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Regulating hydration and microstructure development of reactive MgO cement by citric acids



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densification of the microstructure.

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ARTICLE INFO	A B S T R A C T				
Keywords: Reactive MgO cement Citric acid Hydration Carbonation Carbon curing	Reactive MgO cement (RMC) is a novel binder formed through the hydration and carbonation of MgO, but its low reactivity hinders its wider application. Preliminary research has suggested that citric acids can form compounds with Mg^{2+} that regulate these processes, but the mechanism is yet to be understood well. This study investigated the effects of citric acids on the fresh and hardened properties of RMC. Results showed that the shear yield stress and plastic viscosity of the RMC pastes decreased with the addition of citric acids. Under standard curing, 4 <i>wt</i> % and 8 <i>wt</i> % citric acids increased the compressive strength of RMC by ~100 % at 14 days. The adsorption of citrate on MgO inhibited the formation of brucite, forming an amorphous network-like microstructure crystal-lised after 14 days. Under CO ₂ curing, the compressive strength of RMC with 8 <i>wt</i> % citric acids increased by 12 % at 14 days. which could be ascribed to the porous microstructure formed that promotes the uptake of CO ₂ and the				

1. Introduction

Reactive MgO cement (RMC) has attracted great interest from cement science and engineering communities because of its lower calcination temperature compared to Portland cement (PC) (i.e. 700-1000 °C vs 1450 °C), its ability to sequester CO₂ through mineralisation, and its potential to be fully recyclable at the end-of-life [1–4]. The strength gain of RMC originates from its reactions with water through hydration and subsequently with CO₂ via carbonation following a procedure described by Eqs. (1) and (2) [5–7].

$$MgO + H_2O \rightarrow Mg(OH)_2$$
 (brucite) (1)

$$Mg^{2+} + 2HCO_3^- + x H_2O \rightleftharpoons MgCO_3 \cdot x H_2O + H^+ + HCO_3^-$$
(2)

It is reported that the hydration of rMgO (Eq. (1)) follows the firstorder kinetic equation [6,8], i.e. $\alpha = 1 - \exp(-kt)$, where α is the degree of hydration, *k* is a hydration rate constant and *t* is the hydration time. During hydration, MgO particles dissolve and their size constantly shrinks at the early stage, around which hexagonal Mg(OH)₂ precipitates over time, blocking the diffusion of water to the surface of surrounded MgO, gradually decreasing the hydration rate [9,10]. When the hydration products contact with CO₂, carbonation happens and a variety of carbonates, such as magnesium carbonate (MgCO₃), hydrated magnesium carbonates (HMCs) including nesquehonite (MgCO₃·3H₂O), lansfordite (MgCO₃·5H₂O), artinite (Mg₂CO₃(OH)₂·3H₂O) and hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O), etc., can be formed (Eq. (2)) [8–14]. Besides crystalline HMCs, amorphous HMCs can also be formed. These complex phases are composed of nanoparticles and serve as precursors to crystalline HMCs [15–17].

 CO_2 concentration plays a critical role in the formation of HMCs and significantly affects the compressive strength gain of hardened RMCs. Dung et al. [18] investigated the development of microstructure and mechanical properties of RMC concrete under ambient curing (i.e. CO_2 concentration ~0.04 *vol*%) and accelerated carbonation curing (i.e. with CO_2 concentrations of ~5, 10 and 20 *vol*%). Their results showed that the compressive strength of RMC, with the solution to the binder mass ratio of 0.65 and the solution to coarse aggregate mass ratio of 0.34, under ambient curing for 28 days was ~10 MPa, with the major increase in compressive strength occurring from 3 to 7 days of curing, after which it barely increased. At CO_2 concentrations of 5–20 *vol*%, the compressive strength of RMC showed a notable increase, reaching 55–65 MPa (i.e.,

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increased by 450%–550 %) after 28 days, highlighting the substantial role of carbonation in the strength gain of RMCs. However, it was found that the higher the CO_2 concentration during carbonation curing, the lower the hydration and carbonation degree of RMCs [14,19,20]. At 7 days, the unreacted MgO in the hardened RMC paste under ambient curing was 16.8 % by weight. When the CO_2 concentrations were 5 %, 10 %, and 20 %, the unreacted MgO gradually increased to 19.7 %, 27.4 %, and 34.9 % all by weight, respectively [18]. This inevitably raises the question of whether improving the hydration and carbonation of MgO under accelerated carbonation curing can further enhance the mechanical properties of RMCs.

One answer to this question is to use hydration agents to promote the dissolution of MgO [5,21–23], and an increasing interest in the research community is to focus on enhancing the performance of RMCs through additives and modification of MgO [24-26]. Du and Unluer [26] modified Mg(OH)₂ using an acetate-based solution, resulting in a twofold increase in RMC's compressive strength, because of the alteration in the morphology of the carbonation products further influencing the carbonation process. One of the most effective hydration agents reported is magnesium acetate (Mg(CH₃COO)₂) [19,22,27,28], which can facilitate the dissolution and precipitation process of MgO, significantly enhancing the initial hydration rate of MgO (i.e. by 30–35 %) [22]. Hoang et al. [29] achieved self-carbonation of RMC, with a liquid solution to reactive MgO mass ratio of 0.7, through a synergistic combination of microbial carbonation process and Mg(CH₃COO)₂, resulting in a compressive strength of \sim 15 MPa in the natural environment. Dung et al. [27] observed a larger crystal size and denser carbonate morphology in RMC after introducing Mg(CH₃COO)₂ and high-temperature pre-curing to RMC, resulting in a compressive strength of 56 MPa at 28 days for RMC concrete (with a W/B mass ratio of 0.55). NaHCO₃ can increase the initial pH value of the RMC system and the concentration of CO_3^{2-} in the system [30]. This enhancement in the initial carbonation degree improves the content and microstructure of carbonates, resulting in a 95 % increase in the compressive strength of RMC at 56 days (i.e., 40 vs 78 MPa with a W/B mass ratio of 0.7). Co-applying NaHCO₃ and NaCl [31] resulted in the compressive strength of RMC (with a W/B mass ratio of 0.7) increased from 20 to 50 MPa, representing a 150 % increase, under accelerated carbon curing (i. e. CO₂ concentrations ~10 vol%, 80%RH, and 30 °C). Besides, the dispersant agent (NaHMP) can reduce the water requirement of the RMC system to form a denser network microstructure [10]. Therefore, additives play an important role in dictating the properties of RMCs, as they can potentially regulate hydration, and subsequently influence carbonate precipitation and other properties, such as pH, of RMC.

Citric acid is a type of tricarboxylic organic acid that can affect the rheological properties and hydration of cementitious materials and the microstructure of hydration-hardening pastes. Citric acids can retard the formation of hydration products of PC by delaying the dissolution of C₃A and C₃S [32]. Singh et al. [33] found that the zeta potential of cement decreased with increasing citric acid dosage (i.e. from 0 to 0.4 wt%), evidencing the adsorption of citric acid ions on the surface of cement particles. Citrate can be complex with Ca²⁺ and reduce the concentration of Ca^{2+} in the pore solution [34]. According to thermodynamic analyses, citric acids inhibit the dissolution of cement particles by forming a protective film via adsorbing citrate on the clinker surface, rather than by creating a complex phase. The effects of citric acids on the mechanical properties of different cementitious materials vary. The compressive strength of Portland/calcium aluminate blended cement decreases with the addition of citric acids, regardless of their dosage [36]. However, the compressive strength of self-compacting concrete can increase at 0.025 wt% citric acid dosage, and then gradually decrease with the increase in citric acid dosage (i.e. from 0.05 % to 0.2 wt%) [37]. The compressive strength of magnesium phosphate cement (MPC) significantly increases because the content of hydration products (i.e. struvite) increases with the increase in citric acid dosage (i.e. from 0 to 8 wt%). The compressive strength of MPC at 8 wt% citric acid dosage

Table 1

Chemical compositions (wt.%) of light-burnt MgO.	

MgO	\$10 ₂	CaO	Al_2O_3	Fe ₂ O ₃	SO_3	P_2O_5	Others	LOI (%)
91.78	4.98	1.82	0.61	0.43	0.18	0.04	0.16	4.80

rises from 36.4 to 70.5 MPa (i.e. increased by 94 %) at 28 days [38]. Moreover, citric acids have proven to be effective in enhancing the water-resistance of magnesium oxysulfate (MOS) cement and magnesium oxychloride (MOC) cement, as well as altering the rheological properties and phase composition of MOS cement [39–41].

Citric acids can affect cementitious pastes' rheological properties, hydration, and mechanical properties. However, the effects of citric acids on the compressive strength and microstructural evolution of RMC have not been investigated. It is worth exploring whether citric acids will also affect the degree of carbonation, which would consequently influence the compressive strength of RMCs. In line with these, this study investigated the effects of citric acids on the rheological properties, mechanical properties, microstructural evolution and carbonation of RMCs. The rheological properties and exothermic hydration of fresh RMC pastes mixed with citric acids were first investigated in this study. The compressive strength of RMC mortars mixed with citric acids under standard curing (with $(20 \pm 1)^{\circ}$ C, 95%RH, and ~0.04 vol%CO₂) and accelerated carbonation curing (with $(20 \pm 3)^{\circ}$ C, 70%RH, and 20 vol% CO₂) was measured. XRD and TG were employed to study the effects of citric acids on the evolution of the phase composition of the RMC pastes. The micro-morphology and pore structure evolution obtained by scanning electron microscope (SEM) and nuclear magnetic resonance (NMR) were used to explain the evolution of the compressive strength of RMCs under hydration and carbonation curing.

2. Materials and methods

2.1. Materials and sample preparation

In this study, light-burnt MgO obtained from magnesite was used as the base binding material for all formulations investigated. Table 1 presents the chemical compositions of the MgO, while Fig. 1 shows the MgO's XRD pattern and its particle size distribution. The analytical reagent citric acid ($C_6H_8O_7$) was acquired from Macklin Co. Ltd., Shanghai, China with purity>99.5 % by weight and its molecular structure is shown in Fig. 2.

In this study, the dosages of citric acids varied between 0.05 %, 0.1 %, 0.5 %, 1 %, 2 %, 4 %, and 8 % by mass of the binder. To prepare samples, citric acids were dissolved in deionised water before mixing with other ingredients. Then, the mortar was prepared with a water (with citric acid dissolved)-to-MgO mass ratio of 0.7 and a sand-to-MgO mass ratio of 3.0 before casting cubic samples with the sizes of 40×40 \times 40 mm³. The mortar samples were de-moulded after 48 h of curing in a standard curing room and then placed in a carbonation chamber for carbon curing until the testing age. Thin sheet paste samples (with a thickness of \sim 2 mm) were also prepared at a water-to-MgO mass ratio of 0.6 to investigate their phase composition and microstructural evolution. Both mortar and paste samples were prepared and then subjected to standard curing (with (20 \pm 1) ^{o}C , 95%RH, ${\sim}0.04$ vol%CO_2) or carbonation curing (with (20 \pm 3) °C, 70%RH, 20 vol%CO₂). A sample identification system was adopted in this study. According to this identification system, a sample identifier is represented as B or C followed by a number, in which B represents the samples under standard curing and C under carbonation curing, and the number after B or Crepresents the dosage of citric acids in percentages of the mass of the binder.

The hydration of all paste samples was terminated through solvent exchange with isopropanol (with a liquid (isopropanol)-to-solid (paste samples) volume ratio of 5). After 7 days of solvent exchange, the samples were vacuum dried at 45 $^{\circ}$ C for 48 h. Some samples were



Fig. 1. (a) XRD pattern and (b) the particle size distribution of light-burned MgO.



Fig. 2. Molecular structure and 3D model of a citric acid molecule.



Fig. 3. (a) The rheology test protocol and (b) the shear stress-shear rate relationship conforming to the Bingham model.

employed for SEM analyses, while others were ground to powder with a particle size smaller than 75 μ m for X-ray diffraction (XRD) and thermogravimetric (TG) analyses. All samples were stored under vacuum conditions throughout the experimental programme.

2.2. Methods

2.2.1. Rheology test and data interpretation

The plastic viscosity and shear yield stress of fresh RMC pastes were measured using a MARS 40 rheometer (Thermo Fisher Scientific, Germany). The designated amounts of MgO powder and water with citric acids, if present, were mixed for 2 min to prepare the RMC paste, and the prepared paste was then placed in the rheometer for the rheology test. All paste samples had the same age at the start of the rheology test. The rheology test protocol is depicted in Fig. 3a. Initially, the pre-shearing lasted for 1 min at a constant shear rate of 50 s⁻¹, followed by a 2-min rest period while the shear rate was 0 s⁻¹. Subsequently, the shear rate was increased from 0 to 50 s⁻¹ and then decreased from 50 back to 0 s⁻¹. The Bingham model (Fig. 3b) was employed to fit the shear stress-shear rate data obtained in the descending loading branch (i.e. the "down curve" in Fig. 3a), to determine shear yield stress and plastic viscosity of RMC pastes.

2.2.2. Hydration heat

The isothermal calorimetry was employed in this study to measure the exothermic rate and the cumulative heat release of RMC pastes using



Fig. 4. (a) Shear stress vs shear rate and (b) plastic viscosity vs shear rate of RMC pastes.

a TAM AIR 8-channel micro-calorimeter (TA Instruments Ltd.) at 20 °C. During the test, a designated amount of citric acids (i.e. 0.05 %, 0.1 %, 0.5 %, 1 %, 2 %, 4 %, or 8 wt% of the binder (i.e., in this case, 1.6g MgO)) was pre-dissolved into 1g of deionised water. Then, the solution was mixed with 1.6g of MgO in the channel, and the heat evolution was monitored for 72 h using an internal stirring method at a recording time interval of 20 s.

2.2.3. Compressive strength

The compressive strength of mortar samples at 3, 7 and 14d was determined according to the Chinese Standard GB/T 17671-2021. In line with this, the cubic samples with the sizes of $40 \times 40 \times 40$ mm³ were tested under direction compression using a MTS CMT5504 electrome-chanical test system (MTS Corporation, USA) with a loading rate of 2500N/s (i.e. 1.56 MPa/s), which falls in the loading rate range recommended by the Chinese Standard GB/T 17671-2021. The average strength of four cubic samples of a formulation was taken as the representative compressive strength of the formulation. The strength growth rate was defined as follows to evaluate the effects of citric acid dosage on the compressive strength of RMC mortars:

$$R_i = rac{f_i - f_0}{f_0} imes 100\%$$

Where R_i is the strength growth rate of RMC mortars when the dosage of citric acids is *i* (*in percentage*), f_i is the compressive strength of RMC mortars when the dosage of citric acids is *i* (*in percentage*), and f_0 is the compressive strength of RMC mortars without citric acids.

2.2.4. X-ray diffraction(XRD) analysis

XRD patterns of RMCs aged 3 and 14 days were determined by a Bruker D8 Advance X-ray diffractometer using Cu K α radiation ($\lambda = 1.54184$ Å, 40 kV, 40 mA). The scanning speed was 10°/min and the scanning range was 10–80°. The TOPAS software was employed to perform a quantitative analysis of the present phases by comparing the integrated intensity of a standard phase (i.e. internal standard) with a known proportion to that of the phases being studied. The internal standard used for quantification was corundum (Al₂O₃) at 20 *wt*%.

2.2.5. Thermogravimetric(TG) analysis

The RMC samples were tested using a TGA55 instrument (TA Corporation, USA) under a nitrogen atmosphere, employing a heating rate of 10 °C/min within a 30–800 °C temperature range. About 20–25 mg of RMC paste powder was used for TG-DTG analyses at the curing ages of 3 and 14 days for both non-carbonated and carbonated samples. The mass

loss at the temperature ranges of 300–500 $^\circ C$ was calculated to quantify the amounts of reaction products (e.g. brucite).

2.2.6. Morphology

The microstructures of the hardened RMC pastes were characterised by a GeminiSEM360 scanning electron microscope at an accelerated voltage of 2 kV. The two non-carbonated and carbonated paste samples aged 3d and 14d were coated with gold before the SEM examination.

2.2.7. Low-field nuclear magnetic resonance (NMR) analysis

NMR can measure concrete's total porosity and pore size distribution [42–45]. The Carr-Purcell-Meiboom-Gill (CPMG) experiment can resolve the mobile water into fractions in different types of pores (i.e. depending on pore size) based on their spin-spin relaxation times (T₂). By analysing the T₂ spectrum distribution of water molecules in the sample, the porous microstructure of the material can be characterised. The total porosity and T₂ spectrum distribution of RMC pastes treated with water retention agents were analysed using a MicroMR20-025V low-field NMR analyser.

3. Results and discussion

3.1. Plastic viscosity and shear yield stress

Citric acids significantly affect the rheological properties of cementitious materials [37,39,46], but there is limited research on their impact on the rheological properties of RMCs. The effects of citric acid dosage on the shear yield stress and plastic viscosity of RMC pastes under varying shear rates are illustrated in Fig. 4. The plastic viscosity and shear yield stress of RMC paste B0, B0.05, B0.1 and B8, i.e. without and with 0.05 %, 0.1 % and 8 *wt*% citric acids, respectively, were obtained by fitting the shear stress-shear rate dataset, obtained during the descending loading branch, conforming to the Bingham model.

Citric acids significantly influenced the rheological properties of RMC pastes. The plastic viscosity and shear yield stress of RMC pastes gradually decreased with increasing citric acid dosage. At the dosages of 0.5 %, 1 %, and 2 *wt*%, the shear yield stress and plastic viscosity of the RMC pastes were comparable. The shear yield stress of RMC pastes with 0 % citric acids was 241.78 Pa, which decreased to 192.65 Pa with 0.05 *wt*% citric acids and further down to 71.59 Pa with 8 *wt*% citric acids. The RMC pastes with an 8 *wt*% citric acid dosage exhibited the lowest plastic viscosity. Citric acid is a tridentate complexing ligand that can form multidentate ligands with metal ions and regularly acts as a retardant in Portland cement/magnesium oxychloride cement [32,33, 35,47]. The decrease in shear yield stress and plastic viscosity with



Fig. 5. The exothermic rate (a) and cumulative heat release (b) of RMC pastes.

increasing citric acid dosage in RMC pastes is expected. Changes in the rheological properties of the RMC pastes can be attributed to the formation of the layer on the surface of the RMC particles through hydrogen bonding of OH- groups from citric acids [35], which reduces the internal friction for inter-particle movement. In addition, citrate is known to form complexes with Mg²⁺ that adsorb on the surface of MgO particles [47,48]. Consequently, the formation of OH- layers and Mg²⁺ complexes on the RMC surface hinders the hydration of RMC, resulting in more free water in the RMC pastes and leading to a decrease in their plastic viscosity.

3.2. Hydration heat

To investigate the influence of citric acids on the microscopic hydration process of the RMC systems, the exothermic rate and cumulative heat release of RMC pastes containing various dosages of citric acids were measured and the results are presented in Fig. 5. In Fig. 5a, the first peak is attributed to the dissolution of MgO particles in water, while the second peak is generated because of the heat released during the formation of Mg(OH)₂.

It can be seen that the exothermic rate from the dissolution of MgO gradually increased with the increasing amount of citric acids (Fig. 5a), leading to a rapid increase in the cumulative heat release of the samples with citric acids in the early ages (i.e., before 72 h) (see Fig. 5b). The exothermic rate of hydration increased when citric acids were dosed at 0.05 wt%. Coupled with the increase in heat release from MgO dissolution, the cumulative heat release of RMC pastes reached the highest. The hydration heat peak of RMC pastes shifted to the right, suggesting that the hydration of RMC was delayed. This could be because of the adsorption of citrate on RMC particles and the complexation between citrate and magnesium ions, which leads to delayed hydration [35,49]. When the dosage was 0.1 wt%, the exothermic rate of hydration was lower than that of the control formulation without citric acids, showing the inhibition effects of citric acids on the hydration process of RMC paste when the dosage of citric acids reached a certain level. The delay and inhibition effects became more pronounced as the dosage increased. The second exothermic peak of the RMC paste did not appear within the first 72 h of the reaction when the dosage was 8 wt%. Therefore, the cumulative heat release of RMC pastes decreased gradually with the increase in citric acid dosage, with the final cumulative heat release at 8 wt% dosage being close to that at 2 wt%, primarily because of the increase in heat release from MgO dissolution.

There are two mechanisms for the action of citric acids on RMC pastes. One mechanism is that the hydrogen bonding of OH- groups from citric acids to the RMC surface forms a lubricating layer that reduces friction for inter-particle movement [35]. The other mechanism involves



Fig. 6. Compressive strength (a) and strength growth rate (b) of RMC mortars under standard curing.



Fig. 7. Compressive strength (a) and strength growth rate (b) of RMC mortars under carbonation curing.

citrate complexing with Mg^{2+} to form a complex that adsorbs onto the surface of RMC [47,48]. The results of the hydration heat suggest that the precipitation process of $Mg(OH)_2$ is gradually delayed with increasing citric acid content, which validates the above explanation. Citric acids can influence the dissolution of MgO and the precipitation process of the hydration/carbonation products, but the specific effects of citric acids on the relative rates of these two individual reactions have not been revealed.

3.3. Compressive strength

Figs. 6 and 7 illustrate the evolution of RMC mortars' compressive strength during standard and carbonation curing, respectively. The results show that the compressive strengths of all RMC mortars at 14 days under standard curing were less than 5 MPa (see Fig. 6a), mainly because of the poor binding capability of the MgO-H₂O system and poor mechanical strength of brucite [23]. The effects of citric acids on the compressive strength evolution of RMC mortars under standard curing depended on their dosage. At a citric acid dosage of 0.5 *wt%*, the compressive strength reached its lowest, with a 50 % decrease from that of the control group without citric acids after 14 days of standard curing. As the citric acid dosage further increased, the compressive strength gradually recovered. When the citric acid dosage reached 4 *wt%*, the compressive strength significantly exceeded that of the control group BO

without citric acids. As illustrated in Fig. 6b, the strength growth rates at 3 days for RMC mortars with a citric acid dosage of 4 wt% and 8 wt% were 155 % and 500 %, respectively, suggesting that the mechanical properties of RMC mortars can be significantly improved with a high dosage (i.e. 4-8 wt%) of citric acids. This variation in strength is attributed to the evolution of the phase (to be elaborated in Section 3.4.1) and the development of the microstructure (to be elaborated in Section 3.5.1 and 3.5.2) of the RMC samples. At the dosage of 8 wt% citric acids, the compressive strength gain of RMC mortars was primarily evident between 3 and 7 days, with the compressive strength at 7 days equivalent to that of RMC mortars with a citric acid dosage of 4 wt% at 14 days. It is worth noting that the 14-day strength growth rate for the samples with 4 wt% citric acids was higher than that of the samples with 8 wt% citric acids, with the corresponding strength growth rates of 116 % and 88 %, respectively. This suggests there may be further potential for the growth of compressive strength of RMC mortars at 4 wt% citric acid dosage. The evolution of the microscopic morphology in the crystallinity of the 4 wt% dosed samples was better than that of the 8 wt% samples at 14d may be ascribed to this.

Under carbonation curing, the compressive strength of RMC mortars was higher than that under standard curing (i.e. 15 vs 0.37 MPa at 3 days and 18 vs 4 MPa at 14 days) (see Fig. 7). The influence of citric acids on the evolution of the compressive strength of RMC mortars under carbonation curing also depended on its dosage. When the citric acid



Fig. 8. XRD patterns of RMC pastes at different ages under standard curing: (a) 3d, (b) 14d (P: periclase (MgO), B: brucite (Mg(OH)₂), C: Al₂O₃).



Fig. 9. Quantitative analysis of RMC pastes at different ages under standard curing: (a) 3d, and (b) 14d



Fig. 10. TG-DTG curves of RMC pastes at different ages under standard curing: (a) 3d, (b) 14d, (c) comparison of B0, B0.05, B4 and B8 at 3d and 14d



Fig. 11. (a) XRD patterns and (b) quantitative analysis of RMC pastes at 14 days under carbonation curing. (P: MgO, C: Al₂O₃).

dosage was 0.05 wt%, the strength kept increasing for up to 14 days, suggesting that a small dosage of citric acids enhanced the early-age compressive strength of RMC mortars. Consistent with the results of hydration heat (see Section 3.1), the strength growth rate gradually decreased with the increase in citric acid dosage. At 3 days, the compressive strength of the RMC mortar decreased from 15 MPa at the citric acid dosage of 0 wt% to 6 MPa at the citric dosage of 8 wt%. Nevertheless, the RMC mortars with 8 wt% dosage exhibited the highest compressive strength at both 7 and 14 days, showing an increase of 7 % and 12%, respectively, compared to the control sample (C0). At 14 days, the strength growth rate was positive at dosages of 0.05 wt% and 8 wt%, both by weight, compared to the control sample. The application of citric acids, whether in extremely low or high dosages, proved to be effective in improving the compressive strength of RMC, while it was ineffective at moderate dosages. Moreover, it was observed that the compressive strength loss of RMC mortars between 3 and 14 days decreased when the dosage of citric acids exceeded 1 wt% (see Fig. 7b), thereby demonstrating the favourable effects on the 14-day compressive strength of RMC mortars at elevated dosages. However, the strength losses at dosages of 0.5, 1, 2, and 4 wt% were consistently higher than 10 % at all ages investigated, suggesting that their adverse effects on the compressive strength gain of RMC mortars were significant.

Citric acids have demonstrated different effects on the compressive strength gain of RMC under standard and carbonation curing. Samples B4 and B8 had a significant increase in strength growth rate between 3 and 14 days. However, this positive effect at 4 *wt*% and 8 *wt*% citric acid dosages did not appear in the RMC under carbonation curing. At 14 days, it was the low (0.05 *wt*%) and high (8 *wt*%) citric acid dosages that were beneficial for the compressive strength growth of RMC under carbonation curing. This is mainly related to the development of the pore structure of the RMC, which will be elaborated on in Sections 3.5.3 and 3.5.4. The optimal citric acid dosage was variable under different curing conditions, highlighting that the effects of citric acids on the phase evolution and the development of the microstructure of RMC under standard and carbonation curing are noticeably different.

3.4. Phase evolution analysis

3.4.1. Phase evolution of the RMC pastes under standard curing

To reveal the effects of citric acids on the evolution of compressive strength, qualitative and quantitative investigations on the phase evolution of the RMC pastes under standard curing were studied by XRD, as shown in Figs. 8 and 9. Fig. 10 presents the thermal decomposition curves of all samples investigated.

Periclase (MgO) and brucite (Mg(OH)₂) are the main crystal phases in RMC pastes under standard curing at various ages. The hydration of the control sample (B0) continued over time, manifested by a significant decrease in the diffraction peak of MgO at 14 days. Combined with quantitative analysis (see Fig. 9), it can be found that the MgO content was 38 % at 3 days, but decreased to only 6 % at 14 days. When the citric acid dosage was small (i.e. at 0.05 % and 0.1 % both by weight for samples B0.05 and B0.1, respectively), the change in the Mg(OH)₂ peak was minimal. As the citric acid dosage gradually increased, a noticeable decrease in the peak of Mg(OH)₂ can be observed, as shown in Fig. 8. At 3 days, the Mg(OH)₂ content of the RMC pastes decreased from 62 % (i. e. sample B0) to 2 % (i.e. sample B8), which was consistent with the results of the hydration heat (see Fig. 7a). This is mainly because of the complexation of citrate with Mg²⁺ on the surface of MgO particles, which reduces the contact area between the MgO particles and water, resulting in a decrease in the amount of hydration products generated [47,48]. The extent of the decrease in hydration products depends on how much the citrate reduces the contact area between MgO particles and water. When the concentration of citrate is low, the area occupied by the complexed Mg^{2+} on the surface of MgO particles is very small, which does not significantly hinder the hydration of MgO particles. It is noteworthy that this inhibitory effect resulted in a gradual reduction in the hydration degree of RMC paste with increasing citric acid dosage. At 14 days, the unreacted MgO content in the B8 was 44 %, while that in the B0 was only 6 %, both by weight.

An amorphous phase was detected in the RMC pastes at 3d when the citric acid dosage exceeded 0.5 wt%, and its content rose proportionally with the citric acid dosage, where the amorphous phase contents of B4 and B8 reached 24 % and 37 %, respectively. The formation of the amorphous phases may be related to the large exothermic effect after citric acids were added in the early stages of the RMC pastes, which affected the precipitation of Mg(OH)₂ particles. The mass loss of the amorphous phase in the thermograms appeared at ~ 100 °C and 450 °C (see Fig. 10), attributed to dehydration and dehydroxylation, respectively. At 14 days, some amorphous phases transformed into Mg(OH)2 crystals, followed by a decrease in mass loss at \sim 450 °C in the thermograms. The formation of Mg(OH)₂ crystals in the citric acid samples under standard curing (i.e. B0.5, B1, B2, B4, and B8) can be attributed to both the transformation of amorphous phases and the hydration of raw MgO, as illustrated in Fig. 9b, which suggests that the precipitation of Mg(OH)₂ on the surface of MgO particles in the early stages of hydration was gradually peeled off [8,50], and the inhibition of citric acids in the early stages of RMC paste hydration was gradually weakened over time, allowing the raw MgO to hydrate. It is worth noting that the variability



Fig. 12. TG-DTG curves of RMC pastes at different ages under carbonation curing: (a) 3d, (b) 14d, (c) comparison of C0, C0.05, C4 and C8 at 3d and 14d

of the rheological properties of the RMC paste may be related to the transformation of its crystalline form [51].

Significant mass loss at \sim 400 °C was observed in all the thermograms of RMC pastes under standard curing, attributed to the dehydroxylation of brucite [2,18]. The results show that B8 had a higher mass loss than B4 (i.e. 7.59 % vs 4.95 %), which is not consistent with the results of the brucite content quantified by XRD (see Fig. 9a). This may be because of the partial decomposition of the amorphous phases, confirming the structural similarity of the amorphous phase and brucite. It can be observed that the total mass loss of all citric acids-added samples at 14 days was lower than that of B0 (see Fig. 10b), suggesting a decrease in the MgO reaction degree, consistent with previous calculations (see Fig. 9b). Comparing the thermal decomposition curves of RMC pastes at different ages with citric acid dosages of 0, 0.05, 4 and 8 wt% (see Fig. 10c), the increases and rightward shifts of B0 and B0.05 at \sim 400 °C can be observed. These correspond to an increase in brucite content and grain size over time, respectively, which supports the evolution of RMC compressive strength. At the same time, B4 and B8 only exhibited an increase in mass loss at ~400 °C with curing age, corresponding to the recrystallisation of the amorphous phases. In all thermograms, there was a mass loss at \sim 550 and 650 °C, attributed to the decarbonation of carbonates [52,53]. The weight loss peaks of carbonates on all thermal decomposition curves exhibited no significant difference, inferring that they may be magnesite originating from incompletely calcined raw materials (see Fig. 1a). In Fig. 10c, it was observed that the mass loss peaks at ~550 and 650 °C on the thermal decomposition curves of the RMC samples shift to the right at 14 days. This shift may be because of the amorphous substances adhering to the surface of the magnesite, which increased their thermal decomposition temperature.

3.4.2. Phase evolution of the RMC pastes under carbonation curing

Fig. 11 illustrates the evolution of the phase composition of RMC pastes with different citric acid dosages under carbonation curing. The unmarked characteristic diffraction peaks at $26-32^{\circ} 2\theta$ all originated from the raw materials (see Fig. 1a). Thermal analyses were also conducted on RMC pastes at different curing ages, and all thermograms obtained are shown in Fig. 12.

The addition of citric acids did not result in the formation of any new phases. However, the quantitative XRD results indicated significant changes in the amounts of various phases. Unreacted MgO and amorphous phases were predominantly present in the RMC pastes under



Fig. 13. SEM images of RMC pastes at 3 days under standard curing: (a)-1 and (a)-2 for B0, (b) for B0.1, (c) for B0.5, (d) for B1, (e) for B4, and (f)-1 and (f)-2 for B8.

carbonation curing, with small amounts of hydration products detected in the control sample (CO). When the dosages of citric acids were 4 wt%and 8 wt%, a clear increase in the reaction degree of MgO was noticed (see Fig. 11b). The thermogram shows that only the total mass loss of C4 and C8 was significantly higher than that of C0 (see Fig. 12b). The results of the two different methods all pictured the same trend: the reaction degree of MgO in RMC pastes increased at small (0.05 *wt%*) or high (\geq 4 *wt%*) citric acid dosages under carbonation curing. This may affect the development of the microstructure, resulting in variations in the compressive strength of RMC at different citric acid dosages (see Fig. 7). It is worth noting that at 14 days, the compressive strength of C8 indeed increased by 12 % compared to that of C0. However, the



Fig. 14. SEM images of RMC pastes at 14 days under standard curing: (a) for B0, (b) for B0.1, (c) for B0.5, (d) for B1, (e)-1 and (e)-2 for B4, and (f)-2 for B8.



Fig. 15. The total porosity of RMC pastes under standard curing.

compressive strength of C4 was lower than that of C0. This hints that the development of compressive strength depended not only on the reaction degree of MgO but also possibly on the microstructure of the products and the development of porosity within the RMC system.

Significant mass loss at ~100 °C and 400 °C can be observed in all thermograms, attributed to dehydration and dihydroxylation [54,55], respectively. The mass loss of C2, C4, and C8 at ~100 °C gradually increased compared to that of C0 (see Fig. 11a), resulting in their total mass loss being higher than that of C0. It is clear that at ~400 °C, the thermal decomposition curves of C4 and C8 gradually broadened after 3 days and exhibited an increase in mass loss after 14 days. However, there was no significant difference in the total mass loss of C8 between 3 and 14 days. This may suggest that C8 nearly completed its hydration in 3 days. Therefore, a comprehensive investigation and analysis of its microstructure are necessary to explain why C8 had the lowest compressive strength at 3 days.

3.5. Microstructural analysis

3.5.1. Microstructural evolution of the RMC pastes under standard curing Figs. 13 and 14a-f present the SEM images of RMC pastes, with 0, 0.1, 0.5, 1, 4 and 8 wt% citric acids, at various ages under standard curing. At 3 days, the porous microstructure of the control sample (B0) can explain its low compressive strength. At 14 days, more hydration products with better crystallinity can be observed (corresponds to the increase in

decomposition temperature in Fig. 10c), which could explain the increase in compressive strength and phase evolution. Cone-like Mg(OH)2 crystals [56] can be observed in B0 at 3 days, with little change in B0.1. When the citric acid dosage was 1 wt%, an amorphous phase in the RMC pastes was observed, which agrees well with the previous quantitative XRD and thermogravimetric results. In B4 and B8, the gradually densifying amorphous phase formed a network-like structure, enhancing the interconnection of the microstructure in the RMC system [27]. At 14 days, unlike B0 and B0.1 where only cone-like Mg(OH)₂ crystals were present (see Fig. 14a and b), both cone-shaped and plate-like Mg(OH)₂ [56,57] crystals coexisted in B0.5 (see Fig. 14c). In B1, there were more plate-like, smaller size (i.e. diameter <200 nm and thickness <200 nm) Mg(OH)₂ crystals (see Fig. 14d), while in B4, larger plate-like Mg(OH)₂ crystals (i.e. diameter~300-500 nm and thickness <200 nm) were observed (see Fig. 14e). It is demonstrated that the plate-like Mg(OH)₂ crystals were formed through the transformation of the network-like amorphous phase over time (i.e., the amorphous phase serves as precursors for the Mg(OH)₂ crystals), validating the phase evolution of the RMC pastes during 3–14 days of standard curing (see Fig. 8). It is worth noting that at 14 days, the crystallinity of the amorphous phase in B4 was significantly better than that in B8, suggesting that the complete crystallisation of the amorphous phase in B8 required more time.

3.5.2. Pore structure of RMC pastes under standard curing

Figs. 15 and 16 present the total porosity and T_2 spectrum distribution of RMC pastes with different dosages of citric acids under standard curing. Pore size is positively correlated with relaxation time, which is represented by the horizontal axis of the T2 spectrum. The vertical axis represents signal intensity, which is positively correlated with the number of pores; the stronger the signal, the greater the number of corresponding pores [43,58].

At 3 days, the total porosity of B0 was 36.02 %, which decreased to 26.09 % at 14 days, suggesting a gradual densification of the microstructure of the RMC pastes over time. When the citric acid dosage exceeded 1 *wt*%, the total porosity of the RMC pastes gradually increased. In samples B1, B2, B4, and B8, it reached 40.71 %, 49.59 %, 52.66 % and 55.57 %, respectively. The presence of large pores with relaxation times at 10–1000 ms was observed in samples B4 and B8, and their quantity increased proportionally with the addition of citric acids, which suggests that the formation of the network-like amorphous phase may be responsible for the increase in total porosity of the samples with citric acids. At 14 days, the number of small pores with relaxation times at 0.1–1 ms gradually increased in samples B1, B2, B4, and B8, with the overall distribution curves shifting to the left. In addition, a few large pores with relaxation times at 10–100 ms were observed in samples B1 and B2, and the number of large pores increased in samples B1



Fig. 16. T₂ spectrum distribution of RMC pastes at different ages under standard curing: (a) 3d, (b) 14d



Fig. 17. SEM images of RMC pastes under carbonation curing for 3 and 14 days with different citric acid dosages: (a) 0, (b) 0.5 %, (c) 8 wt%.

These observations partly resulted from the fact that some pores were filled with hydration products generated by the slow dissolution of the raw MgO, and partly from the transformation of the amorphous phase into Mg(OH)₂ crystals, leading to generating large pores.

3.5.3. Microstructure evolution of the RMC pastes under carbonation curing

The SEM images of RMC pastes with citric acid dosages of 0, 0.5 and 8 wt% at different ages under carbonation curing are shown in Fig. 17. At 14 days, a small amount of flake-like Mg(OH)₂ crystals can still be observed in sample C0 (see Figs. 17a-2), while in sample C0.5, there were almost none, which is consistent with the quantitative results of phase analysis (see Fig. 11). The microstructure of C0.5 exhibited no significant changes compared to that of sample C0, while sample C8 underwent noticeable changes because of the increased reaction degree of MgO. It can be seen that the micro-morphology of sample C8 did not change significantly at 3 and 14 days, suggesting that the reaction of RMC pastes with 8 wt% citric acids mainly occurred in early ages,

confirming that the total mass loss in the thermograms did not significantly increase from 3 to 14 days (see TG curves presented in the bottom right corner of Fig. 12a and b). The evolution of the microstructure cannot explain the significant difference in compressive strength (i.e. 5 vs 20 MPa) of sample C8 between 3 and 14 days, warranting that further analysis of its pore structure evolution is necessary.

3.5.4. Pore structure of the RMC pastes under carbonation curing

The total porosity and T₂ spectrum distribution of RMC pastes under carbonation curing are depicted in Figs. 18 and 19, respectively. Compared to RMC pastes under standard curing (see Fig. 15), the RMC pastes under carbonation curing for 3 days exhibited a much denser microstructure with a smaller total porosity. The total porosity of sample B0 decreased from 36.02 % to 26.09 %, with reductions of 8.2 %, 10.9 %, 22.8 %, 33.4 %, and 29.4 % for samples B0.1, B1, B2, B4, and B8, respectively. At 14 days, both carbonation and standard curing regimes led to a stable total porosity of 26 % for samples C0 and B0. The evolution of total porosity in RMC pastes with added citric acids differed



Fig. 18. The total porosity of RMC pastes under carbonation curing.

from that under standard curing, which will be discussed below.

Adding citric acids to the RMC pastes led to a significant increase in the total porosity at 3 days, primarily because it introduced micropores with relaxation times at 0.1 and 1–10 ms. This explains the evolution of its compressive strength. In sample C8, there were visible large pores with relaxation times at 10–1000 ms, resulting in its highest total porosity reaching 39.24 %. At 14 days, the disappearance of macropores caused by the transformation between the phases resulted in a significant reduction in the total porosity to 26.03 %. Combining the results of the phase evolution, it is noteworthy that, although the reaction degree of sample C8 at 3 days was close to that at 14 days, it still required time to densify its microstructure to improve its compressive strength. The significant decrease in total porosity of sample C8 at 3–14 days may be attributed to the porous structure formed at early stages that favoured CO_2 uptake, densifying its microstructure.

Fig. 20 depicts the relationship between strength and total porosity. It can be seen from Fig. 20 (a) that strength and total porosity do not always demonstrate a negative correlation, suggesting that the effects of citric acids on the compressive strength of RMC under standard curing are primarily because of the combined variations in the amount and crystal form of hydration products. In Fig. 20 (b), unlike the trends observed during standard curing, the increase in compressive strength of RMC under carbonation curing primarily relies on the reduction of porosity and the densification of the microstructure.

Therefore, as elaborated above, citric acids modified the rheology, exothermic hydration and microstructure of the RMC pastes with positive/negative effects on their strength development, depending on their dosage. The effects of citric acids on the hydration-hardening process of RMC pastes are schematically presented in Fig. 21. The hydration of the RMC paste proceeded over time, showing a continuous consumption of MgO when citric acid dosage was low (i.e. the unreacted MgO content in samples B0 and B2 were 38 % and 75 % at 3d, which decreased to 6 % and 19 %, respectively, at 14d) and an improvement in the crystallinity of Mg(OH)₂ crystals (see Figs. 13 and 14a-d). The presence of Mg(OH)₂ in the system, which had minimal gelling ability, was crucial in negatively affecting the strength of the RMC (Figs. 6 and 7). The crystalline form existing predominantly in the RMC paste varied when the citric acid dosage was higher than 2 wt%, with an amorphous phase observed as a reticulated structure (see Fig. 13e and f) that could gradually crystalise with the progression of hydration (i.e. 24 % and 37 % in samples B4 and B8 at 3d, decreasing to 9 % and 27 %, respectively, at 14d). Citric acids provide citrate, which can complex Mg^{2+} adsorbed on the surface of MgO, together with hydroxyl groups that can form a film through hydrogen bonding on the surface of RMC. When the amount of citric acids is low (i.e., < 2 wt%), the RMC system exhibited a decrease in Mg(OH)₂ crystals. However, when the citric acid content reaches a certain level (i.e., > 2 wt%), an amorphous phase is generated, and its content increases with the dosage of citric acids, possibly because of the increased overlap of the aforementioned effects. The longer time required to complete the crystallisation process of the amorphous phase may also contribute to the retardation of the RMC paste. Differences in the rheology and microstructure of the RMC pastes may account for the \sim 100 % increase in strength in 14 days (see Fig. 6). In addition, the high porosity of sample C8 (see Fig. 18) was an advantage for the diffusion and capture of CO_2 , which contributed to the increase in the strength of sample C8 under carbonation curing (see Fig. 7).

4. Conclusions

This study investigated the effects of citric acids on the rheological properties, compressive strength and microstructural evolution of reactive magnesium oxide cement (RMC). The main conclusions are drawn as follows.

- (1) The shear yield stress and plastic viscosity of RMC pastes decreased gradually with the increase in citric acid dosage. The shear yield stress of RMC pastes with 8 *wt*% citric acids was 71.588 Pa, while that of B0 without citric acids was 241.778 Pa.
- (2) The effects of citric acids on the compressive strength of RMC depended on their dosage (i.e. between 0.05 and 8 wt%). When



Fig. 19. T₂ spectrum distribution of RMC pastes at different ages under carbonation curing: (a) 3d, (b) 14d



Fig. 20. The relationship between compressive strength and total porosity under (a) standard and (b) carbonation curing.

the citric acid dosage was low (i.e. at 0.05 *wt*% and 0.1 *wt*%), their influence on the compressive strength of RMC was minimal. When the citric acid dosage was between 0.5 and 2 *wt*%, there was a significant adverse effect on the compressive strength of RMC at various ages under both standard and carbonation curing regimes. At 4 *wt*% and 8 *wt*% dosage levels, there was a significant increase in the compressive strength of RMC under standard curing. At the 8 *wt*% dosage level, the compressive strength of RMC carbonated for 14 days increased by ~12 %.

- (3) The hydration of RMC was gradually delayed and inhibited with the increase in citric acid dosage. The presence of an amorphous phase with accumulating content in RMC was observed at citric acid dosages of 0.5-8 *wt%*, and a progressively denser network structure was observed in samples dosed at 4 *wt%* and 8 *wt%*. It gradually transformed into crystals over time, leading to a reduction in the total porosity and a smaller pore size distribution of the RMC pastes.
- (4) During the carbonation curing, the reaction degree of RMC pastes with 4 *wt*% and 8 *wt*% citric acids increased significantly. The porous microstructure of the RMC samples with a citric acid dosage of 8 *wt*% at early ages favoured the adsorption of carbon dioxide, contributing positively to the gain of compressive strength.

The findings of this research contribute to a fundamental understanding of the hydration and carbonation regulation characteristics of reactive MgO cement by citric acids to enhance its reactivity to maximise its application as a more sustainable binder with high CO_2 sequestration potential.

CRediT authorship contribution statement

Huanhuan Wang: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. Shuang Liang: Writing – original draft, Validation, Methodology, Investigation, Formal analysis. Xiangming Zhou: Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization. Pengkun Hou: Writing – review & editing, Validation, Supervision, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Xin Cheng: Supervision, Methodology, Conceptualization.



Fig. 21. Schematic illustration of effects of citric acids on hydration-hardening of RMC paste.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Xiangming Zhou reports financial support was provided by European Commission. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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