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THERMAL CHARACTERIZATION OF PORTLAND CEMENT–MAGNESIA BLENDS

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Due to growing environmental concerns and the need to use less energy-intensive building products, alternatives and improvements to Portland cement (PC) are being actively researched worldwide. Use of supplementary materials is now a common practice where PC is the predominant component of inorganic building products. This study aims to investigate the potential of magnesia (MgO), derived from a naturally occurring raw material magnesite, as a supplementary material. Results from mortar samples prepared with 10 and 20% replacements of ordinary Portland cement (OPC) by MgO are presented. DTA-TG was used to study and characterise the hydration behaviour of MgO in OPC environment after 3, 7, 14, 28, 56 and 90 days of moist curing. Microstructural and compressive strength determinations providing additional information on the influence of hydrated phases are also reported.

Keywords: *DTA, magnesia, mortar, OPC, TG*

Introduction

The use of supplementary materials in cement mortar production is increasing due to the growing pressure placed on industry to reduce carbon dioxide emissions. The largest contribution to carbon dioxide evolution is in the calcination of calcium carbonate ($CaCO_3$), to produce calcium oxide (CaO), which accounts for approximately 64% by mass of a typical Type I ordinary Portland cement (OPC) [1] conforming to ASTM C150–99a [2]. The calcination of $CaCO_3$, represented by Eq. (1), occurs at temperatures in the range of 900–1150ºC [3]:

$$CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)} \quad (1)$$

Calcium oxide is an essential component in cement and, on hydration in the presence of other cement components such as silica, it forms the essential strength contributing phase calcium silicate hydrate (CSH). CSH is considered to have the composition $C_{1.7}SH_4$ [4] and may be generated by the hydration of tricalcium silicate (C_3S) and dicalcium silicate (C_2S) as given by the following Eqs (2) and (3) [5]:

$$C_3S + 5.3H \rightarrow C_{1.7}SH_4 + 1.3CH \quad (2)$$

$$C_2S + 4.3H \rightarrow C_{1.7}SH_4 + 0.3CH \quad (3)$$

The partial replacement of cement for some other naturally occurring mineral such as magnesia (MgO) reduces the volume of cement used in the production of mortar, concrete and other construction and building materials. The temperature of calcination of $MgCO_3$ affects the reactivity of the MgO produced; in order to form a reactive, non dead-burned product, calcination typically occurs at 850–900ºC [6]. The calcination of $MgCO_3$ may be represented by Eq. (4) as follows [7]:

$$MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)} \quad (4)$$

Magnesite, requiring a lower calcination temperature compared to $CaCO_3$ and thus MgO being less expensive to produce, is an attractive raw material for use in inorganic cement-based building materials. In this study the potential of magnesia, derived from a naturally occurring raw material magnesite ($MgCO_3$), as a supplementary material in the production of cements was investigated. TG and DTA-TG along with XRD, SEM and compressive strength determinations, were used to study the hydration behaviour of OPC–magnesia cement blends, in order to assess the effects of MgO as partial replacement of OPC.

Experimental

Materials

Cement

Type I ordinary Portland cement (OPC) from Australian cement, Railton, Tasmania, was used. The chemical composition of the cement as determined by XRF is given in Table 1.

Aggregate

Type 200G ground silica used was supplied by Unimin Australia, Granville, NSW. The 200G ground

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Table 1 Composition of Portland cement used

OPC blaine specific surface: 350 m^2 kg^{-1}	
Composition	Mass/%
CaO	64.2
SiO_2	20.0
Al_2O_3	4.5
Fe_2O_3	3.7
SO_3	2.4
LOI	3.1

quartz contains 98.9% SiO_2 as determined by ICP; with a Blaine surface area of 360 m^2 kg^{-1}.

Magnesia

Grade TGM SF magnesium oxide (MgO) was supplied by Causmag International, Young, NSW. The magnesium oxide percentage given in Table 2 was calculated by difference after the determination of other oxides by wet chemical methods.

Table 2 Composition of MgO used

MgO blaine specific surface: 560 m^2 kg^{-1}, mean particle size of 5 micron	
Composition	Mass/%
MgO	98.1
CaO	1.00
SiO_2	0.65
Al_2O_3	0.18
Fe_2O_3	0.08
LOI	2.10

Mix design

Standard mortar for cement cube casting was prepared according to ASTM 109/C109M [8] with one part cement to 2.75 parts of sand by mass. Water to solids ratio of 0.4 was used to obtain the desired flow. Table 3 outlines the three mix compositions investigated in this study – an OPC control mix, along with mixes containing 10 and 20% replacement of OPC with MgO by mass.

Testing procedure

DTA-TG analysis was conducted using TA-instruments SDT 2960 simultaneous DTA-TG analyser where a sample size of ~20 mg was subjected to a heating rate of 10 K min^{-1} from 30–1200ºC under flowing nitrogen (110 mL min^{-1}). Hydration was evaluated using a Setaram TG instrument where a sample size of ~15 mg was subjected to a heating rate of 10 K min^{-1} from 30–800ºC under flowing air (20 mL min^{-1}). X-ray diffraction (XRD) using a Siemens D-5000 diffractometer operating at 40 kV and 30 mA with CuK_α radiation was used to obtain data on crystalline phase development. Sample powder diffraction data sets were compared to those from the Joint Committee on Powder Diffraction Standards (ICDD-JCPDS) CD-ROM database providing qualitative phase identification. Microstructural analysis by SEM of dried cured mortar samples was conducted using a JEOL 6300 field emission gun-scanning electron microscope (FEG-SEM).

Table 3 Mixing proportions of cements

Mix No.	Cement type	Quantity/g			
		cement	water	quartz	MgO
1	OPC	200	300	550	0
2	90% OPC 10% MgO	180	300	550	20
3	80% OPC 20%MgO	160	300	550	40

Mechanical mixing of cement batches was carried out using an electrically driven mechanical mixer as per ASTM C305-82 [9]. Transfer of the mortar mixture using a spatula into stainless steel 50 mm cube moulds was followed by compaction using a vibrating table as per AS 2350.12-1995 [10]. The cast mortar cement specimens were demoulded following moist cabinet curing for 24 h, and then stored fully immersed in saturated lime water according to ASTM C511-98 [11] until the time of testing. Mortar cubes were removed from water storage containers after 3, 7, 14, 28, 56, and 90 days, a batch size of six samples for each mix composition was mechanically tested as per ASTM C109/C109M-99 [8] using a Tinius–Olsen compression testing machine, and dried in an oven at 50ºC for a minimum of 24 h to cease hydration. Sub-samples from the core of the cement cubes were ground using a tungsten carbide disc mill, and the powders analysed by DTA-TG and XRD. The apparent porosity of hydrated samples was determined as per ASTM C373-88 [12].

Results and discussion

The magnesia examined in this study was produced at a calcination temperature between 550 and 750ºC [13]. As the calcination temperature of magnesite increases, the specific surface area of magnesia decreases due to crystal propagation, thereby reducing the reactivity of the magnesia [6]. By reducing the calcination temperature of magnesite a more reactive product may be formed. The reactivity and hydration behaviour of magnesia may be predicted using the materials activity; activity measurements are based on the time required to cause complete dissolution of magnesia in citric acid. The activity of the magnesia raw material as specified by Causmag International was 16 s, this result exceeding the requirements of reactive magnesia according to Birchal *et al*. [6].

The hydration behaviour of magnesia was evaluated by TG analysis, whereby the magnesia powder was hydrated in a simulated cementitious environment maintained at 50ºC, with an excess of alkaline water (pH~14). Figure 1 illustrates magnesia's hydration behaviour; a 64% conversion of MgO to brucite ($Mg(OH)_2$) was noted within 1 min of water addition and increasing to 79% conversion after 5 h. The hydration of MgO may be represented by Eq. (5) [14]:

$$MgO_{(s)}+H_2O_{(l)}\leftrightarrow Mg(OH)_{2(s)} \qquad (5)$$

The degree of conversion of MgO into $Mg(OH)_2$ was calculated by considering both the TG and DTG curves produced using Setaram TG data analysis software and measuring the maximum deviation in percentage mass loss occurring at ~350ºC indicating brucite formation [15]. The presence of brucite in these samples was confirmed by XRD analysis.

Cured mortar samples were analysed by DTA-TG following grinding with a tungsten carbide disc mill. The phases brucite and portlandite ($Ca(OH)_2$), attributed to the hydration of magnesia and calcium oxide respectively, were monitored by measuring their percentage mass losses (mass%) and calculated using TA instruments DTA-TG data analysis software as described by Klimesch and Ray [1]. Portlandite dehydroxylation occurs between 400–600ºC [16]. The brucite/portlandite peak ratios from mass loss determinations are presented in Table 4 for the three mix compositions (as indicated in Table 3) at different curing ages. It was observed that as the curing age increased the ratio of brucite/portlandite also increased, suggesting the relatively delayed hydration of magnesia to form brucite.

X-ray diffraction (XRD) analysis on ground mortar samples provided additional information regarding the presence of brucite in the cement structure. Crystalline brucite with characteristic *d*-values of 2.37 and 4.77 Å was detected in both Mix 1 and 2 containing 10 and 20% MgO replacement of OPC, respectively [17]. The dominant reflection for brucite (*d*-value of 2.37 Å) was examined for the three mixes. Figure 2 illustrates the relationship between peak area and percentage replacement of OPC by MgO following 90 days of curing.

Table 4 Peak ratio calculation from DTA-TG mass losses for hydration phases

Mix No.	Age/day	Brucite^1/mass%	Portlandite^2/mass%	Ratio$^{1/2}$
1		0	1.298	–
2	3	0.215	1.349	0.159
3		1.082	1.054	1.027
1		0	1.209	–
2	14	0.329	1.013	0.325
3		1.118	1.023	1.093
1		0	1.297	–
2	90	0.687	1.323	0.519
3		1.511	1.091	1.385

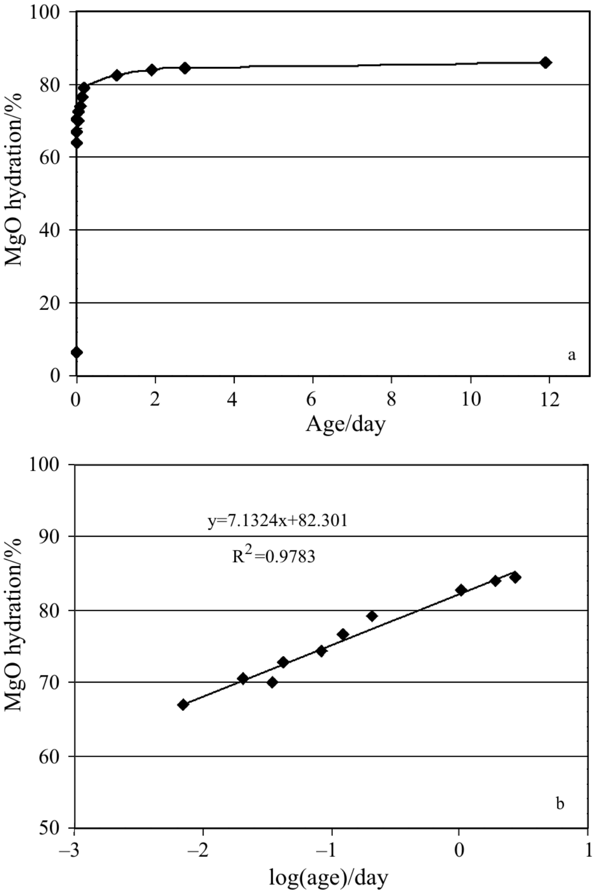

Fig. 1 Percentage hydration of magnesia a – as a function of curing age and b – as a function of the log of age

The compressive strengths (MPa) for the 50 mm cement cubes are shown in Fig. 3. The partial replacement of OPC by MgO resulted in a reduction in compressive strength for samples of equal curing age; the higher the MgO content the lower is the strength. The compressive strength is observed to increase with curing age, which is to be expected due to the hydration of strength contributing phases in OPC [5]. However, on examination of the 90-day cured sample results from Fig. 3, the compressive strength is seen to plateau for the samples containing 0 and 10% replacement of OPC for MgO, while the 20% MgO sample's compressive strength continued to increase. The reason for this observed deviation is as yet unclear. The apparent porosity

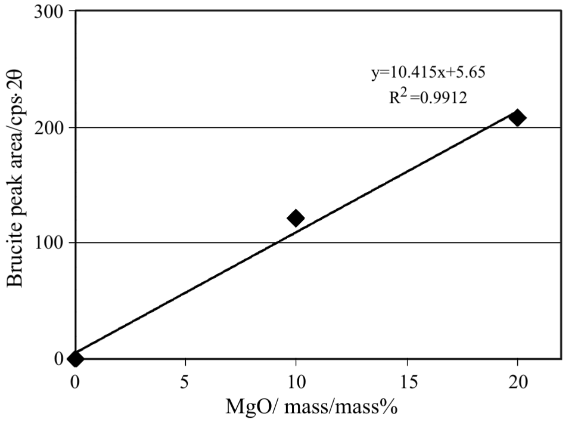

Fig. 2 XRD peak area of brucite at 2θ reflection of 38° for 90-day cured mortar specimens containing 10 and 20% replacement of OPC by MgO, along with an OPC control containing no MgO addition

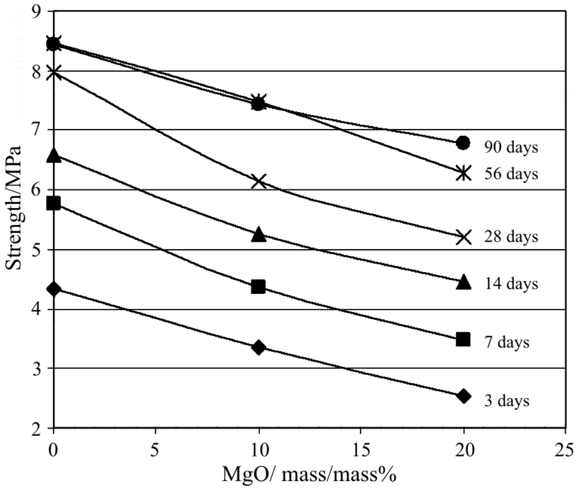

Fig. 3 Compressive strength of 50 mm cube mortar specimens containing 10 and 20% replacement by mass of OPC by MgO, along with a control containing no MgO addition; The average strength resulting from a batch is displayed

data for the 90-day samples of Mix 2 (Table 5) do not indicate a sharp decline in porosity which may otherwise would have correlated with the noted increase in strength. A possible explanation of an increased compressive strength for the 90-day samples may be attributed to the increased formation of brucite and partial carbonation of portlandite both of which acting as a pore filling material.

The apparent porosity of dried mortar samples was measured to provide further insight into the results from compression testing. The apparent porosity, based on Archimedes' principle, was measured according to Eq. (6) [18]; where three mass measurements are required 1) the object's dry mass, 2) its saturated mass immersed in a fluid, and 3) its saturated mass in air:

$$\text{apparent porosity} = \frac{\text{wet mass} - \text{dry mass}}{\text{wet mass} - \text{wet mass (submerged)}} \cdot 100 \qquad (6)$$

Table 5 includes the apparent porosity measurements for Mixes 1–3 for each curing age. The partial replacement of OPC by MgO resulted in a reduction in apparent porosity, the greater the quantity of MgO used to replace OPC the smaller the pore volume, suggesting that hydration of MgO behaves as a filler in these environments. The only deviation observed was for Mix 1 when cured for 90 days, the apparent porosity for the batch dropping below that of the magnesia containing mixes, suggesting that MgO hinders phase development following 56 days of curing.

SEM analysis was used to observe cement phase development for each of the mortar compositions at different curing times, as illustrated by Fig. 4. The SEM images of 7-day cured mortar specimens indicate that as the percentage replacement of OPC by MgO is increased a more crystalline hydration product is developed within the cements pores. MgO thus appears to be acting as a nucleating agent promoting crystallite growth within the cements. Preliminary XRD work suggesting that the plate-like hexagonal crystals, Fig. 3c, are portlandite as indicated by Salgueiro *et al.* [19].

Table 5 Apparent porosity measurements for mortar samples; the average porosity resulting from a batch of at least four specimens is displayed

Mix No.	Age/day	Apparent porosity/%	Mix No.	Age/day	Apparent porosity/%
1	3	45.23	1	28	43.50
2		44.80	2		42.42
3		44.27	3		42.13
1	7	44.30	1	56	43.01
2		43.64	2		40.64
3		43.25	3		40.60
1	14	43.59	1	90	36.62
2		43.28	2		39.75
3		43.12	3		39.01

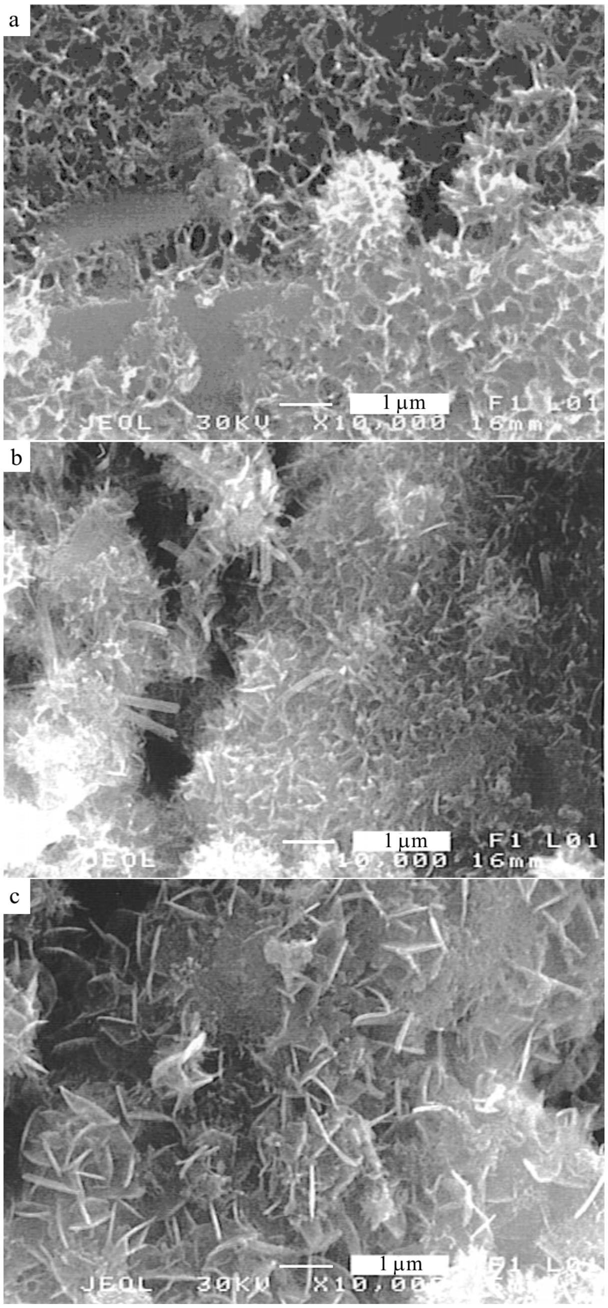

Fig. 4 FEG-SEM pictures of 7-day cured mortar specimens with different mix compositions; a – OPC control containing no MgO replacement, b – 10% replacement of OPC by MgO, c – 20% replacement of OPC by MgO

Conclusions

Thermal experimental data supplemented by XRD, SEM and physical testing results indicated that the addition of reactive MgO as partial replacement of OPC adversely affected the strength of OPC mortars even after 90 days of curing with brucite remaining as a separate phase. Samples with 20% MgO replacement consistently showed less strength than those with 10% replacement. SEM analysis of 7-day cured mortar specimens suggested that as the percentage replacement of OPC by MgO was increased a more crystalline hydration product was evident. MgO thus appeared to be acting as a nucleating agent promoting crystallite growth within the cement. The experimental results using a combination of analytical methods suggested that MgO did not behave as a pozzolan when used alone as a supplementary material in cement mortar production.

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