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Development of MgO concrete with enhanced hydration and carbonation mechanisms

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ABSTRACT

This study proposed the use of hydration agent (HA) and seeds to improve the hydration and carbonation of reactive magnesium cement (RMC)-based concrete formulations. Hydration of RMC was evaluated by isothermal calorimetry. Water absorption and compressive strength results were used to assess the mechanical performance of RMC-based concrete samples. Quantification of hydrate and carbonate phases was performed via XRD and TGA. Formation and morphology of carbonates were observed via BSE and SEM. In addition to increasing the utilization of RMC in the carbonation reaction and facilitating early strength development, the use of HA formed large carbonate phases, while the addition of seeds improved sample microstructures via the development of dense carbonate networks. The improvements in morphology, microstructure and carbonate content in samples involving the simultaneous use of HA and seeds resulted in 56% lower water absorption values and 46% higher 28-day compressive strengths (70 MPa) in comparison to the control sample.

1. Introduction

Reactive magnesium oxide (MgO), produced at much lower calcination temperatures than PC (i.e. 700–1000 vs. 1450 °C) [1,2] is a promising material for the sequestration of CO_2 within construction products. The sequestration of CO_2 in reactive MgO cement (RMC) involves the diffusion and dissolving of CO_2 in the pore space, followed by its reaction with Mg-phases to form a range of hydrated magnesium carbonates (HMCs). Some of the main HMCs that have been observed to provide physical strength in RMC formulations are needle-like nesquehonite ($MgCO_3{\cdot}3H_2O$), rosette-like hydromagnesite ($4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$) and dypingite ($4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$), and acicular artinite ($MgCO_3{\cdot}Mg(OH)_2{\cdot}3H_2O$) [3,4]. The formation of HMCs is primarily responsible for the strength gain of RMC-based formulations by enabling an increase in density as the formation of carbonate phases reduces the overall pore volume. The carbonation reaction also improves the microstructure and increases strength as the morphology and binding strength of the carbonate crystals contribute to the network structure.

Hydration and carbonation reactions are critical for the strength development of RMC samples as they control the degree of HMC formation [5]. The hydration mechanism of MgO involves a dissolution–precipitation process initially controlled by the dissolution of MgO [6]. However, the hydration degree of MgO is quite low under ambient conditions due to its low rate and degree of dissolution [7–12] and the precipitation of hydration and carbonation products on the surface of unhydrated MgO particles, thereby inhibiting further hydration. The precipitation of carbonate phases on unhydrated $Mg(OH)_{2(aq,s)}$ can also prevent the progress of the carbonation reaction. These limitations in the hydration and carbonation of RMC can result in its inefficient use as a binder and limit the strength development of concrete formulations it is incorporated in.

Overcoming the limitations associated with the low dissolution of MgO and the subsequent hydration and carbonation reactions can not only increase the formation of HMCs but also improve the mechanical performance of RMC-based concrete formulations. Two methods that can alleviate these challenges include (i) the use of a hydration agent (HA) to improve the dissolution of MgO and increase the amount of $Mg(OH)_{2(aq,s)}$ available for carbonation and (ii) the provision of additional nucleation sites dispersed into the sample pore space to facilitate continuous hydration and carbonation by increasing the surface area for the nucleation and growth of carbonate phases away from the unhydrated MgO and uncarbonated $Mg(OH)_2$.

One of the most effective HAs reported in literature is magnesium acetate ($(CH_3COO)_2Mg$) [13,14]. The hydration of MgO in the presence of $(CH_3COO)_2Mg$ takes place in a similar mechanism as shown in Eqs. (1)–(4). The complex magnesium acetate ions (CH_3COOMg^+) shown in Eq. (2) migrate away from their original particles [13] to enable the precipitation of a bulk $Mg(OH)_2$ structure in the spore space. Furthermore, the presence of $Mg^{2+}_{(aq)}$ (Eq. (1)) promotes the precipitation of Mg

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$(OH)_2$, whereas $CH_3COO^-_{(aq)}$ facilitates the dissolution of unhydrated MgO. When coupled with the use of HAs, the introduction of additional nucleation sites stimulates the formation of $Mg(OH)_2$ away from the MgO grains. The dispersion of $Mg(OH)_{2(aq,s)}$ into the pore space increases the contact surface area of MgO and $Mg(OH)_{2(aq,s)}$ with water and CO_2, thereby enhancing the hydration and carbonation reactions. These advancements can lead to increased formation of HMCs and therefore improve the mechanical performance of RMC formulations.

Dissociation of magnesium acetate:

$$(CH_3COO)_2Mg_{(aq)} \leftrightarrow 2CH_3COO^-{}_{(aq)} + Mg^{2+}{}_{(aq)} \quad (1)$$

Dissolution of magnesia:

$$MgO_{(s)} + CH_3COO^-{}_{(aq)} + H_2O_{(l)} \leftrightarrow CH_3COOMg^+{}_{(aq)} + 2OH^-{}_{(aq)} \quad (2)$$

Dissociation of magnesium complexes:

$$CH_3COOMg^+{}_{(aq)} \rightarrow CH_3COO^-{}_{(aq)} + Mg^{2+}{}_{(aq)} \quad (3)$$

Precipitation of magnesium hydroxide due to supersaturation:

$$Mg^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \rightarrow Mg(OH)_{2(s)} \quad (4)$$

Differing from previous studies that looked into the incorporation of carbonates within RMC systems, which generally led to a decrease in strength due to the high inclusion levels of carbonates (i.e. up to 50% of the cement content) [15], this study involves the use of small amount of carbonate seeds (i.e. up to 1% of the cement content) to improve the reaction mechanisms. The provision of additional nucleation sites via the introduction of seeds (e.g. C-S-H) has been reported to accelerate the nucleation and growth controlled early age hydration in PC [16] and alkali-activated slag [17] systems. This improvement was reflected as an increase in the compressive strength values of seeded samples, which were up to 5 times higher than those of unseeded samples at early ages [17].

The role of HA in promoting the formation of $Mg(OH)_{2(s)}$ (brucite), rather than HMCs, was demonstrated in previous studies [13,14]. Differing from PC and alkali-activated systems, whose hydration is limited by the nucleation and growth mechanism, the rate-limiting step in the hydration of MgO systems is the dissolution of MgO. Therefore, while the introduction of seeds in the mix design is beneficial in accelerating the hydration of PC and alkali-activated mixes, this approach does not have the same influence on the early hydration rate of MgO [17]. Alternatively, as the strength gain mechanism of MgO systems mainly rely on the degree of carbonation, the introduction of seeds can increase the overall extent of carbonation by increasing the reactive contact surface within the pore space, thereby facilitating the increased formation of carbonate phases. This led to the simultaneous inclusion of HA and seeds in the mixes prepared in this study, which were aimed to enhance the mechanical performance of RMC samples by increasing the degree of hydration and carbonation, respectively.

The presented approach did not only aim to provide increased hydration, but also to stimulate the carbonation reaction throughout the curing process, the combination of which has not been tackled simultaneously in detail in previous studies. In this respect, a comprehensive analysis on the performance and microstructural development of carbonated RMC concrete formulations involving the use of HA and nucleation seeding was presented. Concrete samples with and without HA were prepared with different seed contents and subjected to carbonation curing for up to 28 days. The influence of these additives on the hydration kinetics of MgO was evaluated by isothermal calorimetry. The performance of the prepared formulations was analyzed at different durations by compressive strength testing and water absorption measurements. X-ray diffraction (XRD), thermogravimetric analysis (TGA), backscattered electron (BSE) and scanning electron microscopy (SEM) were employed to analyze the formation of hydration and carbonation products and investigate the microstructural development at the end of the curing process.

Table 1
Chemical composition and physical properties of RMC.

	Chemical composition (%)							Physical properties	
	MgO	SiO_2	CaO	R_2O_3	K_2O	Na_2O	LOI	Specific gravity (g/cm^3)	Specific surface area (m^2/g)
RMC	> 91.5	2.0	1.6	1.0	–	–	4.0	3.0	16.3

2. Materials and methodology

2.1. Materials

The main cement binder used in this study was RMC (commercial name "calcined magnesite 92/200") obtained from Richard Baker Harrison (UK), that was produced at around 1000 °C. The chemical and physical properties of RMC are shown in Table 1. The reactivity of RMC (i.e. measured by the time required for the neutralization of 0.25 M of acetic acid by 5 g of RMC [18]) was recorded as 520 s. Magnesium acetate ($(CH_3COO)_2Mg$), obtained from VWR (Singapore), was used as the HA at a concentration of 0.05 M (i.e. based on previous research [13,14] and preliminary studies) to promote the hydration process. Hydromagnesite ($4MgCO_3{\cdot}Mg(OH)_2{\cdot}4H_2O$) seeds, obtained from Fisher Scientific (UK) with a specific surface area of 43.5 m^2/g, were used to provide additional nucleation sites and stimulate the nucleation and growth of HMCs in the pore space. Fig. 1 shows the microstructure of hydromagnesite seeds, which are spherical agglomerations with a diameter of ~1–7 µm, composed of ~0.5 µm diameter disks. Saturated surface dry (SSD) gravel with a particle size of 4.7–9.5 mm was used to form the aggregate profile in the prepared concrete samples.

2.2. Methodology

Two sets of samples (i.e. with and without HA) were used to investigate the influence of HA and seeding on the hydration and carbonation of RMC formulations. Table 2 lists the compositions of the concrete samples prepared under this study. Each set included seed contents of 0% (samples $H_2O{\cdot}S0$ and HA.S0), 0.5% (samples $H_2O{\cdot}S0.5$ and HA.S0.5) and 1% (samples $H_2O{\cdot}S1.0$ and HA.S1.0) of the total binder content. The ratio of water or HA solution to binder was kept constant at 0.7 for all samples. Before casting the concrete samples, corresponding pastes were prepared to study the effects of HA and seeding on the hydration of MgO via isothermal calorimetry.

To prepare the concrete samples, seeds were dispersed in water/HA

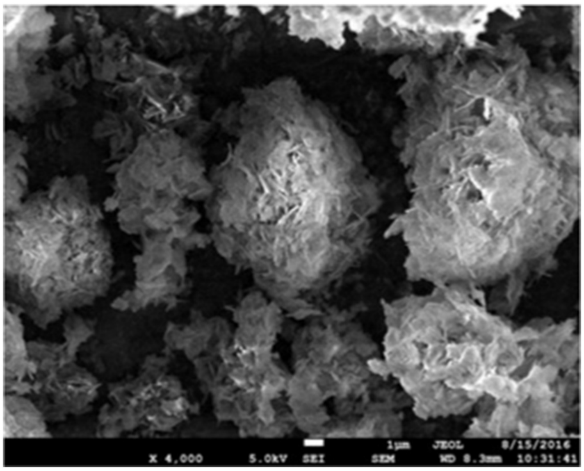

Fig. 1. SEM image of hydromagnesite seeds.