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**PRELIMINARY STUDIES OF PHOTOCATALYTIC NO\textsubscript{x} DEGRADATION BY DIFFERENT TYPES OF CAC INCORPORATING TiO\textsubscript{2}**

Pérez-Nicolás M.\textsuperscript{1}, Fernández J.M.\textsuperscript{1}, Balbuena J.\textsuperscript{2},

Cruz-Yusta M.\textsuperscript{2}, Sánchez L.\textsuperscript{2}, Navarro-Blasco I.\textsuperscript{1}, Alvarez J.I.\textsuperscript{1}

\textsuperscript{1}Departamento de Química y Edafología, Universidad de Navarra; \textsuperscript{2}Departamento de Química Inorgánica, Universidad de Córdoba

e-mail: mperez.52@alumni.unav.es

Different percentages of TiO\textsubscript{2} (1 to 10 wt.\%) were incorporated into two different Calcium Aluminate Cements (iron rich – d-CAC – and iron lean – w-CAC–) which were cured under two curing conditions. The mild hydrothermal curing condition 2 was chosen so as to resemble the natural ageing of aluminate cements in which hydrated hexagonal phases are converted into more stable cubic ones. Fresh and hardened state properties were studied. NO\textsubscript{x} removal under UV illumination was assessed in TiO\textsubscript{2}-bearing mortar samples. NO conversion values were higher in w-CAC than in d-CAC. Retention of NO\textsubscript{2} in w-CAC samples was also more successful than in d-CAC samples due to the presence of ferrite in the latter ones. The presence of ferrite in d-CAC was established by XRD, SEM and EDAX. The interaction of ferrite phases with TiO\textsubscript{2} was monitored in both types of mortars and different behaviours were observed. In the d-CAC, the incorporation of TiO\textsubscript{2} results in the appearance of two new iron containing phases: namely pseudobrookite and in a lesser extent ilmenite, at the expense of brownmillerite. These new phases yielded in an improve photocatalytic efficiency of d-CAC in the visible region of spectrum, as proved by Methyl Orange degradation tests.
Study of NO\textsubscript{x} abatement by calcium aluminate cements modified with TiO\textsubscript{2}

M. Pérez-Nicolás\textsuperscript{a}, J. Balbuena\textsuperscript{b}, M. Cruz-Yusta\textsuperscript{b}, L. Sánchez\textsuperscript{b}, I. Navarro-Blasco\textsuperscript{a}, J.M. Fernández\textsuperscript{a}, J.I. Alvarez\textsuperscript{a*}

\textsuperscript{a} MI MED Research Group, Department of Chemistry and Soil Sciences, School of Sciences, University of Navarra. c/ Irúnlarrea, 1. 31008 Pamplona, Spain
\textsuperscript{b} Department of Inorganic Chemistry, School of Sciences, University of Córdoba, Rabanales Campus, Marie Curie Building, 14071 Córdoba, Spain

Introduction

NO and NO\textsubscript{2} (NO\textsubscript{x}) are toxic gases that cause atmospheric pollution. TiO\textsubscript{2} is able to remove NO\textsubscript{x} from the atmosphere by photocatalytic oxidation assisted process so, its incorporation as photocatalytic additive in building materials has increased in the last years. Calcium aluminate cement (CAC) is used in many building structures but its modification with photocatalytic additives has not yet been addressed. The aim of this work is to obtain depolluting and self-cleaning CAC mortars modified with different amounts of TiO\textsubscript{2}.

Material and Methods

Mortar specimens of two types of CAC (one type of CAC was an iron-rich, dark cement (d-CAC) and the other was an iron-lean, white cement (w-CAC)) were subjected for 28 days to two different curing regimes: curing 1 (20\textdegree C, 95\% R.H.) and curing 2 (60\% C, 60\% R.H.). Mineralogical characterization was carried out by X-ray diffraction and textual characteristics as well as elemental composition were performed by means of SEM-EDAX studies. Photocatalytic activity of TiO\textsubscript{2} was assessed on mortar samples irradiated with UV radiation and exposed to an air flow composed of NO (1000 ppbv) and NO\textsubscript{2} (50-200 ppbv). The accurate measurement of the concentration of NO and NO\textsubscript{2} was carried out through a chemiluminescence analyser. Photocatalytic activity was also evaluated in the visible region adding Methyl Orange solution and measuring the colour loss by a spectrophotometer using colour coordinates in the CIELab colour space.

| Table 1. Chemical and mineralogical composition of the dark-CAC and white-CAC |
|--------------------------|--------------------------|
| Cement                  | Al\textsubscript{2}O\textsubscript{3} (% ) | CaO (% ) | Fe\textsubscript{2}O\textsubscript{3} (% ) | SiO\textsubscript{2} (% ) | SO\textsubscript{3} (% ) | Na\textsubscript{2}O+K\textsubscript{2}O (% ) | Main mineralogical phases |
| d-CAC                    | 42.0                      | 37.8      | 17.0                                   | 3.0                       | 0.1                       | 0.1                               | CaAl\textsubscript{2}O\textsubscript{4} (CA) |
| w-CAC                    | 70.9                      | 28.0      | 0.1                                    | 0.2                       | <0.3                      | <0.5                              | CaAl\textsubscript{2}O\textsubscript{4} (CA) |

Results

![Figure 1](image1.png)

**Figure 1.** XRD analysis shows the presence of pseudobrookite and ilmenite phases in d-CAC as a consequence of the interaction between TiO\textsubscript{2} and ferrie (brownmillerite) phase. In 5wt. % and 10wt. % TiO\textsubscript{2} loaded w-CAC samples, strong diffraction peaks of anatase were identified. However, for d-CAC samples the diffraction peaks of TiO\textsubscript{2} were hardly seen. At the same time, brownmillerite phase (clearly identified in the pure d-CAC sample) underwent a clear reduction in the TiO\textsubscript{2}-bearing d-CAC samples, while the appearance of pseudobrookite (Fe\textsubscript{2}TiO\textsubscript{5}) was found as a result of the TiO\textsubscript{2} reaction.

![Figure 2](image2.png)

**Figure 2.** SEM micrographs of CAC samples after curing condition 1: a) d-CAC (0 wt. % TiO\textsubscript{2}) b) w-CAC (0 wt. % TiO\textsubscript{2}) c) d-CAC (5 wt. % TiO\textsubscript{2}) d) w-CAC (5 wt. % TiO\textsubscript{2}) e) and b) present similar textural appearance with cracked surface and with identical compounds, such as hexagonal plat-like crystals of CaH\textsubscript{3} (CaH\textsubscript{3} (OH)\textsubscript{3} \textsuperscript{2+}) and metastable calcium aluminates. On the other hand, CAH\textsubscript{2} for w-CAC samples can be seen accompanied by spherical-shaped aluminohydrates. For c) inorganic and non-homogeneous aspect was seen with some ill-defined characteristics and no correlation with the TiO\textsubscript{2}-ferrie interaction by EDAX. However, SEM observations for d) allowed to see quasi-prismatic crystals, with well-defined structures covering the main part of the sample.

![Figure 3](image3.png)

**Figure 3.** Profiles of NO, NO\textsubscript{2}, and NO\textsubscript{x} abatements for d-CAC (a) and w-CAC (b) samples loaded with 10 wt.% TiO\textsubscript{2}. Three common stages: i) in the absence of UV radiation the concentration of NO and NO\textsubscript{2} was kept constant during the first 10 min. ii) Under UV radiation (30 min) the heterogeneous photocatalysis reaction took place: iii) When the UV radiation was off, the NO/NO\textsubscript{2} concentration returned to its initial value. Contrary to what is usually observed in previous works dealing with photocatalytic portland cement mortars, the NO\textsubscript{x} gas profile decreased under UV radiation. This fact has been related to a photoacidsorptio plus reaction mechanism owing to the alumina presence.

![Figure 4](image4.png)

**Figure 4.** Percentages of NO abatements for all the samples assayed. It can be observed that w-CAC samples present greater NO abatements (\%) than d-CAC samples. In general, the higher the dosage of additive, the higher NO abatement. Formation of stable phases in CAC systems will not have a negative effect on the photocatalytic activity of the loaded TiO\textsubscript{2}.

Conclusions

Results indicate:

- Better NO\textsubscript{x} abatement in w-CAC than in d-CAC under UV irradiation. Because of the presence of aluminates, CACs are suitable matrices for an effective NO\textsubscript{x} fixation, by a photoacdsorption plus reaction mechanism, yielding good final NO\textsubscript{x} removal.
- XRD and SEM studies show pseudobrookite and ilmenite presence in d-CAC samples because of the interaction between ferrie phase and TiO\textsubscript{2}. These phases present more reduced band gap than TiO\textsubscript{2}, so it causes the drop of the photocatalytic activity of d-CAC samples under UV irradiation. Brownmillerite phase also experiments a decrease in the TiO\textsubscript{2}-doped d-CAC samples.
- However, the new phases allowed d-CAC samples to show better photocatalytic activity under visible irradiation, as confirmed by degradation of methyl orange.

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