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ABSTRACT BOOK

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PREFACE

This book collects abstracts of the papers submitted to the 14th International Congress on the Chemistry of Cement (ICCC 2015), which was held in Beijing, China between October 13~16, 2015, and organized by China Building Materials Academy and the Chinese Ceramic Society. Since the First International Congress on the Chemistry of Cement started in London in 1918, it has become the most influential event for information exchange and promoting global cooperation on cement and concrete science and technology.

This congress attracted papers and attendee from 43 countries. It covers: (1) clinker chemistry, (2) hydration of portland cement, (3) supplementary cementing materials, (4) chemical admixtures and rheology, (5) durability and service life prediction, (6) alternative binders and (7) standard and codes. A large number papers discuss the considerable progress towards understanding chemistry, microstructure, and durability of cement and concrete. The challenge still remains of finding new ways to reduce CO₂ emission during cement and concrete production, to extend the service life of concrete. Considering cement and concrete as viable construction materials must be retained and sustained, considerable efforts still should focus on the environmental challenges that the industry and society now face. The main objective of this congress was to provide a platform for interactions between researchers, producers and engineers all over the world to produce cross-fertilization ideas aimed at developing rational multiple-disciplinary ideas.

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Photocatalytic performance of calcium aluminate cements modified with TiO₂

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Abstract

The photocatalytic activity of powdered TiO₂ (75% anatase, 25% rutile) was tested after the incorporation of the additive in mortars of calcium aluminate cement. Two different CACs were used according to their chemical and mineralogical composition: one of the CAC was a high alumina cement (H-CAC, 70.9% of Al₂O₃) while the other one was a low alumina cement (L-CAC, 42.0% of Al₂O₃) with a large amount of ferrite. One batch of the prepared mortars was tested after being subjected to 28 days under a normal curing regime (20°C and 95% RH). A second batch was tested after a curing regime of 60°C and 100% RH (for 24 hours) and then 20°C and 95% RH. This second curing regime intended to induce the conversion reaction, which is responsible for the formation of stable calcium aluminate hydrates at the expense of metastable hydrates. Different properties such as workability, setting time and compressive strength were determined in the tested mortars in order to study the influence of the TiO₂ addition. The photocatalytic effect was assessed by means of the NO_x abatement under UV irradiation. The TiO₂-H-CAC mortars were found excellent systems to decrease NO₂ concentrations in connection with the more abundant presence of aluminates. The better NO₂ retention improved the NO_x removal. An chemical interaction between ferrite and TiO₂ was suggested to take place in the L-CAC mortars as evidenced by XRD, SEM, EDAX and zeta potential analyses. This interaction originated two new iron titanate phases, namely pseudobrookite and, to a lesser extent, ilmenite. The reduced band-gap energy of these compounds compared with that of TiO₂ improved the photocatalytic efficiency of L-CAC samples in the visible spectrum, as proved by Methyl Orange degradation tests, conferring a self-cleaning ability to the TiO₂-bearing iron-rich L-CAC under visible illumination.

Originality

Although CAC is used in many building as well as industrial structures, its modification upon addition of photocatalytic additives has not yet been addressed and that is precisely the purpose of the present work. We intend to obtain for the first time depolluting CAC mortars modified with different amounts of TiO₂. The effect of the TiO₂ incorporation on setting time, compressive strength and mineralogical composition of the CAC mortars will be assessed. PCO efficiency of these TiO₂-bearing CAC mortars will be also measured by means of the NO_x abatement. The modified depolluting mortars could be then applied in different tunnels, industrial floors and urban areas in which CACs are usually applied.

Keywords: *Calcium Aluminate Cement; X-ray Diffraction; Compressive Strength; NO_x abatement.*

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Introduction

The main aim of this work* is to obtain for the first time depolluting calcium aluminate cement (CAC) modified with different amounts of TiO₂ in order to remove NO and NO₂ (NO_x) from the atmosphere. These toxic gases that caused atmospheric pollution, could be removed by a photochemical oxidation assisted process through TiO₂. So TiO₂ incorporation as photocatalytic additive in building materials has increased in the last years although his activity in CAC has not yet been addressed.

The aim of this work is to obtain depolluting and self-cleaning CAC mortars modified with different amounts of TiO₂.

Material and Methods

Mortar specimens of two types of CAC (one type of CAC was low alumina cement (L-CAC) with 17.0 wt. % in Fe₂O₃, and the other one contains high alumina percentages (H-CAC) with only a 0.1 wt. % in Fe₂O₃). Normal curing condition (20°C and 95% RH) was imposed to half of the samples and the second curing condition (hereinafter, forced curing condition), with high temperatures and RH (60°C and 100% RH, and after 24h, 20°C and 95% RH) to the rest of the samples. Mineralogical characterization was carried out by X-ray diffraction and textural characteristics as well as elemental composition were performed by means of SEM-EDAX studies. Photocatalytic activity of TiO₂ was assessed on mortar samples irradiated with UV radiation and exposed to an air flow composed of NO (1000 ppbv) and NO₂ (50-200 ppbv). The accurate measurement of the concentration of NO and NO₂ 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 L-CAC and H-CAC

Cement	Al ₂ O ₃ (%)	CaO (%)	Fe ₂ O ₃ (%)	SiO ₂ (%)	SO ₃ (%)	Na ₂ O+K ₂ O (%)	Main mineralogical phases	Minor mineralogical phases
L-CAC	42.0	37.8	17.0	3.0	0.1	0.1	CaAl ₂ O ₄ (CA)	Ca ₂ FeAlO ₅ (C ₂ AF), Ca ₁₂ Al ₁₄ O ₃₃ (C ₁₂ A ₇), β-Ca ₂ SiO ₄ (C ₂ S), Ca ₃ TiFe ₂ O ₈ , FeO
H-CAC	70.9	28.0	0.1	0.2	<0.3	<0.5	CaAl ₂ O ₄ (CA), CaAl ₄ O ₈ (CA ₂)	Ca ₁₂ Al ₁₄ O ₃₃ (C ₁₂ A ₇)

Results

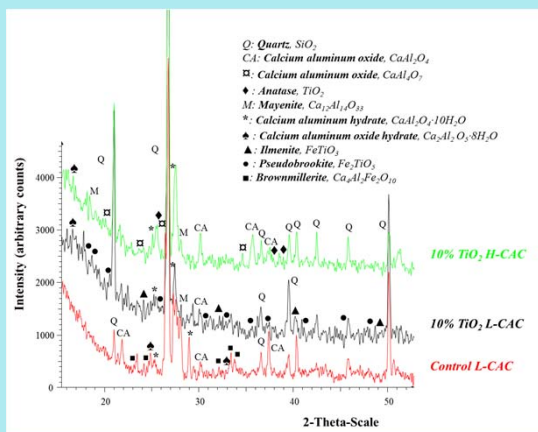


Figure 1. XRD studies of H-CAC showed the absence of any new distinct crystalline phase involving TiO₂, indicating that no strong chemical interaction took place upon addition of the TiO₂ in these samples. In 10 wt. % TiO₂-loaded H-CAC sample, the anatase peaks were identified. Nevertheless, for L-CAC samples, the diffraction peak of anatase almost completely disappeared and the presence of pseudobrookite and ilmenite phases is seen as a consequence of the interaction between TiO₂ and ferrite (brownmillerite) phase.

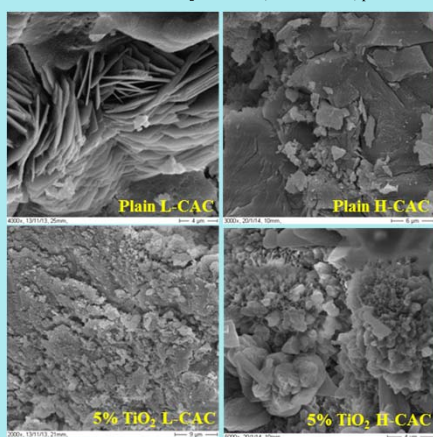


Figure 2. Plain L-CAC samples as well as H-CAC samples present similar textural appearance (with fractured surfaces and with some well identified compounds, such as hexagonal plate-like crystals of C₂AH₄ metastable calcium aluminates). The addition of 5 wt.% of TiO₂ resulted in a different micro-morphology depending on the type of cement: for L-CAC samples irregular and non-geometric aspect were seen with some ill-defined clusters, under normal curing regime. Nevertheless, SEM studies let us see prismatic crystals with well-defined structures in H-CAC samples.

Conclusions

Results indicate:

- XRD and SEM studies show an interaction between the ferrite (brownmillerite) phase present in the L-CAC with the TiO₂ added, is the responsible of the formation of certain amounts of titanates, mainly pseudobrookite. This phases present more reduce band gap than TiO₂ so its photocatalytic activity is higher under visible irradiation.
- Better NO abatements under UV irradiation are seen in H-CAC samples because of the lack of reduce band gap phases.
- However, these new phases allowed L-CAC samples to show better photocatalytic activity under visible irradiation, as confirmed by degradation of methyl orange.

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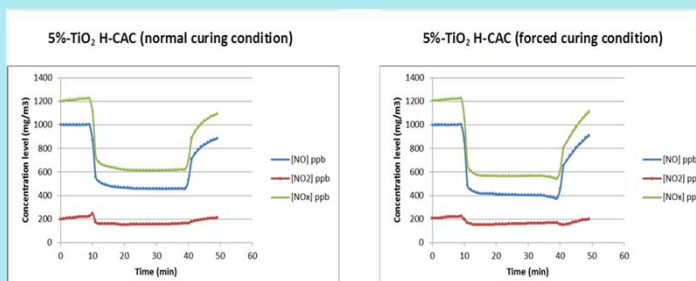


Figure 3. Profiles of NO, NO₂ and NO_x abatements for H-CAC samples loaded with 5 wt.% TiO₂ under normal and forced curing condition. Three common stages are seen: i) in the absence of UV radiation the concentration of NO and NO₂ was kept constant during the first 10 min. ii) Under UV radiation (30 min) the heterogeneous photocatalysis reaction took place iii) When the UV radiation was off, the NO/NO₂ concentration returned to its initial value. Contrary to what is usually observed in previous works dealing with photocatalytic portland cement mortars the NO₂ gas profile decreased under UV radiation. This fact has been related to a photoadsorption plus reaction mechanism owing to the aluminates presence.

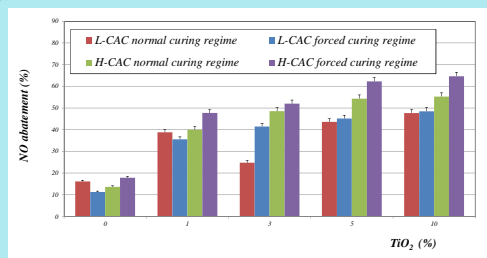


Figure 4. Percentages of NO abatements. H-CAC abatements are clearly greater than L-CAC ones due to the absence of iron phases. The higher dosage of additive, the higher NO removal.

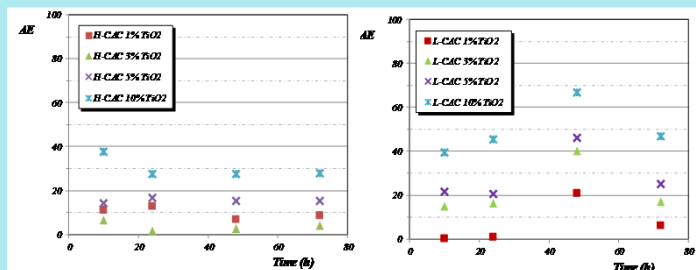


Figure 5. Color variation of methyl orange-treated samples under visible light irradiation in a) TiO₂-doped H-CAC and b) TiO₂-doped L-CAC samples. Contrary to NO abatement results, photocatalytic activity was lower for H-CAC samples than for L-CAC owing to the lack of more reduced band gap phases as pseudobrookite (2,18 eV).