NO\textsubscript{x} sequestration by calcium aluminate cementitious materials

Qingxu Jin\textsuperscript{a}, Sarah L. Hordern\textsuperscript{a,b}, Yuanzhi Tang\textsuperscript{a,c}, Kimberly E. Kurtis\textsuperscript{a,*}

\textsuperscript{a} School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA
\textsuperscript{b} Department of Civil, Architectural and Environmental Engineering, Austin, The University of Texas at Austin, Austin, TX 78712, USA
\textsuperscript{c} School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332, USA

\textbf{A R T I C L E   I N F O}

Keywords:
Calcium aluminate cement
TiO\textsubscript{2} photocatalysts
NO\textsubscript{x} sequestration
Nitrite/nitrate binding
Surface area

\textbf{A B S T R A C T}

This study quantifies NO\textsubscript{x} uptake efficiency and explores NO\textsubscript{x} binding mechanisms in calcium aluminate cementitious (CAC) materials. Comparison between unmodified and TiO\textsubscript{2}-modified CAC separates intrinsic NO\textsubscript{x} binding mechanisms from those related to photocatalysis. Attributed to surface-related heterogeneous reactions, the NO\textsubscript{x} binding occurs in unmodified CAC at nitrite-to-nitrate ratio of 1:1.3 and can be increased with surface area. The photocatalytic reactions in TiO\textsubscript{2}-modified CAC increase NO\textsubscript{x} uptake, and ~50% of converted NO\textsubscript{x} resists releasing back into the environment via dissolution. Compared to previously studied ordinary portland cement (OPC) materials, CAC increases NO\textsubscript{x} uptake capacity and demonstrates a more permanent NO\textsubscript{x} binding, potentially mitigating concerns related to the release of previously bound N-species in OPC. Examination of the interaction between NO\textsubscript{x} and a synthetic pure aluminum-bearing phase shows that the permanent NO\textsubscript{x} uptake in CAC could be largely attributed to the chemical binding of converted NO\textsubscript{x} within aluminum-bearing phases.

\section{1. Introduction}

Nitrogen oxides (NO\textsubscript{x}) are hazardous and highly reactive air pollutants, causing a wide variety of health and environmental problems such as impairment of the human respiratory and visual systems and the formation of tropospheric ozone and urban smog [1]. Although efforts have been made to reduce concentrations of NO\textsubscript{x} in the atmospheric environment, urban NO\textsubscript{x} levels are still increasing due to lack of air flow, increasing use of cars with small combustion engines, and increased industrial zones [2]. As a promising pathway for sequestering atmospheric NO\textsubscript{x}, titanium dioxide (TiO\textsubscript{2}) photocatalysts have been proposed to be used in combination with cement-based materials [3]. In the presence of water, oxygen, and ultraviolet (UV) light, TiO\textsubscript{2} can effectively convert atmospheric NO\textsubscript{x} into nitrite (NO\textsubscript{2}) and nitrate (NO\textsubscript{3}) [4,5], which can be bound within the complex structure of cementitious materials [6,7].

TiO\textsubscript{2}-modified cementitious materials have been used in both exterior and interior applications, such as building facades, exterior tiles, roofs, concrete pavements, tunnels, and interior walls [8]. The global market for photocatalysts has increased exponentially in recent decades, was worth 2.1 billion U.S. dollars in 2017, and is expected to increase to 5.3 billion U.S. dollars by 2025 [9]. One third of this photocatalytic market is attributed to applications of air purification [9]. In Japan, the sale of photocatalytic cementitious materials accounts for more than 60% of their total photocatalytic market [10].

The large potential of TiO\textsubscript{2}-modified cementitious materials has prompted extensive study, including the design of various TiO\textsubscript{2} photocatalysts [11–13], as well as the exploration of the fundamentals of photocatalytic reactions [8,14,15] and the surface and microstructural features that affect the photocatalytic efficiency of NO\textsubscript{x} sequestration [6,7]. Recently, studies have quantified the photocatalytic efficiency in OPC-based cementitious materials, with measurements of NO\textsubscript{2} and NO\textsubscript{3} produced by photocatalysis on the surfaces and the efficiency with which those ions are bound within the cementitious material as a function of the material’s microstructural features [6]. Three types of binding in OPC-based materials have been theorized – I) the adsorption of NO\textsubscript{2} and NO\textsubscript{3} on the surface of cement hydrates such as C-S-H [6,8,16], II) the reaction of these ions with hydroxyls in materials’ alkaline environment [17,18], and III) substitution of these ions into aluminum-bearing hydrates (e.g., AFm) through anion substitution process [19,20]. Moreover, studies have shown when N-substituted phases interact with ingressing Cl\textsuperscript{−} ions, ion exchange reactions can occur, releasing nitrate and nitrate ions into the pore solution [21,22]. The release of nitrate and nitrite into the pore solution can enhance

\begin{itemize}
  \item \textsuperscript{a} Corresponding author.
  \item E-mail address: kkurtis@gatech.edu (K.E. Kurtis).
  \item Standard cement chemistry abbreviations are used in this paper: C=CaO, S=SiO\textsubscript{2}, A=Al\textsubscript{2}O\textsubscript{3}, and H=H\textsubscript{2}O.
\end{itemize}

\texttt{https://doi.org/10.1016/j.cemconres.2021.106381}
Received 29 September 2020; Received in revised form 7 January 2021; Accepted 24 January 2021
Available online 9 February 2021
0008-8846/© 2021 Elsevier Ltd. All rights reserved.
corrosion resistance, relying on chemical interactions at the steel/concrete interface currently associated with nitrate- and/or nitrite-containing corrosion-inhibiting admixtures [23,24].

While Portland cement is, by far, the most widely used cement, it may not be the most advantageous substrate cement for applications intended to bind NOx. One of the major drawbacks is that the binding of photocatalytically converted NO2 and NO3 to OPC substrates is imperfect [6,7]. For example, NO2 and NO3 held within the OPC structure can be extracted by water [6,7]; such leaching can affect groundwater, aquatic and forest systems, and agriculture [25]. In addition, certain amounts of NO2, which are produced in the photocatalytic process (HNO2 + OH− → NO2 + H2O), can be released back into the atmosphere [26,27]. Acid formation during the photocatalytic reactions (NO + OH· → NO2 + H+ and NO2 + OH· → NO3 + H+) is considered another drawback since decomposition of hydrated cement phases, such as C-S-H [28], can compromise surface integrity, strength, and overall durability [29]. These concerns suggest that the binding of NOx within OPC could be transient and even potentially damaging to the substrate and cement-based composite performance.

Therefore, alternative cementitious systems with greater NOx binding capacity, more permanent NOx binding capacity and greater durability through interactions with NOx, particularly to acids that could be formed, should be explored. Calcium aluminates cements (CACs) have been considered a potential candidate [21,22,30] since they are widely available and possess enhanced acid resistance compared to OPC [31,32], which could potentially offer an advantage in case that nitric acid is formed during photocatalytic reactions [29]. The primary component in CAC is monocalcium aluminate (CA), and their hydration products are aluminum-bearing phases. Prior studies on OPC [19,20] and aluminum-rich geopolymers [23,24] have shown the importance of aluminum-bearing phases in chemically binding NO2 and NO3 in those materials. A previous study has demonstrated the photocatalytic NOx binding by TiO2-modified CAC [30]. However, the binding mechanism in CAC materials has not been explored and the inherent NOx sequestration capacity in CAC materials has not been previously quantified.

Going beyond preliminary ‘proof-of-concept’ demonstration of NOx capture by TiO2-modified CAC materials, this study aims to quantify photocatalytic efficiency and to bring new understanding of binding capacity and mechanisms by combining standardized NOx degradation experiments on CAC pastes with photocatalysts, characterization of the substrate materials, and targeted examination of a key aluminum-bearing phase. Long-term efficiency in ordinary (unmodified) and TiO2-modified CAC is examined by performing multiple UV-light ‘on-off’ cycles to replicate diurnal exposure conditions. The effects of TiO2 nanoparticles on the CAC composites, including microstructural properties and TiO2 dispersion are analyzed using N2 adsorption and desorption isotherms, scanning electron microscopy (SEM), and X-ray diffraction (XRD). To quantitatively assess the NOx binding mechanisms in CAC materials, a combination of wet chemical extraction, UV-visible spectrophotometry, and ion chromatography is employed. The NOx uptake capacities of both unmodified and TiO2-modified CAC are quantified and the results are compared with our previously examined OPC-based cementitious materials [30]. In addition, to examine the interaction of NOx with aluminum-bearing phase, studies are performed on an AFm (Al2O3-2FeO3-2Al2O3-monophase) phase, which provides a better understanding on the mechanisms of NOx binding in aluminum-rich cementitious materials.

2. Materials and methods

2.1. Materials

Pastes were prepared from calcium aluminates cement (CAC) (Kernen, Chesapeake, VA, USA) and deionized water (18.2 MΩ·cm) with 0% (control) and 5% (by mass) cement replacement with photocatalytically TiO2 nanoparticles (KRONOClean® 7050, Kronos Worldwide, Dallas, TX, USA). The water-to-solid ratio was kept at 0.40 by mass. The chemical compositions of the CAC and TiO2 photocatalyst, obtained by X-ray fluorescence (XRF) spectrometry, are given in Tables 1 and 2, respectively. Other characteristics of the TiO2 photocatalyst provided by the manufacturer are also provided in Table 2. The photocatalytic performance of TiO2 nanoparticles is optimized under UV irradiance of 10 W m−2.

Two types of samples were prepared for control and 5% TiO2-modified CAC – plate and granular samples – for different purposes and characterization tests. The plate samples were prepared based on ISO 22197 [33] and JIS R 1701 Standards [34] and used to study the NOx degradation of TiO2-modified CAC. TiO2 photocatalysts were first added to deionized water, and the suspension was mixed for 1 min using a handheld electric mixer to facilitate particle dispersion. Cement was then added to the TiO2 suspension and mixed for 2 min. Plate samples of 50 × 50 × 10 mm3 (width × length × height) were cast in polyethylene plastic molds and stored at 23 ± 2 °C under polyethylene sheeting. After 24 h, the plates were removed from the molds and subsequently cured in laminar in a sealed container at 23 ± 2 °C for 28 days. After curing, samples were stored in double sealed plastic bags prior to characterization tests to avoid carbonation or drying.

The preparation of granular samples was adopted from ref [6]. The use of granular samples not only facilitates the examination of the binding mechanism(s) and NOx uptake capacity of CAC samples compared to the greater surface area for reaction, but also allows for direct comparison with OPC-based samples that were prepared and tested in the same manner [6]. The samples were produced by hand-crushing one of the plate samples and sieved to particle sizes of 0.6–1 mm. Granular samples were stored in the same manner as plate samples before characterizations.

To demonstrate the interaction of NOx with aluminum-bearing phase, AFm-SO4 (Al2O3-Fe2O3-2Al2O3-monosulfate) was synthesized according to the protocol developed by Matschei [35]. This phase was selected because it is structurally similar to C2AH8 phase, which is one major phase in hydrated CAC [36]. Also, it can be produced reliably in the laboratory and remains relatively stable under lab conditions. It was prepared by mixing CaSO4 (Mineral Research Processing, Meyzieu, France) and CaSO4·H2O in a 1:1 molar ratio in boiling deionized water with a water/solid mass ratio of around 20. The slurry was then stirred at 85 °C for two weeks in a sealed polytetrafluoroethylene (PTFE) bottle prior to filtration with Whatman grade 1 filter paper and vacuum-drying. XRD analysis (Section 2.2.4) confirmed the phase purity of >99%. The sample was then stored in a double sealed HDPE bottle at 23 ± 2 °C before characterizations.

2.2. Characterization

2.2.1. Thermogravimetric analysis

To identify the hydration phases and quantify the bound water for both unmodified and TiO2-modified CAC samples, thermogravimetric analysis (TGA) was carried out using Hitachi TG/DTA 7300. Approximately 60 mg of cementitious pastes were ground to a particle size of <74 µm (No. 200 sieve) and placed in a 70 µL platinum crucible. Samples were dried at 40 °C for 15 min or until reaching constant mass if mass had not stabilized within 15 min. The sample was then heated from 40 °C to 1000 °C at a rate of 10 °C · min−1. Nitrogen was used to purge at a flow rate of 100 mL min−1.

2.2.2. N2 adsorption and desorption isotherms

The specific surface area (SSA) and pore size distribution (PSD) of the granular samples were measured by Brunauer-Emmett-Teller (BET) N2 adsorption and desorption isotherms [37]. Tests were conducted on ∼2 g of granular samples in a gas analyzer (Micromeritics ASAP 2420) over a pressure range of 0.01 to 0.99 atm. The samples were degassed at 1.33 kPa pressure for 12 h prior to the analysis. Although a previous study has shown that surface area measurements vary with techniques and sample
preparation methods [38], BET adsorption-desorption isotherms are commonly used for detecting the relevant microstructural features and facilitating semiquantitative comparisons among different cementitious materials [6,39,40]. In this study, sample preparation was performed through a procedure consistent as ref [6,39,41], in order to facilitate comparison between samples.

2.2.3. Scanning electron microscopy analysis

To investigate the dispersion of TiO$_2$ nanoparticles, SEM and energy dispersive X-ray spectroscopy (EDS) analyses were performed using a JSM-7600F Schottky Field Emission Scanning Electron Microscope (JEOL, Tokyo, Japan). After curing, a thin sliced specimen was impregnated with low-viscosity epoxy resin, polished, and carbon-coated for better surface conductivity prior to imaging.

2.2.4. X-ray diffraction

XRD was performed on the synthetic AFm-SO$_4$ phase before and after NO$_x$ exposure to identify changes in mineralogy. Approximately 0.2 g of finely ground powders were packed into a sample holder, and the measurements were taken on a PANalytical Empyrean X-ray diffractometer (Malvern Panalytical Ltd., Malvern, United Kingdom) with Cu-Kα radiation (λ = 1.54 Å) at 45 kV and 40 mA. Scans were performed at 5–45° 2θ using a PIXcel3D detector.

### Table 1

|         | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO  | MgO  | SO$_3$ | Na$_2$O | LOI | CA  | CA$_2$ | C$_2$AS | C$_12$A$_7$
|---------|---------|-------------|------------|------|------|--------|--------|-----|------|-------|--------|----------
| Composition (%) by mass |         |             |            |      |      |        |        |     |      |       |        |          |
| 5.5     | 45.2    | 6.9         | 37.7       | 0.2  | 0.1  | 0.3    | 1.9    | 57.0| 8.6  | 16.2  | 1.5    |          |

Table 2

Composition (% by mass) and characteristics of TiO$_2$ photocatalyst.

<table>
<thead>
<tr>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>SO$_3$</th>
<th>Phase</th>
<th>Bulk density</th>
<th>Crystallite size</th>
<th>Specific surface area</th>
</tr>
</thead>
<tbody>
<tr>
<td>92.3</td>
<td>1.0</td>
<td>3.7</td>
<td>2.0</td>
<td>Anatase</td>
<td>300 g L$^{-1}$</td>
<td>~15 nm</td>
<td>&gt;225 m$^2$ g$^{-1}$</td>
</tr>
</tbody>
</table>

2.2.5. NO$_x$ degradation

NO$_x$ degradation was performed following procedures in the ISO 22197 [33] and JIS R 1701 Standards [34], and test setup is shown in Fig. 1. For plate samples, a sealed reaction chamber with a prismatic cross-section and borosilicate glass cover was constructed, as shown in Fig. 1(b). Three identical plates with a total area of 7500 mm$^2$ were placed in the reaction chamber for each composition (control or 5% TiO$_2$-modified CAC). To investigate the long-term photocatalytic efficiency, the plate samples were subjected to three consecutive UV light “on-off” cycles to replicate diurnal exposure conditions. For each cycle, the reaction chamber was pumped with NO$_x$ gas, which was prepared by mixing 1000 ppb nitric oxide in ultrapure dry air at a constant flow rate of 1 L min$^{-1}$ [33,34]. The test was conducted at 23±2°C and 50±5% relative humidity. The sample-loaded reaction chamber was placed under two UV fluorescent lamps of 40 W with peak emission of 365 nm and UV irradiance of 10 W m$^{-2}$ (Actinic BL TL 40W/10 SLV, Philips Lighting). To achieve an optimal photocatalytic performance, the UV intensity at the sample surface was maintained at 10 W m$^{-2}$ by adjusting the distance between the UV light source and the samples. The initial gas concentration was kept at 1000 ppb before turning on the UV light. After ~1 h, the gas concentration stabilized and UV light exposure started and continued for 5 h. The gas concentration was allowed to re-stabilize for another hour after the UV light was turned off. A chemiluminescent NO/NO$_2$/NO$_x$ analyzer (Model 200A, Teledyne API, San Diego, CA, USA)

![Experimental setup for NO$_x$ degradation.](image-url)
was used to measure the gas concentration. The test setup was covered by a black light-blocking canvas to prevent ambient light from affecting the reaction.

Each cycle ended when gas concentration re-stabilized and was followed by 12-hour breaks, during which the samples were not tested or subjected to any surface treatment (e.g., washing the NO) allowed by 12-hour breaks, during which the samples were not tested or subjected to wet chemical extraction for NO.

Q. Jin et al.

was purged by N, reacted samples were suspended in anoxic deionized water that above). To ensure a same period of NO, reacted samples were suspended in anoxic deionized water that contained a Agilent, Santa Clara, CA, USA). Nitrate concentration was determined with the previously examined OPC-based samples [6]. At the end of the photodegradation test, the sample was removed from the photoreactor and stored in double sealed plastic bags with light-blocking foil-wrapped centrifuge tubes to prevent further photodegradation test, using the methods previously described in Q. Jin et al.

The NO degradation capacity that is normalized by sample surface area (SNOx) can be calculated by Eqs. (2) and (3) and in units of mmol m$^{-2}$. The N mass of NOx uptake ($m_{N}$) through photocatalytic reactions is normalized by sample mass and can be quantified by Eqs. (2) and (4) [6], with the units of mg N per kg solid (denoted as mg kg$^{-1}$ for simplicity).

\[
Q_{NOx} = \frac{f}{V} \int_{0}^{T} (C_{NOx,in} - C_{NOx,out}) \, dt
\]

(2)

\[
S_{NOx} = \frac{Q_{NOx}}{A}
\]

(3)

\[
m_{N} = \frac{m_{NOx} \times M_{N}}{m_{S}}
\]

(4)

where $Q_{NOx}$ is the NOx uptake that is measured by the NOx analyzer (mol), $f$ is the duration of NOx absorption (min), $T$ is the total duration of the UV-light exposure (300 min), $f$ is the flow rate of NOx at 23 $^\circ$C and 1.01 kPa (1 L min$^{-1}$), $V$ is the volume of 1 mole ideal gas at 23 $^\circ$C and 1.01 kPa (24.3 L), $S_{NOx}$ is the uptake capacity that is normalized by the UV-exposed surface area (A) of test plate samples (mmol m$^{-2}$), $m_{NOx}$ is the nitrogen mass of NOx uptake (mg kg$^{-1}$), $M_{N}$ is the molar mass of nitrogen (14 g mol$^{-1}$) and $m_{S}$ is the sample mass (kg). The result is then compared with the total nitrogen mass from the NOx ($m_{N}$) and NOx ($m_{N}$) measurements, as shown in the following section.

2.3.2. Quantification of NOx and NOx formation

The N mass from nitrite and nitrate measurements is determined by Eqs. (5)-(8) [6].

\[
m_{NOx} = C_{NOx} \times DF
\]

(5)

\[
m_{NOx} = C_{NOx} \times DF
\]

(6)

\[
m_{N} = m_{NOx} \times \frac{M_{N}}{M_{NOx}}
\]

(7)

\[
m_{N} = m_{NOx} \times \frac{M_{N}}{M_{NOx}}
\]

(8)

where $m_{NOx}$ is the mass of nitrite (mg kg$^{-1}$), $m_{NOx}$ is the mass of nitrate (mg kg$^{-1}$), $C_{NOx}$ is the concentration of nitrite measured by UV--vis spectrophotometer (ppm), $C_{NOx}$ is the concentration of nitrate measured by ion chromatography (ppm), DF is the dilution factor used for wet chemical extraction (400), $m_{N}$ is the mass of nitrogen from nitrite (mg kg$^{-1}$), $m_{N}$ is the mass of nitrogen from nitrate (mg kg$^{-1}$), $M_{NOx}$ is the molar mass of nitrite (46 g mol$^{-1}$), and $M_{NOx}$ is the molar mass of nitrate (62 g mol$^{-1}$).

3. Results and discussion

The effects of TiO2 nanoparticles on the composition and microstructural properties of CAC pastes are determined by using TGA and N2
adsorption and desorption isotherms. Two sample geometries are prepared to examine the material’s photocatalytic performance: plate samples to examine photocatalytic efficiency, as well as granular samples to quantify NO\textsubscript{x} uptake capacity and explore binding mechanisms and to allow for a direct comparison with OPC-based samples that were prepared and tested in the same manner. N-species that are physically bound with hydrated cementitious phases are quantified using a combination of wet chemical extraction, UV-vis spectrophotometry, and ion chromatography. The total NO\textsubscript{x} uptake is estimated by combining the results from surface-related heterogeneous reactions and/or photocatalytic reactions. The presence of chemically bound N-species is then estimated by the difference between the total NO\textsubscript{x} uptake and that which is physically bound.

3.1. Composition, nano-TiO\textsubscript{2} dispersion, and microstructure

The phase composition of both unmodified CAC paste (CAC) and TiO\textsubscript{2}-modified CAC paste (CAC5T) after 28 days of hydration can be identified by TGA (Fig. 2), where the mass losses indicate the decomposition of different phases. The metastable phases of CAH\textsubscript{10} and C\textsubscript{2}AH\textsubscript{8} are identified at temperature of 120 °C and 150 °C, respectively, while stable phases of AH\textsubscript{3} and C\textsubscript{3}AH\textsubscript{6} are identified at temperature of 270 °C, and 320 °C, respectively [42]. The TGA results show lesser amounts of hydration products formed in TiO\textsubscript{2}-modified samples, likely due to the dilution of the cement with non-hydraulic titania [30]. SEM analysis (Fig. 3) shows well distributed TiO\textsubscript{2} particles within the hydrated CAC sample. The images also show these TiO\textsubscript{2} particles are agglomerates in the range from 1 to 2 \(\mu\text{m}\) in diameter.

The measured SSA are \(16.68 \pm 0.29 \text{ m}^2 \text{ g}^{-1}\) for CAC and \(21.33 \pm 0.35 \text{ m}^2 \text{ g}^{-1}\) for CAC5T after 28 days of hydration. The SSA is increased in CAC5T samples by 27\%, which is in the range expected based on the SSA of the material’s components. The PSD profiles of both CAC and CAC5T samples are shown in Fig. 4, with a larger number of small pores (<10 nm) observed in CAC5T. Since the amount of hydration products in CAC5T is in fact lower than CAC (Fig. 2), the higher SSA and greater amount of micropores observed in well-hydrated CAC pastes should be mainly attributed to the inclusion of TiO\textsubscript{2} nanoparticles, which intrinsically exhibit high SSA (Table 2).

3.2. Photocatalytic performance

Fig. 5 shows the long-term photocatalytic performance of TiO\textsubscript{2}-modified CAC plate samples that are exposed to NO\textsubscript{x} and UV (CAC5T-NV) for three consecutive UV “on-off” cycles (the detailed test arrangement can be referred to Section 2.2.5). With a constant NO\textsubscript{x} concentration before the UV light was illuminated, an almost...
instantaneous drop of NO\textsubscript{x} concentration occurred upon initial UV illumination. The magnitude of the initial drop of TiO\textsubscript{2}-modified CAC samples are similar to the CAC samples tested by Pérez-nicolás et al. [30]. However, only a short-term photocatalytic efficiency (30 min) was examined in their study. To show long-term photocatalytic performance, this study examines the NO\textsubscript{x} degradation throughout a 5-hour test period during each cycle. This subsequent decrease over the 5-hour period in CAC samples was also observed in TiO\textsubscript{2}-modified OPC samples [6,15,43], which were tested under similar conditions. When the UV light was off, the NO\textsubscript{x} concentration recovered to its initial level. This phenomenon then occurred repeatedly in the second and third UV light “on-off” cycles.

Table 3 lists the initial and end NO\textsubscript{x} concentrations for each cycle, which correspond with the results of NO\textsubscript{x} degradation shown in Fig. 5. The initial concentration is the measured NO\textsubscript{x} level right after the UV light is on and the end concentration right before the UV light is off. The photocatalytic efficiency ($\eta$) at the initial and the end of each cycle is determined by Eq. (1). The highest $\eta$ of 53% occurred at the initial exposure of the first cycle; it then decreased throughout the 5-hour test period to 46%. When the second cycle began after a 12-hour break from UV exposure, $\eta$ started at 49% and decreased to 43%, and the $\eta$ of third cycle decreased from 46% to 40%. Comparing the end concentration of 1st cycle to the initial concentration of 2nd cycle, a small but consistent fraction of the $\eta$ was recovered (about 3%), and the same restoration phenomenon was also observed between 2nd and 3rd cycles. This restoration phenomenon between cycles, where the test was paused, indicates that a small fraction of NO\textsubscript{x} binding with CAC samples is transient and should be taken into consideration for estimating the material’s NO\textsubscript{x} binding capacity. However, the underlying mechanisms of such restoration phenomenon require further investigations.

The results from Fig. 5 and Table 3 shows a decreasing trend of long-term photocatalytic efficiency over time and with increasing cycles, which implies that the NO\textsubscript{x} uptake for TiO\textsubscript{2}-modified CAC could reach a limit over time. In addition, this decreasing trend also affects the NO\textsubscript{x} degradation capacity ($S$), which can be estimated using Eqs. (2) and (3). The NO\textsubscript{x} uptake capacity for each cycle is also included in Table 3, and it decreases from 800 mmol m\textsuperscript{-2} in the first cycle to 710 mmol m\textsuperscript{-2} in the third cycle. Similar phenomenon was observed in OPC-based plate samples [44–46], where both photocatalytic efficiency and NO\textsubscript{x} degradation capacity decrease over time. Recall that no surface treatment (e. g., washing the exposed sample surface) was performed between UV-exposure cycles, to avoid alteration of the sample surface. The impact of washing, as would be experienced during rain, on photocatalytic efficiency deserves further investigation.

### 3.3. Quantification of NO\textsubscript{x} uptake

#### 3.3.1. NO\textsubscript{x} uptake through photocatalytic reactions

The NO\textsubscript{x} degradation achieved by granular TiO\textsubscript{2}-modified CAC samples that are exposed to NO\textsubscript{x} and UV (CAC5T-NV) is illustrated in Fig. 6. As with the plate samples, an instantaneous drop of NO\textsubscript{x} concentration occurred upon initial UV illumination and the photocatalytic efficiency decreased during the test period. When the UV light was turned off, the NO\textsubscript{x} concentration recovered to the initial level. The trends of NO\textsubscript{x} degradation in the plate and granular samples are essentially the same. The N mass of NO\textsubscript{x} uptake ($m_n$) through photocatalytic reactions, which is represented by the shaded area in Fig. 6 and normalized by sample mass, can be determined by Eqs. (2) and (4). The result is 28.4 ± 0.63 mg N per kg solid (denoted as mg kg\textsuperscript{-1}).

The N mass of NO\textsubscript{x} uptake for plate samples is also calculated and normalized by sample mass for the sake of comparison in this study. For the plate samples, the result is 1.58 ± 0.09 mg kg\textsuperscript{-1}, which is significantly lower than granular samples. This result is expected since the UV-exposed surface area per unit mass is increased when the plate sample is crushed into granular samples, and the increase in surface area in turn increases the NO\textsubscript{x} binding potential of granular samples. As discussed in

![Fig. 5. Photocatalytic performance of plate TiO\textsubscript{2}-modified CAC samples that are exposed to NO\textsubscript{x} and UV light for three consecutive UV “on-off” cycles.](image)

| NO\textsubscript{x} concentration ($C_{\text{NO}_x}$) and NO\textsubscript{x} uptake capacity ($S_{\text{NO}_x}$) of TiO\textsubscript{2}-modified CAC plate samples that exposed to NO\textsubscript{x} and three consecutive UV light “on-off” cycles. The detailed NO\textsubscript{x} degradation can be referred to Fig. 5 and the exposure arrangement can be referred to Section 2.2.5. The NO\textsubscript{x} concentration prior to the illumination of UV light is 1000 ppb, the initial concentration is the NO\textsubscript{x} level right after UV light is on and the end concentration is right before the UV light is off. The unit of $C_{\text{NO}_x}$ is ppb and the unit of $S_{\text{NO}_x}$ is mmol m\textsuperscript{-2}. |
|---|---|---|---|---|---|---|
| 1st cycle | 2nd cycle | 3rd cycle |
| Initial | End | Initial | End | Initial | End |
| $C_{\text{NO}_x}$ (ppb) | 470 | 540 | 510 | 570 | 540 | 600 |
| $S_{\text{NO}_x}$ (mmol m\textsuperscript{-2}) | 800 | 760 | 710 |

![Fig. 6. Photocatalytic performance of granular TiO\textsubscript{2}-modified CAC samples that are exposed to NO\textsubscript{x} and UV light.](image)
3.3.2. NO\textsubscript{3} uptake by unmodified CAC

Fig. 7 summarizes the measured N mass, as NO\textsubscript{2} and NO\textsubscript{3}, in the NO\textsubscript{x}-exposed granular samples. As expected, the samples without NO\textsubscript{x} exposure (CAC and CACST) show no detectable N, as either NO\textsubscript{2} or NO\textsubscript{3}. However, similar N mass as both NO\textsubscript{2} and NO\textsubscript{3} were detected in the unmodified CAC samples after NO\textsubscript{x} exposure (CAC-N and CAC-NV), regardless of the presence of UV light, and the results are expected due to the absence of TiO\textsubscript{2} in the unmodified CAC samples. The N mass is approximately 6.50 mg kg\textsuperscript{-1} for NO\textsubscript{2} and 9.40 mg kg\textsuperscript{-1} for NO\textsubscript{3}. Therefore, this study for the first time quantifies the intrinsic NO\textsubscript{3} binding capability of CAC-based cementitious materials, even in the absence of photocatalysts.

The measured N mass of TiO\textsubscript{2}-modified CAC samples that are exposed to NO\textsubscript{x} (CACST-N) is approximately 8.60 mg kg\textsuperscript{-1} for NO\textsubscript{2} and 11.20 mg kg\textsuperscript{-1} for NO\textsubscript{3}. Compared to unmodified CAC samples (CAC-N), the total NO\textsubscript{x} uptake is increased by 25\%, which is similar to the increase of SSA measured in Section 3.1. The result confirms that the increased SSA induced by the inclusion of TiO\textsubscript{2} nanoparticles promotes the surface-related heterogeneous reactions in CAC samples [6,17]. The detection of NO\textsubscript{2} and NO\textsubscript{3} ions indicates that these ions produced by the heterogeneous reactions are likely to be physically adsorbed by the hydrated cementitious phases in CAC samples and susceptible to water-based wet chemical extraction [6]. According to Fig. 7, the nitrite-to-nitrate concentration ratio is approximately 1:1.3, suggesting that the heterogeneous reactions converted NO\textsubscript{2} more to nitrite than nitrite by 30\% in CAC systems. This discovery is also supported by the work from Pérez-nicolas et al. [30], where they observed that CAC-based samples show a higher NO\textsubscript{2} adsorption than NO\textsubscript{3}, which leads to a higher photo-oxygenation of NO\textsubscript{2}. The product of this photo-oxygenation is nitrate, which is considered a better corrosion inhibitor compared to nitrite when incorporated in cement-based materials [22,47].

3.3.3. NO\textsubscript{3} uptake by TiO\textsubscript{2}-modified CAC

From Section 3.3.1, the NO\textsubscript{3} uptake (m\textsubscript{N}) of TiO\textsubscript{2}-modified CAC sample (CACST) through photocatalytic reactions is approximately 28.4 mg kg\textsuperscript{-1}. If this NO\textsubscript{3} binding is transient, such as physically adsorbed by the hydrated cementitious phases as in unmodified CAC, m\textsubscript{N} should be equivalent to the summation of photocatalytic converted NO\textsubscript{2} (m\textsubscript{N,I}) and NO\textsubscript{3} (m\textsubscript{N,II}). The m\textsubscript{N,I} and m\textsubscript{N,II} can then be determined by their differences between the samples that are only exposed to NO\textsubscript{x} (CACST-N) and those that are exposed to both NO\textsubscript{x} and UV-light (CACST-NV) [6]. However, Fig. 7 shows similar N masses, as NO\textsubscript{2} and NO\textsubscript{3}, in both CACST-N and CACST-NV samples, making the m\textsubscript{N,I} and m\textsubscript{N,II} essentially zero. Therefore, the m\textsubscript{N} = m\textsubscript{N,I} + m\textsubscript{N,II}, suggesting a portion of NO\textsubscript{3} uptake is chemically bound with TiO\textsubscript{2}-modified CAC samples. The mechanisms of how NO\textsubscript{3} is chemically bound in CAC samples will be described in detail in Section 3.4.1.

The total NO\textsubscript{x} uptake of TiO\textsubscript{2}-modified CAC should be determined by separating the contributions from the photocatalytic reactions (m\textsubscript{N,1} = 28.4 mg kg\textsuperscript{-1}) and the surface-related heterogeneous reactions (m\textsubscript{N,2} = 20.5 mg kg\textsuperscript{-1}) since both reactions occur intrinsically in the materials. As a result, the total NO\textsubscript{x} uptake is determined by m\textsubscript{N} = m\textsubscript{N,1} + m\textsubscript{N,2} = 48.9 mg kg\textsuperscript{-1}, showing that 58\% of the NO\textsubscript{x} is chemically bound within the material. The determination of NO\textsubscript{x} uptake through photocatalytic reactions, which has been commonly used to determine total NO\textsubscript{x} uptake capacity of OPC samples [8,16,49], underestimates the capacity of TiO\textsubscript{2}-modified CAC by almost half by neglecting the material’s intrinsic NO\textsubscript{3} uptake capacity. Therefore, the measurement of NO\textsubscript{x} uptake for TiO\textsubscript{2}-modified CAC should include the contributions from both photocatalytic and surface-related heterogeneous reactions.

3.4. Comparison between NO\textsubscript{x} sequestration in CAC- and OPC-based materials

3.4.1. Mechanism and capacity of NO\textsubscript{x} uptake

As discussed in the introduction, the intrinsic NO\textsubscript{x} binding capability of cementitious materials have been observed recently. Three mechanisms for NO\textsubscript{x} binding have been proposed after the oxidation of NO\textsubscript{x} into NO\textsubscript{2} and NO\textsubscript{3} through photocatalytic and surface-related heterogeneous reactions [5,16,17,30,49]: I) the adsorption of NO\textsubscript{2} and NO\textsubscript{3} on the surface of cement hydrates such as C-S-H, II) the reaction of NO\textsubscript{x} with hydroxyl ions in the alkaline pore solution, and III) substitution of NO\textsubscript{2} and NO\textsubscript{3} into aluminum-bearing hydrated phases. Since differences in hydration products and microstructural properties between CAC- and OPC-based materials could affect their binding capacity and mechanisms, this section provides a summary of the characteristics of CAC-based samples that could contribute to their NO\textsubscript{x} uptake, as compared to the previously examined OPC-based samples [6]. The goal with this discussion is to better understand and quantify the differences in NO\textsubscript{x} sequestration between CAC and OPC, considering the three mechanisms noted above.

I. For unmodified cementitious samples, the intrinsic NO\textsubscript{x} uptake is induced by the surface-related heterogeneous reactions [7,16], and a higher surface area can facilitate greater reactions and provide more surface area for the adsorption of N-species [6,7,16]. From the previous study for unmodified OPC samples, which was under the same sample preparation (e.g., water-to-solid ratio and TiO\textsubscript{2} dosage) and test conditions as this study [6], the total NO\textsubscript{x} uptake (the summation of NO\textsubscript{2} and NO\textsubscript{3}) was found to be approximately 8.50 mg kg\textsuperscript{-1}. According to Section 3.3.2, the total NO\textsubscript{x} uptake of unmodified CAC samples is 15.90 mg kg\textsuperscript{-1}, an increase by 85\% compared to OPC samples. Since the heterogeneous reactions are related to the material’s microstructural features, the higher NO\textsubscript{x} uptake can be attributed to the larger surface area of CAC samples prepared in this study. The SSA is approximately 10.20 m\textsuperscript{2} g\textsuperscript{-1} for OPC [6] and 16.70 m\textsuperscript{2} g\textsuperscript{-1} for CAC (Section 3.1). Since the granular OPC and CAC samples have different SSAs, the total intrinsic NO\textsubscript{x} uptakes for both materials are further normalized by their respective SSA in this section for the sake of comparison. The surface area-normalized NO\textsubscript{x} uptake is estimated to be approximately 8.3 × 10\textsuperscript{2} mg mm\textsuperscript{-2} for OPC and 9.5 × 10\textsuperscript{2} mg mm\textsuperscript{-2} for CAC. The higher...
surface area-normalized NO$_x$ uptake of CAC samples suggests other mechanisms, in addition to surface area, could also play a role in the NO$_x$ uptake.

II. The N-species can react with the hydroxyls (OH$^-$) presented in the cementitious material [17,18], but CAC typically has a lower pH than OPC [36]. The pH of the hydrated CAC sample was measured at 12.6 [50] and is slightly lower than the OPC sample, which was measured at 13.2 [50]. However, based on the porosity and pH of the hydrated CAC, Alapati [50] has shown that the concentration of OH$^-$ in the hydrated CAC is approximately 0.01 mmol g$^{-1}$ of solid (or 170 mg kg$^{-1}$). This concentration is 10 times greater than that of the converted N-species, implying there is ample OH$^-$ to react with the N-species exists in CAC. Therefore, the reactions between OH$^-$ and N-species in this CAC-based cementitious environment should be similar to OPC, despite the lower pH of CAC.

III. Section 3.3.3 has shown that the photocatalytic reactions ($m_{\text{N}}$) are not equal to the summation of photocatalytic converted NO$_x$ ($m_{\text{N}}'$) and NO$_x$ ($m_{\text{N}}''$), i.e., $m_{\text{N}} 
eq m_{\text{N}}' + m_{\text{N}}''$ for TiO$_2$-modified CAC samples (CAGST). However, our previous study [6] has quantified that the $m_{\text{N}} = m_{\text{N}}' + m_{\text{N}}''$ for TiO$_2$-modified OPC samples. This discrepancy between CAC and OPC can be attributed to the differences in their hydration products (refer to Section 3.1 for the hydrated CAC phases); CAC forms significantly more aluminum-bearing hydrated phases compared to OPC [51,52]. Therefore, this imbalance between the NO$_x$ uptake and converted NO$_x$ and NO$_2$ should be related to the interactions of converted N-species with these phases.

Studies [19,20] have suggested that the converted NO$_2$ and NO$_3$ could chemically substitute the interlayer sulfate (SO$_4^{2-}$) in AFm phases through an anion exchange process. Thermodynamically, it is understood that these anions have a binding preference within AFm phases, with a preference for NO$_3 > NO_2 > SO_4^{2-} > OH^-$ [53]. The XRD pattern for the AFm-SO$_4$ phase that is exposed to NO$_x$, as shown in Fig. 8, shows a formation of new peaks at 2θ of 9.5° and 15.1°. According to Balonis et al. [20], these two peaks represent AFm-NO$_2$/NO$_3$. Therefore, this study for the first time has experimentally demonstrated the formation of AFm-NO$_2$/NO$_3$ in a solid-gas reaction through the aforementioned anion exchange process. This anion exchange process could also occur in C$_2$AH$_8$ phase, which is one of the major phases in hydrated CAC (Fig. 2), since it is structured similarly to the AFm-SO$_4$ [36].

In practice, because C$_2$AH$_8$ is a metastable phase in CAC and can be converted to more stable phases of AH$_3$ and C$_2$AH$_6$ [42], the conversion of this phase may require control for CAC to be used effectively for NO$_x$ sequestration. Recently, Alapati [50] has demonstrated that carbonation and internal curing could be used to preferentially form C$_2$AH$_6$ and in turn maximize the chemically bound NO$_x$ in CAC-based cementitious materials. Further studies, which examine the NO$_x$ binding in other CAC phases such as AH$_3$, C$_2$AH$_{6}$, and C$_2$AH$_{8}$, are needed to understand the stability of nitrite or nitrate substituted aluminum-bearing phases in CAC over time.

### 3.4.2. Sustainability and durability

Based on the discussion in Part III of Section 3.4.1, this study has shown that these chemically bound NO$_2$ and NO$_3$ in CAC samples are more resistant to being released by water-based extraction. As discussed in the introduction, release of previously bound N-species back into the environment from OPC-based materials or other substrates remains a concern in developing sequestration materials for sustainability. Therefore, because CAC-based materials have demonstrated a more permanent binding with these ions than OPC-based materials, the use of CAC could be preferred for sequestration applications.

It has been proposed that NO$_2$ and NO$_3$-containing compounds in cement-based materials can be used at the steel interface to improve the corrosion resistance of steel-reinforced concrete [22,47]. Falzone et al. [22] have demonstrated that chlorides can be fixed in the AFm phases through the aforementioned anion exchange process (Section 3.4.1 and [53]) due to their more favorable binding preference than NO$_2$ and NO$_3$. Since chloride-induced steel corrosion is a leading cause of OPC-based concrete infrastructure deterioration, this study has demonstrated that CAC-based infrastructure, which contains TiO$_2$ photocatalysts, could offer an additional pathway to enhance the inhibition of such corrosion and prolong its service life. In addition, the greater capacity for non-transient chemical NO$_3$ sequestration in CAC is viewed as advantageous over OPC, with regard to enhanced corrosion resistance through increased nitrate and nitrite concentrations in the pore solution.

### 4. Conclusion and future study

Two sample geometries were prepared to examine the NO$_x$ sequestration performance for both unmodified and TiO$_2$-modified calcium aluminate cementitious (CAC) materials. The long-term NO$_x$ degradation of TiO$_2$-modified CAC was examined using plate samples under a

![Fig. 8. Two new peaks at 2θ of 9.5° and 15.1° were observed in the XRD patterns of AFm-SO$_4$ phases before (control) and after NO$_x$ exposure, indicating the formation of AFm-NO$_2$/NO$_3$ phases.](image-url)
multi-cycle test. Granular samples were used to quantify NO\textsubscript{x} uptake and explore NO\textsubscript{2} binding mechanisms. A combined method of water-based chemical extraction, UV–vis spectrophotometry, and ion chromatography was used to quantify N-species that are bound with hydrated cementitious phases. The effects of composition and microstructural properties on NO\textsubscript{x} uptake were examined and a comparison of NO\textsubscript{x} uptake between OPC- and CAC-based materials was made. Key conclusions include:

1. The photocatalytic efficiency, \(\eta_{\text{NOx}}\), decreased with increased exposure time and test cycles (from 53% in the first cycle to 40% in the third cycle), implying that the NO\textsubscript{x} uptake could reach a limit over time if no surface treatment (e.g., washing) is performed. This decreasing trend also affected the NO\textsubscript{2} degradation capacity, which decreased from 800 mmol m\textsuperscript{-2} in the first cycle to 710 mmol m\textsuperscript{-2} in the third cycle. It was also observed that a small fraction of NO\textsubscript{x} binding with CAC samples was transient. These effects should be taken into consideration when estimating a material’s photocatalytic performance.

2. Similar NO\textsubscript{x} uptake was measured in unmodified CAC samples (CAC-N and CAC-NV) regardless of the UV light exposure, demonstrating the material’s intrinsic NO\textsubscript{x} sequestration capability even in the absence of photocatalysts. The NO\textsubscript{x} uptake increased by 25% in TiO\textsubscript{2}-modified CAC that was only exposed to NO\textsubscript{2} (CACST-N). This increase should be attributed to the increased surface area, which is induced by the inclusion of TiO\textsubscript{2} nanoparticles. The nitrite-to-nitrate concentration ratio was approximately 1:1.3, suggesting that the heterogeneous reactions in CAC systems favor NO\textsubscript{x} conversion to nitrate over nitrite.

3. For TiO\textsubscript{2}-modified CAC that was exposed to both NO\textsubscript{x} and UV light (CACST-NV), the photocatalytically-converted nitrite and nitrate cannot be directly measured by water-based chemical extraction, indicating these ions are chemically bound within the CAC materials and resist releasing back into the environment via dissolution. Therefore, the total NO\textsubscript{x} uptake of CACST-NV can only be determined by separating the contributions from the photocatalytic and surface-related heterogeneous reactions, both of which occur intrinsically in the hydrated CAC materials. Since these chemically bound ions are more resistant to being released back into the environment, the use of CAC can help mitigate the environmental concerns in developing NO\textsubscript{x} sequestration materials.

4. The main difference between OPC- and CAC-based materials, in terms of NO\textsubscript{x} sequestration, is that the NO\textsubscript{x} uptake in OPC through photocatalytic reactions is equal to the summation of photocatalytic converted NO\textsubscript{2} and NO\textsubscript{3}, while such balance cannot be detected in CAC. This discrepancy is attributed to the differences in their hydration products, where CAC has significantly higher aluminum content and tends to form more aluminum-bearing hydrated phases compared to OPC. The examination of mineralogical change of synthetic Afm-SO\textsubscript{4} phase before and after its exposure to NO\textsubscript{x} has shown the converted NO\textsubscript{2} and NO\textsubscript{3} could chemically substitute the interlayer anions through an anion exchange process. These chemically bonded N-species could then enhance the durability of CAC-based concrete infrastructure compared to the OPC-based ones, since NO\textsubscript{2} - and NO\textsubscript{3} -containing compounds can be used at the steel interface to improve the corrosion resistance of steel-reinforced concrete and, in turn, improve the material’s durability.

Based on the findings from this study, future research to improve our understanding of NO\textsubscript{x} sequestration in cementitious materials could consider the impact of surface treatment such as washing on the overall photocatalytic efficiency, the interaction of NO\textsubscript{2} and NO\textsubscript{3} with other aluminum-bearing phases in CAC-based materials, and NO\textsubscript{x} uptake in other aluminum-rich binders such as geopolymers.

CRediT authorship contribution statement

Qingxu Jin: Conceptualization, Investigation, Methodology, Validation, Formal analysis, Data curation, Visualization, Project administration, Writing - Original draft, Writing - Review & editing
Sarah L. Hordern: Investigation, Data curation, Formal analysis, Writing - Review & editing
Yuanzhi Tang: Methodology, Resources, Writing - Review & editing
Kimberly E. Kurtis: Conceptualization, Resources, Project administration, Writing - Review & editing
Supervision, Funding acquisition.

Declaration of competing interest
None.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Science Foundation under Grant No. CMMI-1362843 and EEC-1757579. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation. The authors would like to thank Paul Stutzman from the National Institute of Standards and Technology for his assistance with electron microscopy, Monday Okoronkwo from the Chemical and Biochemical Engineering Department at Missouri S&T for his preparation of Afm-SO\textsubscript{4} phase, and Hongyan Ma from the Civil, Architectural and Environmental Engineering Department at Missouri S&T for his help with X-ray fluorescence analysis of TiO\textsubscript{2} nanoparticles.

References
