DRYING SHRINKAGE OF HYDROTHERMALLY CURED CEMENTS WITH REACTIVE MAGNESIA AND CLAY BRICK WASTE

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ABSTRACT

In recent years, worldwide research and development in the cement industry has gathered momentum with an aim to explore innovative and sustainable methods to deliver environmentally responsible Portland Cement (PC) based construction products. This study investigated physical and mechanical properties of autoclaved cement-quartz sand blends with the addition of clay-brick waste (CB waste) and reactive magnesia (MgO) with the aim to lower CO_2 emissions through the reduction of PC consumption. Mechanical properties and drying shrinkage showed improvements with the incorporation of CB waste due to increased amounts and crystallinity of Al-tobermorite. The addition of reactive MgO to PC in hydrothermal conditions was observed to have a negative effect on the compressive strength. XRD data indicated that MgO did not take part in the reaction during the hydration of the cement and may even retard tobermorite formation. However, the expansive nature from the hydration of MgO to brucite may have compensated for drying shrinkage.

KEY WORDS

Portland cement; magnesia; clay brick waste; autoclave; drying shrinkage; compressive strength.

INTRODUCTION

While strength is an essential property of a building material, the durability characteristics are also regarded as being at least of equal if not of greater importance. It is crucial that a cement-based building material is capable of withstanding the conditions for which it has been designed throughout the life of a structure. Many causes for the lack of durability, categorised as physical, mechanical and chemical, can be attributed to external agents arising from the environment or by internal agents within the building material. One of the critical durability attributes of cement-based products is drying shrinkage. Drying shrinkage is the time dependent non-uniform dimensional change of a cement-based materials caused by the removal of water which can lead to cracking and warping (Juenger and. Jennings, 2002). Even though drying shrinkage may not affect the structural integrity, the durability may be compromised over time (Bissonnette et al, 1999). Hydrothermal treatments are known to reduce drying shrinkage where tobermorite, the main binder in most autoclaved calcium silicate products, shrinks to about half the volume of the tobermorite gel (Kalousek, 1969). Shrinkage reduction is also afforded by the substitution of Al^{3+} in tobermorite under autoclaving. Noorlander (1964) found that with increasing kaolin or gibbsite additions to the raw mix, the drying shrinkage of autoclaved sand-lime bricks decreased progressively. Sun et al. (1983) quantified hydrates in numerous autoclaved aerated concrete (AAC) specimens and reported that the proportion of different

hydrates including tobermorite, C-S-H and hydrogarnet was important to achieve a compromise between strength and drying shrinkage. Drying shrinkage was found as a function of the C-S-H content where the greater the amount of C-S-H, the greater was the drying shrinkage.

This study investigated drying shrinkage properties of autoclaved blends incorporating fired clay-brick (CB) waste fines and reactive magnesia (MgO). CB waste, an abundant industrial waste, is a supplementary cementing material (SCM) rich in alumina and silica and has been shown to exhibit pozzolanic activity under ambient conditions when finely ground (Wild et al, 1998). Reactive or light-burned MgO (produced at calcination temperatures of 600°C to 900°C) has been recognised as a potential additive to produce blended cement where its production, relative to PC, is less energy intensive. It had been suggested in previous studies (Buntoro, 2000, Taylor, 1997, Xu and Deng, 2005) that reactive MgO is utilised as an expansive additive to produce a shrinkage-compensated cement. The hydration of MgO to brucite ($Mg(OH)_2$), which involves a volume expansion of 118% (Rehsi and Majumdar, 1969), may fill in pore spaces when water is evaporated to reduce capillary stress and prevent the pores from collapsing. This paper aims to further studies previously carried out by the authors (Liu et al, 2007) in the subject of strength development and phase characterisation. The Al_2O_3 present in CB waste provided a source of Al ions for the formation of Al-substituted tobermorite and, in conjunction with enhanced formation of C-S-Hs, resulted in strength improvement of approximately 9% for up to 15% addition. The addition of MgO alone resulted in a relative reduction in the proportion of PC available for the formation of hydration products and a reduction in compressive strength of approximately 16% at 20% addition was observed. The addition of MgO had also adversely affected the formation of Al-tobermorite. The combined additions of MgO and CB waste, however, produced a strength gain equivalent to the CB waste only series up to 15% with partial retainment of 5% strength gain at 20% addition. The authors suggested that the volume expansion of MgO to brucite and, to a lesser extent, its subsequent carbonation to $MgCO_3$ had a complementary physical effect in that it behaved as an expanding filler producing more efficient packing leading to retainment of strength as crystallisation of the Al-tobermorite occurred.

EXPERIMENTAL

Raw Materials

Raw materials used in this study were sourced from local suppliers. These are listed as follows with the oxide compositions listed in Table 1.

a) Goliath cement (OPC) was supplied by Australian Cement, Auburn, NSW, Australia. The material has a fineness index (Blaine) of 350m^2/kg.

b) Type 200G ground silica (quartz sand) was supplied by Unimin Australia Limited, Sydney, Australia, with a Blaine value of 360m^2/kg.

c) Natural magnesite ($MgCO_3$), with surface area of 2.3m^2/g, was supplied by Unimin Australia Limited, Sydney, Australia. It has a bulk density of 1.6 g/cm^3 and a particle size range of less than 75μm with a maximum of 2% greater than 75μm. The magnesite was calcined to light-burned magnesia at 600°C for 2 hours. BET surface area of calcined MgO was measured to be 104.2m^2/g.

d) Clay-brick (CB) waste used was from a major clay-brick manufacturer in Sydney, Australia. The pre-screened brick waste was ground by dry ball milling method to produce a surface area comparable to that of the quartz sand. Crystalline phase identification of the CB waste was determined using XRD and these phases are listed in decreasing order of abundance as follows: quartz (SiO_2); mullite ($3Al_2O_3.2SiO_2$); Hematite (Fe_2O_3); cristobalite (SiO_2); rutile (TiO_2).

Table 1. Chemical compositions of the raw materials used in this investigation

Oxides	OPC	Silica	Magnesite	Brick waste
SiO_2	20.0	98.9	6.15	69.71
Al_2O_3	4.5	0.6	1.60	18.64
Fe_2O_3	3.7	0.1	0.60	7.48
CaO	64.2	0.1	1.16	0.21
MgO	1.48	0	44.11*	0.95
K_2O	0.67	-	0.28	1.88
Na_2O	0.052	-	0.42	0.44
TiO_2	0.27	0.06	0.086	0.84
LOI	3.1	0.1	46.47	0.08

Oxides and LOI are in mass %.
*Magnesium Carbonate equivalent = 92.3%
Chemical compositions of OPC and 200G silica were obtained from the suppliers. Chemical compositions of magnesite and brick waste were determined by X-ray Fluorescence (XRF) spectroscopy.

Mix design

Three series of OPC mixtures were prepared using a water-to-total solid mass ratio (w/s) of 0.35 and with a constant total Ca/Si oxide molar atom ratio of 0.49 (i.e. atomic ratio based on a 45:55 cement to quartz % mass ratio). The first series of mixtures is concerned with the addition of MgO (M series) at 0, 5, 10 and 20 mass % and the second series with the addition of CB waste (C series) at 0, 10 and 20 mass %. The third series deals with the addition of both MgO and CB waste (CM series) in equal amounts having the total combined amount of 0, 5, 10, 15, and 20 mass %.

Testing and Analysis

Mechanical mixing was conducted on the mixes in accordance with ASTM C 305-99 (1999) using a Hobart mixer. Pastes were cast into stainless steel moulds and compacted on a vibratory table, followed by a 24 hours curing period in a moist cabinet (temperature $23 \pm 1°C$, 95% relative humidity as per ASTM 511-03 (2003)). Demoulded specimens were autoclaved for 7.5 hours, 6 hours of which were at 180°C under approximately 1 MPa of pressure in saturated steam. Drying shrinkage was measured on three autoclaved prisms per selected mix as per ASTM C 490-04 (2004). Dimensions of the prisms used were $120 \times 16 \times 16$ mm instead of $285 \times 25 \times 25$ mm as suggested by the ASTM method. Specimens were fully saturated in water for 3 days followed by equilibration to a relative humidity (RH) of approximately 50-55% by placing the prisms on racks over a saturated solution of $Mg(NO_3)_2 \cdot 6H_2O$ as per ASTM E104-85 (1996) in a closed plastic box. Relative humidity and temperature were continuously recorded using a HOBO® RH/Temp data logger. A special jig mounted at an angle of 45° was used to measure the prisms. Length measurements, using a Mitutoyo Digimatic caliper recorded to the nearest 0.001 mm, were carried out every 2-4 days until the shrinkage remained constant (approximately 4 weeks).

XRD analyses were performed using a Siemens D5000 diffractometer operating at 40 kV and 30 mA with CuK_α radiation scanning from 3 to 60° 2θ at intervals 0.02° using a step time of 8 seconds per interval. Peak intensity and integrated areas were determined by Scherrer method using TOPAS 2.0 with correction for line broadening using a fundamental parameters approach for X-ray line profile fitting (Cheary, R.W. and A. Coelho, 1992). The crystallinity of the tobermorite phase was determined using the relative intensities of the 002 and 220 reflections Hara, N. and H.G. Midgley, 1980), i.e. ($H_{0.308}/H_{1.1}$).

RESULTS AND DISCUSSION

Figure 1 depicts a general reduction in drying shrinkage of autoclaved blends with increasing addition of CB waste fines in both C and CM series. The observed improvement in drying shrinkage can be explained by the main hydration products formed where the presence of Al in CB waste accelerated the crystallisation of Al-bearing 1.1 nm tobermorite from C-S-H. Al-tobermorite has been shown to be relatively more resistant to drying shrinkage (Noorlander, 1964) whilst reduced proportion of C-S-H, which is highly porous, will additionally improve the dimensional stability (Juenger and Jennings, 2002).
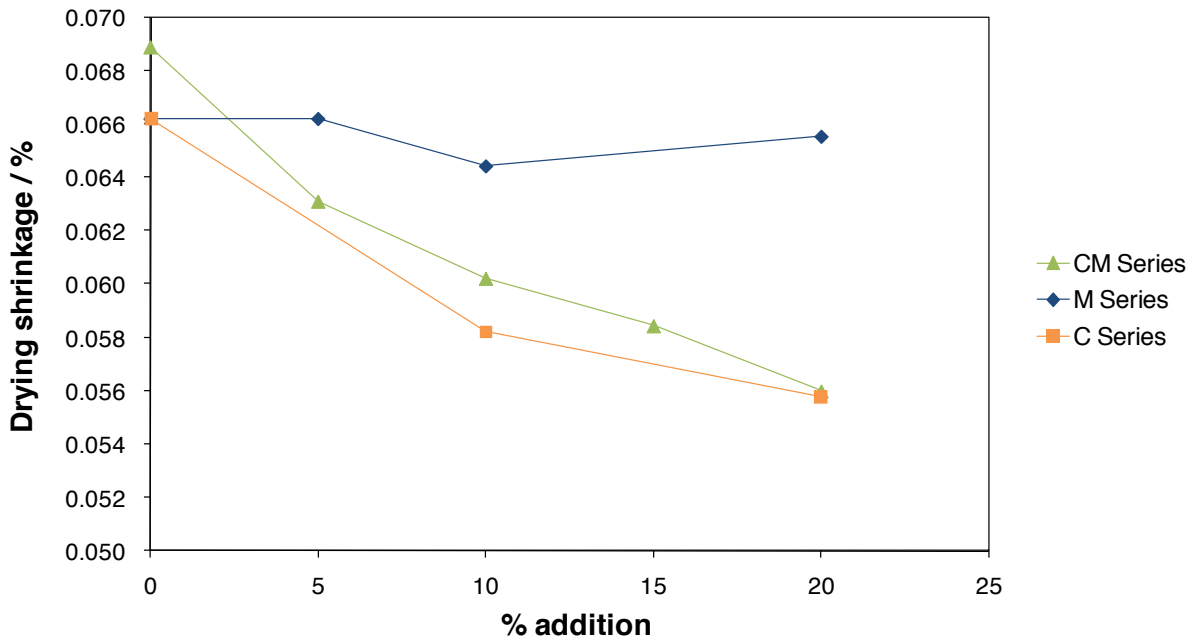

Figure 1 – Average drying shrinkage of selected specimens after approximately 28 days.

The most notable feature is the equivalent degree of drying shrinkage reduction afforded in the C20 and CM20 (10% CB waste, 10% MgO) specimens, despite the fact that the amount of Al-tobermorite is significantly greater in the C20 specimens (Liu et al, 2007). Furthermore, the CM20 specimens exhibited superior drying shrinkage performance when compared to the corresponding CB waste content specimens (C10 specimens). The addition of reactive MgO in the CM20 specimens may have resulted in the high degree of reduction in shrinkage at half the amount of CB waste addition. The volume increase associated with the hydration of magnesia to brucite and subsequent carbonation to magnesite may compensate for the increase in shrinkage from the reduction in the amount and crystallinity (Figure 2) of Al-tobermorite. This may also explain the relatively constant shrinkage values observed for the M series specimens while the tobermorite quantity and crystallinity progressively decreased with increasing MgO additions as the proportion of PC available for the formation of hydration products is reduced. This is evident in Figure 2 where the M series specimens deviated from the main linear trend exhibited by the C series and CM series specimens.
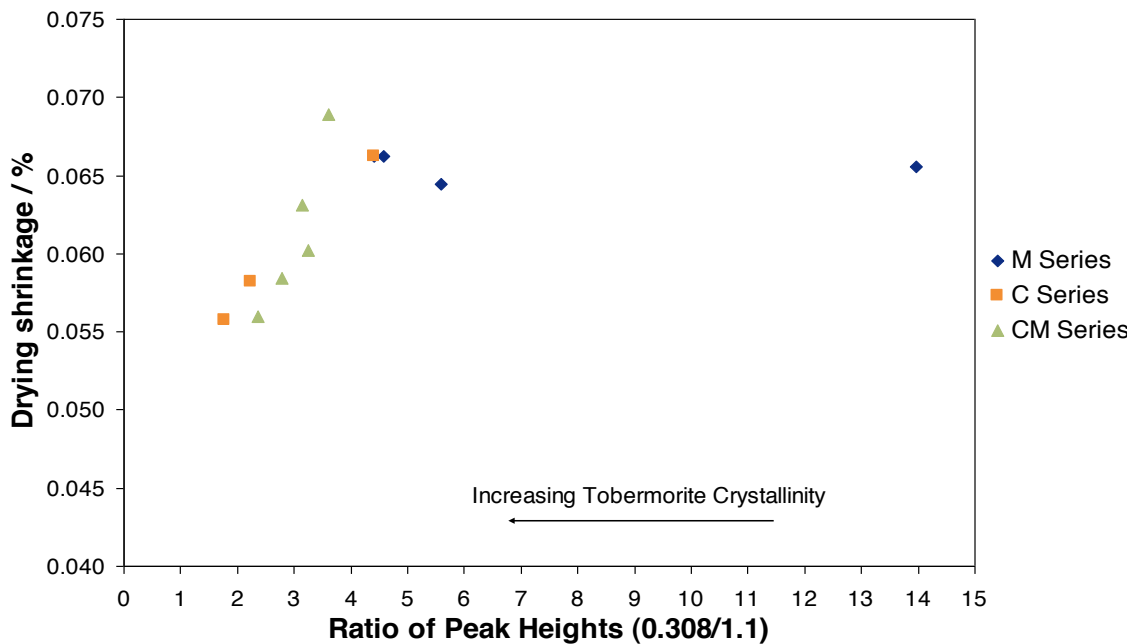
Figure 2 – Drying shrinkage versus the degree of crystallinity of tobermorite calculated from ratio of peak heights of the 0.308 nm and 1.1 nm XRD peaks.

CONCLUSIONS

The proportion and crystallinity of tobermorite was found to have a decisive influence on drying shrinkage where minimum shrinkage was associated with the addition of CB waste leading to the formation of highly crystalline Al-tobermorite from C-S-H. The addition of reactive MgO yielded relatively constant shrinkage values which were attributed to the expansive nature of magnesia converting to brucite and subsequent carbonation to magnesite. The combined CB waste and MgO series produced comparable shrinkage values in comparison to the CB waste added only specimens, which was afforded by complementing physical packing and phase developments.

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