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**INVESTIGATION OF MAGNESIA REACTIVITY IN
BLENDED CEMENT SYSTEMS UNDER
HYDROTHERMAL CONDITIONS**

**by
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Requirements for the
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Certificate of Authorship / Originality

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Abstract

Addition of supplementary cementing materials (SCM) to produce blended Portland cements (PC) is a well established practice in the manufacture of construction materials. It enables an overall reduction in the consumption of PC thereby reducing CO₂ emissions. This study reports findings on the hydrothermal chemistry, physical and mechanical properties of autoclaved PC–quartz blends where PC was partially replaced by reactive magnesia (MgO), which requires less energy for calcination than calcia (CaO) from their naturally occurring carbonates, and alumina-silica rich fired clay-brick (CB) waste fines, an abundant industrial waste and a proven SCM.

The dependence of the reactivity of magnesia on the calcination temperature was initially investigated through the hydration behaviour and an optimum reactivity at a temperature of 600°C was identified. In order to investigate the potential of this reactive magnesia in a cement environment, the reactivity of the magnesia with colloidal silica in model MgO-SiO₂-H₂O slurry systems was first investigated under both 'mild' and 'extreme' hydrothermal reaction conditions. Amorphous magnesium silicate hydrate (M-S-H) phases were identified in the 'mild' conditions at 180°C with increasingly crystalline phases being developed as the temperature and time were increased up to 350°C and 16 hours of hydrothermal treatment. Two different reaction sequences were also established. For M/S ratios of 0.6, 0.8 and 1.0, the principal reaction products were M-S-H gel and talc while for M/S ratios of 1.5 and 2.0, they were brucite, deweylite and chrysotile serpentine. Morphological studies using SEM of the specimens containing chrysotile revealed that the chrysotile was not of a fibrous nature.

The addition of reactive MgO to PC in hydrothermal conditions was observed to have a negative effect on the compressive strength. The only magnesium containing phase observed in XRD was brucite, indicating that MgO did not take part in the reaction during the hydration of the cement. No M-S-H phases were observed in the MgO containing mixes. Experimental results suggested that MgO was not entirely inert as the formation of tobermorite appeared to be retarded in the presence of brucite.

Examination of PC-quartz mortar mixes revealed that alumina-silica rich clay-brick waste is pozzolanic where the Al₂O₃ provided a source of Al ions for the accelerated formation of Al substituted 1.1nm tobermorite. Mechanical properties showed

improvements with the incorporation of CB waste in more silica-rich environments. Moreover, drying shrinkage and resistance to carbonation were improved due to increased crystallinity of Al-tobermorite.

For blended PC with the addition of both CB waste and reactive magnesia (in a 50/50 ratio), an apparent synergy was observed as minimal (or no) reduction in strength was observed for up to 20% additions of the 50/50 blend. The synergy was explained by the contrasting physical and chemical effects as a result of attaining an optimum proportion of amorphous and crystalline material and optimum physical packing conditions.

Autoclaved MgO-SiO₂ only cube specimens were shown to be capable of producing strength up to 10MPa. XRD revealed the presence of talc where the talc crystallinity was higher in the MgO-silica fume specimens which corresponded to higher strength specimens. This has the potential to be used for low strength applications such as interior walls, possibly as a replacement for gypsum plasterboards.

The use of fired clay-brick waste in combination with reactive magnesia as additives for the production of hydrothermally cured cement-based building products has the potential to achieve an overall positive outcome from an environmental viewpoint.

Table of Contents

Abstract	i
Table of Contents	iii
List of Publications by the Author	vii
List of Abbreviations	viii
List of Tables	x
List of Figures	xii
Appendices	xix
1 Introduction	1
1.1 Preface	1
1.2 Portland Cement	2
1.2.1 Manufacture of Portland Cement	2
1.2.2 Energy Consumption and CO ₂ Emission Considerations	4
1.3 Supplementary Cementing Materials (SCM)	5
1.4 Clay-Brick (CB) Waste	8
1.4.1 Production of Clay-Brick	9
1.4.2 Clay-Brick Waste as Partial Cement Replacement in Concrete.....	10
1.5 Magnesium Oxide	13
1.5.1 Sources and Production of Magnesia (MgO).....	13
1.5.2 General Applications of Magnesia	16
1.5.3 Magnesia as a Supplementary Material in Cement	18
1.6 Chemistry of the Autoclave Process	20
1.7 Research Objectives	24
1.8 Structure of the Thesis	25
2 Background	27

2.1 Preface	27
2.2 The CaO-SiO₂-H₂O System	28
2.2.1 C-S-H Formed at Ambient Temperature.....	28
2.2.2 Hydrothermally Prepared C-S-H.....	35
2.2.3 Characteristics of Tobermorite.....	40
2.2.4 Tobermorite Formation	44
2.3 The CaO-Al₂O₃-SiO₂-H₂O System	47
2.3.1 Aluminium Substitution in C-S-H: The Location of Al.....	47
2.3.2 (Al)-C-S-H Structure.....	52
2.3.3 Al Substituted Tobermorite.....	53
2.3.4 Al-Tobermorite: The Location of Al.....	54
2.3.5 Al-Tobermorite: Silica Reactivity.....	55
2.3.6 Al-Tobermorite: Basal Spacing and Thermal Behaviour.....	55
2.3.7 Hydrogarnet.....	58
2.4 Strength	62
2.5 Durability	63
2.5.1 Drying Shrinkage	63
2.5.2 Carbonation.....	64
2.6 Magnesia	68
2.6.1 Calcination of Magnesite	68
2.6.2 Sintering of Magnesia	74
2.6.3 Hydration of Magnesia.....	76
2.6.4 Magnesia in Cement.....	79
2.6.5 Hydrothermal Reaction of MgO	85
3 Experimental Procedure	96
3.1 Preface	96
3.2 Materials	97
3.2.1 Ordinary Portland Cement (OPC).....	97
3.2.2 Ground Quartz Sand.....	97
3.2.3 Clay-brick (CB) Waste.....	98
3.2.4 Natural Magnesite (MgCO ₃)	99
3.2.5 Basic Magnesium Carbonate.....	100
3.2.6 Gibbsite (Al(OH) ₃).....	100
3.2.7 Silica Fume.....	101
3.2.8 Glenium 51	101
3.2.9 Colloidal Silica.....	101
3.2.10 Calcined Magnesias	101
3.3 Sample Preparations Methods	102
3.3.1 Hydration of Differently Calcined Magnesium Oxide.....	102
3.3.2 Slurry Preparation	103
3.3.3 Paste Preparation.....	105

3.4 Evaluation of Specimens.....	105
3.4.1 Compressive Strength	105
3.4.2 Drying Shrinkage	106
3.4.3 Degree of Carbonation (DoC).....	107
3.5 Methods of Characterisation.....	108
3.5.1 X-ray Diffraction (XRD).....	108
3.5.2 X-Ray Fluorescence (XRF).....	110
3.5.3 Scanning Electron Microscopy (SEM)	111
3.5.4 Thermal Analysis (TA)	112
3.5.5 ²⁷ Al and ²⁹ Si Nuclear Magnetic Resonance (NMR) Spectroscopy	115
3.5.6 BET Surface Area	117
3.5.7 Acid-Insoluble Residue (AIR) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).....	119
4 Hydration of Differently Calcined Magnesia.....	121
4.1 Preface.....	121
4.2 Results	122
4.2.1 Degree of Calcination	122
4.2.2 Scanning Electron Microscopy	125
4.2.3 Degree of Hydration.....	129
4.2.4 Summary	129
5 Phase Development of Hydrothermally Treated MgO-SiO₂-H₂O System	131
5.1 Preface.....	131
5.2 Results	132
5.2.1 X-Ray Diffraction	132
5.2.2 Scanning Electron Microscopy	138
5.2.3 Thermal Analysis	146
5.2.4 ²⁹ Si MAS Nuclear Magnetic Resonance	151
5.2.5 MgO-Al ₂ O ₃ -SiO ₂ -H ₂ O System.....	154
5.2.6 Summary	157
6 Hydrothermally Cured PC-Quartz Pastes with Clay-Brick Waste and Reactive Magnesia Additions.....	158
6.1 Preface.....	158
6.2 Workability	161
6.3 Results of Constant Ca/Si = 0.58 Specimens.....	165
6.3.1 Compressive Strength	165
6.3.2 X-Ray Diffraction	166
6.3.3 Scanning Electron Microscopy	170

6.3.4	Thermal Analysis	173
6.3.5	²⁷ Al Nuclear Magnetic Resonance	175
6.3.6	Evaluation of Acid-Insoluble Residue	178
6.3.7	Degree of Carbonation	183
6.3.8	Physical Properties	185
6.3.9	Drying Shrinkage	187
6.4	Results of Constant Ca/Si = 0.49 Specimens	189
6.4.1	Compressive Strength	189
6.4.2	X-Ray Diffraction	190
6.4.3	Scanning Electron Microscopy	192
6.4.4	Thermal Analysis	195
6.4.5	²⁷ Al Nuclear Magnetic Resonance	196
6.4.6	Evaluation of Acid-Insoluble Residue	196
6.4.7	Degree of Carbonation	197
6.4.8	Physical Properties	199
6.4.9	Drying Shrinkage	200
6.5	Results of Constant Ca/Si = 0.41 Specimens	202
6.5.1	Compressive Strength	202
6.5.2	X-Ray Diffraction	203
6.5.3	Scanning Electron Microscopy	205
6.5.4	Thermal Analysis	208
6.5.5	²⁷ Al Nuclear Magnetic Resonance	208
6.5.6	Evaluation of Acid-Insoluble Residue	209
6.5.7	Degree of Carbonation	210
6.5.8	Physical Properties	210
6.5.9	Drying Shrinkage	212
6.6	Strength Development of Autoclaved Cement Blends with Addition of MgO Calcined at 850°C	214
6.7	Strength Development of Autoclaved MgO-SiO₂ Only Cubes Specimens	216
6.7.1	Compressive Strength	216
6.7.2	X-Ray Diffraction	217
6.7.3	Scanning Electron Microscopy	219
6.7.4	Thermal Analysis	220
6.7.5	²⁹ Si MAS Nuclear Magnetic Resonance	222
7	Conclusions	224

List of Publications by the Author

1. B. Liu, A. Ray, and P.S. Thomas (2008). "Physical and mechanical properties of autoclaved alumina-silica rich industrial waste cement systems incorporating reactive magnesia." Concrete Forum 1(1): 18-22.
2. B. Liu, A. Ray, and P.S. Thomas (2007). "Autoclaved alumina-silica rich industrial waste cement systems incorporating magnesia." International Congress on the Chemistry of Cement, Montreal, Canada.
3. B. Liu, A. Ray, and P.S. Thomas (2007). "Strength development in autoclaved aluminosilicate rich industrial waste-cement systems containing reactive magnesia." Journal of the Australian Ceramic Society 43(1): 82-87.
4. B. Liu, P.S. Thomas, A.S. Ray, and J.P. Guerbois (2007). "A TG Analysis of the Effect of Calcination Conditions on the Properties of Reactive Magnesia." Journal of Thermal Analysis and Calorimetry 88(1): 145-149.
5. B. Liu, A. Ray, P.S. Thomas, D. Klimesch and J.P. Guerbois (2007). "Mechanical properties of hydrothermally treated alumina-silica rich industrial waste cement systems - effect of magnesia addition." Journal of Solid Waste Technology and Management 33(2): 61-66.

List of Abbreviations

AAC	Autoclaved Aerated Concrete
AFm	$\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-mono phase, } [\text{Ca}_2(\text{Al,Fe})(\text{OH})_6]\text{X}\cdot\text{xH}_2\text{O}$, X = one formula unit of a singly charged anion, or half a formula unit of a doubly charged anion.
(Al)-C-S-H	Al substituted C-S-H
AIR	Acid Insoluble Residue
ASTM	American Society for Testing and Materials
ATH	Aluminium Trihydrate
C_2S	Dicalcium Silicate
C_2SH	Dicalcium Silicate Hydrate
C_3A	Tricalcium Aluminate
C_3AH_6	Hydrogarnet
C_3ASH_4	Katoite
C_3AS_3	Grossular
C_3S	Tricalcium Silicate
C_4AF	Tetracalcium Aluminoferrite
$\text{C}_6\text{S}_6\text{H}$	Xonotlite
CB	Clay-Brick
CH	Calcium Hydroxide (Portlandite)
CS	Wollastonite
C-S-H	Calcium Silicate Hydrate
DDT	2 nd Derivative Differential Thermal
DoC	Degree of Carbonation
DTA	Differential Thermal Analysis
EGA	Evolved Gas Analysis
ESEM	Environmental Scanning Electron Microscope
FESEM	Field Emission Scanning Electron Microscope
FID	Free-Induction Decay
FT	Fourier Transform
GGBFS	Ground Granulated Blast-Furnace Slag
ICCD	International Centre for Diffraction Data
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
LOI	Loss on Ignition
M/S	MgO/SiO ₂ Ratio
M-A-S-H	Magnesium Aluminium Silicate Hydrate
M-S-H	Magnesium Silicate Hydrate
MAS	Magic Angle Spinning
MK	Metakaolin
MPa	Megapascal

NMR	Nuclear Magnetic Resonance
OPC	Ordinary Portland Cement
PC	Portland Cement
PFA	Pulverised Fuel Ash
ppm	Parts Per Million
PSA	Particle Size Analyses
RH	Relative Humidity
SCM	Supplementary Cementing Materials
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
TGA	Thermogravimetric Analysis
TMS	Trimethylsilylation
WDS	Wavelength Dispersive Spectrometry
w/c	Water/Cement Ratio
w/s	Water/Solid Ratio
wt. %	Weight Percent
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

List of Tables

Table 1.1 Main Clinker Compounds (Shreve and Brink 1977).....	2
Table 1.2 Approximate composition limits of Portland cement (Neville and Brooks 1987). Oxides are given in mass percent.	3
Table 1.3 Worldwide reserves of magnesite (Kramer 2006).....	14
Table 1.4 Terms related to the production conditions and resultant MgO properties (Manocha 2000).....	17
Table 2.1 ²⁹ Si NMR notation examples with and without Al substitution modified from LaRosa Thompson (1995).	33
Table 2.2 Hydration states of tobermorite (Taylor 1992).....	40
Table 3.1 Chemical compositions of raw materials used. Oxides and LOI are in mass percentage.....	97
Table 3.2 Definitions and criteria for C-S-H and tobermorite (T) used in this thesis (Kalousek 1969; Mitsuda and Taylor 1975).	110
Table 4.1 Calcination results: (i) Degree of calcination based on the mass loss of the decarbonation peak compared to their respective uncalcined raw material. (ii) BET surface area of calcined magnesias and raw materials. (iii) Crystallite size determined from periclase (200) X-ray diffraction line.	123
Table 5.1 Phases identified by x-ray diffraction.....	137
Table 6.1 Chemical compositions of mortar specimens made with constant Ca/Si ratio of 0.58.	159
Table 6.2 Chemical compositions of mortar specimens made with constant Ca/Si ratio of 0.49.	159
Table 6.3 Chemical compositions of mortar specimens made with constant Ca/Si ratio of 0.41.	160
Table 6.4 Mix design of MgO-quartz sand and MgO-silica fume blends.	160
Table 6.5 Volume of Glenium 51 superplasticiser required to achieve comparable flow to the control specimens.	162
Table 6.6 List of the absolute values of the average compressive strength versus % addition. The 0% addition values are used as a reference for the normalisation of the data in Figure 6.2.	163
Table 6.7 Average compressive strength for autoclaved blends. The 0% addition (control specimens) values are used as a reference for the normalisation of the data in Figure 6.3.	165
Table 6.8 Average compressive strengths for autoclaved blends. The 0% addition (control specimens) strengths are used as a reference for the normalisation of the data presented in Figure 6.21.....	189
Table 6.9 Average compressive strength values for autoclaved blends. The 0% addition (control specimens) values are used as a reference for the normalisation of the data in Figure 6.32.	202

Table 6.10 Average compressive strength values for autoclaved cement blends with the addition of MgO calcined at 850°C. The 0% addition (control specimens) values are used as a reference for the normalisation of the data in Figure 6.42.	214
Table B.1 ²⁹ Si NMR peak positions of M-S-H specimens.	274
Table C.1 Physical properties of autoclaved prisms made with constant Ca/Si = 0.58.....	279
Table C.2 Physical properties of autoclaved prisms made with constant Ca/Si = 0.49.....	289
Table C.3 Physical properties of autoclaved prisms made with constant Ca/Si = 0.41.....	299

List of Figures

Figure 1.1 Schematic diagram of a dry process cement plant	3
Figure 1.2 Global greenhouse gas emissions (CO ₂ eq.) in year 2000 and contribution of cement production (Rehan and Nehdi 2005).	4
Figure 1.3 Locations of magnesia production in Australia (Shand 2006).	16
Figure 1.4 Effects of partial replacement of cement by finely ground silica on the compressive strengths of mixes cured normally and in the autoclave. From Menzel (1934).	21
Figure 2.1 XRD powder diffraction pattern (spacings in Å, where 1 Å = 0.1nm) of a fully reacted 23 years old β-C ₂ S paste. From Taylor (1997).	28
Figure 2.2 A single layer of 1.4 nm tobermorite (A and B) in bc- and ac-projections, respectively. In ac- projections the chains are seen end on. The suggested structure for a single layer of jennite (C) is consisting of chains of silica tetrahedra (Δ) and Ca (•) oxide sheets. B = bridging tetrahedron, P = paired tetrahedron, H = hydroxyl groups. From Taylor (1997).	30
Figure 2.3 Silicate chain of the type present in jennite and 1.4nm tobermorite, showing the probable positions of the H atoms (marked A) and suggest modification (at B) by the omission of a bridging tetrahedron. The oxygen atoms at the bottom of this diagram are also part of the central CaO ₂ layer. From Taylor (1986).	31
Figure 2.4 Percentages of the total silicon in C ₃ S or alite pastes recovered as monomer, dimer and polymer by a trimethylsilylation method. From Mohan and Taylor (1982).	34
Figure 2.5 XRD patterns of samples cured for 2 hours at 150°C made from CaO-silicic acid mixtures of various Ca/Si as indicated. C = C-S-H, P = portlandite, T = tobermorite. From Okada et al. (1994a).	37
Figure 2.6 TG curves of samples made with Ca/Si = 1.5, 1.3, 1.0, 0.8, 0.6 and 0.5 (bottom to top). From Mitsuda et al. (1986).	38
Figure 2.7 Q ² /Q ¹ intensity ratio vs. bulk Ca/Si ratio shows gradual decrease for 150° and 180°C cured samples; a more abrupt transition occurs for 120°C curing (Okada et al. 1994a).	39
Figure 2.8 ‘Anomalous’ tobermorite Ca ₅ Si ₆ O ₁₆ (OH) ₂ ·4H ₂ O. The bridging tetrahedra in one chain are bonded to those in the chain across the interlayer region forming double-chains (Q ³). From Komarneni and Tsuji (1989).	42
Figure 2.9 A three dimensional view of ‘normal’ tobermorite comprised of single dreierketten chains. The dotted Ca-atoms (Ca5 and Ca6) are statistically distributed among these sites. From Hamid (1981).	43
Figure 2.10 Schematic model of C-S-H. From Sato and Grutzeck (1992).	46
Figure 2.11 Dependence of the percentage of Al ⁴ and Al ⁶ on the Ca/Si ratio of the C-S-H phases. From Stade and Müller (1987).	48
Figure 2.12 Schematic representation of: (a) unsubstituted pentameric silicate chain with (b) Al substitution in the bridging site or (c) a non-bridging site. Richardson et al. (1993) found case (b) to be the most likely arrangement of Al and Si tetrahedra.	49

Figure 2.13 Different types of configurations for the Si substitution by Al in (Al)-C-S-H with the corresponding approximate chemical shifts. Modified from Faucon et al. (1999).....	50
Figure 2.14 Differential thermal analysis curves of C/(S+A) = 0.8 reaction products: (1) pure tobermorite; (2) tobermorite containing 5.7% combined Al ₂ O ₃ ; (3) C ₃ ASH ₄ containing 9.3% combined Al ₂ O ₃ ; (4) products containing 14.4% Al ₂ O ₃ ; (5) products containing 20.7% Al ₂ O ₃ . From Kalousek (1957).....	57
Figure 2.15 XRD patterns of autoclaved CaO-metakaolin-fine quartz mixtures with Al/(Al+Si) ratios of a) 0.03 and b) 0.13, hydrothermally cured at 180°C for 1, 2, 4, 9 and 23 hours. H = hydrogarnet, T = tobermorite, Q = quartz, C = C-S-H, P = portlandite. From Klimesch and Ray (1998).	61
Figure 2.16 Stepwise processes involved in thermal dissociation of magnesite. From Shand (2006).	69
Figure 2.17 Calcination of MgCO ₃ to active (dilated lattice) and inert (normal lattice) MgO. Modified from Eubank (1951).....	70
Figure 2.18 Schematic diagram of a crystal plane of MgO, produced by low temperature calcination, which is pseudomorphic after MgCO ₃ . From Eubank (1951).	71
Figure 2.19 Effect of time and temperature of calcination of natural magnesite on the BET specific surface area. From Fernández et al. (1999).....	73
Figure 2.20 Schematic of the pathway of particle sintering. From Shand (2006).....	75
Figure 2.21 Hydration mechanisms of polycrystalline magnesia. From Salomão et al. (2007)..	79
Figure 2.22 Average compressive strength of cube mortar specimens containing 0, 10 and 20% replacement by mass of PC by MgO. From Lawry et al. (2005).....	82
Figure 2.23 Unconfined compressive strength (UCS) versus binder composition for specimens air-cured for 28 days. From Vandeperre et al. (2006).....	83
Figure 2.24 Diagram showing composition (in moles) of the several phases in the system, MgO-SiO ₂ -H ₂ O. From Bowen and Tuttle (1940).	85
Figure 2.25 Structure of serpentine layer: (a) tetrahedral Si ₂ O ₅ network in plan, (b) tetrahedral network as viewed along y-axis, (c) tri-octahedral component of serpentine layer (plan), (d) serpentine layer as viewed along y-axis. From Zussman (1954).....	88
Figure 2.26 X-ray pattern of a typical deweylite, with basal reflections from the talc (T) and serpentine (S) indicated. From Bish and Brindley (1978).....	89
Figure 2.27 The structure of brucite (Deer et al. 1966).....	90
Figure 2.28 DTA curves of bentonite-MgO mixtures (M/S = 1.63), cured at 126°C for different periods. From Wang and Handy (1966).	91
Figure 2.29 XRD patterns showing the transition from M-S-H to poorly crystalline talc to highly crystalline talc. From Mitsuda (1977).	94
Figure 3.1 Particle size distribution of type 200G ground quartz sand.	98
Figure 3.2 Particle size distributions of the CB after various milling times (minutes).	99
Figure 3.3 Particle size distribution of natural magnesite used.	100
Figure 3.4 Bomb setup in a fan-forced oven	104
Figure 3.5 ²⁹ Si NMR chemical shift ranges for phases with Si in tetrahedral co-ordination. The shifts and regions related to cement phases are highlighted in black (Engelhardt and Michel 1987).....	116

Figure 4.1. X-ray diffraction patterns of (a) natural magnesite and calcined natural magnesite and (b) basic MgCO ₃ and calcined basic MgCO ₃ . M = Magnesite, P = Periclase (MgO), T = Talc (Mg ₃ Si ₄ O ₁₀ (OH) ₂), Q = Quartz, D = Dolomite (CaMg(CO ₃) ₂).	124
Figure 4.2. BET surface area of calcined and uncalcined natural magnesite and basic MgCO ₃ .	125
Figure 4.3 SEM micrograph of (a) raw natural magnesite; and (b) the N600 specimen showing the presence of fine protrusions on the surfaces of MgO particles.	126
Figure 4.4 SEM micrograph of (a) the N1000 specimen showing growth of the fine protrusions and; (b) raw basic MgCO ₃ with randomly ordered scaly particles.	127
Figure 4.5. SEM micrograph of (a) the B600 specimen and; (b) the B1000 specimen showing relatively smaller changes in the crystallite size compared to the natural MgO.	128
Figure 4.6. Degree of hydration, in a constant RH atmosphere, of calcined natural MgO to Mg(OH) ₂ (Corrected for impurities).	130
Figure 4.7. Degree of hydration, in a constant RH atmosphere, of basic MgO to Mg(OH) ₂	130
Figure 5.1 XRD patterns of (a) M/S = 0.6, (b) M/S = 0.8, (c) M/S = 1.0, (d) M/S = 1.5 and (e) M/S = 2.0 specimens hydrothermally treated at 180, 250, 300 and 350°C for 16 hours. • = M-S-H gel, B = brucite, T = talc (JCPDS #02-0571), C = chrysotile (JCPDS #02-0350), S = amorphous SiO ₂ (JCPDS #29-0085), D = deweylite (Speakman and Majumdar 1971; Bish and Brindley 1978), with basal reflections from the talc (T) and serpentine (S) indicated by the subscript.	136
Figure 5.2 SEM micrograph of specimens made with M/S = 0.6 treated at (a) 180°C for 8 hours and, (b) and (c) 350°C for 16 hours.	141
Figure 5.3 SEM micrograph of specimens made with M/S = 0.8 treated at (a) 180°C for 8 hours and, (b) and (c) 350°C for 16 hours.	143
Figure 5.4 SEM micrograph of specimens made with M/S = 1.5 treated at (a) 180°C for 8 hours and (b) 350°C for 8 hours.	144
Figure 5.5 SEM micrograph of specimens made with M/S = 2.0 treated at (a) 180°C for 8 hours and (b) 300°C for 16 hours.	145
Figure 5.6 DTA curves of (a) M/S = 0.6, (b) M/S = 0.8, (c) M/S = 1.0, (d) M/S = 1.5 and (e) M/S = 2.0 specimens hydrothermally treated at 180, 250, 300 and 350°C for 16 hours.	149
Figure 5.7 TGA/EGA curves of the MS2.0-250°C-8H specimen.	150
Figure 5.8 XRD patterns of specimens heated to 1000°C. E = Enstatite (JCPDS #019-0768), F = Forsterite (JCPDS #034-0189) and C _E = Clinoenstatite (JCPDS #035-0610).	150
Figure 5.9 ²⁹ Si NMR single pulse spectra of (a) M/S = 0.6, (b) M/S = 0.8, (c) M/S = 1.0, (d) M/S = 1.5 and (e) M/S = 2.0 specimens hydrothermally treated at 180, 250, 300 and 350°C for 16 hours.	154
Figure 5.10 X-ray diffraction patterns of specimens made with M/S ratio of 1.0 hydrothermally treated at 180°, 250°, 300° and 350°C for 16 hours with 10% gibbsite additions.	155
Figure 5.11 X-ray diffraction patterns of specimens made with M/S ratio of 1.0 hydrothermally treated at 300°C for 8 hours with 10, 20 and 30% of gibbsite additions. Bo = Boehmite (JCPDS #021-1307).	156
Figure 6.1 Average flow for C, M, and CM series, with associated error.	162

Figure 6.2 Normalised compressive strength curves for autoclaved blends containing Glenium 51 superplasticiser with constant Ca/Si of 0.58. The normalised data are calculated as a percentage relative to the control specimens for a particular autoclave run. Strength curves for M and CM series without Glenium 51 superplasticiser are included for comparison (denoted by dashed lines). 164

Figure 6.3 Normalised average compressive strength curves for autoclaved blends. The normalised data are calculated as a percentage relative to the control specimens for a particular autoclave run. 166

Figure 6.4 XRD patterns of (a) CM series specimens, (b) M series specimens and (c) C series specimens, additions at 0, 5, 10, 15 and 20%. T = tobermorite, Q = quartz, B = brucite, C = calcite, M = magnesite, H = hydrogarnet. 169

Figure 6.5 Ratio of peak heights of the 0.308 nm and 1.1 nm XRD peaks versus percentage addition. The $H_{0.308} / H_{1.1}$ ratio is inversely proportional to crystallinity..... 169

Figure 6.6 SEM micrographs of (a) control specimen, (b) 20% MgO addition specimen (M20), (c) 20% CB fines addition specimen (C20) and (d) 20% CB + MgO addition specimen (CM20). 172

Figure 6.7 DTA curves of CM series specimens (CB + MgO additions) at 0, 5, 10, 15 and 20%. 174

Figure 6.8 Total bulk Al_2O_3 content in the initial mix versus the variation in the β -CS exotherm temperature. 174

Figure 6.9 ^{27}Al NMR single pulse spectra of (a) C series specimens, (b) M series specimens and (c) CM series specimens. *-spinning side band..... 177

Figure 6.10..... 178

Figure 6.11 ^{27}Al MAS NMR spectra of calcined MgO derived from natural magnesite. 178

Figure 6.12 Average acid-insoluble residue versus percentage addition..... 179

Figure 6.13 Composition of bulk and combined AIR of autoclaved blends with MgO addition: (a) % SiO_2 ; (b) % Al_2O_3 ; (c) % MgO. 180

Figure 6.14 Composition of bulk and combined AIR of autoclaved blends with CB addition: (a) % SiO_2 ; (b) % Al_2O_3 ; (c) % MgO..... 182

Figure 6.15 Composition of bulk and combined AIR of autoclaved blends with CB + MgO addition: (a) % SiO_2 ; (b) % Al_2O_3 ; (c) % MgO. 183

Figure 6.16 Degree of carbonation of selected autoclaved blends. 184

Figure 6.17 XRD patterns of carbonated CM series specimens (CB + MgO) additions at 0, 5, 10, 15 and 20%. T = tobermorite, Q = quartz, B = brucite, C = calcite, M = magnesite, H = hydrogarnet..... 185

Figure 6.18 Bulk density of autoclaved prisms as a function of compressive strength..... 186

Figure 6.19 Average drying shrinkage values of selected specimens after approximately 28 days..... 188

Figure 6.20 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 estimated trend curve is drawn to accentuate the observed trend; it is not a calculated mean curve. 188

Figure 6.21 Normalised average compressive strength curves for autoclaved blends. The normalised data are calculated as a percentage relative to the control specimens for a particular autoclave run.	190
Figure 6.22 Integrated intensities of 1.1 nm Al-tobermorite peak versus percentage addition.	191
Figure 6.23 Ratio of peak heights of the 0.308 nm and 1.1 nm XRD peaks versus percentage addition.	192
Figure 6.24 SEM micrographs of (a) the control specimen showing platy lath-like tobermorite, (b) the M20 specimen showing lath needle-like tobermorite, (c) the C20 specimen showing dense crystalline platy tobermorite and (d) the CM20 specimen showing dense lath-like tobermorite.	194
Figure 6.25 Total bulk Al ₂ O ₃ content in the initial raw mix versus the variation in the β-CS formation temperature.	196
Figure 6.26 Average acid-insoluble residue versus percentage addition.	197
Figure 6.27 Degree of carbonation of selected autoclaved blends.	198
Figure 6.28 XRD patterns of carbonated M series specimens (MgO only) additions at 0, 5, 10, 15 and 20%. T = tobermorite, Q = quartz, B = brucite, C = calcite, M = magnesite, H = hydrogarnet.	198
Figure 6.29 Bulk density of autoclaved prisms as a function of compressive strength.	199
Figure 6.30 Average drying shrinkage of selected specimens after approximately 28 days.	200
Figure 6.31 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.	201
Figure 6.32 Normalised average compressive strength curves for autoclaved blends. The normalised data are calculated as a percentage relative to the control specimens for a particular autoclave run.	203
Figure 6.33 Integrated intensities of 1.1 nm Al-tobermorite peak versus percentage addition.	204
Figure 6.34 Ratio of peak heights of the 0.308 nm and 1.1 nm XRD peaks versus percentage addition.	205
Figure 6.35 SEM micrographs of (a) the control specimen showing lath-like tobermorite, (b) the M20 specimen showing lath needle-like tobermorite, (c) the C20 specimen showing lath-like tobermorite and (d) the CM20 specimen showing dense lath-like tobermorite.	207
Figure 6.36 Total bulk Al ₂ O ₃ content in the initial raw mix versus the variation in the β-CS formation temperature.	208
Figure 6.37 Average acid-insoluble residue versus percentage addition.	209
Figure 6.38 Degree of carbonation of selected autoclaved blends.	210
Figure 6.39 Bulk density of autoclaved prisms as a function of compressive strength.	211
Figure 6.40 Average drying shrinkage values of selected specimens after approximately 28 days.	212
Figure 6.41 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.	213
Figure 6.42 Normalised average compressive strength curves for autoclaved cement blends with the addition of MgO calcined at 850°C. The normalised data are calculated as a percentage relative to the control specimens.	215

Figure 6.43 Average compressive strength values of autoclaved MgO-quartz sand and MgO-silica fume blends	216
Figure 6.44 XRD patterns of (a) MQ series specimens and (b) MSF series specimens at 40, 50 and 60 wt.% MgO. B = brucite, D = dolomite, Q = quartz, T = talc (JCPDS #02-0571).	218
Figure 6.45 SEM micrographs of (a) MQ60 and (b) MSF60 specimens.	220
Figure 6.46 DTA curves of (a) MQ series and (b) MSF series specimens.....	221
Figure 6.47 ²⁹ Si NMR single pulse spectra of (a) MQ series and (b) MSF series specimens. ..	223
Figure A.1 (a) XRD pattern, (b) DTA-TGA curves and (c) ²⁷ Al MAS NMR spectra of Goliath Cement (OPC).	245
Figure A.2 (a) XRD pattern, (b) DTA-TGA curves and (c) ²⁷ Al MAS NMR spectra of ground quartz sand.....	247
Figure A.3 (a) XRD pattern, (b) DTA-TGA curves and (c) ²⁷ Al MAS NMR spectra of natural magnesite.....	249
Figure A.4 (a) XRD pattern and (b) DTA-TGA curves of basic magnesium carbonate.....	250
Figure A.5 (a) XRD pattern, (b) DTA-TGA curves, (c) ²⁷ Al and (d) ²⁹ Si MAS NMR spectra of clay-brick fines. *- spinning side band.....	252
Figure A.6 (a) XRD pattern, (b) DTA-TGA curves and (c) ²⁹ Si MAS NMR spectra of silica fume.....	254
Figure A.7 (a) XRD pattern and (b) ²⁹ Si MAS NMR spectra of colloidal silica.....	255
Figure A.8 (a) XRD pattern, (b) DTA-TGA curve and (c) ²⁷ Al MAS NMR spectra of gibbsite.	257
Figure B.1 XRD patterns of (a) M/S = 0.6, (b) M/S = 0.8, (c) M/S = 1.0, (d) M/S = 1.5 and (e) M/S = 2.0 specimens hydrothermally treated at 180, 250, 300 and 350°C for 4 hours. • = M-S-H gel, B = brucite, T = talc, C = chrysotile, D = deweylite, with basal reflections from the talc (T) and serpentine (S) indicated by the subscript.	260
Figure B.2 XRD patterns of (a) M/S = 0.6, (b) M/S = 0.8, (c) M/S = 1.0, (d) M/S = 1.5 (e) M/S = 2.0 specimens hydrothermally treated at 180, 250, 300 and 350°C for 8 hours. • = M-S-H gel, B = brucite, T = talc, C = chrysotile, D = deweylite, with basal reflections from the talc (T) and serpentine (S) indicated by the subscript.	263
Figure B.3 DTA curves of (a) M/S = 0.6, (b) M/S = 0.8, (c) M/S = 1.0, (d) M/S = 1.5 and (e) M/S = 2.0 specimens hydrothermally treated at 180, 250, 300 and 350°C for 4 hours.....	266
Figure B.4 DTA curves of (a) M/S = 0.6, (b) M/S = 0.8, (c) M/S = 1.0, (d) M/S = 1.5 and (e) M/S = 2.0 specimens hydrothermally treated at 180, 250, 300 and 350°C for 8 hours.....	268
Figure B.5 ²⁹ Si NMR single pulse spectra of (a) M/S = 0.6, (b) M/S = 0.8, (c) M/S = 1.0, (d) M/S = 1.5 and (e) M/S = 2.0 specimens hydrothermally treated at 180, 250, 300 and 350°C for 4 hours.....	271
Figure B.6 ²⁹ Si NMR single pulse spectra of (a) M/S = 0.6, (b) M/S = 0.8, (c) M/S = 1.0, (d) M/S = 1.5 and (e) M/S = 2.0 specimens hydrothermally treated at 180, 250, 300 and 350°C for 8 hours.....	273
Figure C.1 DTA curves of (a) M series and (b) C series specimens made with constant Ca/Si = 0.58, additions at 0, 5, 10, 15 and 20%.....	277
Figure C.2 XRD patterns of carbonated M series specimens made with constant Ca/Si = 0.58 for MgO additions at 0, 5, 10, 15 and 20%.	278

Figure C.3 XRD patterns of carbonated C series specimens made with constant Ca/Si = 0.58 for MgO additions at 0, 5, 10, 15 and 20%.	278
Figure C.4 XRD patterns of (a) M series, (b) C series and (c) CM series specimens made with constant Ca/Si = 0.49, additions at 0, 5, 10, 15 and 20%.	281
Figure C.5 DTA curves of (a) M series, (b) C series and (c) CM series specimens made with constant Ca/Si = 0.49, additions at 0, 5, 10, 15 and 20%.	282
Figure C.6 ²⁷ Al NMR single pulse spectra of (a) C series specimens, (b) M series specimens and (c) CM series specimens. *-spinning side band.	284
Figure C.7 Composition of bulk and combined AIR of autoclaved blends with MgO addition: (a) % SiO ₂ ; (b) % Al ₂ O ₃ ; (c) % MgO	285
Figure C.8 Composition of bulk and combined AIR of autoclaved blends with CB addition: (a) % SiO ₂ ; (b) % Al ₂ O ₃ ; (c) % MgO.	286
Figure C.9 Composition of bulk and combined AIR of autoclaved blends with CB + MgO addition: (a) % SiO ₂ ; (b) % Al ₂ O ₃ ; (c) % MgO	287
Figure C.10 XRD patterns of carbonated (a) C series and (b) CM series specimens made with constant Ca/Si = 0.49.	288
Figure C.11 XRD patterns of (a) M series, (b) C series and (c) CM series specimens made with constant Ca/Si = 0.41, additions at 0, 5, 10, 15, 20 and 40%.	291
Figure C.12 DTA curves of (a) M series and (b) C series specimens made with constant Ca/Si = 0.41, additions at 0, 5, 10, 15 and 20%.	292
Figure C.13 ²⁷ Al NMR single pulse spectra of (a) C series specimens, (b) M series specimens and (c) CM series specimens. *-spinning side band.	294
Figure C.14 Composition of bulk and combined AIR of autoclaved blends with MgO addition: (a) % SiO ₂ ; (b) % Al ₂ O ₃ ; (c) % MgO	295
Figure C.15 Composition of bulk and combined AIR of autoclaved blends with CB addition: (a) % SiO ₂ ; (b) % Al ₂ O ₃ ; (c) % MgO.	296
Figure C.16 Composition of bulk and combined AIR of autoclaved blends with CB + MgO addition: (a) % SiO ₂ ; (b) % Al ₂ O ₃ ; (c) % MgO	297
Figure C.17 XRD patterns of carbonated (a) M series, (b) C series and (c) CM series specimens made with constant Ca/Si = 0.41.	299

Appendices

Appendix A: Starting Materials	244
Appendix B: Phase Development of Hydrothermally Treated MgO-SiO₂-H₂O System	258
Appendix C: Hydrothermally Cured PC-Quartz Pastes with Clay-Brick Waste and Reactive Magnesia Additions	276