



# Photocatalytic cement exposed to nitrogen oxides: Effect of oxidation and binding



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## ABSTRACT

The photocatalytic oxidation and binding capacity of cement containing titanium dioxide nanoparticles under nitric oxide and nitrogen dioxide gas exposures were examined experimentally both in the presence and absence of ultraviolet (UV) light, to examine independently the contributions of photocatalysis and potential additional mechanisms for binding of nitrogen oxides (NOx) inherent in cement-based materials. The overall, photocatalytic efficiency was similar for both gas exposures, with faster initial rates of initial NO binding for higher water-to-cement ratio pastes, due to higher surface area. In the absence of UV light, greater binding of NO<sub>2</sub> gas was found compared to NO gas, perhaps due to the greater polarity of the NO<sub>2</sub> molecule, although further examination of this phenomenon is warranted. Overall, these experiments show not only the fact that cementitious materials can be tailored to decrease NOx levels through photocatalysis but also the fact that Portland cements possess the inherent ability to bind NOx, and in particular NO<sub>2</sub>.

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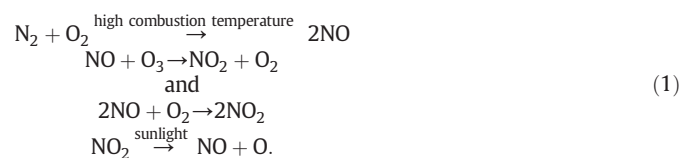
## 1. Introduction

Although the adverse effects of atmospheric nitrogen oxides (or “NOx”) on human and environmental health are well-known [1], NO<sub>2</sub> levels in many large cities exceed the World Health Organization (WHO) guideline of 40 µg/m<sup>3</sup> (0.021 ppm) for air quality [1]. One proposed way of reducing the NOx concentration in the atmosphere is the use of photocatalytic titanium dioxide (TiO<sub>2</sub>) in construction materials near mobile sources (e.g., photocatalytic concrete roads) [2–6]. Nano-anatase titanium dioxide (TiO<sub>2</sub>) is perhaps the most well-known photocatalytic semiconductor and one which possesses a strong oxidizing capability. A review of the mechanisms of photocatalytic oxidation can be found in [7,8]. Generally, the photocatalytic oxidation reactions occur in the presence of water, oxygen, and under UV and near-UV light [9] which enable nano-TiO<sub>2</sub> to oxidize or decompose NOx, as well as organic and inorganic compounds [7,9]. Thus, the applications of nano-anatase TiO<sub>2</sub> include self-cleaning, air and water purification, self-sterilizing, and anti-fogging surfaces [4].

Here, the effect of nano-TiO<sub>2</sub>-containing cementitious materials on oxidation and binding of nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>)

gases is examined, with and without photocatalysis. To assess photocatalytic efficiency, tests such as the ISO standard [10] and JIS standard [11] have been established for advanced ceramics, where a photocatalyst is added by coating, impregnation, and mixing. However, both of these standards utilize only NO gas in their experimental procedures. As a result, significantly more research effort has been put toward measurements of NO gas oxidation than NO<sub>2</sub> gas oxidation by photocatalysis. Since NO gas being emitted by combustion sources is typically converted to NO<sub>2</sub> gas relatively quickly (i.e. within hours) it is important to also determine the extent to which NO<sub>2</sub> is oxidized by photocatalytic surfaces.

Yet, NO<sub>2</sub> gas is – like NO – a major air pollutant that threatens human health and also participates in the formation of photochemical smog and ozone (O<sub>3</sub>) [1], ultimately contributing to climate change. During high-temperature combustion (e.g., power generation, engine combustion in vehicles), nitrogen and oxygen combine to produce NO, which then readily transforms into NO<sub>2</sub> through reaction with ozone and/or oxygen. The NO<sub>2</sub> is then photolyzed by sunlight to reform NO:



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As a result, NO and NO<sub>2</sub> coexist in equilibrium in the atmosphere. While the NO/NO<sub>2</sub> ratio is determined by the intensity of solar radiation and the concentration of ozone, it has been reported that the annual average on-road NO<sub>2</sub>/NO<sub>x</sub> ratio was 28% [12], meaning that the more harmful NO<sub>2</sub> gas [1] is as much as 39% of the NO gas overall. The NO<sub>2</sub>/NO<sub>x</sub> ratio tends to increase with increasing distance from the emitting source, and that most NO<sub>x</sub> in the lower troposphere over the US is in fact NO<sub>2</sub> and not NO. The atmospheric NO<sub>2</sub> concentrations are commonly monitored, because of its contributions to ground level ozone formation and fine particulate formation and its adverse effects on the human respiratory systems and because its concentration is viewed as an indicator of overall NO<sub>x</sub> [13]. Taking into consideration the severe implications of NO<sub>2</sub> gas, its quantity fraction in the atmosphere, and its significance to ambient air quality standards, there is a need to investigate the photocatalytic behavior of cementitious materials under NO<sub>2</sub> as well as NO exposure.

In addition to the relative dearth of information regarding the photocatalytic efficiency of cementitious materials under NO<sub>2</sub> exposure, some preliminary work has suggested that NO<sub>2</sub> can be bound into cementitious materials without the benefit of photocatalysis. For example, Cassar [14] observed a decrease in NO<sub>x</sub> concentration during exposure to cement paste without a photocatalyst, suggesting that the decrease may be due to NO<sub>x</sub> adsorption by the hydroxides present in the cement matrix. Vallee et al. [15] performed de-polluting experiments exposing photocatalytic surfaces to NO<sub>2</sub> gas, and mentioned the possibility that NO<sub>2</sub> can be adsorbed into cementitious materials in the absence of UV-radiation that is later oxidized in the day time. Yoshio et al. [16] also tested TiO<sub>2</sub>-coated cement on NO<sub>x</sub> removal, noting that NO<sub>2</sub> gas can be adsorbed on the porous surface structure of cement. However, not much effort has been made in the published literature to either quantify and compare NO<sub>x</sub> binding capacity to photocatalysis or examine the NO<sub>x</sub> binding mechanism of cementitious materials in the absence of UV light, or photocatalysis.

The potential of cementitious materials to decrease the amount of the NO<sub>2</sub> in the atmosphere is potentially important for a comprehensive assessment of the potential environmental impact of cement-based infrastructure. For example, NO<sub>x</sub> binding in the cementitious structure in the absence of photocatalysis (i.e., in the absence of UV-radiation) could potentially facilitate subsequent photocatalytic reaction by providing nitrogen oxides near the TiO<sub>2</sub> particles. Thus, a detailed examination of NO<sub>x</sub> binding – including examination of NO and NO<sub>2</sub> binding – in cementitious systems is warranted.

The objectives of this research are to examine and compare the photocatalytic efficiency and NO<sub>x</sub> binding capacity of TiO<sub>2</sub>-containing cement-based materials under both NO and NO<sub>2</sub> gases. Additional studies are also conducted in the absence of photocatalysis, with both NO and NO<sub>2</sub> gases. The effect of different water-to-cement ratios (w/c) of the cementitious materials on the photocatalytic efficiency is also studied.

## 2. Materials and experimental procedure

Hardened cement pastes at varying w/c and containing varying amounts of photocatalytic TiO<sub>2</sub> nanoparticles were prepared. Tests were performed to assess photocatalytic binding of NO and NO<sub>2</sub>, with UV-radiation (i.e., “photocatalysis series”). Additional tests were performed to examine the potential for NO and NO<sub>2</sub> binding in the absence of UV-radiation (i.e., “NO<sub>x</sub> binding series”).

### 2.1. Materials

The cement used was ASTM C 150 Type I Portland cement with potential Bogue composition of 54% C<sub>3</sub>S, 18% C<sub>2</sub>S, 7% C<sub>3</sub>A, and 10% C<sub>4</sub>AF. (The cement chemistry notations of these oxides are defined as C = CaO, S = SiO<sub>2</sub>, F = Fe<sub>2</sub>O<sub>3</sub>, and A = Al<sub>2</sub>O<sub>3</sub>.) The TiO<sub>2</sub> used was selected as one more commonly used in the concrete industry (Aeroxide TiO<sub>2</sub> P25, Evonik Industries), which consisted of 80% anatase and 20% rutile

titania. The average crystal size is 21 nm, the surface area is 50 ± 15 m<sup>2</sup>/g, and the sample purity is 99.5%, as stated by the manufacturer. The average agglomerate size was found to be 0.58 μm. NO and NO<sub>2</sub> gases were obtained at 100 ppm each and were mixed with ultra pure zero air (~80% nitrogen and ~20% oxygen) to reach the desired concentration.

### 2.2. Sample preparation

Two series of cement paste samples were prepared. For the photocatalysis series, pastes were prepared at water-to-cement ratios (w/c) of 0.40, 0.50, and 0.60, all with 5% TiO<sub>2</sub> replacement by mass of cement. For the NO<sub>x</sub>-binding series, samples were prepared with a consistent composition at w/c of 0.60 with 10% TiO<sub>2</sub> replacement by mass of cement.

To prepare the samples, the TiO<sub>2</sub> particles were mixed with deionized water for 1 min using a hand-held mixer at a low speed. Cement was then added to the TiO<sub>2</sub> slurry and mixed for 1 additional minute at a low speed and another 1 min at a medium speed. Samples were cast in plastic molds with dimension of 4.8 cm × 4.8 cm × 0.8 cm. They were allowed to cure in 100% relative humidity and at 23 ± 2 °C for the initial 24 h, and continued to be cured in lime water at 23 ± 2 °C for complete hydration after demolding. For the photocatalysis series, samples were cured for at least 28 days, a period sufficient to minimize any potential effects of hydration on subsequent moist exposures. After curing, they were progressively polished to 15 μm using 600 grit wet sandpaper to ensure uniform surface roughness. Finally, samples were conditioned in a 30 °C oven until the mass change within a 24 hour time period was less than 0.5%.

For the NO<sub>x</sub> binding series, samples were prepared and cured in the same manner, except they were cured for 28 days of age and polished up to 5 μm, and dried for 3 days. In order to investigate the influence of moisture state on binding and to better understand the binding mechanisms, NO<sub>x</sub> binding series samples were conditioned to be either ‘wet’ or ‘dry’ during NO or NO<sub>2</sub> exposure. Wet samples were fully immersed in deionized water for 3 h under vacuum, and kept wet in plastic bags until tested. Saturation was confirmed by breaking a control sample and visually examining the broken surface. Dry samples were conditioned in 40 °C oven until mass change was less than 0.1% within 24 h.

### 2.3. Methodology

Both series of tests utilized a UV reactor, shown with the UV light on in Fig. 1 and schematically in Fig. 2, that largely conforms to the ISO and JIS standards [10,11] for measurements of removal of nitric oxide gas during photocatalysis. The inner width of the reactor was manufactured to be 8 cm compared to the standard 5 cm to accommodate larger

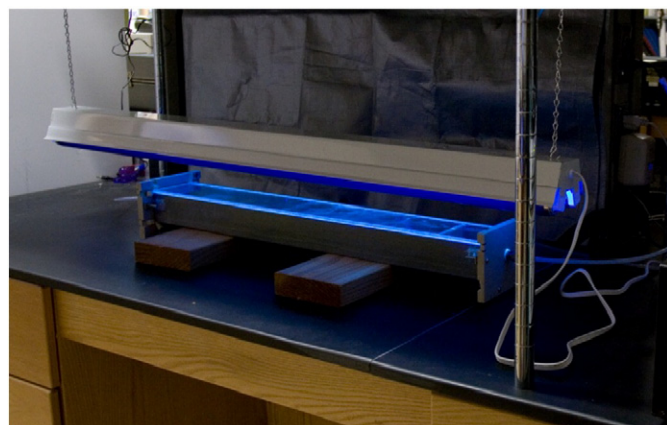


Fig. 1. NO<sub>x</sub> reactor with UV light on.

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