work activities, the ROS production observed during bag emptying with photocatalytic cement was three-fold greater than the one measured with regular cement. Again, even in the absence of UV irradiance, this photocatalytic activity may be attributed to the visible light energy present in the experimental setup, though nano-TiO_2 can produce ROS also under dark conditions (Kakinoki et al. 2004). More

Table 1 ROS concentration originated from airborne aerosols of photocatalytic and regular cement, with and without UV irradiance

	ROS concentration (nmol/pt)	TiO_2 content (wt%)*	Avg. particle concentration (pt/cm^3)	Distribution interval (nm)
Photocatalytic cement exposed UV	$3.34{\cdot}10^{-9}$ (SD = $1.32{\cdot}10^{-9}$)	37.35	214,482	100–930
Photocatalytic cement non-exposed UV	$1.58{\cdot}10^{-9}$ (SD = $0.11{\cdot}10^{-9}$)	37.35	182,996	100–930
Average particle concentration (pt/cm^3)			198,739	
Regular cement exposed UV	$0.51{\cdot}10^{-9}$ (SD = $0.20{\cdot}10^{-9}$)	0.16	139,132	550–1000**
Regular cement non-exposed UV	$1.12{\cdot}10^{-9}$ (SD = $0.54{\cdot}10^{-9}$)	0.16	76,616	550–1000**
Average particle concentration (pt/cm^3)			107,874	

*From Batsungnoen et al. 2019

**Top range detection limit for SMPS measurements

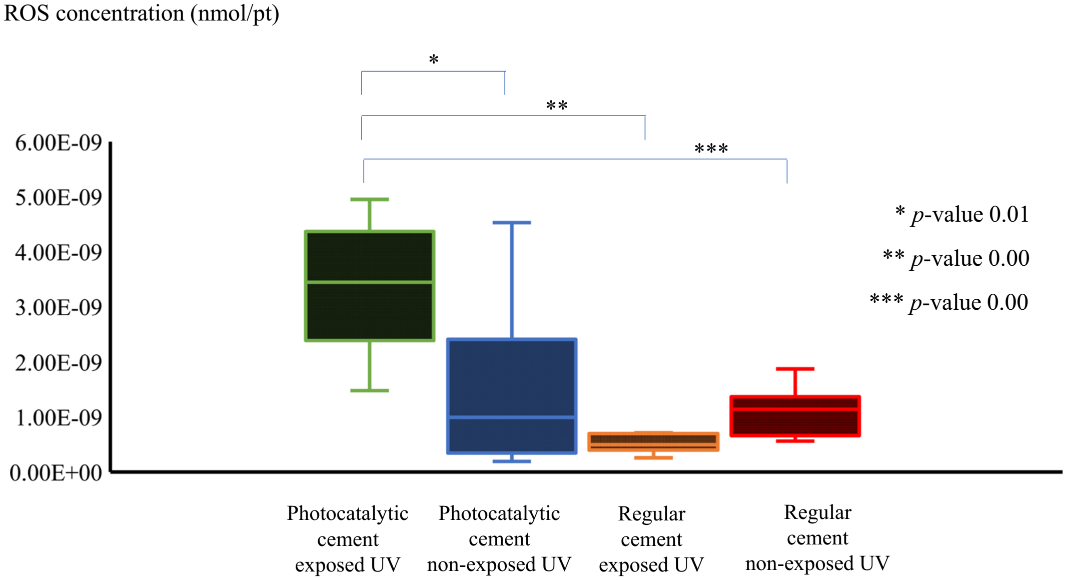

Fig. 4 Box plot showing the normalized ROS production (nmol/pt) originated from photocatalytic and regular cement airborne particles

interestingly, one can notice that in the case of concrete cutting no significant difference is shown between photocatalytic and regular concretes, while in parallel, the corresponding TiO_2 contents in the generated aerosols are relatively low (max. 2%) as shown in Table 2. The different TiO_2 content observed depending on the work activity is explained by the fact that bag emptying process favors the smaller size fraction to remain airborne (16.5% of TiO_2 detected airborne), while the larger cement powder particles will sediment rapidly. In contrast, aerosols created from cement concrete cutting roughly reflects the initial composition of the initial cement powder in the bag (2.0% nano TiO_2) because the TiO_2 has become part of the cement matrix and is no longer present as individual nano TiO_2 particles. It is worthily to notice that the ROS concentration measured during bag emptying using photocatalytic cement was in the same order of magnitude than the value obtained in

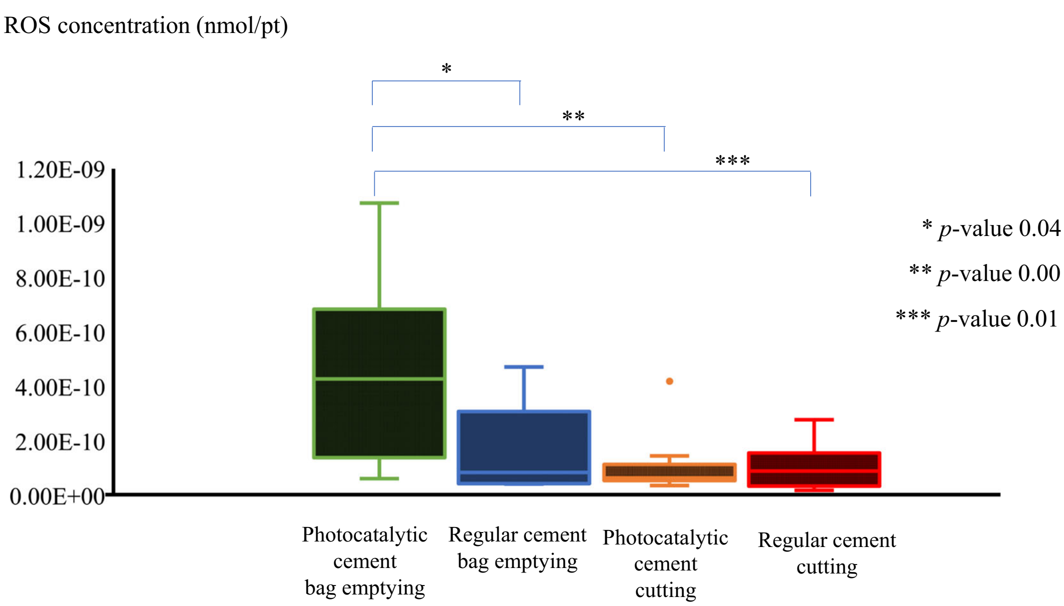

Fig. 5 The ROS production from cement bag emptying and concrete cutting

Table 2 ROS concentration originated from aerosols generated during cement bag emptying and concrete cutting activities

	ROS concentration (nmol/pt)	TiO_2 content (wt%)	Avg. particle concentration (pt/cm^3)	Distribution interval (nm)
Photocatalytic cement bag emptying	$4.60 \cdot 10^{-10}$ (SD = $3.47 \cdot 10^{-10}$)	16.46	3715	240–1000*
Regular cement bag emptying	$1.58 \cdot 10^{-10}$ (SD = $1.81 \cdot 10^{-10}$)	0.19	3662	240–1000*
Photocatalytic concrete cutting	$1.10 \cdot 10^{-10}$ (SD = $1.09 \cdot 10^{-10}$)	2.03	10,549	150–1000*
Regular concrete cutting	$1.12 \cdot 10^{-10}$ (SD = $1.01 \cdot 10^{-8}$)	0.10	19,143	150–1000*

*Top range detection limit for SMPS measurements

prior work with pure nano TiO_2 once normalized by TiO_2 content (Vernez et al. 2017).

Finally, health effects related to airborne nano TiO_2 exposure in photocatalytic cement should integrate its reactivity—in the presence of environmental UV/vis irradiance—by considering the associated ROS products as secondary airborne toxicants. In terms of toxic effects, ROS are associated to various metabolic/pathological paths such as oxidative stress, inflammation, genotoxicity, cytotoxicity, DNA damage, and cancer (Li et al. 2014; Brieger et al. 2012; Scherz-Shouval and Elazar 2011; Jaeger et al. 2012; Yin et al. 2012; Jaeger et al. 2012; Wang and Fan 2014).

Conclusion

The combination of an efficient aerosol generation setup coupled with a solar simulation lamp and a sensitive photonic detection device made it possible to assess the production of ROS by photocatalytic and regular cement aerosols. As expected, the presence of nano TiO_2 in photocatalytic cement has a strong impact on the ability of the corresponding aerosol to produce exogenous airborne ROS in the presence of UV light. Moreover, the level of ROS generated during work activities was found to be linked to the amount of airborne nano TiO_2 present in the cement aerosol. Thus, concrete cutting activities appear to be considerably less problematic in terms of ROS production than bag emptying for which the nano TiO_2 content in the aerosol reaches 16%. Considering the photoreactivity of aerosolized photocatalytic cement under UV irradiance and the high content of airborne nano TiO_2 generated during bag emptying, worker protection procedures should not only consider nano TiO_2 exposure but also its ability to produce ROS as secondary airborne potential toxicants. Providing the specific reactivity of its aerosol under environmental conditions, photocatalytic cement should not only be considered a novel promising material but also a potential new hazard in construction sites.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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