

# Physical and Mechanical Properties of Autoclaved Alumina-silica Rich Industrial Waste Cement Systems Incorporating Reactive Magnesia

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## ABSTRACT

The utilisation of industrial waste products as supplementary cementitious materials to produce blended Portland cement has increased worldwide in recent years. This study aims to investigate physical and mechanical properties of the addition of clay-brick waste and reactive magnesia (MgO) as a low-emission alternative to ordinary Portland cement (OPC) binders in autoclaved calcium silicate based building products. The addition of clay-brick waste was found to be beneficial for drying shrinkage reduction but had an adverse effect on strength development. The addition of reactive MgO also showed a decrease in compressive strength but had some positive effects on bulk density. For the combined addition of clay-brick waste and magnesia an apparent synergy was observed which has been explained by the complementary physical and chemical effects.

Keywords: autoclaving, bulk density, clay-brick waste, compressive strength, drying shrinkage, magnesia

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## 1. Introduction

The highly energy intensive manufacturing process of Portland cement and its generation of approximately 5% of the total global carbon dioxide emissions<sup>5</sup> have provided the incentive to utilise appropriate industrial waste in minimising the consumption of Portland cement. Industrial wastes such as fly ash, blast furnace slag and other pozzolanic materials have been successfully used as supplementary cementing materials (SCM) in the production of blended Portland cement. Traditionally, magnesia (MgO) has been avoided as an additive to Portland cement, since, under the calcining conditions of >1400°C during the production of Portland cement, a highly crystalline and unreactive form of magnesia, periclase, is formed from the raw material magnesium carbonate (MgCO<sub>3</sub>).<sup>16,17</sup> Periclase, in cement clinker, is considered an undesirable component as its slow hydration from MgO to Mg(OH)<sub>2</sub> (brucite) involves a volume expansion of 118%<sup>16</sup> in the hardened paste, thereby leading to micro-cracks. Limits of 4-6% of MgO have been set in Standard Specifications for Portland cement<sup>8</sup> in order to prevent the long term volume instability. By comparison, reactive magnesia (or light-burned magnesia), which may be produced at lower calcination temperatures (600-900°C)<sup>15</sup>, is significantly more reactive and can undergo a high rate of hydration. The lower calcination temperature for the production of reactive magnesia results in less energy consumption and CO<sub>2</sub> emission.

As reactive magnesia is not pozzolanic, finely ground clay-brick waste which has been demonstrated to be a pozzolanic SCM<sup>20</sup>, was investigated in this study in

conjunction with reactive magnesia to aid the reduction of Portland cement consumption in the manufacture of construction materials. Annually, substantial quantities of clay-brick waste are generated on a global scale where large amounts are broken during production and handling.

Under autoclaving conditions pozzolanic materials are well known to be highly reactive.<sup>19</sup> Autoclaving or high pressure steam (hydrothermal) curing of cement-based building products, which is an established process, allows the development of permanent high early strength and improved chemical and physical properties.<sup>4</sup> Klimesch and Ray<sup>10,9,12</sup> have demonstrated that the addition of finely ground clay-brick waste to blends of ordinary Portland cement (OPC) and quartz enhances the formation of 1.1 nm tobermorite, the principal binder of most autoclaved calcium silicate based building materials. More specifically, Al present in clay-brick waste has been shown to accelerate the crystallisation of Al-bearing 1.1 nm tobermorite from calcium silicate hydrate (C-S-H). From a durability perspective this Al-tobermorite is regarded as more beneficial than Al-free tobermorite.<sup>18</sup> While strength continues to be the indispensable characteristic of a construction material, durability aspects are also considered to be at least of equal importance.

An important durability property of hardened cement paste is drying shrinkage. Drying shrinkage involves non-uniform dimensional changes of hydrated cement paste which is associated with loss water leading to cracking and warping.<sup>6</sup> Even though drying shrinkage may not affect the structural integrity, durability problems are increased with time.<sup>2</sup> This paper investigates some aspects of physical and mechanical properties, including drying

shrinkage and bulk density, of autoclaved blends made with clay-brick waste and reactive magnesia.

## 2. Experimental

### 2.1 Raw Materials

- Goliath cement (OPC) was supplied by Australian Cement, Auburn, NSW, Australia. The material has a fineness index (Blaine) of 350m<sup>2</sup>/kg.
- Type 200G ground silica (quartz sand) was supplied by Unimin Australia Limited, Sydney, Australia, with a Blaine value of 360m<sup>2</sup>/kg.
- Natural magnesite, with surface area of 2.3m<sup>2</sup>/g, was supplied by Unimin Australia Limited, Sydney, Australia. The magnesite was calcined to light-burned magnesia at 600°C for 2 hours. BET surface area of calcined MgO has a value of 104.2m<sup>2</sup>/g.
- Brick waste used was from a major clay-brick manufacturer in Sydney, Australia. The pre-screened brick waste was ground using a dry ball milling method to produce a surface area comparable to that of the quartz sand. Crystalline phase identification of the clay-brick waste was determined using XRD and these phases are listed in decreasing order of abundance as follow: quartz (SiO<sub>2</sub>); mullite (3Al<sub>2</sub>O<sub>3</sub>.2SiO<sub>2</sub>); hematite (Fe<sub>2</sub>O<sub>3</sub>); cristobalite (SiO<sub>2</sub>); rutile (TiO<sub>2</sub>).

Chemical compositions of OPC and silica were obtained from the suppliers. Chemical compositions of magnesite and brick waste were determined by X-ray Fluorescence (XRF) spectroscopy.

### 2.2 Mix design

Three series of OPC mixtures were prepared using a water-to-total solid ratio (w/s) of 0.35 and a constant total Ca/Si molar atom ratios of 0.38 i.e. atomic ratio based on a 1:1 cement to quartz % mass ratio. The first series of mixtures is concerned with the addition of MgO at 0, 5, 10, 15, and 20 mass % and the second series with the addition of clay-brick waste at the same amounts. The third series deals with the addition of MgO and clay-brick waste in equal amounts at the total combined amount of 0, 5, 10, 15, and 20 mass %. Each specimen was designated according to the material added (C = clay-brick waste, M = MgO and CM = combined MgO and clay-brick waste additions) followed by the % total addition.

### 2.3 Testing and analysis

Mechanical mixing for compressive strength and drying shrinkage specimens was conducted on the mixes in accordance with ASTM C 305-99. Pastes were cast into 50mm<sup>3</sup> stainless steel moulds or drying shrinkage prisms and compacted on a vibratory table, followed by pre-curing for 24 hours in a moist cabinet. Demoulded specimens were autoclaved with 1.5 hours ramping up to 180°C followed by 6 hours of steam saturation under approximately 1 MPa of pressure. After autoclaving, specimens were allowed to air dry for 2 days followed by compressive strength testing as per ASTM C109/C. Three specimens per mix were loaded under compression until failure using a Tinius Olsen instrument. The tested

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

Oxides	OPC	Silica	Magnesite	Brick waste
SiO <sub>2</sub>	20.0	98.9	6.15	69.71
Al <sub>2</sub> O <sub>3</sub>	4.5	0.6	1.60	18.64
Fe <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	0.67	-	0.28	1.88
Na <sub>2</sub> O	0.052	-	0.42	0.44
TiO <sub>2</sub>	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%

specimens were immediately oven dried at approximately 105°C overnight. Samples from the core of the cement cubes were ground using a tungsten carbide disc mill, and the powders characterised by XRD. XRD analyses were performed using a Siemens D5000 diffractometer operating at 40kV and 30mA with CuK $\alpha$  radiation scanning from 3 to 60° 2 $\theta$  at intervals 0.02° using a step time of 8 seconds per intervals.

Based on compressive strength data, selected blends were tested for drying shrinkage. Drying shrinkage was measured on three autoclaved prisms per mix as per ASTM C 490-04. Dimensions of the prisms used were 120 × 16 × 16 mm instead of 285 × 25 × 25 mm as suggested by the ASTM method. Specimens were fully saturated in water for 2 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<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (ASTM E104-85) 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 and mass measurements were determined using a Mitutoyo Digimatic Indicator measuring to the nearest 0.001 mm. Length measurements were carried out every 2-4 days for 2 weeks. A 150 mm stainless steel standard bar was used to calibrate the jig prior to length measurements. Average bulk density was determined on all drying shrinkage prisms followed by the completion of length measurements using the evacuation method as per Australian Standard AS 1774.5-2001. Test specimens were immersed in water at the pressure of 2.5 kPa overnight to

ensure complete saturation. Masses were determined to the nearest 0.1 g.

### 3. Results and discussion

In two recent papers<sup>13,14</sup>, the authors have reported the compressive strength characteristics and the relationships between phase characteristics and compressive strength development in these mixes. While a general decrease in strength was observed on the combined additions of both additives, these blends produced relatively higher strength than those containing either reactive MgO or clay-brick waste. The CM10 specimen (5% clay-brick waste, 5% MgO), in particular, was found to have improved strength resulting in only a 2% reduction in strength relative to the control.

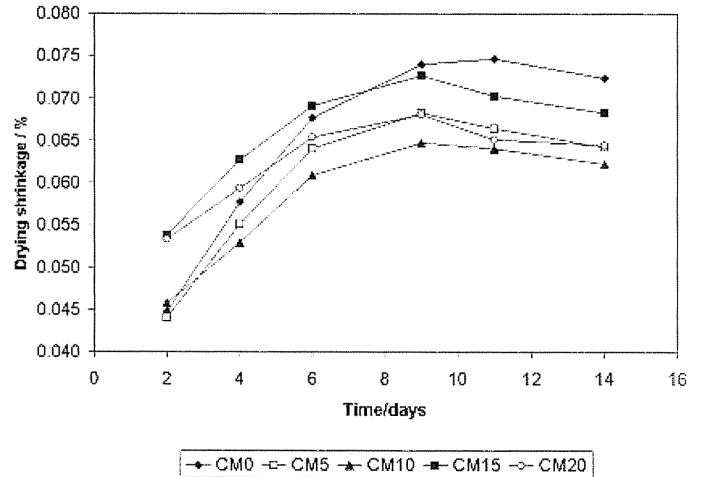
**Table 2. Summary of compressive strength development with MgO and clay-brick additives.<sup>14</sup>**

% Addition	MgO (MPa)	Clay-brick waste (MPa)	Clay-brick and MgO (MPa)
0	86.6 ± 1.2	91.6 ± 4.1	85.3 ± 4.4
5	77.6 ± 5.2	87.7 ± 4.0	79.3 ± 4.1
10	72.1 ± 1.0	83.6 ± 0.0	83.3 ± 2.5
15	67.1 ± 1.7	81.0 ± 3.0	77.2 ± 2.7
20	62.6 ± 1.6	67.1 ± 0.7	75.8 ± 2.9

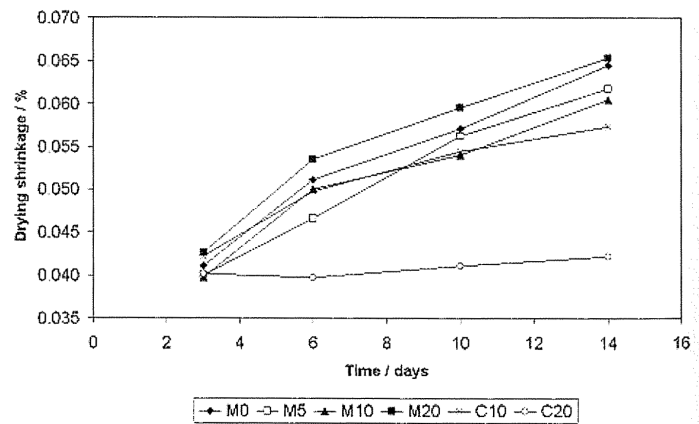
Results of the drying shrinkage measurements on selected specimens after 14 days are depicted in Figures 1 and 2. Figure 1 shows the drying shrinkage has reached maximum around 9 days for all specimens. The CM10 specimens show the lowest shrinkage at 14 days which offers a possible explanation for the observed increase in strength mentioned above. For all specimens the addition of clay-brick waste is also found to reduce shrinkage and this is most noticeable for C20 specimens. The addition of reactive MgO, on the other hand, had little effect on shrinkage relative to the control specimens. Drying shrinkage values at 14 days are generally larger for the CM specimens and they seem to have reached equilibrium while the slope of M and C specimens indicates that further shrinkage may be expected. Additional shrinkage measurements are required to further investigate the maximum level obtainable by the clay-brick waste and reactive MgO specimens.

The degree of crystallinity of the tobermorite, determined from the XRD peak intensity ratio of the 0.308 nm and 1.1 nm ( $H_{0.308} / H_{1.1}$ )<sup>11</sup>, in relation to drying shrinkage is shown in Figure 3. The  $H_{0.308} / H_{1.1}$  ratio is inversely proportional to crystallinity. A non-linear trend is observed where increase in crystallinity results in decrease in drying shrinkage. This observation is in good agreement with test results of autoclave aerated concrete.<sup>1</sup> The crystallinity was found to have a decisive influence on shrinkage where minimum shrinkage is associated with the addition of clay-brick waste leading to the formation of highly crystalline tobermorite from calcium silicate hydrate (C-S-H). The reduced C-S-H amount from its conversion

tobermorite reduces shrinkage as C-S-H is highly porous, and thus will be expected to shrink upon drying.<sup>6</sup>

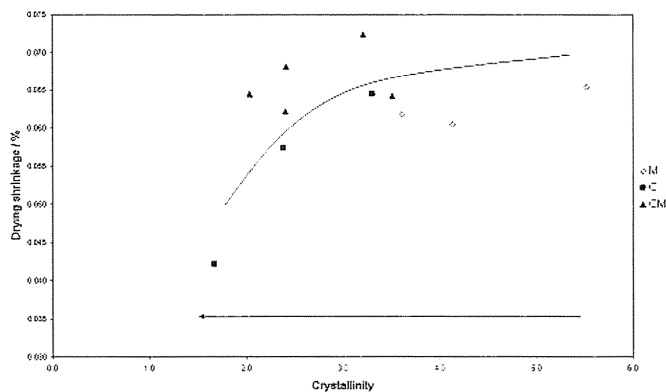


**Figure 1. Average drying shrinkage of combined clay-brick waste and reactive MgO added blends.**

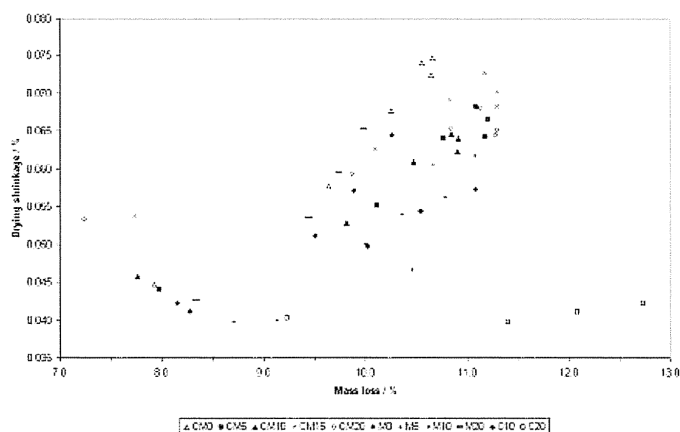


**Figure 2. Average drying shrinkage of independent addition of clay-brick waste and reactive MgO added blends.**

The relationship between shrinkage and water loss for all blends investigated is shown in Figure 4. The data show shrinkage is approximately proportional to the loss of water. The gradient of each curve is dependent on the degree of crystallinity of tobermorite. Higher crystallinity specimens generally show a smaller gradient and vice versa. Figure 4 provides a summary of the inter-relationships of drying shrinkage, water loss and the degree of tobermorite crystallinity.

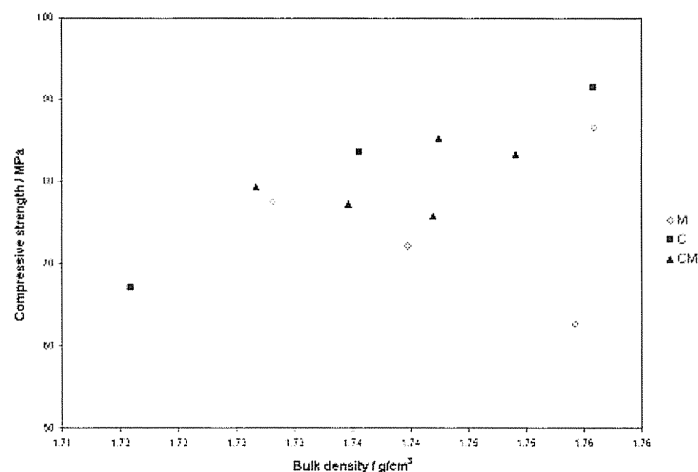


**Figure 3. Drying shrinkage versus the degree of crystallinity of tobermorite calculated from ratio of peak heights of the 0.308 nm and 1.1 nm XRD peaks. The arrow indicates increase in crystallinity. The estimated trend curve is drawn to accentuate the observed trend, it is not a calculated mean curve**



**Figure 4. Relation between shrinkage and weight loss associated with loss of water**

Compressive strength and corresponding bulk densities are plotted in Figure 5. The data show that an increase in compressive strength is associated with increase in bulk density. Similar results were observed by other authors<sup>8,3</sup>, thus confirming that strength is largely dependent on the amount of air voids or pores present. The increased compressive strength was the outcome of available pore volume being filled up with the formation of hydration products including tobermorite. The M20 specimen (1.756 g/cm<sup>3</sup>, 62.6 MPa) suggests the addition of reactive MgO improved the bulk density possibly from the hydration of reactive MgO to brucite (Mg(OH)<sub>2</sub>) which involves a significant volume expansion. Carbonation of brucite to magnesite (MgCO<sub>3</sub>) may also play a part in filling up of pore volume of which the process involves a volume expansion of ~12%. The improved bulk density is not reflected in an increase in strength since with increasing additions of reactive MgO progressively lesser amounts of CaO and Al<sub>2</sub>O<sub>3</sub>, are available for the formation of tobermorite. The amount of binders in this case masks the



**Figure 5. Bulk density of autoclaved prisms as a function of compressive strength**

trends observed in Figure 5. The CM10 (1.749 g/cm<sup>3</sup>, 83.3 MPa) specimen demonstrating the optimum synergy between reactive MgO and clay-brick waste is of physical interactions as evident from the high bulk density value. The expansion of MgO to brucite may compensate, at least partially, for the decrease in volume caused by the crystallinity of 1.1 nm tobermorite and hence producing specimens with relatively higher bulk density and strength.

## 4. Conclusions

Independent additions of reactive MgO and clay-brick waste to Portland cement in autoclave conditions had a negative effect on the compressive strength due to a relative decrease in the proportion of Portland cement available for the formation of strength contributing hydration products. The addition of reactive MgO at 20%, however, showed improvements in its physical properties in terms of bulk density possibly originating from volume expansion associated with the formation of brucite and its carbonation thereafter. A decrease in compressive strength was also observed for the combined reactive MgO + clay-brick waste additions although to a much lesser extent. The presence of Al from clay-brick waste accelerates the crystallisation of Al-bearing 1.1 nm tobermorite from C-S-H, hence, minimising drying shrinkage, where the addition of MgO had improved the bulk density. Hence, the synergy between reactive MgO and clay-brick waste may be explained by the complementary physical and chemical effects.

Drying shrinkage values at 14 days are generally larger for the CM specimens, however, they seem to have reached equilibrium while the slope of M and C specimens indicates that further shrinkage may be expected. A non-linear relationship between drying shrinkage and crystallinity was established. Increasing crystallinity generally results in decreasing shrinkage as C-S-H amounts are reduced from its conversion to tobermorite.

## 5. References

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