

Article Influence of Magnesium Oxide on Carbonation of Cement Paste Containing Limestone and Metakaolin

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Abstract: One of the major durability concerns for limestone calcined clay cement (LC^3) concrete is its high susceptibility to atmospheric carbonation that could lead to an early onset of electrochemical corrosion of reinforcing steel in concrete structures. Aimed at designing innovative LC^3 formulations with potentially enhanced carbonation resistance, this preliminary study investigates the influence of reactive magnesia (MgO) on the early-age strength development, hydrates assemblage, and atmospheric carbonation resistance of ternary ordinary Portland cement-metakaolin-limestone blends with a constant 45% ordinary Portland cement (OPC) replacement level. The results show that the MgO addition impedes the formation of AFm phases (hemicarbonate and monocarbonate), likely through interfering reactions between metakaolin and portlandite. The formed brucite due to MgO hydration can uptake atmospheric CO_2 to some extent, but at a considerably slower rate, in comparison with other hydrates in LC^3 including AFm, AFt, and portlandite. The enhancement of carbonation resistance of LC^3 pastes is insignificant by MgO addition of less than 5%.

Keywords: LC3; low-carbon binder; natural carbonation; durability of concrete; MgO

1. Introduction

Due to the high demand for concrete in the global construction industry, the massive production of OPC clinkers generates a great carbon footprint, accounting for approximately 8% of the total anthropogenic carbon emission [1,2]. Partially substituting OPC clinkers with supplementary cementitious materials (SCMs), including coal fly ash, ground granulated blast-furnace slag, limestone, calcined clays, and volcanic ash, has been an industrial practice to improve the ecoefficiency of concrete [3–7]. In addition, SCMs, particularly those with a chemical composition rich in alumina and silicon, can benefit from the long-term mechanical and durability performance of SCMs-blended OPC concrete. However, due to the phasing out of coal combustion plants worldwide, the long-term availability of high quality coal fly ash is uncertain. In addition, the production of ground granulated blast-furnace slag is relatively small considering the huge demand for low-carbon concrete, and its majority has already been consumed in modern concrete construction. As such, there exists a strong incentive to identify and develop alternative SCMs that are abundant, cost-competitive, and performance-efficient, for low-carbon concrete production. One of these promising SCMs is calcined clays, known as natural pozzolan in the concrete communities [8].

Limestone calcined clay cement (LC³) material refers to the ternary binder mixture of calcined clay (including calcined kaolinite, also known as metakaolin) and limestone, substituting a certain portion of OPC clinker in concrete [9]. One of the most chemically reactive and geographically abundant clay minerals is kaolinite, and its anhydrous calcined form, namely metakaolin, has been a well-recognized SCM in the concrete industry [8]. The manufacturing cost of metakaolin (MK) is comparatively higher than conventional



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). SCMs (e.g., coal fly ash and ground granulated blast-furnace slag), although its calcination temperature (700 to 850 °C) is generally low and no special equipment is needed. However, limestone (LS) is easily accessible due to its abundance in waterbeds or quarries, making it a cost-efficient material to be blended into cement pastes, which, to some extent, offset the cost of MK. As an economical and environmentally friendly material, LS has a stable long-term supply, but when its addition exceeds 10% of OPC clinker by weight, it may compromise the concrete properties [10,11]. The combination of MK and LS offsets these deficiencies, so they are often mixed to achieve a result comparable in material performance and affordability.

Although LC³ has been shown to possess excellent long-term mechanical and, on some occasions, superior durability performance (particularly the chloride and sulfate resistance) than conventional OPC [12–14], it tends to have relatively poor carbonation resistance [9,15–17], thus increasing the corrosion risk of reinforcing steel embedded in carbonated concrete. The comparatively poor carbonation resistance of LC³ primarily originates from a low amount of portlandite, which serves as a pH buffer in carbonating concrete. As the conversion of portlandite to calcium carbonates occurs in concrete due to carbonation, the pH of pore solution decreases, which leads to instability and dissolution of the protective passive film on reinforcing bars. As such, there is a pressing need to identify suitable additives or admixtures that could effectively mitigate and slow down the atmospheric carbonation of LC³ concrete.

The reactive magnesia (magnesium oxide, MgO) as an additive in concrete has demonstrated benefits in enhancing the carbonation resistance of conventional OPC [18,19] and alkali-activated concrete [20,21]. However, to the best of the authors' knowledge, no work regarding the influence of reactive MgO addition on the reaction and carbonation of LC^3 systems has been documented in the literature. In this work, the influence of reactive MgO addition on the strength development, hydrates assemblage, and atmospheric carbonation resistance of LC^3 pastes is studied. The outcome of this research may contribute to the development of mitigation strategies against the carbonation of LC^3 concrete and thus promote its wider acceptance in the construction industry.

2. Materials and Methods

As shown in Table 1, the reference LC^3 paste (as control) was formulated by blending OPC, calcined kaolinite (metakaolin, MK), limestone (LS), and anhydrite calcium sulfate (Cs) powders at a mass ratio of 52.5:30:15:2.5 (following the work of reference [17]). To study the influence of MgO addition on the properties of LC^3 pastes, three incorporation dosages, including 2.5%, 5%, and 7.5% by powder mass (powder means the summation of anhydrous OPC+MK+LS+Cs) were considered, and the corresponding mixes were denoted as LC^3 _2.5M, LC^3 _5M, and LC^3 _7.5M, respectively. All four designed LC^3 pastes had the same water-to-powder (excluding MgO) mass ratio of 0.4. In addition, pure OPC mixture with the same water-to-powder was prepared. The oxide composition of the raw powder materials determined by X-ray fluorescence spectrometry (JEOL JSX-3201Z) is as follows: The OPC contains 66.5% CaO, 20.2% SiO₂, 4.0% Al₂O₃, and 0.9% MgO; metakaolin contains mainly 55.3% SiO₂ and 43.6% Al₂O₃; limestone contains about 54.6% CaO; and MgO powder has a purity of 97.4%. In addition, the median particle sizes (D50) of the used OPC, MK, LS, and MgO powders, measured by laser diffraction technique, were 12.5 µm, 2.4 µm, 2.1 µm, and 7.8 µm, respectively.

It should be noted that adding calcium sulfate to the LC³ mixture is to supply extra sulfates to balance the sulfate amount, thus compensating the acceleration of aluminate hydrates peak in the isothermal calorimetry due to the filler effect of fine particles (i.e., metakaolin, limestone, and MgO) in LC³ [22]. The anhydrous OPC, MK, LS, Cs, and MgO (if any) were dry blended for at least 5 min in a mixer to obtain a homogenous powder mixture. Then, deionized water incorporating a proper dosage of superplasticizer was added to the mixer. After being homogenously mixed, the freshly mixed pastes were immediately poured into 40-mm cubic stainless-steel molds (conforms to EN 196), lubricated with mineral oils, and then demolded after 23 ± 1 h. Afterwards, the specimens were placed and cured in sealed plastic bags stored in a closed moist cabinet at room temperature (~20 °C) until reaching designated ages. The cubic compressive strength of the specimens was measured at ages of 1, 7, and 28 days on three duplicates.

Table 1. Mixture parameters of LC³ pastes containing MgO additive.

Mixture ID	OPC (%)	MK (%)	LS (%)	Anhydrite CaSO ₄ (%)	MgO (%)	Water/Powder Ratio
LC ³ _Control	52.5	30.0	15.0	2.5	-	0.4
$LC^{3}_{2.5M}$	52.5	30.0	15.0	2.5	2.5	
LC^3_5M	52.5	30.0	15.0	2.5	5.0	
LC ³ _7.5M	52.5	30.0	15.0	2.5	7.5	

All percentages are weight-based.

To investigate the effects of MgO on the phase assemblage of LC³, materials characterization on hardened paste samples at 1, 7, and 28 days was conducted by using X-ray diffraction and thermogravimetric analysis. X-ray diffraction (XRD) analysis was performed by a PANAlytical X'Pert PRO X-ray diffractometer. Cu-K α radiation with $\lambda = 1.5418$ Å was employed and the diffraction patterns were measured from 5 to 45° 20 with a step size of 0.02° 20. Thermogravimetric analysis (TGA) was carried out by a PerkinElmer TGA 4000. Approximately 50 mg of the fine powder was loaded into a ceramic crucible and heated from 30 to 900 °C at a rate of 20 °C/min during N₂ purging at 30 mL/min. Prior to measurements, the specimens with hydration stopped by immersion in isopropanol alcohol for 7 days were vacuum-dried in a desiccator for at least 3 days.

After 28 days of sealed curing at room temperature, the 40-mm cubic specimens were exposed to an indoor environment (approximately 60% relative humidity and 20 °C on average) for natural carbonation. After being carbonated for ~46 weeks, the specimens were split in the middle section and sprayed with phenolphthalein solution. In parallel, carbonation tests of powder samples were conducted, which allowed specific investigation of carbonation-induced phase alterations [21]. After 28 days of sealed curing, the samples were pulverized and sieved through 150 μ m, and subsequently exposed to the same indoor environment for natural carbonation. The phase alternations of atmospherically carbonated samples at various time intervals were studied by XRD and TGA.

3. Results and Discussion

3.1. Compressive Strength

The early-age compressive strength development of LC^3 containing various dosages of MgO additive is shown in Figure 1. In comparison with the OPC reference of the same water-to-powder (binder) ratio, the control LC^3 paste (without MgO addition) shows lower strength at 1 day but then surpasses at 7 days. The catching up of strength gain of control LC^3 is due to the progressive pozzolanic reaction of MK that forms additional strength-giving products, including calcium-aluminosilicate-hydrate (C-A-S-H) and AFm phases (hemicarbonate and monocarbonate) [13,23]. On the other hand, the 1-day strength of LC^3 paste seems to be lowered by MgO addition, seemingly related to its impact on the hydration process, as will be elaborated later. This finding is consistent with the general observation in the literature that incorporating MgO leads to a strength decrease in cementitious matrices [24]. At 7 days and onwards, the strength of LC^3 with a 2.5% MgO addition is consistently lower than that of the control LC^3 paste, whilst those with higher MgO addition percentages show comparable or even slightly higher compressive strength.



Figure 1. Compressive strengths of OPC and LC³ cubic specimens at 1, 7, and 28 days (The mean value is the average of three duplicates).

3.2. Phase and Molecular Analysis

The XRD and TGA results of LC3 containing various dosages of MgO additive are shown in Figures 2 and 3, respectively. A significant reduction in the amount of portlandite (CH) in LC3 pastes from 1 day to 7 days is apparent, which is congruent with the greatest strength increase during this period due to the ongoing MK reaction. On the other hand, with the increasing MgO addition in LC3 pastes, it can be seen that the diffraction peak intensity related to CH at various ages tends to be higher at the same ages. This observation implies that the MgO incorporation in LC3 slows down the chemical reaction of MK with CH. This argument is also supported by the lower diffraction intensity of AFm phases in LC3 pastes with a higher amount of MgO additive at the same ages. It is known that in LC3, the reaction of MK (idealized as AS2) with CH produces both C-A-S-H and AFm phases, as described in reference [25]. As the MK slows down the chemical reaction between MK and CH, the small amount of incorporated MK may result in a reduction in compressive strength, as observed in Figure 1. However, as the incorporating percentages of MgO increases from 2.5% to 7.5%, the reduction of free water-to-powder (here, the powder include MgO) ratio may dominate the strength development of hardened pastes, resulting in comparable strength as the reference mixture.

The TGA results support the conclusion that the MgO addition slows down the reaction of MK in LC³. It is evident that the mass loss humps assigned to dehydration and dehydroxylation of AFm phases, at ~180 °C and ~250 °C, respectively, are noticeably smaller in LC³ with a higher amount of MgO. Meanwhile, after 7 days and 28 days of reaction (see Figure 3), the presence of CH is still detectable in LC³ containing MgO, while it is untraceable in plain LC³. Moreover, the decomposition peak related to brucite (MH), whose content increases with the increase in MgO addition dosage, can be unambiguously identified in the TGA curves.



Figure 2. The XRD results of LC³ pastes containing various dosages of MgO at ages of 1 day, 7 days, and 28 days.



Figure 3. The TGA results of LC³ pastes containing various dosages of MgO at ages of 1 day, 7 days, and 28 days.

3.3. Carbonation Resistance

The split cross-sections of cubic specimens colored by phenolphthalein solution are shown in Figure 4. Although marginally, it shows that an addition of 7.5% MgO in LC³ slightly reduces the carbonation depth of LC pastes. However, for LC³ pastes with a lower dosage of MgO addition, their carbonation depths are comparable to the plain LC³. It remains unclear if the slightly reduced carbonation depth in LC³_7.5M is due to an improved CO₂ binding capacity and/or reduced penetrability due to reduced water-topowder ratio (powder here includes MgO). As discussed earlier, the MK slows down the chemical reaction between MK and CH, thus leaving a greater amount of CH for CO₂ uptake. In addition, the hydrated MgO can bind CO₂ itself [26,27], which contributes to a potentially higher CO₂ binding capacity.



(a) LC3-Control

(b) LC3-2.5MgO



(c) LC3-5.0MgO

(d) LC3-7.5MgO

Figure 4. Photos of the sliced LC³ specimens sprayed with phenolphthalein after natural carbonation for ~46 weeks after 28 days of sealed curing. (**a**) LC³-Control; (**b**) LC³-2.5 MgO; (**c**) LC³-5.0 MgO; (**d**) LC³-7.5 MgO.

The XRD and TGA results of LC^3 pastes after being naturally carbonated for 1 week, 2 weeks, 3 months, and 6 months are shown in Figures 5 and 6, respectively. It is clear that the natural carbonation of LC^3 leads to virtually complete decomposition of AFt and AFm phases, rendering the simultaneous formation of calcium carbonates, i.e., calcite and aragonite. In addition, it shows that the remaining CH in LC^3 containing MgO is rapidly carbonated after exposure to air for ~1 week (see Figure 6a). In contrast, the hump related to MH remains remarkable even after a 6-month carbonation in the air. However, it is evidenced that the MH content is gradually lowered as the carbonation proceeds (see Figure 6c,d), suggesting that MH can uptake CO_2 to some extent, but at a much slower rate than the other hydrated phases including AFm, AFt, and CH in LC^3 systems. It should be noted that the samples used in the carbonation tests were powders, in which the carbonation kinetics of MH did not seem to be limited by the contact area, but by the carbonation potential and thermodynamic constrains of MH phases.



Figure 5. The XRD results of LC³ pastes containing various dosages of MgO after natural carbonation for 1 week, 2 weeks, and 3 months.



Figure 6. The TGA results of LC^3 pastes containing various dosages of MgO after natural carbonation for 1 week, 2 weeks, 3 months, and 6 months. (a) 1-week carbonation; (b) 2-week carbonation; (c) 3-month carbonation; (d) 6-month carbonation.

4. Conclusions

In this work, the influence of reactive magnesium (MgO) on the strength development, phase assemblage, and carbonation resistance of limestone calcined clay cement (LC³) pastes was studied, and aimed towards developing magnesium-based additives for carbonation mitigation. Based on the experimental results, the following conclusions can be drawn:

(1) The addition of MgO in LC³ tends to reduce the very early-age strength but has a somewhat detrimental effect on the later-age strength.

(2) The addition of MgO slows down the chemical reaction of MK in LC³, forming a smaller amount of AFm phases and leaving more CH in LC³. As such, small amounts (2.5%) of incorporated MK can result in the reduction in early-age compressive strength. However, as the incorporating percentages of MgO increases to 7.5%, the reduction in free water-to-powder ratio can dominate the strength development of hardened pastes, resulting in comparable strength as the reference mixture.

(3) The improvement of carbonation resistance of LC^3 by MgO addition is insignificant based on the present experimental results. The formed brucite can uptake CO₂ to some extent but at a much slower rate, in comparison to hydrated phases including AFm, AFt, and CH. Although MgO may be capable of gradually binding some CO₂, its impact on the hydration and phase formation of LC^3 can offset this beneficial impact.

Future works regarding the (i) influence of physiochemical characteristics of MgO on the hydration and performance of LC³ systems; (ii) optimum design of MgO-modified LC³ with significantly enhanced carbonation resistance while preserving remarkable strength achievement; and (iii) Stargates to increase the carbonation rate of MgO particles in LC³ systems, are recommended.

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