Autoclaved alumina-silica rich industrial waste cement systems incorporating magnesia

A. Ray, B. Liu and P.S. Thomas
University of Technology, Sydney, P.O. Box 123, Broadway, Sydney, NSW 2007 Australia.

1. Abstract

Worldwide interest in utilising supplementary cementitious materials (SCM) such as fly ash, blast furnace slag and alkali activated slag, to produce blended Portland cement (PC) stems from the need to reduce PC consumption. Finely ground fired clay brick, an alumina silica rich industrial waste generated from construction and demolition practice in many parts of the world, is a relatively new addition to the list of SCM. The potential to incorporate fired clay brick waste as a SCM for the manufacture of autoclaved or hydrothermally cured calcium silicate based building products has been established recently. Autoclaving, typically carried out between 160° and 200°C under saturated steam, is well suited for utilising industrial by-products. This paper reports the results of investigation on hydrothermally cured quaternary blends comprised of PC, finely ground clay brick waste, reactive magnesia and quartz sand, based on 1:1 cement to quartz ratio. Analytical techniques used in this investigation for characterisation of the autoclaved specimens include thermal analysis, x-ray diffractometry (XRD), scanning electron microscopy (SEM) and compressive strength testing.

2. Introduction

Portland cement (PC) is considered to be one of the most important and widely used construction materials. The manufacturing process of PC is, however, highly energy intensive. As a consequence, the cement industry is amongst the largest single contributors to the greenhouse effect accounting for approximately 5% of the total global carbon dioxide emissions [1]. In order to address the issues of energy consumption and carbon dioxide emission, the utilisation of industrial waste or supplementary cementing materials such as fired clay-brick (CB), fly ash, blast furnace slag and other pozzolanic materials, has been one control measure directed at minimising the consumption of PC and, hence, reducing carbon dioxide emissions [1].

An alternative approach to the minimisation of PC consumption is the addition reactive magnesia as an additive. Traditionally, magnesia has been avoided as an additive, since, under the calcining conditions (>1400°C) required to produce the PC, a highly crystalline form of magnesia, periclase, is formed [2, 3]. Periclase, in cement clinker, is considered an undesirable component as its slow hydration from MgO to $Mg(OH)_2$ (brucite) involves a volume expansion of 118% [2] in the hardened paste, thereby leading to micro-cracks and, ultimately, failure. Limits of 4-6% of MgO have been set in Standard Specifications for PC [4] in order to prevent the long term volume instability or unsoundness. The origins of this problem lie partly in the high temperatures used in the manufacture of PC. The high temperature causes sintering of magnesia resulting in an increase in its crystal size and a decrease in surface area and, thus, a decrease in reactivity [5]. By comparison, reactive magnesia (or light-burned magnesia) is significantly more reactive and can undergo a high rate of hydration. Additionally, reactive magnesia is obtained at lower calcination temperatures (600-900°C [6]), resulting in less energy consumption and CO_2 emission. Another advantage of reactive magnesia for the cement-based building industry is its potential to be used as a flame retardant filler. The hydrated brucite releases H_2O when decomposed to MgO at about 300°C [7].

As reactive magnesia has not yet been demonstrated to be a suitable additive in the highly alkaline cement environment, a pozzolanic SCM, clay brick (CB) waste was also investigated to aid the reduction of PC consumption. Annually, substantial quantities of CB waste are generated on a global scale where large amounts are broken during production and handling. CB waste is rich in alumina and silica and has been shown to exhibit pozzolanic activity under ambient conditions [8]. CB waste is, therefore, a potential renewable resource. The use of CB waste, as a partial replacement for PC in cements, also reduces pressure on landfill.

It is well known that pozzolanic materials under autoclaving conditions are rendered highly reactive [9]. Autoclaving or high pressure steam (hydrothermal) curing of cement-based building products is a well established process typically carried out between 160° and 200°C for several hours. Hydrothermal treatments allow rapid strength development and enhanced chemical and physical properties [10]. The formation of 1.1 nm tobermorite, the principal binder of most autoclaved calcium silicate based building materials, is enhanced by the addition of finely ground CB waste to blends of ordinary Portland cement (OPC) and quartz as demonstrated by Klimesch and Ray [11-13]. More specifically, the presence of Al from CB waste accelerates the crystallisation of Al-bearing

1.1 nm tobermorite from calcium silicate hydrate (C-S-H). Autoclaving blends comprised of $Ca(OH)_2$ + quartz + MgO has also been reported to be capable of producing considerable strength through the MgO hydration reaction [14]. This paper presents variation in strength development with systems containing MgO and CB waste additions at various amounts. Relationships between strength development and phase formations, tobermorite morphology and composition are discussed.

2. Experimental

2.1 Raw Materials

Raw materials used in this study were sourced from local suppliers. These are listed as follows:

(a) Goliath cement (OPC) produced by Australian Cement, Auburn, NSW, Australia, was used. 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. The magnesite was calcined to light-burned magnesia at 600C for 2 hours. BET surface area of calcined MgO has a value of $104.2m^2/g$.

(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 follow: 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 silica were obtained from the suppliers. Chemical compositions of magnesite and brick waste were determined by X-ray fluorescence method.

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 involves the addition of MgO at 0, 5, 10, 15, and 20 mass % and the second series was the addition of CB waste in same amounts. The third series deals with the addition of MgO and CB waste in equal amounts at the total combined amount of 0, 5, 10, 15, and 20 mass %.

2.3 Testing and Analysis

Mechanical mixing was conducted on the mixes in accordance with ASTM C 305-99 [15]. Pastes were cast into 50mm^3 stainless steel moulds and compacted on a vibratory table, followed by precuring 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 [16]. Three specimens per mix were loaded under compression until failure using a Tinius Olsen instrument. The tested specimens were immediately oven dried at approximately 105°C overnight. Small fractured pieces were retained for SEM while the remainder sub-samples from the core of the cement cubes were ground using a tungsten carbide disc mill, and the powders characterised by thermal analysis and XRD.

SEM was conducted using a LEO Supra 55VP Scanning Electron Microscope at an accelerating voltage of 1.3 and 2.0kV. XRD analyses were performed using a Siemens D5000 diffractometer operating at 40kV and 30mA with CuKα radiation scanning from 3 to 60° 2θ at intervals 0.02° using a step time of 8 seconds per intervals. The XRD data was compared with powder diffraction data sets from the Joint Committee on Powder Diffraction Standards (ICDD-JCPDS) CD-ROM database providing qualitative phase identification. Thermogravimetric (TG) and differential thermal (DTA) analyses were performed on 20mg $\pm$ 0.2mg samples using a TA-instruments' SDT 2960 at a heating rate of 10°C/min under flowing air (20mL/min) from ambient to 1000°C.

3. Results and Discussion

3.1 Compressive Strength

In a recent paper [17], compressive strength characteristics of these mixes have been reported. The normalised compressive strength plots (Figure 1) are reproduced in this paper to illustrate that the addition of MgO and CB waste fines exhibit inferior compressive strength relative to the control specimens. A general decrease in strength is observed on the combined additions of both additives yet these blends produced, relatively, higher strength specimens than those containing either MgO or CB waste. The 10% combined addition (5% CB, 5% MgO), in particular, was observed to have improved strength resulting in only a 2% reduction in strength relative to the control. 20% combined CB waste and MgO (CB + MgO) is shown to have 11% reduction in strength. This shows a marked improvement in strength when compared to the independent 20% additions of either MgO or CB waste which showed approximately 27% reduction in strength. A value of 75.8MPa for the 20% total additions of CB + MgO specimen is considered to be adequate for building products used in construction.
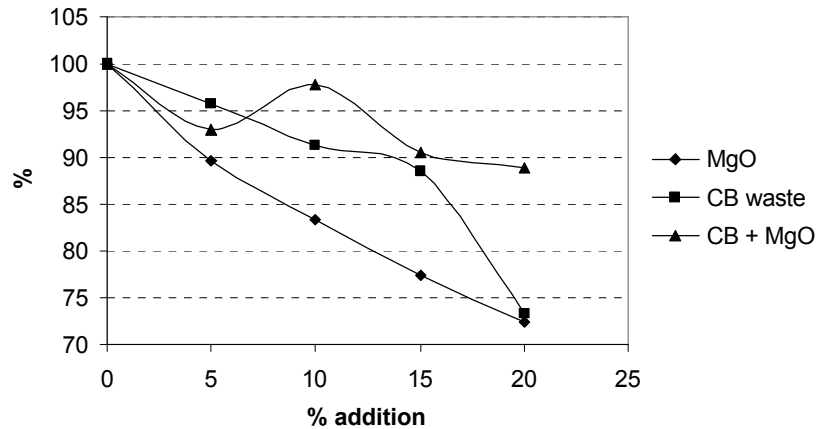
Figure 1. Normalised compressive strength curves for autoclaved blends. The normalised data are calculated as a percentage relative to the control specimens for a particular autoclave run [17].

3.2 X-ray Diffraction

Phase identification using XRD for CB + MgO specimens is shown in Figure 2. Similar data was acquired for both the MgO and CB only additions. For blends including MgO addition, the XRD patterns show an increase in the amount of brucite with increasing proportion of MgO addition, indicating the non-pozzolanic nature of MgO. Of the calcium silicate hydrates, tobermorite was observed in each system and, in particular, in the blends containing CB waste where 1.1 nm tobermorite was evident (Figure 3). The 1.1 nm tobermorite peak (Figure 3) was ill defined in the MgO only specimens and showed a decrease with increasing MgO addition. This was attributed to the decrease in the OPC amounts as the more MgO is introduced to the system. The tobermorite peak in CB waste and CB + MgO additions showed an increase in the peak height confirming the notion that magnesia possesses no pozzolanic activity. The presence of Al ions, originating from the mullite contained in CB waste, appears to accelerate the formation of tobermorite under hydrothermal conditions as has been reported elsewhere [12].
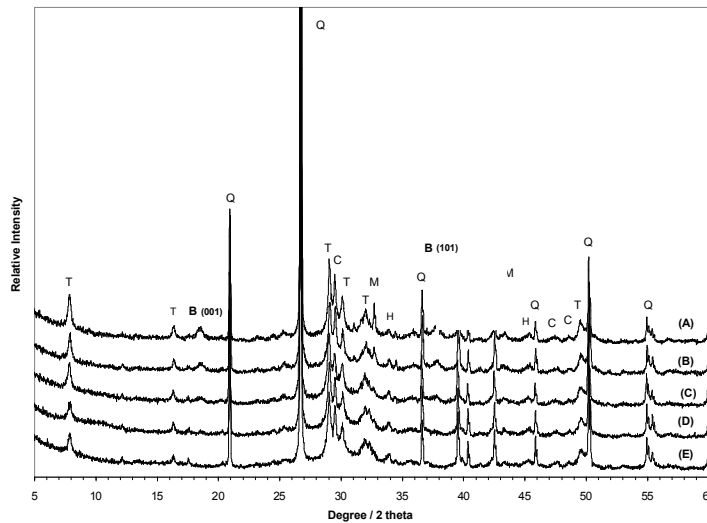
Figure 2. XRD patterns of CB + MgO additions at (A) 20% (B) 15% (C) 10% (D) 5% (E) 0%.
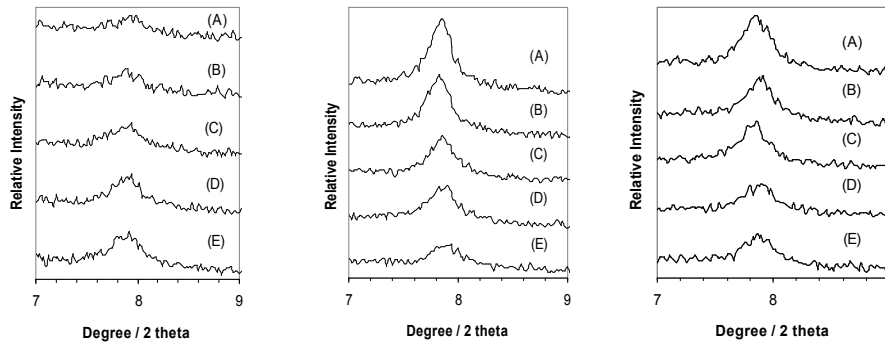T = tobermorite, Q = quartz, B = brucite, C = calcite, M = magnesite, H = hydrogarnet

Figure 3. XRD patterns of 1.1 nm ($2\theta \approx 7.9$) tobermorite peak of MgO, CB waste, and CB + MgO additions (from left to right) at (A) 20% (B) 15% (C) 10% (D) 5% (E) 0%.

The degree of crystallinity of the tobermorite determined from the XRD peak intensity ratio of the 0.308 nm and 1.1 nm ($H_{0.308} / H_{1.1}$) [18] is shown in Figure 4. The $H_{0.308} / H_{1.1}$ ratio is inversely proportional to crystallinity. The addition of magnesia resulted in the formation of poorly crystalline tobermorite phase. The CB waste and CB + MgO specimens both showed a general increase in crystallinity, however, the compressive strength was observed to decrease with increasing addition.
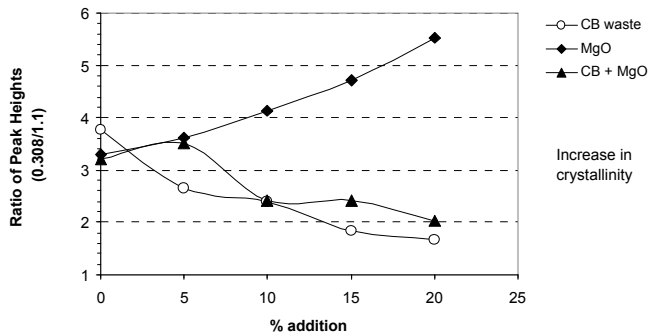
Figure 4. Ratio of peak heights of the 0.308 nm and 1.1 nm XRD peaks versus percentage addition

3.3 Thermal Analysis

Differential thermal analysis (DTA) curves of CB + MgO addition is shown in Figure 5. The main observations of endotherms (endo) and exotherms (exo) are ascribed to:

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ca. 105° - 260°C (endo)	presence of C-S-Hs including 1.1 nm tobermorite (Tob, $C_5S_6H_5$)
ca. 260° - 350°C (endo)	presence of a member of the hydrogarnet series, $C_2AS_{3-x}H_{2x}$, x = 0 to 3
ca. 350° - 440°C (endo)	dehydration of brucite
ca. 440° - 550°C (endo)	decarbonation of magnesium carbonate
ca. 573°C (endo)	crystalline inversion due to unreacted quartz
ca. 600° - 700°C (endo)	decarbonation of calcium carbonate
ca. 850° - 900°C (exo)	crystallisation of beta-wollastonite (β-CS) from C-S-Hs including ($C_5S_6H_5$)
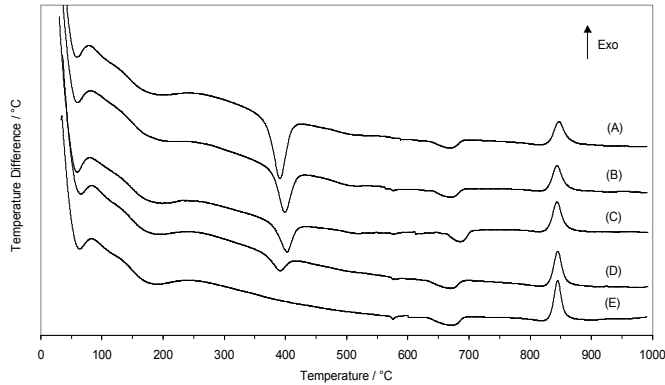
Figure 5. DTA curves of CB + MgO additions at (A) 20% (B) 15% (C) 10% (D) 5% (E) 0%

The increase in Al substituted tobermorite is evident by the gradual reduction in height of the exothermic peak at 850° - 900°C (beta-wollastonite) accompanied by a progressive shift of this peak towards higher temperatures [19]. The relationship between the β-CS and % addition is shown in Figure 6. The CB waste specimens show a considerable increase in the Al-tobermorite amounts with increasing Al_2O_3 content in the system. The CB + MgO in Figure 5 and 6 show a general increase in the Al-tobermorite while the MgO addition (Figure 6) showed a decrease in the peak temperatures. The thermal analysis data agrees well with the XRD data in terms of establishing trends in quantity of Al-tobermorite present.
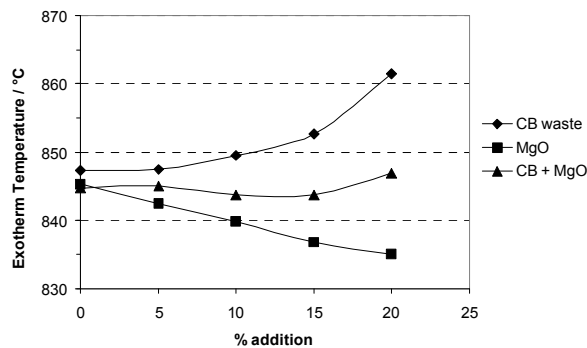

Figure 6. β-CS exotherm temperature versus % addition

3.4 SEM

Differences in tobermorite morphology for different % additions were also observed. It has been reported a decrease in tobermorite crystallinity is associated with the morphology change of: plate → lath-like → needle-like

[20]. Results from SEM are in good agreement with XRD and thermal analysis results. The control specimens were of platy lath-like morphology as shown in Figure 7 (a). The gradual loss of the platy lath-like structure towards need-like structure was observed for the MgO addition specimens. Figure 7 (b) shows a more needle-like structure in the 20% MgO addition specimen indicating a lower crystalline tobermorite. Both CB waste and CB + MgO specimens developed a more dense plate-like morphology with increase in percentage addition as shown in Figure 7 (c) and (d) indicating a more crystalline tobermorite. A dense crystalline plate-type morphology is also associated with higher strength [11], however, for the CB and CB MgO blends characterised in this study, the reverse is apparently observed, although this may be associated with the reduction in PC content. To further underline the non-participating nature of MgO in the principal cement hydration phases, energy dispersive x-ray analysis (EDX) did not show presence of magnesium within the airholes where the micrographs were taken. Magnesium was identified only on the cleaved surface of the specimen indicating that brucite exists as a separate phase.

(a)   (b)

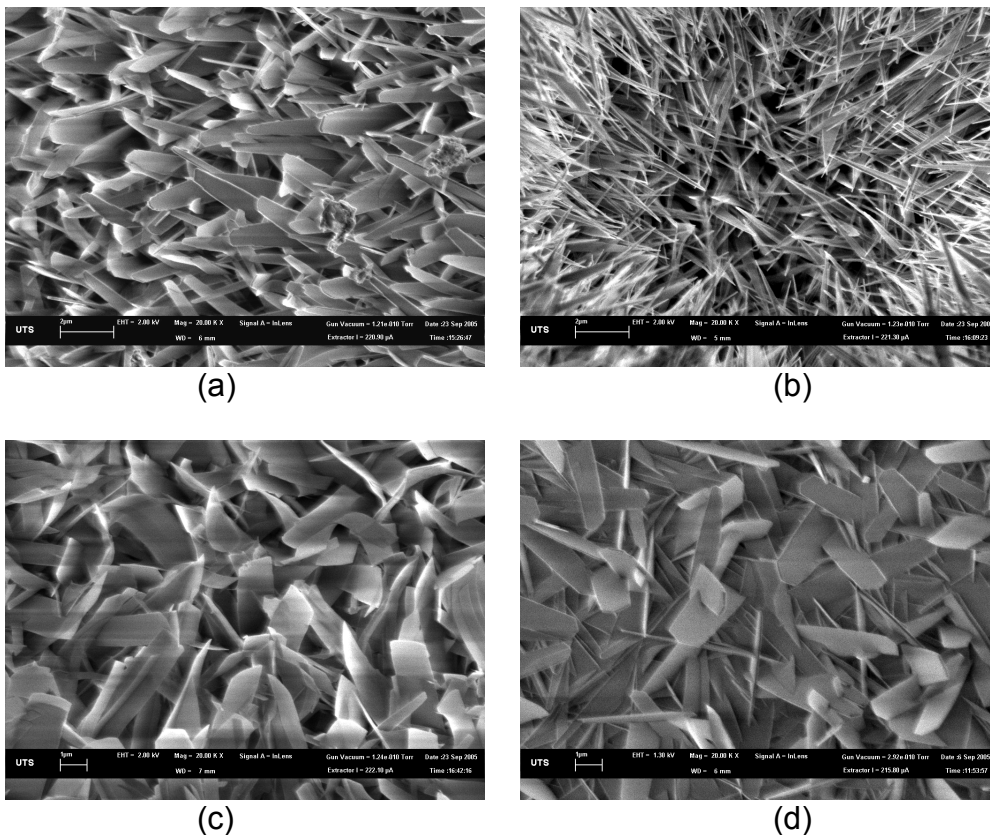(c)   (d)

Figure 7. SEM micrographs of (a) control specimen; (b) 20% MgO addition; (c) 20% CB waste addition; (d) 20% CB + MgO addition

Results from the various techniques used once again confirmed that CB waste is pozzolanic where the Al_2O_3 provided a source of Al ions for the formation of Al substituted tobermorite. From a durability perspective this Al-tobermorite is regarded as more beneficial than Al free tobermorite [21]. It is noteworthy that the incorporation of alumina-silica rich brick waste fines was found beneficial in terms of strength development as reported by Klimesch and Ray [10-13], however, their findings contradict with the trends observed in this study where an additional oxide component MgO was added. The increasing additions of MgO lead to the progressively lesser amounts of CaO and Al_2O_3, hence, decreased amounts of tobermorite resulting in lower strength specimens. XRD data show the presence of brucite, an expanded product of hydration of MgO, indicates that MgO is not reacting with PC nor CB waste. The increasing addition of MgO resulted in the formation of poorly crystalline tobermorite, the principal strength contributing phase. Crennan et al. [22] and Taylor [9] suggested that some optimum degree of crystallinity exists fore strength development. Therefore, it seems that the optimum degree of crystallinity was not realised in the system studied.

The relatively improved strengths observed in samples containing combined additions of MgO and CB waste suggest a synergy between these two materials where brucite from hydrated MgO contributed in a different manner to the CB waste in PC blends, achieving an optimum with a maximum strength specimen produced at 10% CB + MgO additions. In terms of physical aspects, it can be explained 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. A further supporting evidence of the physical interaction comes from the partial carbonation of brucite to magnesite ($MgCO_3$), the presence of which was confirmed by XRD. The carbonation of brucite is accompanied by a volume expansion of ~12%. It had been suggested [9, 23] the use of expansive additive such as MgO to produce a shrinkage-compensated cement. The shrinkage may be outweighed by the expansion of the MgO. The MgO may also fill in pore spaces when water is evaporated to reduce capillary stress and prevent the pores from collapsing. Pore size distribution was found to be one of the major factors controlling strength [9], along with other important factors such as morphology and density of the particles. Further work is underway to examine physical properties in relation to strength.

4. Conclusions

Techniques such as XRD, DTA-TGA, and SEM were found to complement one another in providing critical information about the changes in

composition, crystallinity, and morphology in blends with reactive MgO and CB waste added at various amounts.

The addition of MgO to PC in autoclave conditions had a detrimental effect on the compressive strength due to a relative decrease in the proportion of PC available for the formation of strength contributing hydration products. The brucite phase was observed from XRD data as a separate phase, indicating that the MgO did not take part in the structure of the lime-based hydration products. CB alone also had an adverse effect on the strength with increasing amounts of addition. The same effect was observed for the MgO + CB additions; however, the decrease in strength in these specimens was significantly less. The synergy between MgO and CB waste may be explained by the contrasting physical and chemical effects where hydration of MgO to brucite cancelled out the reactivity of CB waste in PC blends. Future work aims to establish the effect of pore size distribution, using techniques such as mercury intrusion porosimetry (MIP), and crystallinity on mechanical properties. Further experimental data on samples with different Ca/Si ratios are being investigated to examine the viability of light-burned MgO as an additive in PC based construction materials.

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