

Magnesium oxide based binders as low-carbon cements

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I, Fei Zhang, declare that this thesis, submitted for the degree of Doctor of Philosophy of Imperial College London, is the result of my own work and all information derived from other researchers has been specifically acknowledged. No part of the work has previously been presented for another a qualification elsewhere.

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ABSTRACT

Portland cement (PC) is a fundamental component of the construction industry. However, its manufacturing process is responsible for ~5 % of global anthropogenic CO₂ emissions. Given current demand for PC which is expected to triple by 2050, there is an urgent need for the production of alternative binders with a lower carbon footprint. One type of such alternative binder are magnesium oxide (MgO) based cements. This research has investigated the properties of three novel magnesium oxide based cement systems as potential binders that could be used for some standard cement applications.

Previous research at Imperial College London found that the addition of a hydrated magnesium carbonate to MgO prior to hydration resulted in the production of setting and strength gaining samples. One of the main objectives of this research was to understand how the addition of magnesium carbonate gave the system cement-like properties and to investigate the types of strength possible from a basic system as well as to identify the main parameters that affect strength, thus allowing for future optimisation. It was found that the presence of carbonate and its effect upon the system pH alters the type of Mg(OH)₂ formed, giving a more stable microstructure that accounts for the strengths achieved. The type of MgO was found to be an important parameter, as was particle size. Due to water demand, a 10 % carbonate – 90 % MgO mix was chosen as the optimum mix.

The second system studied was the silica (SiO₂) – MgO system. This was investigated in order to assess the potential of the reaction between MgO and silica to form M-S-H gel and to study the mechanism of formation of reaction products. It was found that reactive MgO and amorphous silica can react together upon hydration to form a mixture of M-S-H gel and Mg(OH)₂, dependent upon the SiO₂/MgO ratio. These systems have considerable compressive strengths the extent of which depends upon the type of silica. An optimum mix of 30 % silica – 70 % MgO (by dry weight) was found

Finally, a simple ternary system of magnesium carbonate - silica - MgO was investigated in order to assess if the presence of the combination of both ‘additives’ could create a better system than either of the two-component systems. Strength results suggested that there is no added benefit to the system in combining the two-component systems. For all three systems studied, the high w/s ratios required were found to be a significant limiting factor.

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NOTATION

920d	920d Elkem silica fume
A	Surface area (mm ²)
B	Peak width (radians)
CCS	Carbon capture and storage
CO ₂	Carbon dioxide
CSA	Calcium sulfoaluminate
d	Interplanar spacing
DTA	Differential thermal analysis
F _{max}	Force at which sample fails (N)
FTIR	Fourier Transform infrared
FWHM	Full width half maximum
HY	Hydromagnesite
I _{max}	Maximum intensity
ICP-AES	Inductively coupled plasma - atomic emission spectroscopy
L	Crystallite size (Å)
LOI	Loss on ignition
LSF	Lime saturation factor
m _{cal}	Mass of sample after calcining at 950 °C (g)
m _{dry}	Mass of oven dried sample (g)
MAP	Magnesium phosphate
MOC	Magnesium oxychloride cement
MOS	Magnesium oxysulphate cement
M-S-H	Magnesium silicate hydrate
n	Diffraction order
NY	Nyasil nanosilica
PC	Portland cement
PFA	Pulverized fuel ash
PSD	Particle size distribution
SEM	Scanning electron microscopy
SF	Silica fume
TGA	Thermogravimetric analysis
UCS	Unconfined compressive strength (MPa)
V _{dry}	Volume occupied by sample (cm ³)
w/s ratio	water/solids ratio
x	Final degree of MgO hydration (%)
XRD	X-ray diffraction
XRF	X-ray fluorescence
y	LOI for dried MgO - HY samples
θ	Angle of diffraction
λ	Wavelength of incident x-rays
%	Weight %

Note that all notation relating to PC hydration is in the relevant section of Chapter 1.

Notation used in XRD spectra:

B	Brucite
C	Calcite
H	Hydromagnesite
M	Magnesite
P	Periclase
Q	Quartz
S	Silica
SC	Silicon carbide

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1 INTRODUCTION

1.1 CONCRETE AND CEMENT

Concrete is by far the most important, the most versatile and the most widely used building material worldwide and with global population rising, has a vital role in meeting the growing infrastructure needs of the 21st century (Meyer, 2004). It is currently estimated that annual world consumption of concrete is around 11 billion tonnes (Mehta and Monteiro, 2008).

The wide use of concrete and the fact that its components are inexpensive and readily available in all parts of the world mean that it is by volume the largest globally manufactured material (Gartner, 2004). Concrete is a composite made by mixing a binder, sand, aggregate and water. It also can contain admixtures. The binder commonly used is Portland cement (PC) (Damtoft et al., 2007). It is estimated that 2,550 million tonnes of cement are produced globally each year (Worrell et al., 2009). Cements have been classified into 27 varieties, summarised in Table 1-1.

Table 1-1: Summary of the 27 different varieties of cement according to EN 197-1 specification requirements.

Type	CEM I	CEM II	CEM III	CEM IV	CEM V
Possible percentage of constituents other than PC (%)	up to 5	6 - 20 21 - 35 6 - 10 (silica fume)	36 - 65 66 - 80 81 - 95	11 - 35 36 - 55	36 - 60 61 - 80
Example constituent	Gypsum	Blast furnace slag, Siliceous fly ash, Silica fume	Granulated blast furnace slag	Blast furnace slag, Fly ash, Other pozzolans	Blast furnace slag, Fly ash, Other pozzolans
Description	Ordinary PC	Blended PC cements	Blended PC - slag cements	PC - pozzolan cements	Composite PC with a mixture of blended components
Number of varieties	1	19	3	2	2

The primary constituents of PC are calcium silicates, so the raw materials for PC production must provide calcium and silica in sufficient amounts and forms. Common industrial sources of calcium include limestone, chalk, marl and sea-shells, whilst clays or shales are used to supply silica. At the start of PC production, these proportioned raw materials are subjected to a series of crushing, grinding and mixing in order to homogenize the mix before heat treatment. This process can be either ‘wet’ or ‘dry’, where in the wet process the raw materials are contained within a slurry. As water needs to be evaporated before heat treatment, the dry process, as summarised in Figure 1.1 below, is preferred in modern cement plants as it is more energy efficient.

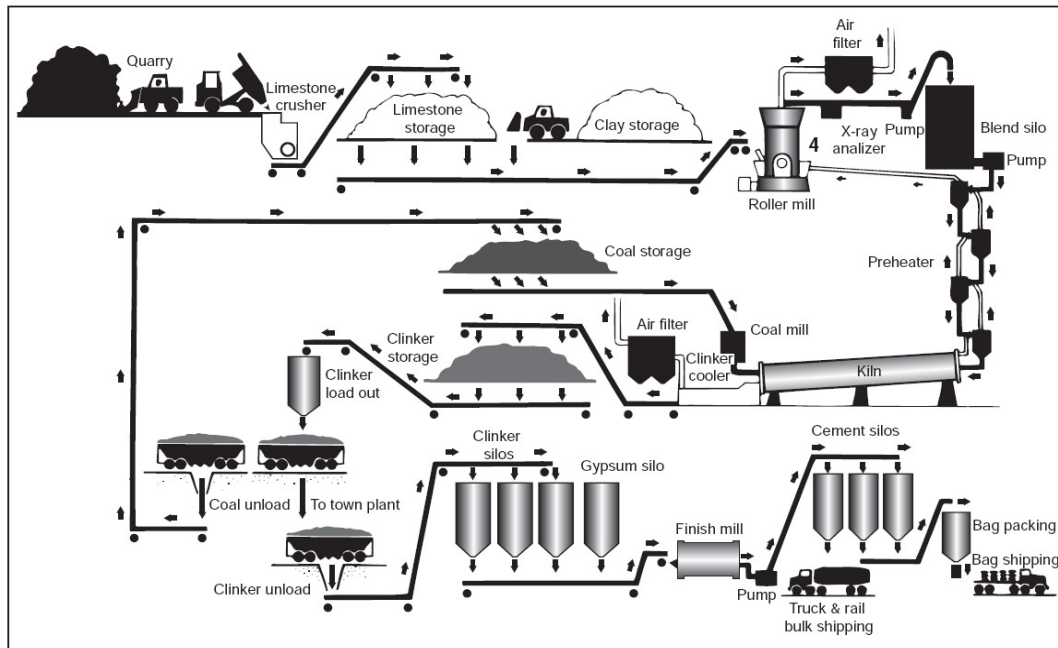


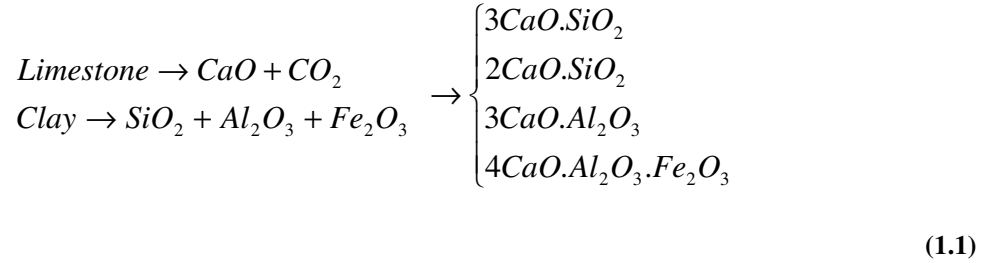
Figure 1.1: Flow diagram of a simplified dry process for PC manufacture (Mehta and Monteiro, 2008).

After homogenisation, the mixture is heated as it passes through a series of pre-heaters until it reaches a rotary kiln where temperatures of 1450 °C are reached. During this heating period, a series of chemical reactions occur, causing the materials to fuse together and create nodules of cement clinker. The four products formed during clinkering as seen in equation 1.1. Table 1-2 summarises the cement notation used in this work.

Table 1-2: Summary of the cement notation used and related chemical formula and names.

Notation	General formula	Name
C_3S / alite	$3\text{CaO}.\text{SiO}_2$	Tricalcium silicate
C_2S / belite	$2\text{CaO}.\text{SiO}_2$	Dicalcium silicate
C_3A	$3\text{CaO}.\text{Al}_2\text{O}_3$	Tricalcium alite
C_4AF	$4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$	Tetracalcium aluminoferrite
$C - S - H$ / $C_3S_2H_3$	$x\text{CaO}.y\text{SiO}_2.z\text{H}_2\text{O}$ (x, y, z are variable) / $3\text{CaO}.2\text{SiO}_2.3\text{H}_2\text{O}$	Calcium silicate hydrate
$C_6A\bar{S}_3H_{32}$ / Aft	$3\text{CaO}.\text{Al}_2\text{O}_3.3\text{CaSO}_4.32\text{H}_2\text{O}$	Calcium trisulphoaluminate hydrate
$3C_4A\bar{S}H_{12}$	$4\text{CaO}.\text{Al}_2\text{O}_3.\text{SO}_4.12\text{H}_2\text{O}$	Monosulphate
CH	$\text{Ca}(\text{OH})_2$	Calcium hydroxide
C_4AH_{13}	$4\text{CaO}.\text{Al}_2\text{O}_3.13\text{H}_2\text{O}$	n/a
C_3AH_6	$3\text{CaO}.\text{Al}_2\text{O}_3.6\text{H}_2\text{O}$	Hydrogarnet phase

The four major phases of cement clinker are abbreviated by cement chemists to C_3S , C_2S , C_3A and C_4AF , as seen in Table 1-2, and in ordinary PC are present in the percentages, 45 – 60 %, 15 – 30 %, 6 – 12 % and 6 – 8 % respectively.



Some of the nodules of clinker can be the size of marbles so the final stage in PC clinker manufacture is grinding this clinker to a powder of average 10 – 15 μm diameter. Roughly 5 % gypsum (CaSO_4) is added during grinding in order to control the setting and hardening of the cement, in particular the C_3A phase, on addition to water.

1.2 HYDRATION OF PC

When the PC is dispersed in water, the CaSO_4 from the gypsum and the clinker products C_3S , C_2S , C_3A and C_4AF start to dissolve and go into solution, rapidly saturating the water with various ions. Interactions between these calcium, sulphate, aluminate and hydroxyl ions then begin to happen. These chemical reactions occur at different rates and influence each other and can be seen later in equations 1.2 – 1.7. Initially, hydration is controlled by the dissolution rate of the gypsum and clinker products. As hydration progresses, the nucleation and crystal growth rate of the hydration products increasingly control the reaction rate. Finally, the rate is controlled by the diffusion rate of water and dissolved species. Hydration can be broken into 3 main periods (Taylor, 1990):

Early period of hydration

Within a few minutes of hydration, a layer of $C-S-H$ precipitates upon the surfaces of cement particles as a result of the dissolution of C_3S . The hyphens in ‘ $C-S-H$ ’ indicate that there is no particular composition implied. Crystals of calcium trisulphoaluminate hydrate, $3\text{CaO}.\text{Al}_2\text{O}_3.3\text{CaSO}_4.32\text{H}_2\text{O}$ abbreviated to $C_6\bar{A}\bar{S}_3H_{32}$ Aft also start to appear as Ca^{2+} and SO_4^{2-} ions, from gypsum and C_3A , react. This hydration product is known as ettringite and its crystals, which also form on cement particles, are needlelike in morphology. The C_4AF phase also produces ettringite, while only a tiny amount of C_2S reacts giving more $C-S-H$ and

calcium hydroxide ($\text{Ca}(\text{OH})_2$), which is abbreviated to *CH*. *CH* crystals are large and prismatic whilst *C-S-H* is a more are amorphous gel like material. After these initial fast hydration reactions, the overall hydration rate decreases and progresses very slowly (Lea, 1998).

Middle period of hydration

3 - 12 hours later, other types of products start to form in the spaces left by the dissolving PC particles and by the water. Both C_3S and C_2S hydration accelerates. More large *CH* crystals form in the spaces originally filled with water and the *C-S-H* layer around cement particles thicken and start to engulf the ettringite rods. By 4 hours, all cement grains are completely covered. The shells grow outwards and begin to coalesce with those of neighbouring grains. The shells start to fracture so spaces appear between shells and unreacted material. Eventually the shells become porous enough to allow ions to migrate through and further dissolution and precipitation occurs. Grains initially smaller than 5 μm have completely reacted by the end of this period.

Late period of hydration

Hydration rate slows down again as it becomes diffusion controlled. The formation of *C-S-H* continues as C_2S and C_3S phases continue to hydrate. Once the SO_4^{2-} concentration declines, ettringite starts to react with any remaining C_3A to produce plate like crystals of monosulfate ($4\text{CaO}.\text{Al}_2\text{O}_3.\text{SO}_4.12\text{H}_2\text{O}$), abbreviated to AFm or $3\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$. The C_3A also reacts with *CH* to form C_4AH_{13} which is $4\text{CaO}.\text{Al}_2\text{O}_3.13\text{H}_2\text{O}$.

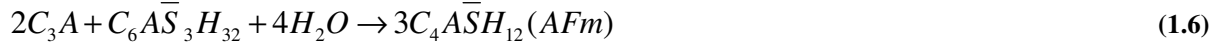
The reactions of tricalcium aluminate, alite and belite that take place during hydration can be seen in equations 1.2 to 1.7 (Lea, 1998):

In the presence of gypsum (i.e. relatively high SO_4^{2-} concentrations):





As the concentration of SO_4^{2-} decreases and C_3A remains:



In the absence of gypsum (i.e. in low SO_4^{2-} concentrations):



C_3AH_6 is a hydrogarnet phase with the formula $3CaO \cdot Al_2O_3 \cdot 6H_2O$. The hydration products of C_4AF are similar to those of C_3A but with Fe^{3+} substituting for some of the Al^{3+} .

In concrete, it is these hydration products of PC that effectively lock together the sand and aggregate constituents into an inert matrix.

1.3 CARBON EMISSIONS FROM CEMENT

There are several environmental and sustainability issues associated with PC manufacture, but with the global prominence of climate change, a significant problem is the amount of carbon dioxide (CO_2) this process creates. The synthesis of Portland cement (PC) is responsible for 5 – 8 % of anthropogenic CO_2 emissions worldwide (Pade and Guimaraes, 2007). The origins of such high CO_2 emissions are twofold. Firstly, as mentioned previously, the production of PC clinker requires heating the raw materials up to temperatures of 1450 °C. This requires the consumption of a huge amount of energy from fossil fuels such as oil and coal, creating CO_2 as a byproduct. Other manufacturing processes, such as grinding also require energy and hence generate further CO_2 emissions. Secondly, during clinkering, one of the raw materials of PC clinker, calcium carbonate, $CaCO_3$, in the forms such as limestone, or marl, decomposes releasing CO_2 . Overall, CO_2 emissions mainly occur during clinkering,

with ~ 60 % coming from the chemical reaction and ~ 40 % from the combustion of fuels used to heat the kiln to high temperature (Quadrelli and Peterson, 2007).

The total carbon emissions from pure PC clinker manufacture have been at approximated at 0.83 tonnes of CO₂ being released for every one tonne of PC clinker produced (Gartner, 2011). This CO₂ value depends upon whether a dry or semi-dry manufacturing process is used, with the semi-dry process producing more CO₂ as more energy is required to dry off any excess water. Either way, when considering that worldwide, 2,550 million tonnes of mostly Portland cement are currently produced each year and that cement demand is expected to double or triple by 2050, it is a significant amount (Worrell et al., 2009).

1.4 CO₂ MITIGATION BY THE CEMENT INDUSTRY

In response to international concerns about climate change, governments around the world have been enforcing taxes on industrial energy use and CO₂ emissions. For example the Climate Change Levy was introduced to the UK in 2001. It essentially works by taxing the energy use of industrial and commercial businesses therefore encouraging increased energy efficiency and CO₂ reductions in industry as well as motivating investment in 'greener' types of energy. As a consequence of such CO₂ reduction strategies, there is a huge pressure on the construction industry and cement manufacturers to reduce their CO₂ emissions and considerable effort has been made in regards to this. There are a number of approaches which limit the energy requirements and CO₂ release, many of which are currently in use although no single approach is likely to make significant reductions for reasons mentioned below.

One idea to reduce emissions is to capture emitted CO₂ and then trap it in a stable form by mineral sequestration, ultimately preventing it from entering the atmosphere and contributing to climate change. Whilst carbon capture and storage (CCS) has the potential to have a strong role in reducing the PC industry's emissions, further research as well as substantial public and private investment is needed to make it commercially viable. Also, CCS does not actually prevent CO₂ being emitted, only prevents its release to the atmosphere so this method is rather a last resort.

In order to reduce energy consumption, energy demand needs to be reduced. By making the manufacturing process and plant more energy efficient, less energy will be wasted therefore reducing overall energy requirements and related CO₂ emissions.

During the 1970s, the cement industry was indirectly forced to increase energy efficiency due to the oil crisis of 1973, which also caused the industry to move away from dependency on oil towards other fuels such as coal, coke and waste fuels. A number of new process technologies have emerged and have been applied so modern cement plants are much more efficient than those of the 1970s, having reduced kiln fuel energy requirements by up to 40 % (Gartner, 2004). In terms of the best available PC manufacturing technology, energy efficiency is already at a comparatively high level, leaving little room for further improvements and CO₂ reductions. However, considering that PC production and use is global, there are likely to be a large number of plants in developing countries which are still operating below levels associated with best available technology so with some investment, energy efficiency improvements are possible in such locations.

It has been suggested that by using fuels that do not directly use fossil fuels, in the manufacture of PC, CO₂ emissions could be reduced. Whilst in theory the idea of electric furnaces sounds like a good way to minimise CO₂ emissions, studies have found that this is not a practical option as most electricity is made from fossil fuels converted with an energy efficiency of less than 40 %. Solar or nuclear powered electric furnaces would also be impractical mainly due to the intermittency of sunshine and the issues associated with nuclear energy.

The use of low-energy clinkers can reduce energy demands by reducing the maximum temperature and thus energy required. There are several types of low-energy clinkers. They are essentially PC clinkers with a small percentage of mineraliser, for example CaF₂, added which causes clinkering of the raw materials to occur at lower temperatures than the standard 1450 °C thus leading to energy savings of up to 5 % (Sahu, 1994). The temperature reduction is dependent upon the type of mineraliser used. The lower temperature requirement also allows the use of alternative fuels.

The use of alternative fuels instead of traditional fossil fuels can help abate CO₂. Currently, a number of different such fuels exist which have been successfully employed in the cement production process to provide energy. Fuels consisting wastes such as scrap tires or selected components of commercial waste, can be beneficial from a waste management perspective whilst also reducing the demand for finite fossil fuels. However, although agricultural biomass, biodegradable municipal waste and animal waste are considered to be carbon neutral other alternative fuels, such as plastics and waste tyres are not, or are only partially.

Whilst some reductions in emission can be made by the above methods, compared to CO₂ derived from fuel, CO₂ arising from the raw materials of clinker production is relatively high so reducing these emissions may be more beneficial (Damtoft et al., 2007).

1.5 REDUCING RAW MATERIAL RELATED CO₂ EMISSIONS

1.5.1 BELITE CEMENTS

Reductions in CO₂ can also come through the use of belite cements produced by reducing the lime saturation factor (LSF). During the heating and sintering of these oxides in the production of ordinary PC clinker, four main compounds are formed, including alite and belite. The LSF (see equation 1.8) is the ratio of CaO to the other main oxides in raw PC feed and controls the ratio of alite to belite.

$$LSF = \frac{CaO}{2.8SiO_2 + 1.18Al_2O_3 + 0.7Fe_2O_3} \quad (1.8)$$

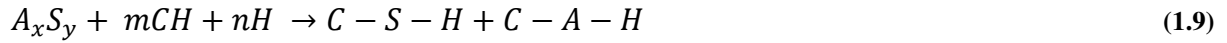
In normal PC clinker, alite makes up the largest proportion of the four components in PC clinker, usually 45 – 60 % (Mehta and Monteiro, 2008). By using a belite based rather than an alite based cement, a reduction in the CaO content of the final PC clinker occurs, meaning that less CaCO₃ is needed in the raw feed so less CO₂ is released. This is done by reducing the LSF of the raw feed. However, even in a belite rich cement, the overall reduction in CaCO₃ consumption is no more than 8 % (Gartner, 2004). Also strength development of cements with an LSF of less than 84 % is much lower than that of ordinary PC although steps such as the inclusion of calcium sulfoaluminate to increase early strength development can be taken to reduce this negative effect (Quillin, 2001).

1.6 ALTERNATIVE LOW - CO₂ BASED CEMENTS

Many methods to reduce emissions are aimed at minimising the amount of CaCO₃ that requires calcining and hence related CO₂ emissions. Much work has been carried out in this area aimed at the production of binders that are generally not based purely upon PC so do not have such high CO₂ emissions. Some of the most promising low CO₂ alternatives to PC include pozzolan based cements, calcium (sulfo) aluminate based cements and calcium sulfate based cements.

1.6.1 POZZOLAN – BASED CEMENTS

Perhaps the best understood group of pozzolan – based cements are those based on lime activation. The underlying generalised pozzolanic reaction of these cements where the pozzolan is defined as a reactive aluminosilicate (A_xS_y) is as follows in equation 1.9 (Gartner, 2004):



Pozzolan + lime + water → calcium silicate hydrated + calcium aluminate hydrates

The exact composition of the reaction products varies depending upon other compounds present and the reaction parameters. The lime (mCH) in the reaction can be from an indirect source. This is usually formed from the hydration of alite and belite in PC.

Using blended cements which partially replace PC clinker with pozzolans is a viable and common CO₂ reducing option. Pozzolans can be natural volcanic glasses or diatomaceous earth, manmade glasses such as silica fume or semicrystalline, for example metakaolin. Using industrial byproducts such as pulverized fuel ash (PFA), fly ash and silica fume can also provide a means of disposal of these wastes. Several engineering advantages such as increased durability due to conversion of soluble lime to less soluble C-S-H gel have been reported from the use of such pozzolan based cements. However, since the production of fly ash occurs in coal fired power stations and steel production plants, they have associated high CO₂ emissions so in future may not be so readily available as these plants are replaced, and the volumes available are limited.

Instead of being activated by lime, some pozzolans can also be activated by other bases. This includes the important class of alkali – activated cements. The use of alkali-activated cements involves activating various aluminosilicate containing materials (AS_y) such as bfs and PFA, with alkaline solutions ($RS_{z(aq)}$) resulting in a highly linked polymeric network with high mechanical strength (Roy, 1999). The reaction is often called geopolymerisation, a type of condensation reaction (equation 1.10):



Alkali - activated cements have a good track record for a wide range of applications and due to the low energy input required in their production as well as the absence of CO₂ release from raw materials, have low associated carbon emissions. Some of the properties of these systems include high compressive strengths, fire resistance up to 1000 °C and good resistance

to a range of acids and salts (Davidovits, 1991, Lee and Van Deventer, 2002). However, common alkali activators are sodium hydroxide, which is manufactured by the electrolysis of brine solutions and sodium silicates produced by melting silica and soda in a glass furnace, both processes of which are energy intensive and CO₂ producing. It should also be noted that there is currently no single system which has all of the best properties observed (Duxson et al., 2007). Also, in order for the use of alkali-activate cements to be scaled up, the capacity to produce alkali solutions such as sodium hydroxide (NaOH) and as well as sodium silicates would need to be increased.

1.6.2 CALCIUM SULPHATE – BASED CEMENTS

Several researchers have highlighted the importance of calcium sulphate based cements (O'Rourke et al., 2009, Gartner, 2004). These cements are based on one of the world's oldest cementing reaction, the hydration of calcium sulphate hemihydrate, $C\bar{S}H_{0.5}$ [$CaSO_4 \cdot 0.5H_2$] to form gypsum, $C\bar{S}H_2$, [$CaSO_4 \cdot 2H_2O$] as shown in equation 1.11:



This system has very rapid but controllable setting and hardening rates and the raw material is widely available worldwide, although natural calcium sulfate sources are far less abundant than limestone. No CO₂ is devolved from the raw natural sources and the manufacturing process has a low energy demand (O'Rourke et al., 2009). The major disadvantage of these cements is the low durability of the gypsum based mortars due to the high solubility and softness of gypsum. However, a more durable and stronger product can be created from a very dense gypsum. In addition, by combining gypsum with low amounts of fairly cheap additives such as silicates, the system is further stabilised towards softening by water. Research has also shown that a stronger and more durable product, resistant to even humid or wet environments, can be produced by the addition of 25 % of a suitable Portland – pozzolan cement to gypsum plasters (Bentur et al., 1994, Colak, 2002).

As mentioned, raw materials are less abundant and less globally available than limestone. However, large amounts of man-made calcium sulfates are being produced as a by-product of gas desulfurization processes linked to oil- and coal- fired electric power plants (Gartner, 2004). Most sulphur control methods utilise limestone in some way as a neutralizer so whilst this process produces calcium sulfate sources, a mole of CO₂ is generated for every mole of SO₂ captured. Nonetheless, considering that SO₂ is a toxic gas, this is currently an

unavoidable carbon emission and making use of the calcium sulfate by-product in cement systems could be seen as a way of disposing of this ‘waste’ material.

1.6.3 CALCIUM SULFOALUMINATE (CSA) CEMENTS

It should be noted that CSA cements are different to belite-rich PCs mentioned in the previous section. One of the most promising alternative cementing systems for use in concrete applications are those based upon calcium sulfoaluminate, $4\text{CaO} \cdot 3\text{Al}_2\text{O}_3 \cdot \text{SO}_3$ ($\text{C}_4\text{A}_3\bar{\text{S}}$) abbreviated to CSA. Typical raw materials include CaCO_3 , CaSO_4 and a source of alumina. The sulfates and alumina required can come from industrial process wastes such as fly ash, bfs and bauxite fines. Raw materials are combined and then heated at temperatures 200 – 300 °C lower than that required for PC production. Although these cements still require CaCO_3 , less limestone is required than for PC production. Consequently, CO_2 emissions per unit of cement are significantly lower than PC. CSA hydrates readily to give ettringite and calcium silicate hydrate phases, depending upon on the availability of sulphate and lime (Garcia-Mate et al., 2012). Research has shown that CSA-based cements can be made which have properties comparable to those of standard PC concrete (Beretka et al., 1993). Two main paths of research have been followed so far. One is research into blends of CSA rich cements with materials such as ggbs and gypsum. Some blends of cements have been found to give concretes with good properties. These types of cements are suitable for the manufacture of precast concrete blocks. Research into clinkers containing CSA, belite and calcium aluminoferrite ($\text{Ca}_2\text{AlFeO}_5$) has also been completed. These clinkers have the potential to be manufactured for a wide range of raw materials, emitting 20 – 25 % less CO_2 than PC (Gartner, 2004). Again, compressive strengths of concretes based upon these clinkers are claimed to be comparable to those of PC based concretes, with 28 day strengths of up to 100 MPa observed (Glasser and Zhang, 2001).

Although CSA based cements are increasingly being used for specialist applications, currently their use for general concrete applications has been limited to China, where a range of cements have been developed and used under the generic name “Third Cement Series” (Gartner and Quillin, 2007). Lafarge has also recently patented a class of cements based upon an activated belite/CSA/ferrite clinker interground with anhydrite abbreviated to BCSAF cements. These clinkers can be made in existing PC plants, when used in concrete have equivalent strengths to PC containing concretes but emit 25 % less CO_2 . However, the

high cost of bauxite means that costs are still much higher than for PC in the majority of locations (Damtoft et al., 2007).

1.7 SUMMARY

There is little doubt that global climate change is one of the biggest problems of the 21st century and is most likely the result of increased anthropogenic emissions. In order to mitigate the possible effects of climate change, governments around the world have put in place legislation enforcing the reduction of CO₂ emissions. For its part, the UK has published the Climate Change Bill, committing it to decreasing its CO₂ emissions by 26 – 32 % by 2020 and 60 % by 2050 based upon 1990 levels (Defra, 2007).

The manufacture of Portland cement is responsible for 5 % of CO₂ emissions and with current production estimated at around 1.5 billion tonnes per year and demand growing, there is significant pressure on the cement and concrete industry to come up with ways to reduce their carbon footprint. Solutions have included increasing the energy efficiency of production plants, the use of alternative fuels and belite cements. However, it appears that measures to reduce PC production related CO₂ emissions are not enough and there is an urgent need for the development of novel cementitious binders with a low CO₂ footprint. This chapter has discussed some of the most promising alternative low – CO₂ cement systems currently available. Another group of alternative cements based upon an entirely different system are magnesium oxide (MgO) based cements. These cements are discussed in Chapter 2.

2 MAGNESIUM OXIDE (MgO) BASED SYSTEMS

2.1 MAGNESIUM OXIDE

MgO, an alkaline earth metal oxide also known as magnesia, consists of a magnesium ion and an oxygen ion held together by an ionic bond. MgO has a density of 3.58 g ml^{-1} , a room temperature solubility of $6.2 \text{ g} \times 10^{-6} \text{ g}$ per gram of water and a melting point of $2827 \pm 30 \text{ }^{\circ}\text{C}$. It has a cubic crystal structure and its molecular mass is 40.3 g mol^{-1} (Shand, 2006).

Table 2-1: Worldwide reserves of magnesite (Vlasopoulos, 2007)

Country	Reserves (million tonnes of contained Mg)
Australia	91
Austria	14
Brazil	41
China	345
Greece	27
India	13
North Korea	408
Russia	589
Slovakia	37
Spain	9
Turkey	59
United States	9
Other	354

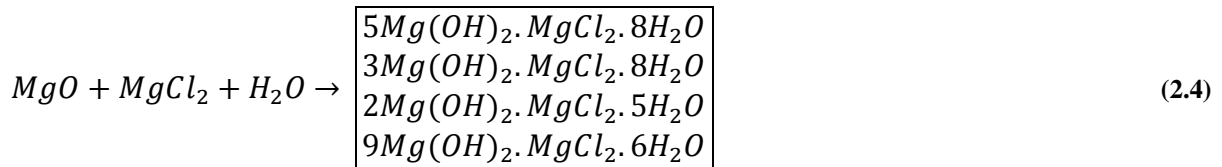
The element magnesium is the 8th most abundant in the world and the 3rd most plentiful in seawater. However, of the many magnesium containing minerals that exist, only a few are of commercial importance (Shand, 2006). These include magnesite [MgCO_3], dolomite [$\text{CaMg}(\text{CO}_3)_2$], brucite [$\text{Mg}(\text{OH})_2$], carnallite [$\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$] and olivine [$(\text{Mg,Fe})\text{SiO}_4$] (Kramer, 2001). MgO is not usually found in nature but must be extracted from other magnesium containing compounds. There are two main methods for acquiring MgO. One is the thermal decomposition of a magnesium carbonate, for example magnesite (equation 2.1). The second involves the precipitation of $\text{Mg}(\text{OH})_2$ from MgCl_2 brines or from seawater using a base such as lime $\text{Ca}(\text{OH})_2$ or dolomitic lime [$\text{Ca}(\text{OH})_2 \cdot \text{MgO}$] (equation 2.2) (Bhatti et al., 1984). After precipitation, the $\text{Mg}(\text{OH})_2$ is treated thermally to remove water so that MgO is formed (equation 2.3).





2.2 SOREL CEMENTS

The first MgO cement was produced in the 18th century when Sorel created a magnesium oxychloride cement (MOC). MOCs are formed by the addition of a magnesium chloride ($MgCl_2$) solution to a fine MgO powder produced by calcinations at relatively low temperatures i.e. 700 – 900 °C. Chemical reaction between reactants can be achieved at ambient temperature as opposed to sintering at high temperature as is required in PC. The hardened cement which forms consists of a MgO - $MgCl_2$ - H_2O system. Four types of oxychloride compound can exist in this system depending upon the reaction conditions: $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, $2Mg(OH)_2 \cdot MgCl_2 \cdot 5H_2O$ and $9Mg(OH)_2 \cdot MgCl_2 \cdot 6H_2O$, see equation 2.4. Continued exposure of magnesium oxychloride to air produces the magnesium chlorocarbonate $Mg(OH)_2 \cdot MgCl_2 \cdot 2MgCO_3 \cdot 6H_2O$. The interlocking of crystals and resulting dense microstructure created by the intergrowth of the two main crystal phases, phase $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ and $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, is a major source for strength development of MOCs.



These cements can have many excellent properties such as rapid hardening rate and good fire and abrasion resistance as well as higher compressive and flexural strengths than PC. They can also be used in combination with several aggregates that may not be suitable for use in combination with PC (Beaudoin and Ramachandran, 1975). Due to their excellent properties, MOCs have a wide range of applications, the main ones being industrial flooring, fire protection products, lightweight wall panels and artificial stone ornaments. They can also be used in decorative panels, rendering wall insulation panels, interior plasters and exterior stuccos (Chau and Li, 2008).

However, the major drawback of these cements is their poor water resistance, particularly at higher temperatures (Li et al., 2008). Prolonged contact of MOCs with water, results in the leaching of $MgCl_2$ and a consequential strength decrease of the binder, which means they

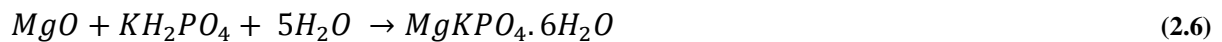
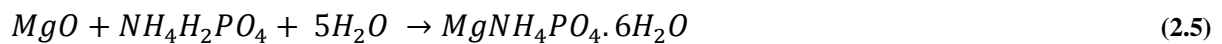
have very limited use in engineering applications (Shand, 2006). Due to this issue, much research has been carried investigating the water resistance of MOCs (Mathur and Misra, 2007). It has been found that the water resistance of MOCs can be greatly improved by the addition of various additives, including phosphoric acid and soluble phosphates such as the phosphates of alkali metals and ammonia (Deng, 2003). However, little data exists documenting the behaviour of MOC concretes.

Another MgO based cement, also considered to be a Sorel cement whose potential has been realized almost as long as that of MOCs, is magnesium oxysulphate cement (MOS cement). These cements are formed by the reaction between MgO and magnesium sulphate (MgSO_4) solution. Depending upon reaction conditions, four different oxysulphate complexes can make up the resulting $\text{MgO} - \text{MgSO}_4 - \text{H}_2\text{O}$ system (Beaudoin and Ramachandran, 1975).

Like MOCs, MOS cements have several properties superior to those of PC such as compressive strength and abrasion resistance, although these properties are not as good as those of MOC cements. MOS cements are used in the production of light weight insulating panels but like MOCs, MOS cements suffer from low water resistance.

2.3 MAGNESIUM PHOSPHATE CEMENTS

Magnesium phosphate cements (MAP cements) are formed by reaction between MgO and a soluble phosphate. Depending upon the phosphate source, different types of cement can be produced. Two common types of MAP cement are magnesium ammonium phosphate cements, consisting of the mineral struvite, and magnesium potassium phosphate cements, made up of a hard dense ceramic of magnesium potassium hexahydrate, formed from ammonium dihydrogen phosphate, and potassium dihydrogen orthophosphate, respectively (see equations 2.5 and 2.6).



These chemical reactions are rapid and exothermic and initially form a hydrogel, followed by crystallisation of insoluble phosphate products.

Unlike MOCs and MOS cements MAP cement systems have good water resistance. They are also reported to have some properties superior to PC such as high early-age and long-term strengths, and higher freeze-thaw and sulphate resistance, so are very attractive for use in

special applications. Applications include their use in dental cements, as refractory materials, waste management applications and structural repair works (Al-Tabbaa and Iyengar, 2007). The fact they set rapidly means they are very useful for repairing runways and roads. However, setting time can sometimes be too fast causing difficulties with manipulation although selection of MgO reactivity, i.e. the use of a dead burned magnesia, can help reduce this problem for small volume works although for mixing larger volumes, the reaction still proceeds too fast and retarder additions, such as boric acid, are necessary (Al-Tabbaa and Iyengar, 2007, Quoi et al., 2008). Sources of phosphate are also limited and this means that MAP cements can be expensive.

2.4 TecEco CEMENTS

More recently, in 1999, reactive magnesium oxide (MgO) cements were proposed. Reactive MgO cements, developed by TecEco Pty Ltd, are essentially blended cements, containing PC, reactive MgO and an optional pozzolan such as pulverized fuel ash (PFA). The contribution to setting by the reactive MgO in these cements is believed to be due to the hydration of MgO to form magnesium hydroxide ($\text{Mg}(\text{OH})_2$) (Harrison, 2005). Although this reaction of MgO in normal PC gives rise to unsoundness in PC, such cracking should only occur if the hydration rate of the MgO is slow and thus $\text{Mg}(\text{OH})_2$ formation occurs much later than the main hydration reactions that take place in PC. By using a suitably reactive MgO as opposed to a dead burned MgO, with low reactivity, hydration is claimed to occur at a rate not dissimilar to PC and thus cracking is avoided. It is thus important for the MgO used to be of a substantially high enough reactivity to hydrate at a similar rate to PC.

TecEco reports that when a hydraulic cement, such as PC, is blended with a reactive MgO, not only is less PC required, thus reducing associated emissions, but the properties of the cement are seen to improve when compared to a non-blended cement. The reactive MgO used for TecEco cements is produced using a special kiln, a Tec-Kiln, patented by TecEco (Harrison, 2003). TecEco claim that the Tec-Kiln:

- Runs at low temperatures ($< 750\text{ }^\circ\text{C}$) so it can produce reactive MgO;
- Can be powered using alternative energy sources to fossil fuels, such as solar energy;
- Calcines as it grinds materials thus increasing its energy efficiency than if these two processes were carried out separately;

- Captures CO₂ released during calcination so it can be re-used or sequestered.

There are three main TecEco cements which vary in composition but overlap to some extent (Harrison, 2001):

1. Tec-cements: consist of 10 % MgO / 90 % PC. TecEco reports that the addition of this relatively small proportion of MgO enhances the physical properties and durability of PC.
2. Enviro-cements: contain higher proportions of MgO (25 – 75 %) to PC (75 – 25 %) and are reported to be highly durable and suited to toxic and hazardous waste immobilization.
3. Eco-cements: are reported to be suited to the production of building productions and like Enviro-cements, contain more MgO (50 – 75 %) to PC (50 – 25 %) than Tec-cements.

Several claims have been made for the TecEco cements. Those of most significance are listed as follows (Harrison, 2005):

- Reactive MgO hydrates at the same rate as PC to form Mg(OH)₂;
- Eco-cement concretes can have up to 90% recycled industrial materials such as PFAs in their composition;
- For higher proportions of MgO and waste, porous materials made of Eco-cement concrete sequester CO₂ by carbonating to form hydromagnesite (Mg(OH)₂.4MgO.4CO₂.4H₂O);
- Mg(OH)₂, MgCO₃ and hydromagnesite bond well to many different materials.

Research has been carried out in order to investigate the claims of TecEco cements as little data is available for these materials (Vandeperre et al., 2007). This research involved the production and testing of a wide range of MgO - PC compositions, with and without pozzolans in the form of pfa and waste derived aggregates. The overall findings of the research were that the replacement of PC with MgO had a detrimental effect upon resulting sample strengths and durability, with little evidence of interaction between the hydration products of these two materials (Vandeperre et al., 2008). This was found to be due to the slow rate of MgO carbonation and the lack of cementitious properties of the Mg(OH)₂ formed

as well as the slow rate at which carbonation of this hydration product occurred under ambient conditions. The standard production of MgO is also carbon intensive.

2.5 MgO – HYDRATED MAGNESIUM CARBONATE CEMENTS

The effects of magnesium carbonates on the properties of MgO pastes have been investigated and it was concluded that the addition of certain hydrated magnesium carbonates, significantly accelerated the hydration of MgO as well as increasing the strength of MgO-aggregate samples and CO₂ sequestration rates. A basic mechanism of a particular MgO – hydrated magnesium carbonate system was suggested (Vlasopoulos, 2007). The company Novacem was established on these findings and aims to optimise this system with a view to making a sellable low CO₂ binder product.

2.5.1 CEMENT COMPOSITION

MgO - hydrated magnesium carbonate cements are a new class of binder based on MgO and hydrated magnesium carbonate and have the potential to be carbon negative. These cements can contain 50 – 80 % MgO with the remaining percentage comprising of hydrated magnesium carbonates, $x\text{MgCO}_3 \cdot y\text{Mg}(\text{OH})_2 \cdot z\text{H}_2\text{O}$, where $x > 1$ and at least one of y or $z > 0$ (Vlasopoulos and Cheeseman, 2009). The presence of the carbonate appears to modify the hydration of MgO and is believed to allow the rapid development of strength regardless of whether CO₂ is present. It is also proposed that the hydrated MgO – hydrated magnesium carbonate system also gains further strength by absorbing CO₂ and forming one or more carbonate phases such as nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$) and dypingite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$). The current performance of these cements requires considerable optimisation by Novacem.

2.5.2 PRODUCTION PROCESS

These cements consist of MgO and a hydrated magnesium carbonate. Both materials can be produced from magnesium silicate. Magnesium silicate containing materials are widely dispersed with accessible worldwide reserves estimated to far exceed the amount needed to carbonate all of the CO₂ that could be emitted from even the most optimistic estimate of the world's fossil fuel reserves (Maroto-Valer et al., 2005).

By using magnesium silicates, CO₂ emissions from raw materials processing are significantly reduced. A summary of the MgO production can be seen in Figure 2.1 (Vlasopoulos and Cheeseman, 2009):

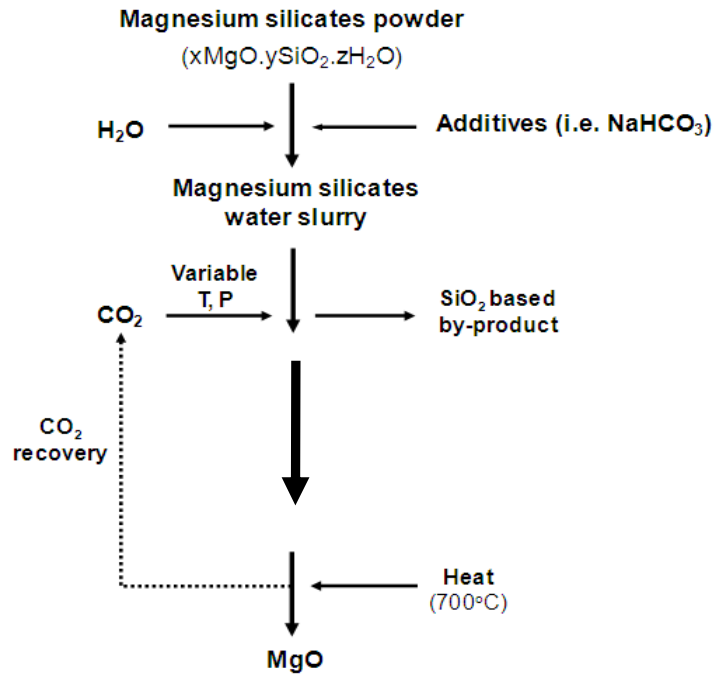


Figure 2.1: The MgO-hydrated magnesium carbonate production process for the synthesis of MgO from magnesium silicates and CO₂.

The production process involves the addition of water and additives such as NaHCO₃ and NaCl or NaNO₃ to powdered magnesium silicates to make a slurry. Magnesium carbonate is then produced and precipitated by the application high temperature and pressure to the slurry. The magnesium silicate slurry is heated at 150 °C and pressurised to 100 – 150 bar using CO₂ inside a high pressure reactor. Under these conditions, the dissolved CO₂ reacts with the magnesium silicate thus precipitating MgCO₃ and SiO₂. The precipitated carbonate is then calcined at relatively low temperatures to produce MgO. The low temperature (650 °C) calcination of the produced magnesium carbonates allows fuels with lower carbon contents than those required in for PC raw material calcination to be used, thus reducing energy related carbon emissions. CO₂ generated during calcination is captured and recycled back into the production process. Current MgO production methods, which involve the thermal decomposition of MgCO₃ or Mg(OH)₂ precipitated from seawater using Ca(OH)₂ are highly carbon intensive emitting 1.2 – 1.6 tonne of CO₂ per tonne of MgO. MgO - carbonate's MgO production method means that MgO can be produced with 0.2 – 0.4 tonnes of CO₂ per tonne

of MgO, over three times lower CO₂ emissions than conventional MgO production processes (Vlasopoulos and Cheeseman, 2009).

The hydrated magnesium carbonate component of MgO – hydrated magnesium carbonate cements can be produced by carbonating some of the synthesised MgO. Carbonation can occur by either exposing MgO powder to gaseous CO₂ concentrations, or via a slurry by bubbling CO₂ through an Mg(OH)₂ slurry to precipitate carbonates. The source of CO₂ can be either atmospheric CO₂ or industrial CO₂ such as that produced during the calcination process used in the MgO production step. Therefore, depending on the efficiency of the carbon capture, Novacem cements could potentially have a neutral carbon footprint.

The long term goal is that Novacem cements will replace some of the uses of standard PC based cements, thus reducing cement related CO₂ emissions. However, in order to reach this goal, the MgO – hydrated magnesium carbonate system requires engineering to have mechanical properties, durability and eventually costs comparable to those of PC. To carry out this optimisation, a thorough understanding of the reactions and mechanisms of the hydration and eventually the carbonation of the MgO – hydrated magnesium carbonate system is essential. This requires an understanding of the hydration and carbonation of MgO as a foundation.

2.5.3 CURRENT UNDERSTANDING OF MgO REACTIONS

a) Hydration of MgO systems

The rate and final hydration extent of a cement system strongly influences properties such as compressive strength. The addition of magnesium carbonate to an MgO system was found to affect the rate and extent of hydration of the system. Current understanding of MgO hydration is summarised below.

The hydration of MgO with both water vapour and liquid water has been studied in several investigations starting from the 19th century (Glasson, 1963, Feitknecht and Braun, 1967, Smithson and Bakhshi, 1969, Maryška and Blaha, 1997, Birchall et al., 2001).

In 1967, a study by Feitknecht and Braun established a mechanism for MgO hydration in water vapour. The proposed mechanism exists of four main steps and is essentially a shrinking core model as suggested by Lievenspiel (1972):

- Stage 1:** Water molecules are first chemisorbed and then physically adsorbed onto MgO particles to form a liquid layer on the MgO solid surface;
- Stage 2:** The liquid layer of water then reacts with the MgO to form a surface layer of $\text{Mg}(\text{OH})_2$;
- Stage 3:** The $\text{Mg}(\text{OH})_2$ layer then dissolves into the water layer;
- Stage 4:** As the water layer becomes more saturated with dissolved $\text{Mg}(\text{OH})_2$, the hydroxide precipitates as solid $\text{Mg}(\text{OH})_2$ particles.

Feitknecht and Braun also suggested that the hydration rate was limited to the rate at which $\text{Mg}(\text{OH})_2$ is removed from the MgO surface, i.e. step 2 in above mechanism (Feitknecht and Braun, 1967).

Smithson and Bakhshi studied the hydration of MgO in water in a stirred reactor (Smithson and Bakhshi, 1969). It was observed that MgO particles in the aqueous slurry decreased in size over time which led to the conclusion that a dissolution-precipitation reaction occurs and not in fact a solid state reaction as initially proposed by Glasson (1963^b). It was also suggested that the shrinking core model was not adequate to describe the kinetics of magnesia hydration. This was corroborated in more recent studies (Rocha et al., 2004).

Kitamura suggested an altered version of the shrinking core model which accounted for the influence of the product deposited on the solid reactant. This kinetic model was applied to real data and found to describe well the hydration mechanism well for temperatures in the range of 135 – 200 °C but not for lower temperatures (Kitamura et al., 1966). Reasons for this may be because different mechanisms govern hydration at different temperatures (Rocha et al., 2004).

In summary, the mechanism of MgO hydration is essentially controlled by the formation of $\text{Mg}(\text{OH})_2$ on the surface of MgO particles and the subsequent precipitation and removal of this $\text{Mg}(\text{OH})_2$ from the MgO surface.

Other parameters which have been found to affect MgO hydration include pH, MgO particle size and surface area (Jost et al., 1997, Henrist et al., 2003, Matabola et al., 2010)

b) Hydration of an MgO – hydrated magnesium carbonate system

As mentioned in section 2.5, previous work has proposed a basic hydration mechanism for a specific type of MgO – hydrated magnesium carbonate system (Vlasopoulos, 2007). This

system was the MgO – hydromagnesite, HY $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$ system. The proposed mechanism is as follows:

- Stage 1:** Water adsorbs to the surfaces of MgO particles and diffuses into MgO pores;
- Stage 2:** $\text{Mg}(\text{OH})_2$ forms on the surface of the HY instead of on MgO surfaces as it is believed to in the absence of HY. The absence of a $\text{Mg}(\text{OH})_2$ film on the MgO surface means that there is little barrier to further MgO dissolution so MgO dissolution rate increases;
- Stage 3:** As hydration is now unimpeded, the temperature of the solution increases with respect to normal MgO hydration. The extra heat increases MgO solubility and decreases $\text{Mg}(\text{OH})_2$ solubility so the solution becomes saturated with Mg^{+2} and OH^- ions;
- Stage 4:** Supersaturation of the solution with these ions leads to fast nucleation producing very small nuclei. Rapid $\text{Mg}(\text{OH})_2$ crystallisation due to low $\text{Mg}(\text{OH})_2$ solubility induced by the increased temperature of solution leads to small crystallites that grow on existing $\text{Mg}(\text{OH})_2$ particles upon the HY surface.

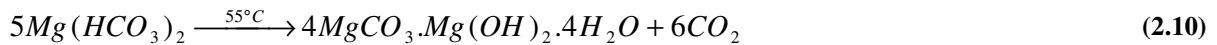
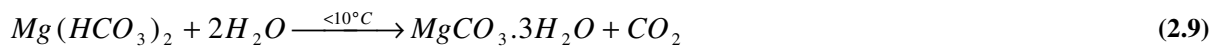
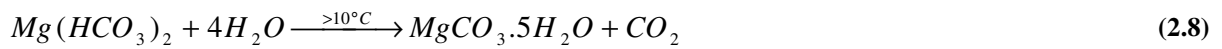
c) Carbonation of MgO systems

Having an understanding of MgO carbonation, including under what conditions different Mg-hydrated magnesium carbonates can be produced is vital for producing hydrated magnesium carbonates from MgO in order to use it as part of the MgO – hydrated magnesium carbonate binder. It is also an essential step in optimising the amount of CO_2 that can be absorbed by MgO – hydrated magnesium carbonate cements and assessing the stability of MgO – hydrated magnesium carbonate systems. Current understanding of MgO carbonation without hydrated magnesium carbonate is summarised.

There are many types of magnesium carbonates that can be acquired from the $\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$ system. Hydrated carbonates identified included hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), dypingite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$), nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), lansfordite ($\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$) and artinite ($\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$). Other unidentified magnesium carbonates have also been found (Sawada et al., 1979, Botha and Strydom, 2003). During carbonation of MgO and $\text{Mg}(\text{OH})_2$ in solution, different carbonates can be formed and can convert to each other depending on the reaction conditions such as temperature and slurry pH. Time of carbonation

and the temperature at which the carbonates are dried can also affect the final carbonate formed.

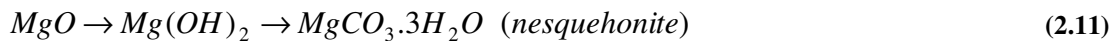
Much work has completed that has studied MgO carbonation in solution. It has been suggested that MgO hydration is an intermediate step in the carbonation of aqueous MgO slurries and a mechanism was proposed for the precipitation of magnesium carbonate (Smithson and Bakhshi, 1969). Whilst studying the leaching of calcined magnesite using CO₂, Fernandez observed two different processes during carbonation; the formation of magnesium bicarbonate (Mg(HCO₃)₂) solution (see equation 2.7) followed by the precipitation of hydrated magnesium carbonate (equations 2.8, 2.9 and 2.10) (Fernandez et al., 1999). The particular phase of hydrated magnesium carbonate depends upon the reaction conditions, particularly temperatures:



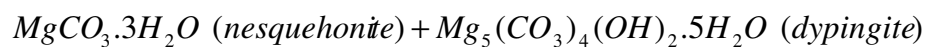
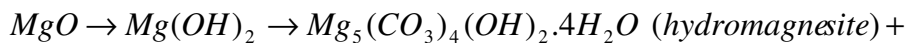
In general, air sparging to remove CO₂ from solution and increasing solution temperature speed up precipitation of carbonates from solutions (Canterford and Moorrees, 1985).

Dheilly et al., reported that the carbonation process of the MgO-CO₂-H₂O powder system is dependent on both CO₂ concentration and temperature and proposed the following three reactions (see equations 2.11 – 2.13) (Dheilly et al., 1998):

- Atmosphere rich in CO₂, temperature lower or equal to 20 °C :

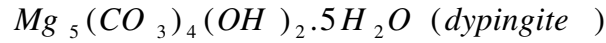
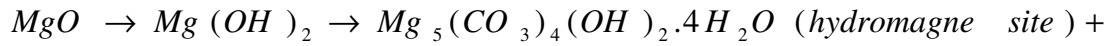


- Atmosphere rich in CO₂, temperature equal to 40 °C:



(2.12)

- Normal levels of CO₂ , irrespective of temperature:



(2.13)

These findings agree with those of Lagmuir, who studied the different phases formed within the CO₂-H₂O-MgCO₃ system under different temperatures and CO₂ pressures (Lagmuir, 1965).

2.5.4 UNDERSTANDING OF THE MgO – HYDRATED MAGNESIUM CARBONATE SYSTEM

Whilst extensive literature exists regarding the hydration and carbonation reactions of MgO alone, other than Vlasopoulos' proposed mechanism of MgO – HY hydration, there is little information available with regards to the hydration of MgO in the presence of a HY (Vlasopoulos, 2007). Therefore, in order to be able to optimise MgO – hydrated magnesium carbonate binders for use in low carbon concrete systems, a significant amount of research is required to fully understand how this system both hydrates and carbonates. However, it is expected that current understanding of MgO hydration and carbonation will provide a useful basis on which to devise research in order to gain further knowledge about how MgO – hydrated magnesium carbonate systems react.

2.6 MgO – SILICA SYSTEMS

Another MgO based system which has been gaining attention as a potential alternative binder is the MgO – silica (SiO₂) system, where SiO₂ and MgO can react to form M-S-H gels analogous to C-S-H gels (Zhang et al., 2011, Brew and Glasser, 2005a, Sandberg and Mosberg, 1988). It is generally recognised that the principal hydration product and binding phase within hydrated PC is that of calcium silicate hydrates, C-S-H (Bjornstrom et al., 2004, Mehta and Monteiro, 2008). Therefore a system based upon MgO that results in the formation of M-S-H analogous to the C-S-H system could have potential as an alternative binder. Work on basic castables by Sandberg and Mosberg (1989) found that MgO reacts with water and SiO₂ to form an amorphous type of M-S-H gel and that aggregate containing

samples based on this system achieved strengths almost twice as much as PC based concrete (Sandberg and Mosberg, 1988). The reaction of SiO_2 and MgO is therefore a promising candidate for producing a cement free binder, although little further information is available about this system and much research is required.

2.7 CONCLUSIONS

The previous chapter (Chapter 1) discussed the problem of the high CO_2 emissions associated with PC production along with several of the most promising low – CO_2 alternatives. This chapter has focused on MgO – based alternative systems, in particular novel MgO – hydrated magnesium carbonate binders which may have the potential to be carbon negative whilst providing a cementitious system. Research has found that the simple addition of hydrated magnesium carbonates to reactive MgO samples, results in a material that sets and gains strength upon hydration. A mechanism for MgO hydration in the presence of the hydrated magnesium carbonate hydromagnesite, HY [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$] was also proposed.

Much research still needs to be carried out in order to understand and optimise this MgO - HY binder system, in particular the hydration and carbonation mechanism and to determine the level of CO_2 sequestration as well as the long term performance and durability of these materials in comparison with conventional PC. A potential MgO – SiO_2 binder system which is thought to work by producing M-S-H gel analogous to C-S-H gel upon hydration has also been reported.

However, as mentioned, both of these systems require significant further investigation into both the mechanisms and properties in order to determine if they can seriously be considered as MgO – based low- CO_2 alternatives to PC.

The following chapter outlines the key aim and objectives of the work. The subsequent chapters report on the systematic investigation of into the properties of the MgO – hydromagnesite system, the MgO – SiO_2 system and the ternary MgO – SiO_2 – hydromagnesite system.

3 AIM AND OBJECTIVES OF THIS WORK

3.1 AIM

The aim of this research is to optimise cementitious binder systems based on the use of MgO. The three selected systems are MgO blended with hydromagnesite (HY), MgO blended with silica (SiO₂) and the three component MgO - HY - SiO₂ system. The aim is to optimise the properties of the binders formed from these blends of materials and understand the hydration reactions and hydration products that occur. This aim will be accomplished by meeting the following objectives.

3.2 OBJECTIVES

- a) Determine the optimal MgO - HY and MgO – SiO₂ ratios of these two systems and the potential achievable compressive strengths;
- b) Determine the rate of set and strength development in these systems;
- c) Characterise the reaction products and microstructures in optimised MgO – HY and MgO – SiO₂ systems in order to understand their contribution to strength;
- d) Understand the reaction mechanisms that lead to strength formation;
- e) Investigate the strengths and microstructure of the three-component MgO – HY – SiO₂ system in order to assess if there is any potential benefits of this system over those of MgO - HY and MgO – SiO₂;
- f) Assess the potential of each of the systems investigated to be used as a cementitious binder highlighting major issues, deficiencies and improvements that are required.

3.3 THESIS STRUCTURE

The following chapter (Chapter 4) describes in detail the materials, methods and experimental procedures used in the research. Chapter 5 reports on the optimisation of the MgO - HY system and the microstructural characteristics of the pastes formed. Chapter 6

reports on the MgO – SiO₂ system, while Chapter 7 describes the basic properties of tertiary blends of MgO – HY – SiO₂. Discussions relevant to each system are included in the relevant chapters. Chapter 8 gives key conclusions from the research and recommendations for further research are given in Chapter 9. The Appendix can be found at the back.

4 MATERIALS AND METHODS

4.1 INTRODUCTION

A range of experimental and analytical methods have been used in this research in order to characterise both the raw materials and reaction products of the hydrated binder systems studied.

Raw materials were characterised using; laser diffraction particle size analysis to characterise particle size distribution, scanning electron microscopy to gauge particle morphology and in some cases size, and XRD analysis to determine the crystalline phases present. The chemical composition of raw materials was analysed using external XRF if data sheets were unavailable or contained insufficient information. Bulk density and pH were also measured for the majority of raw materials. The citric acid reactivity test was carried out on MgO samples to assess their relative reactivities and ICP-AES was used to determine the solubility over time and with pH of SiO₂ samples.

Characterisation of reaction products involved the use of; XRD for crystalline phase identification, SEM for microstructural analysis, TGA for estimation of Mg(OH)₂ and M-S-H gel development (in the SiO₂ – MgO system) and FTIR and Raman for bond type comparison and to aid reaction product identification (in the HY- MgO system). LOI was also carried out to determine hydration extent in samples of the MgO – HY system. Compressive strength tests were also carried out. Mixture pH, and heat of chemical reaction via isothermal calorimetry were also measured for some samples.

This chapter describes the materials and the experimental and analytical techniques used. The reasons why each technique was used and further information about the materials are included in the relevant sections of later chapters.

4.2 RAW MATERIALS

Three different types of material were used throughout this investigation; magnesium oxide [MgO], hydromagnesite, HY, [Mg₅(CO₃)₄(OH)₂·4H₂O] and silica [SiO₂]. The specific types used, names and abbreviations used for this investigation, the company they are from are listed. Two high reactivity commercial MgO powders made from calcined magnesite were used, Baymag 30 MgO (B30; Baymag Inc., Alberta, Canada) and Magox Ag Grade 100 (Magox; Premier Chemicals LLC, PA, USA). A technical grade chemically pure Calmag HY

(Calmag; CALMAGS GmbH, Germany) was used for the majority of studies in the HY – MgO system although one study involved the use of an HY synthesised from B30 MgO and Calmag HY. This HY is named IC HY within this study. The two SiO₂ sources used were a silica fume (920d; Elkem Materials Ltd.) and Nyasil 5 nanosilica (NY; Nyacol Nanotechnologies Inc., MA, USA). A PC, CEM I 42,5N (CEM I; Lafarge, UK) was used to make control samples for compressive strength testing. The chemical and physical characteristics of the as received commercial materials are shown in Table 4-1.

Table 4-1: Chemical and physical characteristics of the raw materials.

	B30	Magox	920d	NY	Calmag	CEM I
	MgO	MgO	SiO ₂	SiO ₂	HY	PC
Chemical composition (wt. %)						
MgO	91.88	92.09	0	–	86.1	1.09
SiO ₂	3.49	2.85	97.6	99.7	–	20.47
Al ₂ O ₃	1.15	0.78	0	–	–	5
Fe ₂ O ₃	0.66	0.58	0	–	–	2.9
CaO	1.46	3.32	<1	–	–	64.4
TiO ₂	–	–	–	–	–	–
K ₂ O	–	–	–	–	–	0.69
Na ₂ O	0.61	0.08	–	–	–	0.18
SO ₃	0.66	0.21	<2	–	–	3.28
LOI	2	2.7	1.3	<1	55.5	–
pH	10 – 11	10 – 11	7.8	5	10.5	–
Specific gravity (g/cm³)	–	3.56	2.2	2.2	–	3.15
Loose bulk density (kg/m³)	520	960	640	150	385	1080
Mean particle size (µm)	27.2	122	135(0.15)	3	40	20
BET surface area (m²/g)	30	20	18.4	284	56	–
Citric acid reactivity (s)	67	165	n/a	n/a	n/a	n/a

From Table 4-1 the chemical compositions of the two MgO powders used can be compared. The Magox MgO contains approximately twice as much CaO as B30 MgO although this is still less than 4 wt. %. The B30 contains 0.66 wt. % sulphate and 1.15 wt. % Al_2O_3 compared to the lower content of 0.21 wt. % and 0.78 wt. % respectively in the Magox MgO. B30 also contains more Na_2O than Magox, but again, in amounts less than 1 wt. %. However, both MgO powders contain approximately 92 wt. % MgO content. It can also be seen from Table 4.1 that the two SiO_2 sources have very high purities. The 920d SiO_2 , the silica fume, has a slightly lower purity of 96.6 wt. % compared with the NY (nanosilica) powders at > 99 wt. %. This difference is to be expected considering that 920d is silica fume, a by-product of the silicon and ferrosilicon industry, rather than a purpose made SiO_2 powder. As mentioned, the Calmag HY was bought as chemically pure HY.

The particle size distributions (PSDs) of the raw materials as measured according to 4.4.1 are shown in Figure 4.1.

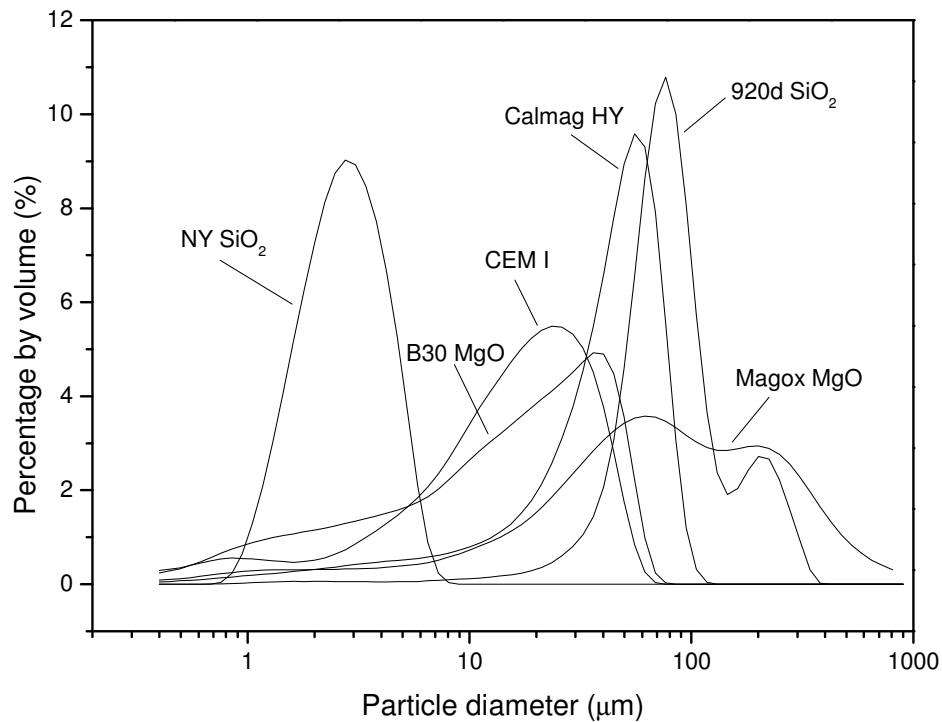


Figure 4.1: Particle size distributions of the raw materials used in this research.

Unlike Baymag 30 MgO, Magox MgO is almost bimodal, with a wide particle size range. This allowed Magox MgO to be used to investigate MgO size effects later in this research. The Calmag HY has a narrower average particle size distribution than the MgO samples. The NY SiO_2 powder has the smallest average particle size of all of approximately 3 – 4 μm as

shown in Table 4-1. The 920d SiO₂ has a bimodal PSD. Two values are given for its mean particle size in Table 4-1. The larger number represents the measured average particle size of the agglomerates, which is 135 µm, in the as received material. The smaller value of 0.15 µm seen in brackets, is that of the individual SF particles which make up the agglomerates according to the data sheet which came with this SF. The CEM I had a PSD similar to that of the B30 MgO.

4.3 PREPARATION OF SAMPLES

4.3.1 SAMPLES FOR MOULDING

For the production of paste samples, the following method was used. Pre-calculated masses of MgO and HY and/or SiO₂ were weighed out and mixed together to homogenise before contact with water. After homogenisation, this mixed dry HY and/or SiO₂ – MgO sample was added to a predetermined amount of water, whose volume was calculated depending upon the required w/s ratio, in a plastic beaker over 30 seconds while mixing on slow speed using a Dualit Professional hand-mixer, model HMR2. Mixing on slow speed was continued for a further 30 seconds after which followed 30 seconds of mixing at high speed. No mixing was then carried out for 90 seconds, the first 30 seconds of which a spatula was used to push material off the sides and bottom of the bowl and into the centre. The mixing process was completed with a final 60 seconds at high speed. This mixing method was used as it is similar to the method, without the addition of sand, recommended for mixing mortar pastes in BS EN 196-01:2005 (BSI, 2005).

After mixing, the paste was placed into the mould and placed on a vibration table for approximately 5 minutes. Moulded samples were then covered with a glass plate to prevent loss of moisture and left to set for 24 hours in a temperature controlled room at 22 ± 1 °C after which they were demoulded and placed in water filled and sealed boxes to cure at temperature of 22 ± 1 °C.

4.3.2 SAMPLES FOR ESTIMATION OF HYDRATION RATE

In order to study the effect of HY content on MgO hydration rate, sample pastes were mixed according to the method in 4.3.1. However, instead of being placed into moulds, pastes were sealed in plastic bags using the vibration table to remove air bubbles. Bags were placed in the curing room set at 22 ± 1 °C. For curing at 65 °C, a water bath was used. At set time periods,

pastes were removed from bags and ground with excess acetone in a pestle and mortar. This powder slurry was then filtered and rinsed with acetone using vacuum filtration. The residue was oven dried at 60 °C to constant weight after which LOI tests were performed and hydration rates calculated according to the methods in 4.6.5.

4.4 TESTING OF PHYSICAL PROPERTIES

4.4.1 PARTICLE SIZE ANALYSIS BY LASER DIFFRACTION

The measurement of particle size distribution by laser diffraction is based upon the fact that particles passing through a laser beam will scatter light at an angle that is directly related to their size. Smaller particles scatter light at larger angles than bigger particles. The intensity of the scattering also depends on particle size. Once a scattering pattern has been obtained, comparison with a suitable optical model allows the calculation of particle size distribution. Typically, two different models are used; the Fraunhofer Approximation and Mie Theory.

A Coulter LS100, which measures a size distribution between 0.4 and 900 µm, was used to analyse particle size by laser diffraction. Approximately 0.2 g of powder (dependent upon the density) was mixed with a couple of drops of surfactant and distilled water in order to aid deglomeration of particles. This mix was then added to the sample holder of the laser diffraction equipment and sonicated for 30 seconds in order to cause disaggregation of particles. Results were analysed using the Fraunhofer model.

4.4.2 BULK DENSITY

The bulk density of materials can change depending on how the material is handled. It can be reported as the “freely settled” bulk density or the “tapped” bulk density. The tapped bulk density refers to the bulk density when the powder has been compacted in some manner whereas the freely settled bulk density is the density calculated from volume and mass measurements made without any compaction. The freely settled bulk density was measured for materials by equation 4.1:

$$\text{Bulk density (kg/m}^3\text{)} = \frac{m_{dry}}{V_{dry}} \quad (4.1)$$

m_{dry} = mass of material after drying at 100 ± 5 °C

V_{dry} = volume occupied by the sample (50 cm^3)

A glass beaker of 50 cm^3 total volume was weighed and then filled and the top of the sample was levelled off to create a flat plane level. During filling, the sample was poured in as gently as possible and the beaker was not moved or tapped, nor was pressure applied to the surface whilst it was being levelled, in order to avoid any compaction. The filled beaker was then weighed, allowing the total mass of sample, m_{dry} , to be calculated. This was repeated three times and an average m_{dry} taken and used in equation 4.1 to calculate the freely settled bulk density.

4.4.3 SETTING TIME

Whilst final set indicates the onset of mechanical strength development, initial setting time essentially refers to the change of a paste from a fluid-like state to a rigid state and is accompanied by a rapid temperature increase in the sample (Mehta and Monteiro, 2008). Knowing the initial setting time helps to determine the time available for the transportation, placement and consolidation of concrete and cement. Setting time can be determined using several techniques including the Vicat needle method, the Gilmore test and methods involving ultrasonic waves (Pessiki and Carino, 1988, Zheng et al., 2012). The most commonly used method is that of the Vicat needle (Sleiman et al., 2010). This test uses a cylindrical needle of 1 mm^2 cross section which is moved vertically at set time intervals to penetrate a mass of cement paste contained within a mould. The time at which the needle no longer penetrates past a certain distance from the top of the sample is defined as initial set. When penetration of the needle can no longer occur, final set has been reached (Sleiman et al., 2010).

In this work, setting time was determined using the Vicat needle method in accordance with British standard (British Standard Institution, 2005). Initial setting time was taken as the time, taken to the nearest 5 minutes, at which the distance between the base of the sample and the needle is $6 \pm 3 \text{ mm}$. Final setting time was defined as being the time at which the needle only penetrates 0.5 mm into the surface of the sample.

4.4.4 COMPRESSIVE STRENGTH TESTING

The unconfined compressive strength (UCS) of samples was measured as follows. If the samples had not been cured in water, they were immersed in a water bath at room temperature for 24 hours prior to testing. Samples were then removed, surface dried and tested. An ADR – Auto strength machine from ELE International was then used to apply a force at a constant loading rate of 0.08 kN/s and the force at which the sample failed ($F_{\max}$) was recorded. The UCS (MPa) of each block was calculated by dividing this maximum force, in newtons (N) applied by the area (A , in mm^2) of the block in contact with the loading plate (see equation 4.2).

$$UCS = \frac{F_{\max}}{A} \quad (4.2)$$

Six identical samples were made and tested for each specific sample mix and the average measurement, $\bar{x}$ used. The average was calculated using equation 4.3, where n is the total number of samples (usually six) and x is the compressive strength measurement.

$$x = \frac{1}{n} \sum_{i=1}^n x_i = \frac{1}{n} (x_1 + \dots + x_n) \quad (4.3)$$

The error was calculated and shown on graphs in the form of standard deviation which is used to show the variation of a set of data from its mean or average. A high standard deviation indicates a wide spread of measurements from the mean whilst a low value for standard deviation shows that the measurements were close to the mean and therefore very similar to each other. If the data is normally distributed, it is expected that 68.3 % of the measured data falls within $\pm$ one standard deviation of the mean, whilst two 95.4 % of the measured data falls within $\pm$ two standard deviations. These percentages are also known as confidence intervals. Standard deviation, σ , is calculated using equation 4.4 below:

$$\sigma = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2} \quad (4.4)$$

After testing, fractured samples were conserved in acetone for 10 days in order to stop cement hydration. Samples were then dried in an oven at 40 °C to constant weight and stored in sealed plastic bags in a dessicator for future testing.

4.5 CHEMICAL TESTS

4.5.1 pH ANALYSIS

The early age pH of materials, both as received and when in various mixes was measured by premixing the dry powders (if applicable) in order to homogenise them, and then adding the homogenised mix to distilled water at a w/s ratio of 3. After 1 minute of mixing the wet and dry components to form a slurry, the pH was then measured immediately and then at various time periods. In between measurements, the ‘slurry’ was stirred using a magnetic stirrer.

The pH electrode used for all testing was a Fischerbrand Hydrus 500 pH meter with an Inlab Routine Pro electrode by Mettler Toledo. The pH meter was calibrated using buffer solutions of pH 4, 7 and 10. Whilst it was apparent that the methods used for measuring pH for binder pastes and hydrated samples are not standard, the pH values obtained were generally used for comparison with other samples that had been treated in the same way so the lack of use of a standardised test was not thought to be of issue.

4.5.2 INDUCTIVELY COUPLED PLASMA – ATOMIC EMISSION SPECTROSCOPY

The overall aim of analytical atomic spectroscopy is to identify and quantify concentrations of elements in various media. Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP – AES) uses plasma, which is an electrically neutral, high ionised gas consisting of ions, electrons and atoms, to atomise and excite the source element. As the excited electrons relax back to lower energy levels, they emit electromagnetic radiation at wavelengths characteristic of the particular element they are from. The spectrometer component of the ICP – AES then separates and resolves the detected wavelengths and measures their strength. As the spectrum of each element is unique, and intensity is proportional to the concentration of that element, both the identity and concentration of elements present can be determined.

The equipment used in this work was an ICP - AES Optima 7300 DV manufactured by Perkin Elmer. Argon gas was used as an atmosphere for the plasma. Before measurement,

solutions of samples that required measurement were filtered through 0.45 μm filter paper and the filtrate diluted with distilled water in order to ensure concentrations of the species of interest were within the detection limit of the machine. 1 molar HCl solution was used as a matrix for the samples. For each different element whose concentration was measured, three calibration samples of different concentrations of that element were used, as well as a blank HCl solution, to ensure calibration.

4.5.3 ISOTHERMAL CALORIMETRY

Isothermal conduction calorimetry is a method used to evaluate the heat generation when a sample is under isothermal conditions. In order to keep the conditions isothermal, i.e. to keep the temperature of the sample constant, any heat emitted through hydration (or other exothermic reactions) of the paste sample, are released to the environment via a heat flux meter. Electric potential is measured at the heat flux meter and is directly proportional to the heat production rate (Poppe and De Schutter, 2005).

An isothermal JAF conduction calorimeter from Wexham Developments Ltd was used in this study to measure the heat of hydration of MgO in various mixtures. The temperature was set to 20.0 ± 0.1 °C. Approximately 25 g of paste was used for each sample. Samples were mixed by hand for 2 minutes before using a vibration table to insert the pastes into the plastic calorimetry bags which were then sealed and inserted into the calorimeter.

4.5.4 CITRIC ACID TEST

The reactivity of MgO powders was determined using the citric acid test (Van der Merwe et al., 2004, Strydom et al., 2005). A 0.4 N (0.133 M) solution of citric acid was prepared by dissolving 28 g of monohydrous or 25.6 g of anhydrous citric acid crystals in 1000 ml of distilled water. 100 ml of this bulk citric acid solution was then measured out into a 250 ml conical flask and a couple of drops of phenolphthalein were added as an indicator. The solution was then stirred for 1 minute using a magnetic flea and stirrer stand at medium speed. Approximately 2 g of MgO was then added to the solution and a stopwatch started. The time taken for the *bulk* solution to turn from white/cream to a first detectable shade of pink which does not disappear upon further mixing, was recorded. This is the citric acid reactivity time and indicates the time taken for the solution to neutralise the acidic solution.

Industry classes of MgO reactivity can be found in Table 4-2. The phenolphthalein indicator was produced by dissolving 0.5 g of phenolphthalein crystals in 50 ml ethanol. After dissolution, 50 ml of deionised water was added to produce the final indicator solution. This test was repeated three times for each sample and the average taken.

Table 4-2: Industry MgO reactivity classes in accordance with reactivity times achieved in the citric acid reactivity test (Van der Merwe et al., 2004)

Reactivity grade	Citric acid reactivity time (s)
High	<60
Medium	180 - 300
Low	>600
Unreactive (dead burnt)	>900

4.6 MICROSTRUCTURAL AND COMPOSITION ANALYSIS

4.6.1 X-RAY DIFFRACTION

X-ray diffraction (XRD) is used to determine the crystalline phases present in a material. Solid matter can be divided into two categories; amorphous and crystalline. Whilst an amorphous material is made up of atoms arranged in a random, disordered way, crystalline material consists of atoms arranged in a regular three-dimensional array. Typically, the wavelengths of X-rays are of the same order of magnitude as the small d-spacings between the crystal planes. Therefore, when a concentrated monochromatic X-ray beam is directed at a crystalline sample, the repeated pattern of the crystal acts as a diffraction grating and if the X-rays scattered/diffracted by the atoms in the crystal plane interfere constructively, intense ‘reflected’ X-rays will leave the crystal at an angle equal to that of the incident beam. For this to occur, it is required that the plane of the crystalline material is parallel to the plane surface of material. Bragg’s Law (expressed as equation 4.5) relates the wavelength of the incident X-ray, the interplanar or ‘d’ spacing and the angle of incidence (Langford and Louer, 1996). It is the underlying equation of XRD analysis.

$$2d \sin \theta = n\lambda \quad (4.5)$$

n = the diffraction order (this must be an integer for constructive interference)

λ = the wavelength of incident x-rays

d = the ‘d’ or interplanar spacing

θ = the angle of diffraction

In powder XRD, by scanning a sample through a range of 2θ angles, all possible constructive interference diffraction for that material should be detected as the random orientation of crystallites in the powdered material should ensure that representatives of all of the crystal planes are parallel to the surface. As the wavelength of the incident X-ray is known, as well as the incident angle at which constructive interference occurs, Bragg's Equation can be solved to give the d-spacing set for that material across the 2θ angles scanned. As each different crystalline material has a unique set of d-spacings, comparison of these d-spacings with a database of known reference samples allows sample identification.

An X-Pert PRO MPD by PANalytical was used with Cu $K\alpha$ radiation in the range of 5 to 65 ° 2θ . An acceleration voltage of 40 Kv and a current of 40 mA were applied. Samples were ground to a fine powder before use. Analysis of spectra was carried out using X'Pert HighScore Plus.

Crystallite dimensions were estimated by calculating the widths of the broadened XRD peaks (via X'Pert Data Viewer) and inserting these values into the Scherrer Equation, shown in equation 5.1 (Klug and Alexander, 1974). It was assumed that instrument broadening was negligible.

$$L = \frac{0.89\lambda}{B \cos \theta} \quad (4.6)$$

For equation 4.6, L is crystalline size, B is the peak width in radians and θ is that angle at which the peak in question is centred. λ represents the wavelength which for CuK α radiation was 1.542 Å. B was estimated using the full width half maximum (FWHM) method which uses the width of the diffraction peak at a height which is equal to half the intensity of the maximum intensity, $I_{\max}$, of the peak as shown in Figure 4.2.

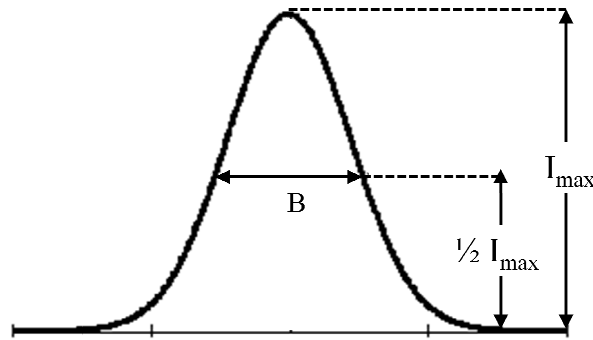


Figure 4.2: Diagram depicting the estimation of B using the FWHM method. $I_{\max}$ is the intensity from an assumed background level to the maximum intensity of the peak.

4.6.2 SCANNING ELECTRON MICROSCOPY

Scanning Electron Microscopy (SEM) is used to obtain magnified images of a materials microstructure. It is based on detecting the scattering of electrons that occurs when a beam of electrons is fired at a specimen. The electron beam is produced by a tungsten filament thermionic electron source. After acceleration of the electron beam to a high voltage (1 KeV to 50 KeV), the beam is de-magnified so that when it hits the specimen, it has a diameter of around 1 – 5 nm. Electrons from the beam hit the sample and a mixture of these incident electrons and electrons produced by excitation of the sample are emitted back from the sample to form an image. The ‘emitted’ electrons can be divided into two categories depending upon their energy. Secondary electrons are those which have energies below 50 eV. They originate within a few nanometers of the sample surface. Electrons belonging to the incident electron beam which hit the sample and are emitted back possessing a large fraction of their initial energy are known as backscattered electrons. Two different types of image can be produced depending upon which of these two types of electron is detected. A scintillator-photomultiplier device can be used to detect secondary electrons to produce well-defined

images of three-dimensional appearance (Goldstein et al., 2007). Alternatively, backscattered electrons can be used to detect contrast between areas of different chemical composition.

The morphology of the raw materials was examined in powder form using a JEOL JSM 5610 SEM machine. Powders were mounted onto the sample stand using black carbon tape and then gold coated for 2 minutes using a current of 20 mA before SEM analysis. For reaction products, fractured surfaces of solids, which had previously been dried using an oven set at 40 °C were used instead of powders but were otherwise prepared in the same way. Both types of sample were analysed by secondary electron imaging in order to obtain three-dimensional images.

4.6.3 INFRARED AND RAMAN SPECTROSCOPY

Spectroscopy can be a very powerful tool for identifying types of chemical bonds. Infrared (IR) and Raman spectroscopy are largely used to determine energy differences between vibrational states of molecules and to identify a compound by comparison of experimental spectra with those of authentic samples. These methods can also be used to identify specific structural features such as CO group in a molecule and can give additional information about the symmetry and shape of simple molecules. However, these two techniques have slight differences.

a) INFRARED SPECTROSCOPY

In IR spectroscopy, a photon of IR radiation of a known frequency is absorbed by the sample causing molecules to be promoted to higher vibrational states. If the energy of the photon is equal to that of the energy separation between vibrational states of the molecule, energy will be absorbed to induce vibrational excitation of the covalent bonds of the molecule and absorption spectra can be obtained. As the wide range of vibrational motions of molecules is dependent on their component atoms, the absorption that occurs corresponds to the energy of these vibrations and the spectra will therefore give an insight into the molecular structure of the sample (Shriver and Atkins, 1999).

For this investigation, a Thermo Scientific Nicolet iS10 spectrometer using Fourier Transform (FT) was used. Approximately 0.1 g of sample was mixed with 10 g of KBr and pressed to form discs in order to be analysed by this technique.

b) RAMAN SPECTROSCOPY

In Raman spectroscopy, it is the inelastic scattering of a incident photon after interaction with the sample molecules that is of interest. The scattered radiation occurs over all directions and results in wavelength changes.

There are several components to light scattered by a molecule; the Rayleigh scatter and the Stokes and Anti-Stokes Raman scatter. Rayleigh scattering involves a scattering process where the incident and scattered radiation have the same frequency. Raman scattering however is when the wavelength of the incident light is changed after interaction with the molecule. Depending upon the vibrational state of the molecule, the shift in the energy of the photons can be higher or lower. Photons emitted by Stokes-Raman scattering are generally lower in energy and frequency than the incident photons absorbed. Scattering of the photon at higher energy (causing shortening of the wavelength) is called Anti-Stokes Raman. However, this is much less likely to occur as only a very small number of molecules will be at a higher vibrational energy level.

The incident photons will interact with the molecule and the loss or gain of energy by the photon resulting from this interaction is characteristic of the type of each bond (vibration) present. Although not all vibrations can be observed using Raman spectroscopy, sufficient information is usually available to enable a precise characterisation of the molecular structure (Thygesen et al., 2003).

The Raman spectrometer used for this study was a Renishaw invia Raman Microscope. A laser of 785 nm wavelength was used. Powdered samples were smoothed with a glass slide in order to create a flat smooth surface. Paste samples were moulded into a small specially made plastic holder using a vibration table to aid moulding and minimise air bubbles. Surfaces were then smoothed flat using a palette knife. Samples were then covered with plastic tape in order to avoid moisture loss. The tape was removed before insertion into the Raman machine.

4.6.4 THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) is an analytical technique that measures the change in mass of a material over a temperature range and has a wide range of use. Measurements can be carried out in air or an inert atmosphere (using gases such as helium or nitrogen) and the sample weight is recorded as a function of temperature. This weight change over specific temperatures can be used to characterise samples and indicate thermal stability amongst other

applications (Wendlandt, 1974). Depending upon the exact instrument used, it is also possible to record the temperature difference between the sample and a reference pan (differential thermal analysis, DTA) or the heat flow into the sample pan (differential scanning calorimetry, DSC). DSC allows any energy release or absorption due to chemical reactions taking place in the sample to be monitored. The applications of DSC and DTA are similar and can be used to observe events such as fusion and crystallisation as well as glass transition temperatures.

TGA was used in this study to measure the mass loss due to dehydration upon heating $\text{Mg}(\text{OH})_2$ within dried hydrated samples in order to partially quantify their composition. It was also used with DSC to check for the presence of M-S-H gel in hydrated SiO_2 – MgO samples. Specific details of how this was done are explained in the relevant chapters.

The thermal analyser used for this project was a Polymer Laboratories PL-STA-1640 with a Rheometric Scientific system interface. TGA measurements were carried out under an inert atmosphere of nitrogen set at a flow rate of 60 ml/min. Samples, which had previously been dried to constant mass at 60 °C and ground to a powder, were heated from room temperature up to 1000 °C at a heating rate of 10 °C per minute. The weight of the sample was measured at 6 second intervals. Approximately 25 mg of powder was used for each run and an identical but empty crucible was used as a control. The crucibles used were alumina.

4.6.5 CALCULATION OF HYDRATION DEGREE

In order to calculate the percentage of MgO that had hydrated to $\text{Mg}(\text{OH})_2$ in MgO – HY samples, a method was derived that was based on mass loss of samples subjected to a loss on ignition (LOI) test. The mass losses, calculated as percentages, for each sample were then inserted into the derived equations in order to calculate the MgO hydration degree, as a percent. The method is as follows.

LOI was measured by weight loss after subjecting a known mass of material at 950 °C for 2 hours and then reweighing the sample. Beforehand, the material was dried at 60 °C until a constant mass was achieved. This was repeated twice for each sample and the average taken.

Equation 4.7 was used to calculate ‘y’ or LOI as a percentage:

$$LOI(\%) = y = \frac{m_{dry} - m_{cal}}{m_{dry}} \times 100 \quad (4.7)$$

m_{dry} = mass of material after drying at 60 ± 5 °C

m_{cal} = mass of material after calcining at 950 °C

This value for LOI, ‘y’ can then be inserted into the relevant equation out of 4.8 to 4.11, which is of the form of equation 4.12, and the equation solved using the quadratic equation solving formula equation 4.13.

Samples that prior to hydration contained 10 % HY – 90 % MgO, 20 % HY – 80 % MgO and 30 % HY – 70 % MgO are represented in equations 4.9, 4.10 and 4.11 respectively. For samples which contained no HY, equation 4.98 is used.

$$-0.0011x^2 + 0.419x + (0.163 - y) = 0 \quad (4.8)$$

$$-0.0009x^2 + 0.359x + (5.809 - y) = 0 \quad (4.9)$$

$$-0.0007x^2 + 0.303x + (11.463 - y) = 0 \quad (4.10)$$

$$-0.0006x^2 + 0.255x + (17.081 - y) = 0 \quad (4.11)$$

Where;

x = final degree of MgO hydration

a , b and c = pre-calculated values

$$ax^2 + bx + c = 0 \quad (4.12)$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (4.13)$$

As the equations are quadratics, their solution will produce two different values, one of which will be an ‘impossible’ value. Therefore the other value should be taken as a value representing percentage hydration of MgO. These equations are based upon the fact that HY does not change to a different carbonate during hydration and assumes that carbonation of the samples is minimal. Explanations and working through of their derivation can be found in Appendix.

4.7 CONCLUDING REMARKS

This chapter has described the raw materials and the methods, both chemical and physical, that were used in this research. In the following experimental chapters, the raw material will be referred to in their abbreviated names listed in this chapter. Methods used will be described by referring to the relevant section of this chapter.

It should also be noted that when the composition of a sample is written, ‘%’ refers to ‘wt. %’ of the relevant material in the original pre-hydrated dry sample mix, unless otherwise stated. This is true for all main text, figures and tables throughout the work.

5 THE MgO – HYDROMAGNESITE (HY) SYSTEM

5.1 INTRODUCTION

Hydration of MgO forms $\text{Mg}(\text{OH})_2$ which does not set and gain compressive strength over time. However, previous research at Imperial College London found that the addition of a hydrated magnesium carbonates, to MgO, produces a paste that sets and gains strength on hydration (Flatt et al., 2012). A reaction mechanism was also suggested (Vlasopoulos, 2007). However information on basic binder properties and further explanation as to how hydrated magnesium carbonates effect and gives strength to the MgO system is not available in the literature (Schneider et al., 2011).

This chapter therefore reports on research that aims to understand a specific MgO – hydrated magnesium carbonate system, the MgO - hydromagnesite (HY), $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$, cement system. The first section reports on research that has investigated the optimisation of MgO - HY cements through compressive strength testing of prismatic samples. This was completed in order to find the optimum MgO to HY ratio. It also provides an overview of the compressive strengths achievable from this system in comparison with Portland cement (CEM I) paste samples. The effect of HY content on hydration rate and on reaction product type and morphology was studied. The effect of the presence of HY on hydration rate was also examined. An optimum MgO – HY system was then selected and its properties investigated and the effects of MgO and HY particle size on strength and reaction product are reported. Particle reaction mechanisms are proposed.

5.2 MATERIALS

A commercial HY powder, Calmag HY, and B30 MgO were used the experiments described in 5.3 and 5.4. Magox MgO and IC HY were used in the experiment described in 5.5. Deionised water was used throughout.

5.3 OPTIMISATION OF THE MgO – HY RATIO

This section reports on experiments that have optimised the HY to MgO ratio in terms of compressive strength. The effect of HY content on early-age hydration rate, type of crystalline reaction product and sample morphology was also determined.

5.3.1 MATERIALS

Calmag HY and B30 MgO were used in these optimisation experiments.

5.3.2 METHODS

a) *Sample production*

The method described in 3.2 was used for the production of prismatic 10 x 10 x 60 mm³ paste samples, with six bars made for each sample type. In order to optimise the MgO -HY composition a range of samples were formed and compressive strengths determined. The addition of HY to MgO required increasing the water content in order to produce a mouldable paste. This meant that increasing the percentage of HY in a sample increased the minimum w/s ratio required. The HY content was thus limited to a maximum of 30 % HY. The minimum w/s ratio required to mould a sample containing this maximum content of HY was used for all samples regardless of HY content in order to negate any water content effects. A sample prepared from 100 % MgO was also produced with a minimum mouldable w/s ratio of 0.6 in order to illustrate that even when a lower w/s ratio is used, MgO pastes will not produce a sample with strength. The samples prepared are listed in Table 5-1. A control sample containing 100 % CEM I was also prepared to provide a reference compressive strength. This was also made using the minimum water required to enable the paste to be moulded using the method described above. This w/s ratio was determined to be 0.3.

Table 5-1: Paste samples made for compressive strength tests.

HY and MgO content in dry mix (wt. %)		w/s ratio	Curing time (days)
HY	MgO		
0	100	0.6	
0	100		
10	90	0.66	7, 28
20	80		
30	70		
100% CEM I		0.3	

Whilst HY containing samples were cured in water in order to avoid carbonation, the 100 % MgO samples were cured in the curing room in sealed plastic bags lined with damp cloths to ensure a high humidity environment, of > 95 % relative humidity. This difference in curing method was because moulded MgO samples started to disintegrate once immersed in water.

The samples made in accordance with 4.3.2 to test the effect of HY content on MgO hydration are summarised in Table 5-2.

Table 5-2: Samples made in order to determine the effects of HY content on the hydration degree of MgO.

HY and MgO content in dry mix (wt. %)		w/s ratio	Hydration time (hours)	Curing temperature (°C)
HY	MgO			
0	100	0.8	0.5, 6, 24, 72, 168	20, 65
10	90			20
20	80			
30	70			

b) Test methods

Compressive strengths tests were carried out using the method described in 3.3.4 on all moulded 10 x 10 x 60 mm³ samples summarised in Table 5-1. After testing, crushed samples were stored in acetone for 10 days to prevent further hydration and then dried at 60 °C to constant mass. These dried samples were then crushed and ground to a fine powder using a pestle and mortar for XRD analysis and small fracture surface pieces were used for SEM analysis.

Powder samples prepared from the pastes summarised in Table 5-2 via the method in 4.3.2, were subjected to the LOI test and related calculations applied as described in 4.6.5 in order to estimate the hydration extent. Crystallite dimensions of broadened peaks were estimated using the widths of broadened XRD peaks as described in 4.6.1.

5.3.3 RESULTS

Compressive strength

Figure 5.1 shows the relationship between HY content and compressive strength measured at 7 and 28 days in the form of a bar chart. The 7 and 28 day compressive strengths of the 100 % CEM I control samples are also shown.

It was found that all of the 100 % MgO samples made, for both 0.6 and 0.66 w/s ratios, were very delicate and compressive strength could not be accurately measured as upon the slightest application of pressure from the force plates of the testing machine, the samples began to crumble so the machine would not register a definitive breaking load. This was observed after both 7 and 28 days curing. For this reason, it has been assumed that 100 % MgO samples have zero compressive strength after 24 hours curing in bags at 98 % RH and are not included in Figure 5.1.

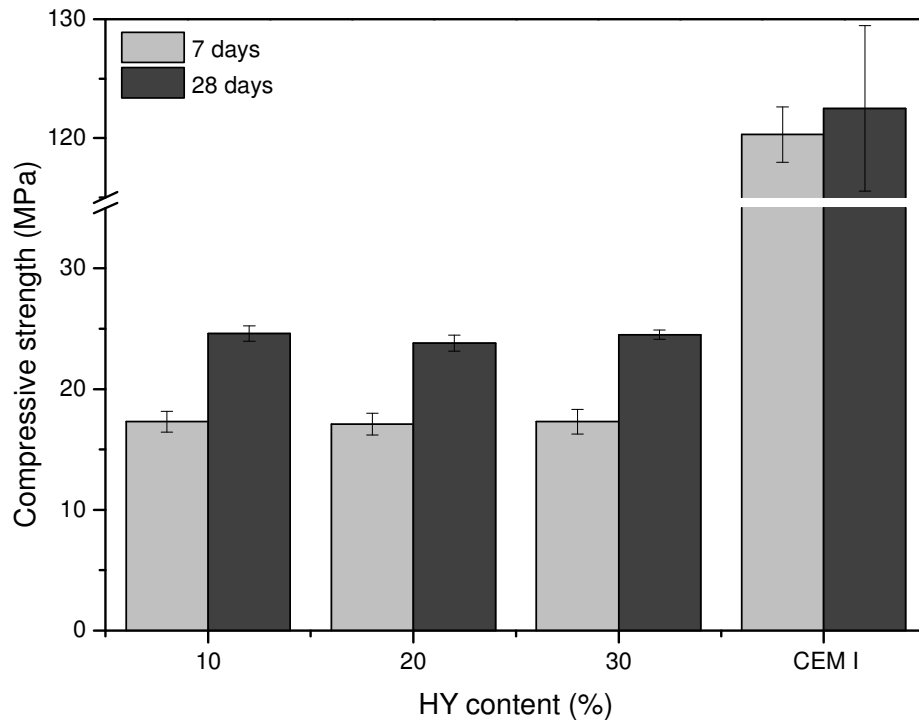


Figure 5.1: Graph showing the compressive strength of samples containing different percentages of HY at 7 and 28 days. 7 and 28 day compressive strengths are also shown for CEM I samples.

From this graph, it appears that under the experimental conditions used, increasing the content of HY from 10 % to 30 % does not make a difference to compressive strength, regardless of curing time. All of these samples had strengths of approximately 17 MPa and 25 MPa after curing at 7 and 28 days respectively showing that strength increases between these time periods. Whilst increasing the percentage of HY in the range of 10 % to 30 % does not significantly increase strengths, the addition of 10 % HY makes a substantial increase to the compressive strength.

Figure 5.1 also shows the strength of samples prepared using CEM I. These strengths of approximately 120 MPa are significantly higher than any of the measured HY – MgO

hydrated sample strengths. However, the significantly lower w/s ratio of the CEM I system cannot be equalled in the MgO – HY samples.

Hydration study

Figure 5.2 shows the effect of HY content on the extent of MgO hydration over time. The measurement for the 20 % HY sample at 24 hours has been omitted as its value of 70 % hydration extent seemed anomalous compared with the other values.

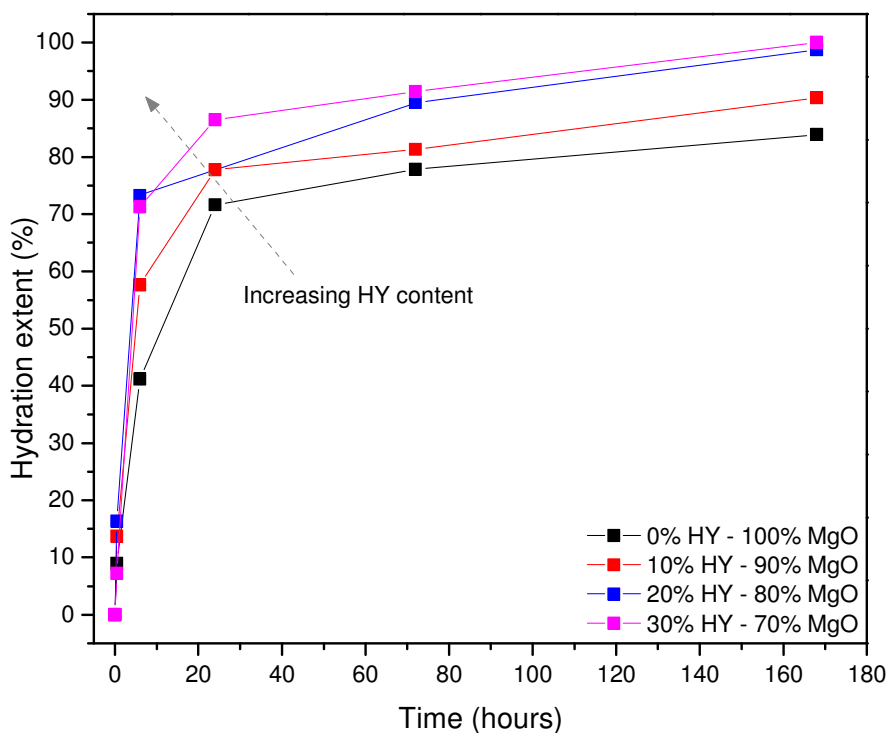


Figure 5.2: Graph showing the relationship between HY content and the hydration rate of MgO.

The term ‘hydration extent’ refers to the percentage of the available MgO that has been hydrated to $\text{Mg}(\text{OH})_2$. The graph indicates that all of the samples containing HY hydrated more rapidly than the 100 % MgO sample, and that the higher the HY content, the faster the hydration rate although the rates of the 20 % and 30 % HY are very similar. For all samples, the fastest stage of hydration, depicted by the steepest lines, occurs at the start of the hydration period, after which the rate of hydration generally slows with time. According to the graph, by 7 days, 20 % and 30 % HY samples have achieved close to maximum hydration extent whilst the 10 % HY sample is ~ 90 % hydrated. However, the 100 % MgO sample has only achieved 84 % of the maximum possible hydration extent.

Figure 5.3 displays the hydration rates, calculated using the method in section 3.7.1, of 100 % MgO samples cured at two different temperatures, ambient $\sim 20^\circ\text{C}$ and 65°C .

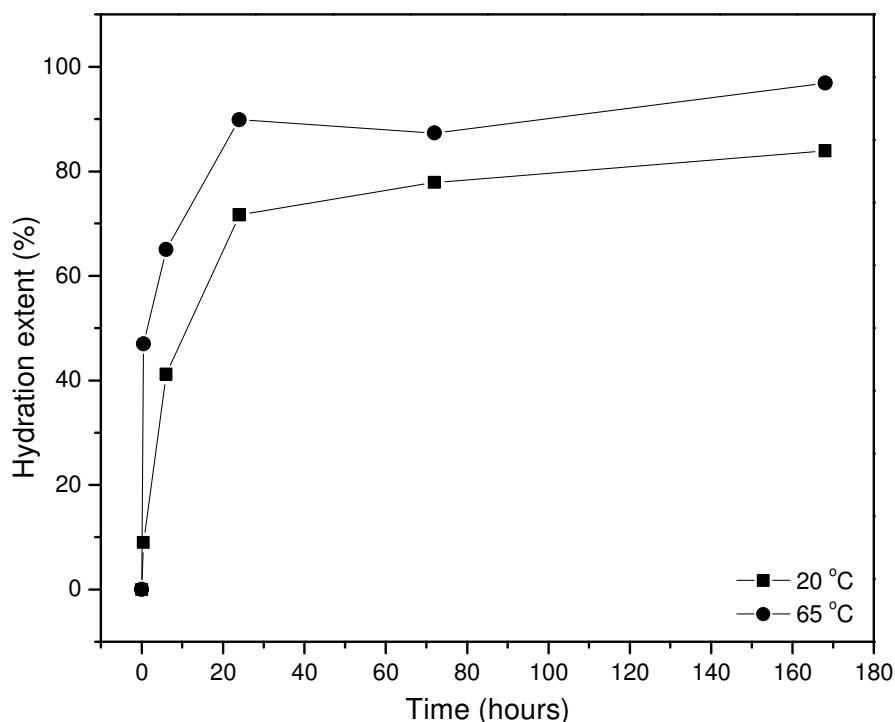


Figure 5.3: Graph showing the effect of two different curing temperatures on the hydration rate of 100 % MgO samples

It is clear from the graph that hydration rate is faster when the sample is cured at 65°C than at ambient temperature. By 7 days (168 hours), 97 % hydration extent has occurred compared to the 84 % achieved by sample cured at the lower temperature.

Analysis of crystalline reaction products

The XRD spectra of MgO - HY samples prepared containing different percentages of HY and a 0.66 w/s ratio after 7 and 28 days curing are shown in Figure 5.4. The crystalline materials have been identified and labelled where B is brucite [$\text{Mg}(\text{OH})_2$], C is calcite [CaCO_3], H is hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$], M is magnesite [MgCO_3] and P is periclase [MgO].

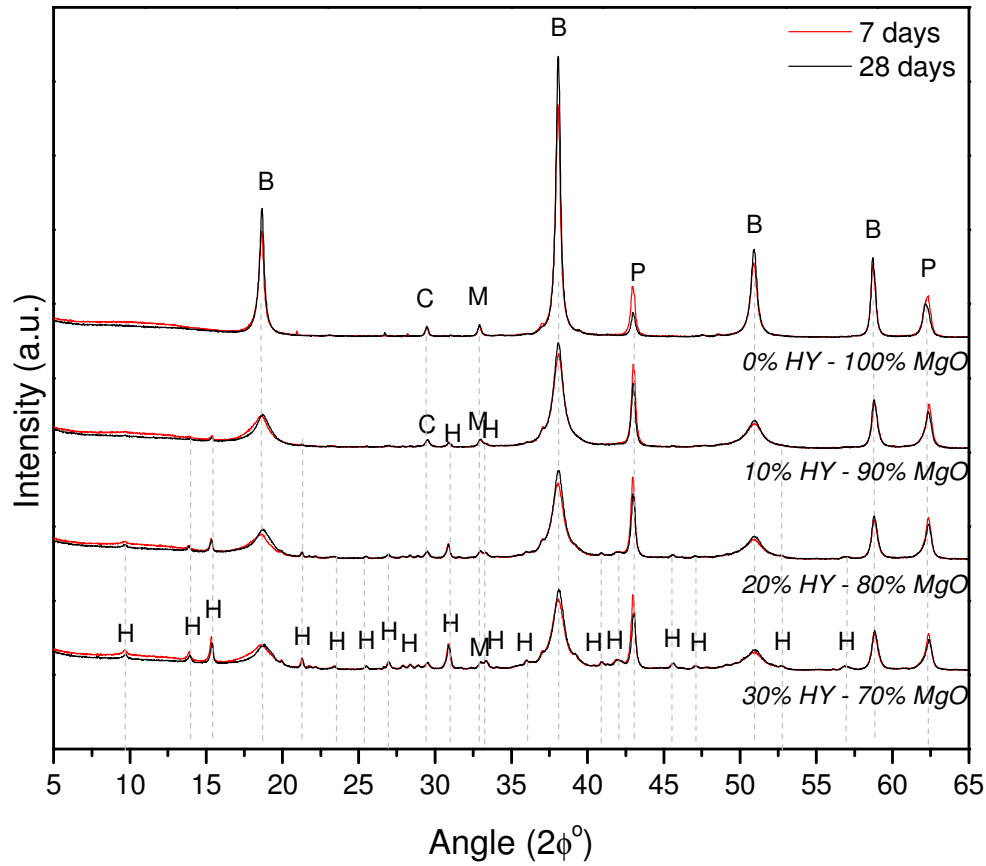


Figure 5.4: XRD spectra from top to bottom of hydrated a) 100% MgO; b) 10% HY – 90% MgO; c) 20% HY – 80% MgO; d) 30% HY – 70% MgO after 7 days curing (red) and 28 days curing (black). B = brucite $[\text{Mg}(\text{OH})_2]$, C = calcite $[\text{CaCO}_3]$, H = hydromagnesite $[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}]$, M = magnesite $[\text{MgCO}_3]$ and P = periclase $[\text{MgO}]$. ‘%’ refers to ‘wt. %’ in the dry start mix.

The major reaction product in all samples is brucite, $\text{Mg}(\text{OH})_2$. Some unreacted periclase, MgO, remains and peaks arising from calcite, CaCO_3 and magnesite, MgCO_3 are present in all samples. These materials are from the raw material MgO as it is extremely unlikely that carbonation to MgCO_3 would be able to occur at the ambient temperature, pressure and CO_2 levels that samples were exposed to during curing (Mo and Panesar, 2012). Given that these impurities are present in all samples, but they do not contribute any strength in the 100 % MgO sample, this is a clear indication that they have insignificant contribution to strength.

The only other crystalline phase identified was HY. This was observed in the three samples containing HY although not all of the peaks are observable for the samples containing lower percentages of HY. No other phases were identified. When comparing different HY contents, there is very little difference between spectra other than the increasing intensity of HY peaks and broadening of some of the $\text{Mg}(\text{OH})_2$ peaks with increasing HY content. Differences in

Mg(OH)₂ peak intensity between samples with different HY content, cannot be taken to mean that there is less Mg(OH)₂ present, as all samples have different HY – MgO ratios and so peaks cannot be compared directly in a quantitative manner.

All of the spectra are very similar after 7 and 28 days with the only obvious difference being the ratio of the MgO to Mg(OH)₂ peaks which is lower after 28 days. This indicates that MgO continues to hydrate to Mg(OH)₂ between 7 and 28 days.

Whilst Mg(OH)₂ peaks are observed in all samples, regardless of whether HY is present, certain Mg(OH)₂ peaks are seen to be broader for all of the samples containing HY than for the 100 % MgO samples. These peaks also appear to become broader with increasing HY content.

Peak broadness can be related to crystallite size, with broader Mg(OH)₂ peaks indicating the presence of crystallites of dimensions smaller than 100 nm (Navarro et al., 1998). Therefore it appears that the presence of HY can affect hydration of MgO in such a way that Mg(OH)₂ crystallites have smaller dimensions than they would if HY is not present. Broadening Mg(OH)₂ peaks are seen at 18.7, 38.1 and 50.1 2 θ ° but not observed for that at ~ 58 2 θ °. These peaks correspond to the (001), (101) and (102) Mg(OH)₂ crystal planes respectively, whilst that which showed no broadening corresponds to the (110) plane. The broadening of each single peak is the product of crystallite dimensions in the direction perpendicular to the planes.

In order to approximate the effect of HY content on the crystallite dimensions, the Scherrer Equation (equation 5.1, 5.3.1) was used to estimate the crystallite size perpendicular to the (001), (101) and (102) Mg(OH)₂ plane directions of all the MgO - HY hydrated samples. Results after 7 days and 28 days curing are shown in Figure 5.5. It should be noted that the calculation of crystallite size via the Scherrer Equation of the analogous peaks for hydrated 100 % MgO samples cannot be approximated due to their larger crystallite size and the sharpness of the peaks which limits the accuracy of the equation but it can be assumed that these crystallite sizes are in the region of 100 nm.

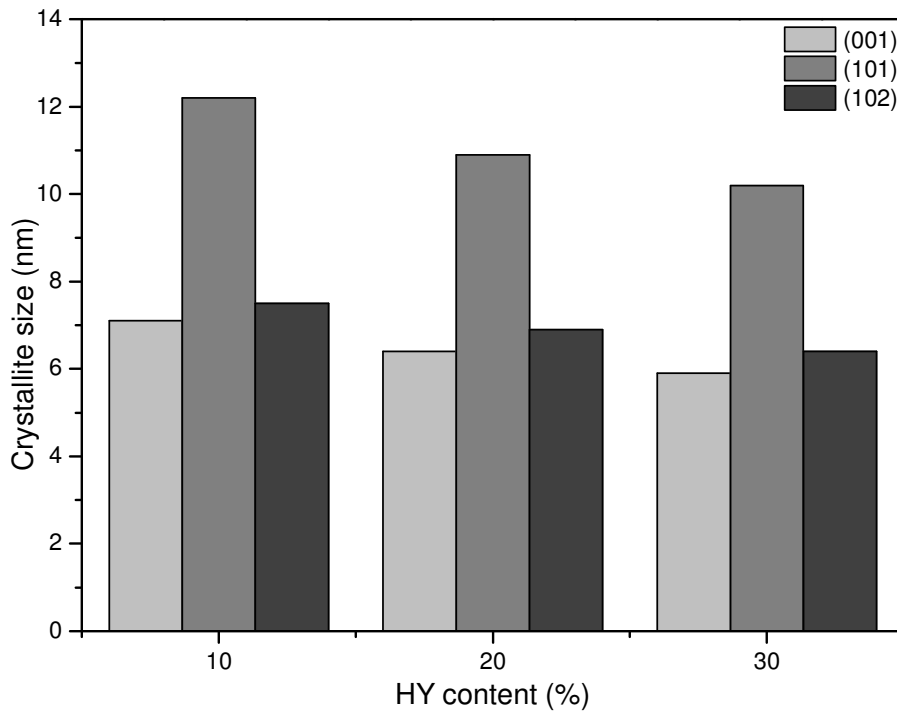


Figure 5.5: Graph showing the change in crystallite size perpendicular to the three Mg(OH)_2 planes with HY content after 7 days curing

It can be seen that increasing HY content causes a slight decrease in crystallite size for all three planes. Crystallite size is very similar in the (001) and (102) planes but slightly larger in the (101) plane.

The XRD spectra of the two 100 % MgO samples cured at different temperatures is shown in Figure 5.6. Identified peaks have been labelled so B is brucite [Mg(OH)_2], C is calcite [CaCO_3], M is magnesite [MgCO_3] and P is periclase [MgO]. As expected based on the hydration extent calculations shown in Figure 5.3, the sample cured at the lower temperature of 20 °C has more intense MgO peaks and less intense Mg(OH)_2 as less hydration has occurred. It is also noted that there is no difference in the sharpness or broadness of the formed Mg(OH)_2 peaks between the two samples. This indicates that increasing the curing temperature has no effect on reaction product crystallinity. As mentioned earlier, unfortunately no specific values can be assigned to crystallite size as the Scherrer Equation can only be applied to peaks which show significant broadening and those depicted in Figure 5.6 show no such behaviour.

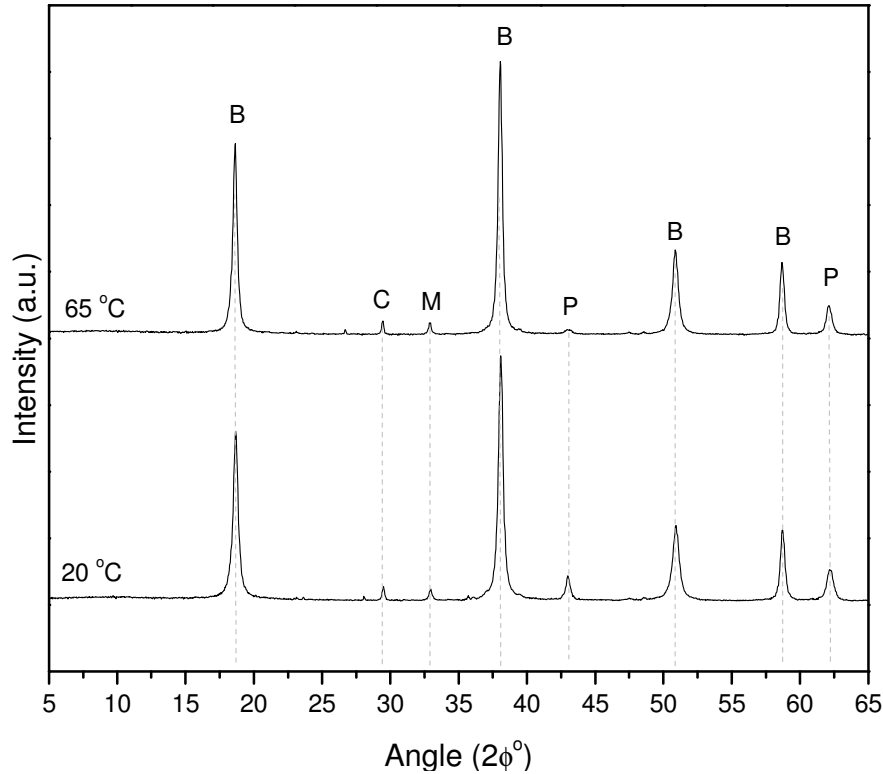


Figure 5.6: XRD spectra of the 100 % MgO samples cured for 7 days at different temperatures of 20 °C and 65 °C

XRD analysis has indicated that the only crystalline reaction product formed on hydration in MgO - HY cements is $\text{Mg}(\text{OH})_2$ and that the crystallites that make up this $\text{Mg}(\text{OH})_2$ are produced with some smaller dimensions in the presence of HY and when a higher percentage of HY is present.

SEM analysis

Images of the two raw material powders MgO and HY are shown in images (a) and (b) respectively. SEM images of a fracture surface from hydrated 100 % MgO, 10 % HY, 20 % HY and 30 % HY samples are shown in Figure 5.7 in images (d) to (f) respectively. The samples were all made with a 0.66 w/s ratio. The red box in image (e) highlights an area of microstructure of particular interest that will be discussed in the following paragraphs.

It is clear that the morphology of the HY containing samples is very different to both that of the MgO and HY raw materials in images (a) and (b) respectively, confirming that a new type of microstructure has been formed. It can be seen that the HY particles appear to be made up of many small particles of different shape.

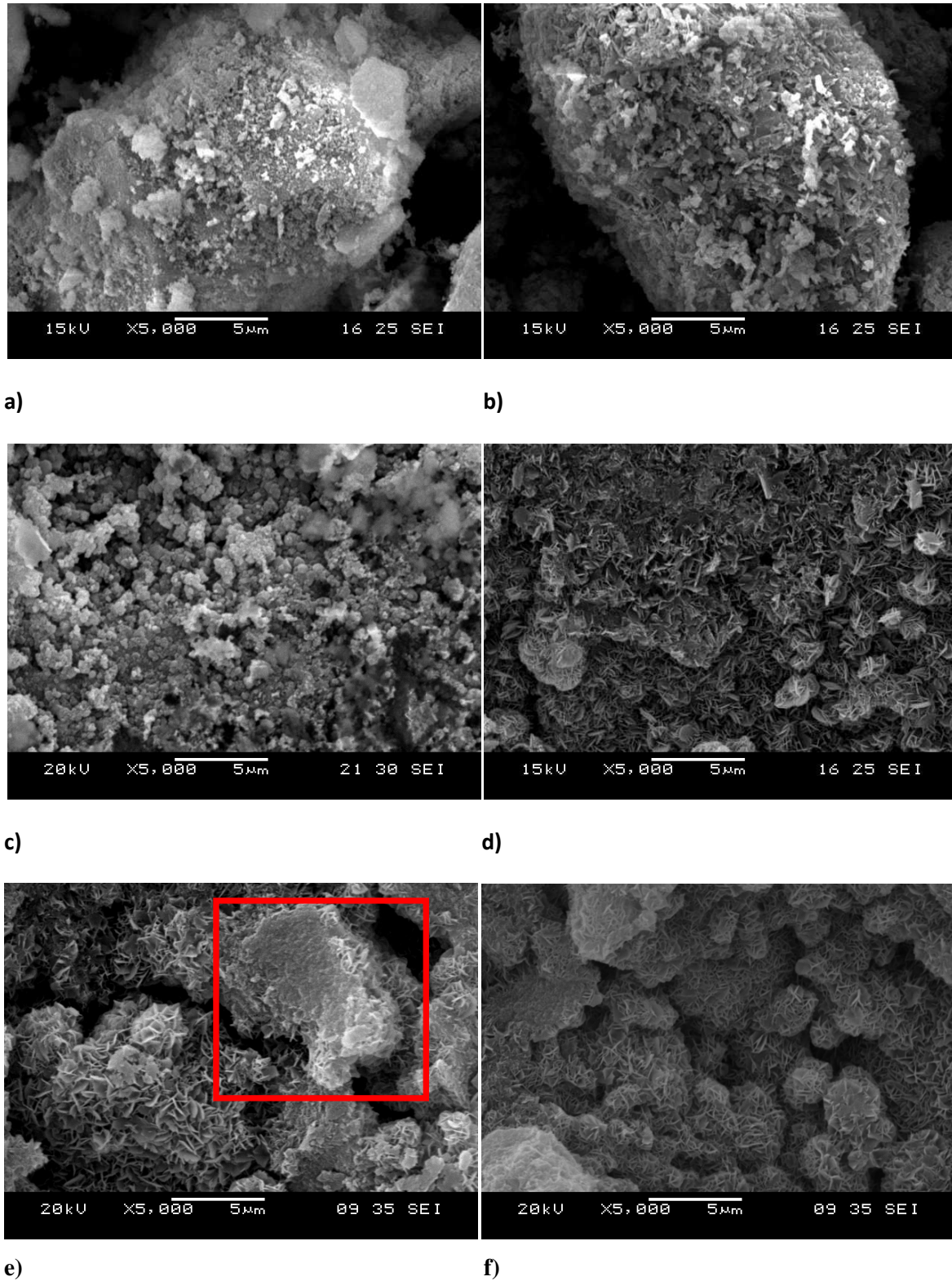


Figure 5.7: SEM images of fractured surfaces of hydrated a) raw material MgO; b) raw material HY; c) 100 % MgO; d) 10% HY – 90 % MgO; e) 20 % HY – 80 % MgO; and f) 30 % HY – 70 % MgO samples after 7 days of curing. Magnification in these images is x5000. The red box highlights an area of interest which is discussed in the main text.

It can be seen from the images that the reaction products of HY containing and non-HY containing hydrated samples have very different morphologies. Whilst the 100 % MgO sample consists of small, globular-like particles clumped together with no particular structure, the products formed in the presence of the HY (images (d), (e) and (f)) consist of interlinked particles of an entirely different shape. The particles are more prismatic, almost like three-dimensional ‘stars’, linking to other ‘stars’ or small platelets stuck together and radiating out in seemingly random directions. Unlike the 100 % MgO sample, it is difficult to differentiate between individual particles as it appears that they have become linked together, producing a sort of coating over other particles. Image (e) in particular suggests that the microstructure forms on the surface of one of the starting materials. In the red box in image (e) can be seen a slightly curved smoother surface, presumably the shell of a particle of a starting material, from the back of which the cross-linked system can be seen growing.

The cross-linked platelet morphology is seen in all samples containing HY regardless of the content of HY. HY content does not appear to make a significant difference to the morphology of the hydration product except that perhaps a more ordered and tightly packed system is observed with increasing HY content.

XRD and SEM results are in agreement, confirming that the crystallinity of $\text{Mg}(\text{OH})_2$ formed is different when HY is present during MgO hydration, with XRD indicating the presence of smaller $\text{Mg}(\text{OH})_2$ crystallites in certain planes and SEM revealing a microstructure of cross-linked $\text{Mg}(\text{OH})_2$ platelets.

5.3.4 DISCUSSION

Results reveal that for a set w/s ratio, whilst the addition of a small percentage of HY to MgO creates a significant increase in strength, increasing the HY content from 10 % HY – 90 % MgO to 30 % HY – 70 % MgO does not result in further compressive strength gain.

XRD reveals that the only crystalline reaction product formed when MgO – HY samples hydrate is $\text{Mg}(\text{OH})_2$. Some amount of unreacted MgO was observed. The major difference in crystalline phases between hydrated MgO – HY samples and 100 % MgO samples is the smaller size of $\text{Mg}(\text{OH})_2$ crystallites reflected in the broadening of certain $\text{Mg}(\text{OH})_2$ peaks in the presence of HY. Considering this and the fact that no other crystalline reaction product was identified, it seems likely that the strength of samples is not based on a reaction between MgO and HY, but rather on the cross-linked $\text{Mg}(\text{OH})_2$ microstructure, which was observed in

SEM images of hydrated MgO – HY samples. This microstructure was not observed when HY was absent.

Images of MgO – HY samples also indicate that the cross-linked platelets are growing on the surface of the starting materials. If the surfaces on which they were growing were HY particles, then this would explain hydration studies which revealed that the presence of HY increases hydration rate. Also, increasing HY content may further increase hydration rate. In the absence of HY, i.e. for the hydration of pure MgO systems, there are no free surfaces for Mg(OH)_2 precipitation so Mg(OH)_2 remains on MgO surfaces for longer, retarding hydration (Feitknecht and Braun, 1967). HY particles may provide surfaces for Mg(OH)_2 , initially formed on the surface of MgO particles, to precipitate on, revealing fresh MgO surfaces allowing faster Mg(OH)_2 formation. This is in agreement with the proposed mechanism of MgO – HY hydration described in 2.5.3 (Vlasopoulos, 2007).

The mechanism also suggests that an increase in hydration rate is responsible for the formation of smaller Mg(OH)_2 crystallites. This is because it is proposed that HY particles act as nucleation sites for the formation of Mg(OH)_2 particles, freeing up surfaces on the MgO particle for further dissolution, thus increasing hydration rate, leading to increased solution temperature. This increased temperature, as explained in 2.5.3 essentially causes faster nucleation and crystallisation of Mg(OH)_2 , leading to smaller crystallites (Vlasopoulos, 2007). If this were true, then it seems logical that increasing the temperature of the solution of 100 % MgO pastes, would have a similar effect on crystallisation speed and thus crystallite size, i.e. significantly smaller crystallites would be formed. However, results in this section have shown that although increasing solution temperature results in an increased rate of hydration, XRD spectra show no broadening of Mg(OH)_2 peaks, which is seen when MgO – HY samples hydrate as a result of smaller crystallite formation, and SEM did not reveal the cross-linked microstructure of hydrated MgO – HY samples. Therefore, it is suggested that the increase in hydration rate as a result of temperature increase is not responsible for the changed crystallite size, microstructure and resulting strength increase.

It is also implied, from SEM images and hydration extent values, that increasing HY content produces a denser microstructure and also increases MgO hydration rate. If this is so, then it would be reasonable to expect that increasing HY content could also result in stronger samples due to closer contact between particles and higher Mg(OH)_2 contents at early time periods. However, this was not observed in the compressive strength results. The reason for this is probably related to the problem that the addition and increase of HY in a sample

increases water demand. This higher water demand of HY may be related to the fact that SEM imaging showed HY particles appear to consist of small particles packed together. The many void spaces in between the particles created areas into which water can become trapped and unavailable for dispersion of the main particles (Jiang et al., 1993, Nehdi, 2000). Therefore, higher HY contents require more water. As the HY content of a sample is increased, MgO content is decreased meaning that there is less MgO to hydrate to $\text{Mg}(\text{OH})_2$ and therefore increased excess water is present. Any benefits of having more HY in the system due to denser cross-linked particles will be negated to some extent by the excess water and porosity this creates within other parts of the microstructure. This makes it difficult to determine the optimum HY/MgO ratio for the system. For this reason, supported by the fact that increasing HY content had little effect on sample strength indicating that any benefits of adding more HY to the system do not outweigh excess water effects, it has been decided that a 10 % HY – 90 % MgO mix is the optimum.

5.3.5 CONCLUSIONS

- MgO hydrated in the presence of HY, as in the MgO – HY system, results in strength giving samples of a cross-linked platelet morphology of $\text{Mg}(\text{OH})_2$, resulting from the formation of small crystallites on the surface of HY particles, which is responsible for achieved strengths;
- A major concern regarding the MgO - HY cement system is the high water demand when compared to that required for CEM I samples. This is problematic as it does not allow a wide range of HY/MgO ratios to be investigated and can limit the maximum achievable strengths;
- For a set w/s ratio, increasing the HY content from 10 % to 30 % has little effect upon 7 and 28 day compressive strength and considering increasing HY content requires an increase in water demand, a 10 % HY – 90 % MgO system was selected as the optimum binder ratio;
- The addition of HY and an increase in HY content in an MgO – HY system of up to 30 % HY content results in an increased hydration rate;
- The observed change in microstructure and strength properties is not likely to be simply due to this increase in hydration rate as the proposed MgO – HY mechanism of Vlasopoulos in section 2.5.3 suggests;

- Some other factor may be responsible for the resulting change in microstructure and resulting compressive strength of MgO – HY systems. The selected MgO/HY ratio system of 10 % HY – 90% MgO will be used as a basis in which to further explore the mechanism behind this novel system in 5.4 along with the basic properties of this ‘optimised’ system.

5.4 STUDY OF THE 10 % HY – 90 % MgO SYSTEM

In this section, further characteristics of the optimised 10 % HY – 90 % MgO system are reported. In addition, supplementary analysis of reaction products and system chemistry in order to further understand the strength giving mechanism is presented.

5.4.1 MATERIALS

B30 MgO and Calmag HY were used in this section as the optimum 10 % HY – 90 % MgO had been selected based on results (from 5.3) of samples made with these materials.

5.4.2 METHODS

Setting time

A paste sample of 10 % HY – 90 % MgO at 0.62 w/s ratio (the minimum to allow moulding) was mixed according to 4.3.1 and setting time measurements taken using a Vicat needle in accordance with the standardised method of 4.4.3.

Heat of hydration

Heat of hydration was measured via isothermal calorimetry (4.5.3) for paste samples of 10 % HY – 90 % MgO sample made with w/s ratio of 0.62 and of 100 % MgO made with w/s ratio of 0.6. These w/s ratios were chosen as they were the minimum possible to make a mouldable sample. Samples were mixed according to the method in 4.3.1.

Compressive strength

In order to observe the development of strength over time, samples of 10 % HY – 90 % MgO were made using the method stated in 4.3.1 and six bars tested for compressive strength after various curing time periods. As mentioned, this content of HY was chosen based on results of 5.3. The minimum w/s ratio necessary to make a mouldable paste for this HY content was used. Table 5-3 summarises the samples made and compressive strength testing times. Compressive strength tests were carried out on all moulded samples via the method described in 3.3.4.

Table 5-3: Samples made in order to observe the strength development over time of the optimised paste samples cured in water.

HY and MgO content in dry mix (wt. %)		w/s ratio	Curing time (days)
HY	MgO		
10	90	0.62	3, 7, 10, 14, 28, 56

Compressive strength tests were carried out on moulded samples via the method described in 3.3.4. After testing, crushed samples were stored in acetone for 10 days to prevent further hydration and then dried at 60 °C to constant mass. Dried samples were then used in further analysis of the 10 % HY – 90 % MgO system.

Further analysis

Dried samples were crushed and ground to a fine powder using a pestle and mortar for XRD analysis. Small fractured pieces were used for SEM analysis.

According to the XRD results of 5.3, no other product, apart from $\text{Mg}(\text{OH})_2$ is formed during hydration reactions. However, XRD can only be used to analyse crystalline reaction products (Langford and Louer, 1996). If amorphous reaction products have been formed that may contribute to the strength of HY – MgO systems, they would probably not have been detected by XRD amongst the other crystalline materials and may be unobservable in SEM. For this reason, powdered samples were also analysed by FTIR and Raman spectroscopy (4.6.3). Samples analysed by FTIR were 100 % MgO hydrated fully to $\text{Mg}(\text{OH})_2$, 30 % HY – 70 % MgO hydrated for 7 days and HY. A control sample containing 23 % HY – 77 % $\text{Mg}(\text{OH})_2$ was also tested. This sample was made as this is the ratio of HY to MgO that would exist after a 30 % HY – 70 % MgO sample had fully hydrated, only forming $\text{Mg}(\text{OH})_2$ and no other reaction product. This sample was not hydrated but merely dry mixed, the $\text{Mg}(\text{OH})_2$ having previously been produced from B30 MgO.

Finally, the pH of 10 % HY – 90 % MgO and 100 % MgO powder mixes was also measured by the method described in 4.5.1.

5.4.3 RESULTS

Setting time

Figure 5.8 shows the setting time of the 10 % HY – 90 % MgO sample. It accounts for the time spent mixing and filling the Vicat mould and shows that the start of set occurs at 43 ± 3 minutes and final setting time at 69 ± 3 minutes.

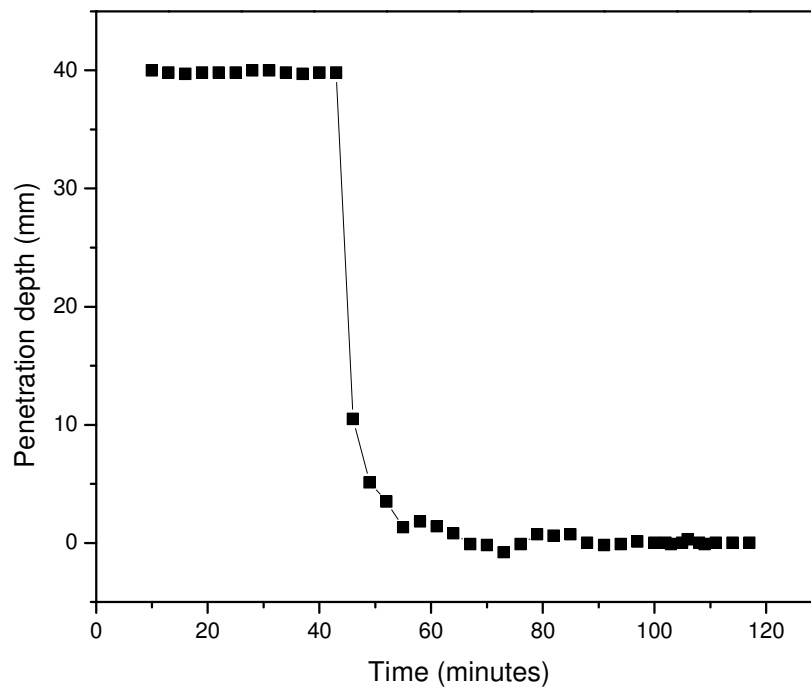


Figure 5.8: Graph showing penetration depth of the Vicat needle with time for the 10 % HY - 90 % MgO sample at 0.62 w/s.

Heat of hydration

Figure 5.9 shows the results of the isothermal calorimetry tests carried out on 100 % MgO and 10 % HY – 90 % MgO paste samples.

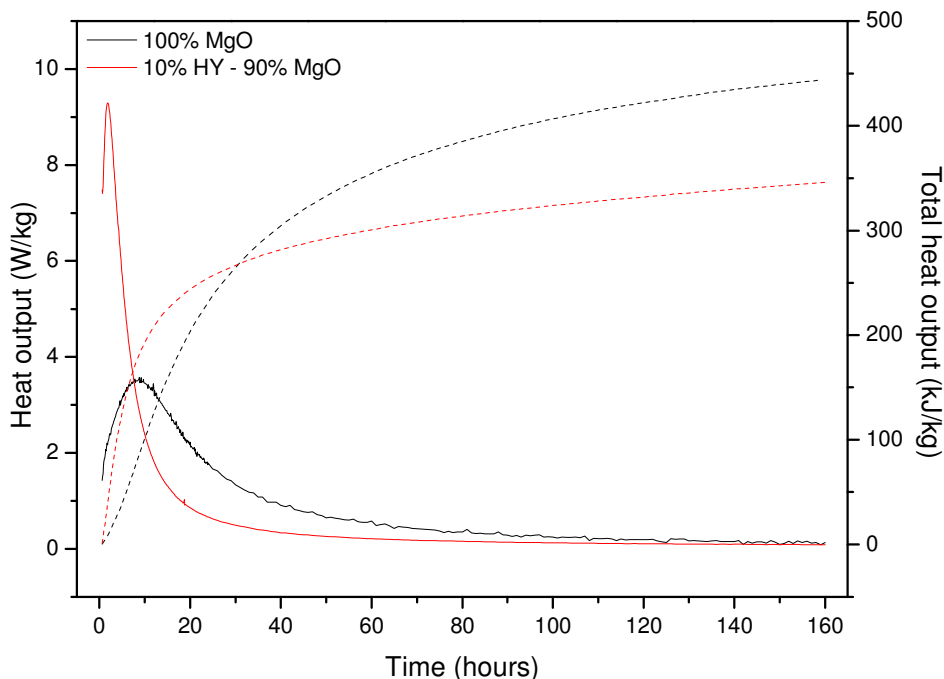


Figure 5.9: Graph of isothermal calorimetry results for the 100 % MgO and a 10% HY – 90 % MgO paste samples. Dotted lines represent total heat output.

It should be noted that since materials were prepared external to the calorimeter, any initial exothermic reaction which occurred during wetting and mixing could not be measured. This period took around 10 minutes.

The graph shows a sharper and more intense peak for the 10 % HY – 90 % MgO paste than for the 100 % MgO paste as maximum heat output occurs significantly earlier at 1.8 ± 0.1 hours (108 ± 6 minutes) than that for the 100 % MgO sample, at 8.8 hours ± 0.1 hours (528 ± 6 minutes). Taking into consideration preparation time outside of the calorimeter, this equates to ~ 118 and 538 minutes. Heat output at these times is also higher for the HY containing sample reaching ~ 9.2 W/kg compared to ~ 5.5 W/kg emitted by the 100 % MgO paste. However, total heat output for the HY containing pastes measured at 160 hours, the end of the measurement period, is lower. This is assumed to be because a 10 % HY – 90 % MgO sample contains less material (i.e. MgO) that can hydrate to produce heat than the 100 % MgO sample. Both curves of total heat output have not completely levelled off suggesting that further hydration beyond the measurement period is likely. Also, considering that the

total heat output of the 10 % HY – 90 % MgO samples is expected to be ~ 10 % lower than that of the 100 % MgO sample, but is at the end of measuring, is ~ 20 % lower, this supports the fact that hydration has not completed by the end of the measurement period.

Strength development over time

Figure 5.10 shows the strength development of samples made from 10 % HY – 90 % MgO mixes over time. This ratio of HY to MgO was considered to be the optimum based on compressive strength data and water demand.

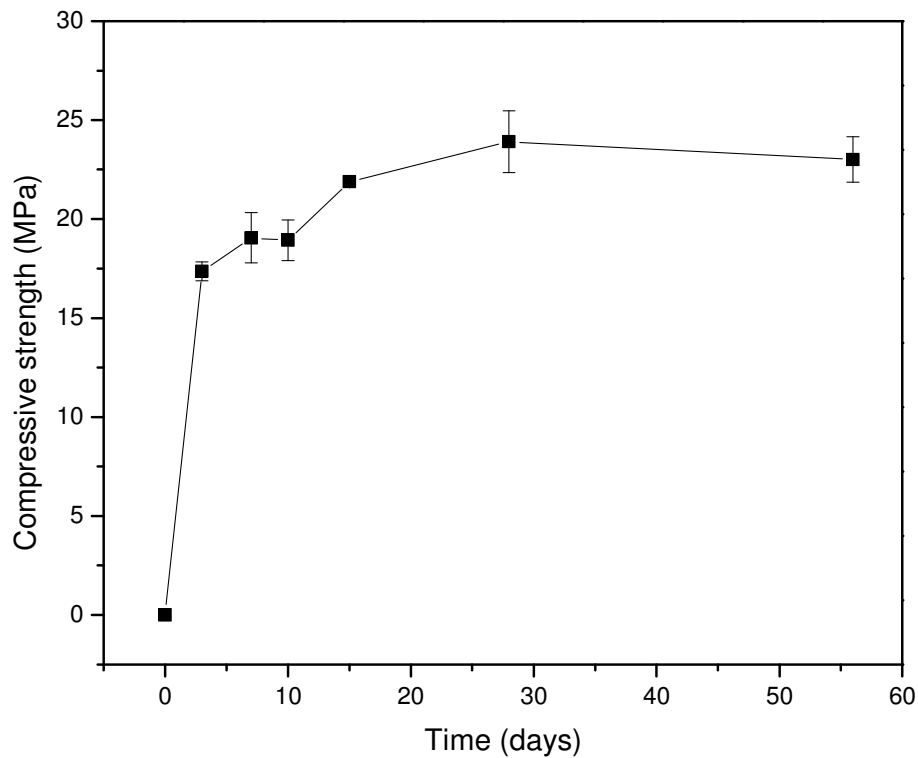


Figure 5.10: Graph showing the development of compressive strength over time for hydrated 10 % HY – 90 % MgO samples made with a w/s ratio of 0.62.

The largest increase in compressive strength occurs within the first three days. It can be seen that compressive strength then continues to increase with time up to 28 days, although at a slower rate, after which it levels off up to 56 days, with the highest strength of approximately 23 MPa achieved after 28 days.

Analysis of crystalline reaction products

Figure 5.11 shows the XRD spectra of the 10 % HY – 90 % MgO samples different curing periods. B is brucite [$\text{Mg}(\text{OH})_2$], C is calcite [CaCO_3], H is hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$], M is magnesite [MgCO_3] and P is periclase [MgO].

As in 5.4.1, $\text{Mg}(\text{OH})_2$ is the only reaction product, with small amounts of unreacted MgO present along with HY (some peaks of which are unobservable in the figure) and minor amounts of CaCO_3 and MgCO_3 . The only difference between the spectra is that the intensity $\text{Mg}(\text{OH})_2$ peaks increase with time and MgO peaks decrease as MgO hydrates. However, MgO has not fully hydrated by the end of the testing period, with small MgO peaks observed in the spectrum at 56 days. No change in $\text{Mg}(\text{OH})_2$ peak broadness was observed over time. For the 3 day sample, the $\text{Mg}(\text{OH})_2$ peak centred at $18.7^\circ 2\theta$ for the other time periods, appears shifted to the higher angle of $19.0^\circ 2\theta$.

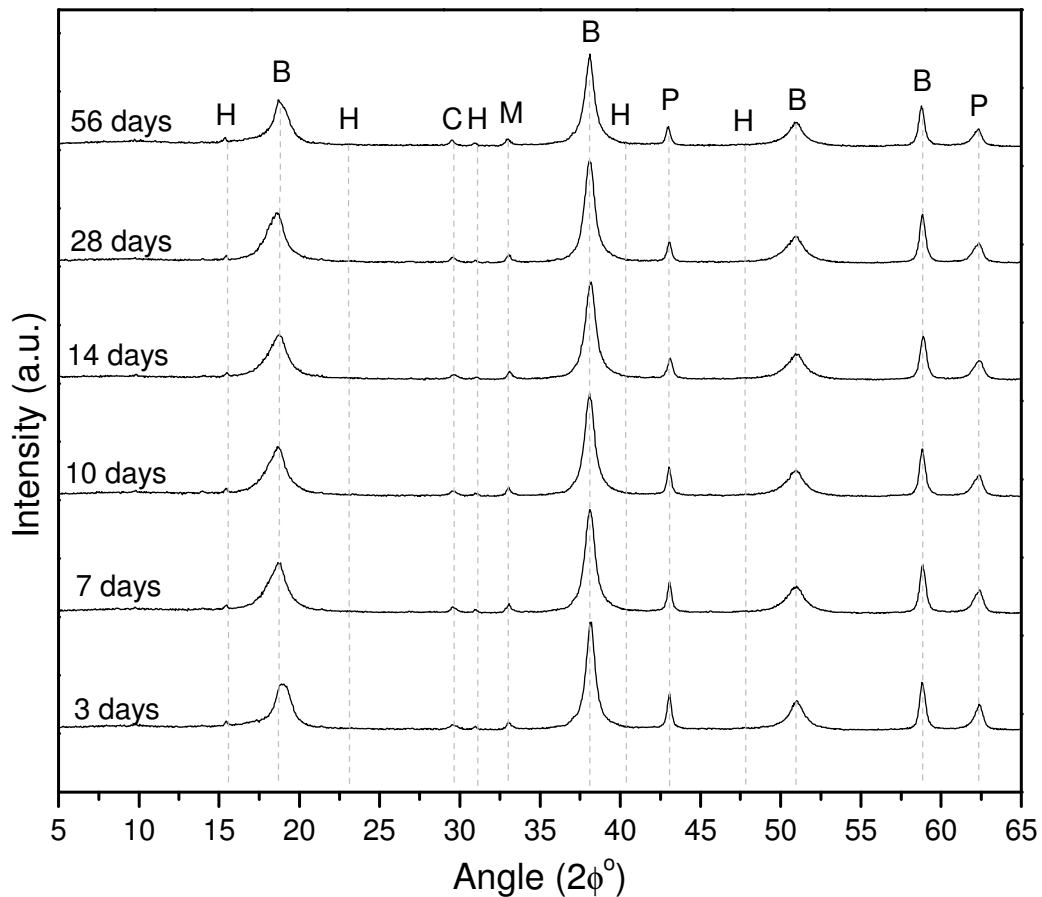


Figure 5.11: XRD spectra of the 10 % HY - 90 % MgO made using a 0.64 w/s ratio cured time periods of 3, 7, 10, 14, 28 and 56 days.

SEM analysis

Figure 5.12 contains SEM images of 10 % HY - 90 % MgO samples after 7 and 28 days curing, labelled (a) to (b), and (c) to (d) respectively. Although both samples display the cross-linked platelet microstructure observed previously in 5.3.2, in many areas of the sample, crystal structures observed at 28 days appear to have grown approximately 5 times in size from those observed at 7 days.

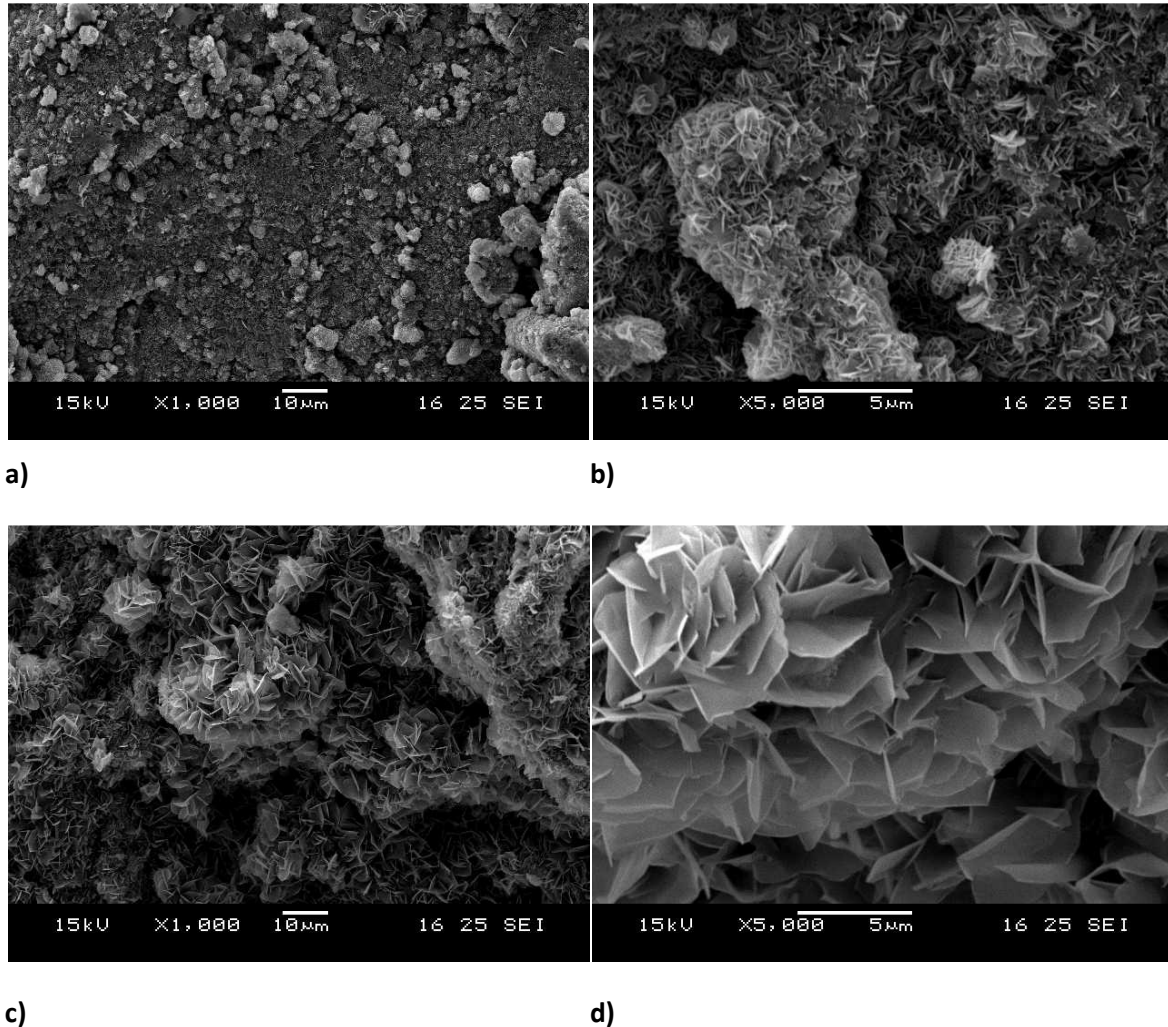


Figure 5.12: SEM images of 10 % HY – 90 % MgO samples after 7 days; (a) and (b) and after 28 days; (c) and (d), at x1000 and x5000 magnification.

Measurement of pH

Figure 5.13 shows the pH development over time up to 28 days for a 100 % MgO slurry and a 10 % HY – 90 % MgO slurry.

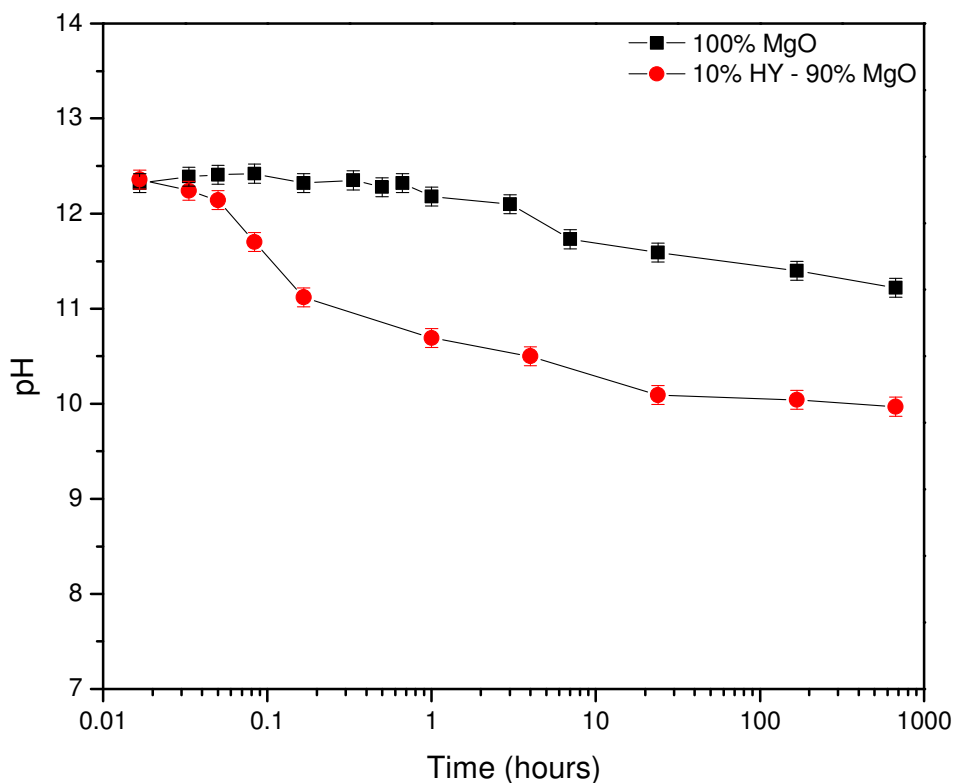


Figure 5.13: Graph showing the pH development over time of slurries containing 100% MgO and 10% HY - 90% MgO mixes. The final point on the graph is 28 days.

The first point on the graph is the pH value measured for both slurries at 1 minute. It can be seen that for both samples the pH immediately rises to around 12.4 on mixing with water, as a result of hydration of MgO, and then decreases. For the slurry containing only MgO, the pH remains high, decreasing slowly from 12.4 to 11.5 after 7 days. The sample containing HY however, displays a rapid decrease in pH to around pH 11 within 10 minutes. The pH then continues to decrease, albeit at a slower rate, to a pH of approximately 10 after 7 days where it appears to level off. A small proportion of pH decrease for both slurries is accredited to CO₂ dissolving in the solution although the slurries were kept in sealed containers between measurements so this should be minimal.

FTIR

FTIR was used to analyse several samples in order to determine if additional amorphous phases that could not be detected in XRD were present in the reaction products. It has been found by other researchers that when HY is present in minor amounts in a mix, corresponding

bands may be too weak and are thus unobservable (Bruni et al., 1998). Therefore, a sample of hydrated 30 % HY – 70 % MgO was analysed, as opposed to the optimum 10 % HY – 90 % MgO sample, as if additional reaction products apart from $\text{Mg}(\text{OH})_2$ had formed, it would be easier to detect these when higher amounts of HY were present.

Figure 5.14 shows FTIR spectra of pure HY, and a 30 % HY – 70 % MgO sample and a 100% MgO sample, hydrated for 28 days, and a dry mix of HY and $\text{Mg}(\text{OH})_2$ made from the sample MgO made-up in proportions that would mimic 30% HY – 70% MgO sample that had fully hydrated with the only reaction product being $\text{Mg}(\text{OH})_2$.

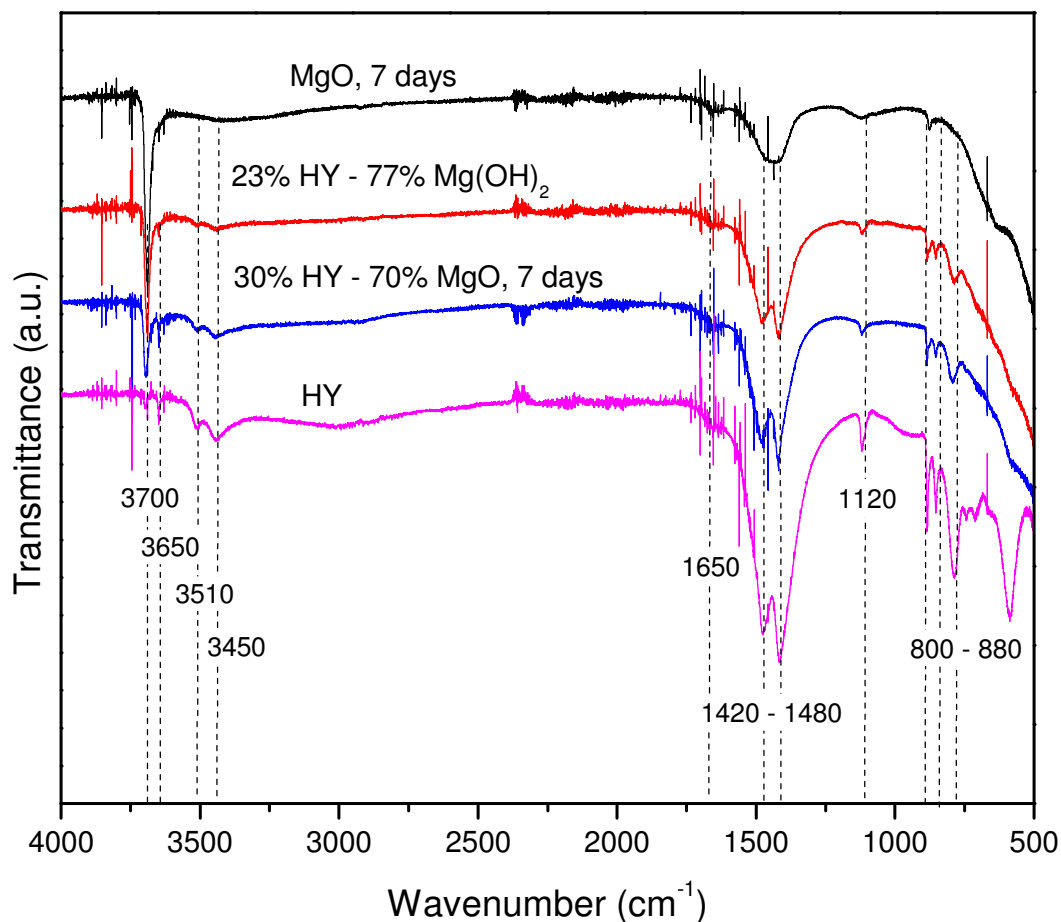


Figure 5.14: FTIR spectra of hydrated MgO after 28 days, a dry mix of 23% HY - 77% $\text{Mg}(\text{OH})_2$, 30% HY - 70% MgO hydrated 28 days and the raw material HY, from top to bottom. The peaks of interest are indicated with dotted lines and their wavenumber labelled.

Previous work by other researchers has characterised IR bands associated with HY and with $\text{Mg}(\text{OH})_2$. Bands observed in the FTIR spectra in Figure 5.14 and the origins of these bands

according to these researchers are summarised in Table 5-4. All of the identified bands are seen in the spectra for the three samples containing HY except for that due to O-H bonds in brucite located at 3700 cm^{-1} which are understandably not observed in the pure HY sample. Most of the bands also appear, although are weaker, in the hydrated MgO sample although those arising due to HY water of crystallisation at 3450 and 3510 cm^{-1} are absent. This is probably due to the MgO containing a small amount of non-hydrated carbonate, probably magnesite, a fact also observed in FTIR studies of brucite (Frost and Kloprogge, 1999). Previous research has shown that for pure magnesite, a single band is observed between 1478 and 1450 cm^{-1} whilst the presence of two bands, as seen for HY containing samples here, indicates the presence of a two different types of carbonate ion, possibly in the form of bicarbonate (Bruni et al., 1998, Choudhari et al., 1972, Sawada et al., 1979).

It is not known what the band in the HY spectrum at $\sim 600\text{ cm}^{-1}$ is, although this band has been observed by other researchers studying HY, but not identified (Botha and Strydom, 2003).

Table 5-4: Summary of the bands detected and their origins from the FTIR spectra seen in Figure 5.14.

Band position (cm ⁻¹)	Origin	Movement	Reference
~ 600	Unknown	Unknown	Observed by Botha and Strydom, 2003 but unidentified (Botha and Strydom, 2003)
800 - 880	CO ₃ ²⁻ from HY	Bending vibrations	(Choudhari et al., 1972, Han et al., 2011)
1120	CO ₃ ²⁻ from HY	V ₁ symmetric stretching vibration	(Choudhari et al., 1972, Han et al., 2011)
1420 - 1480	CO ₃ ²⁻ / HCO ₃ ⁻ from HY	V ₃ asymmetric stretching vibration	(Choudhari et al., 1972, Sawada et al., 1979, Han et al., 2011)
1650 (shoulder)	H ₂ O	Bending vibration	(Raade, 1970, White, 1971)
3450, 3510	HY water of crystallisation		(Choudhari et al., 1972, Han et al., 2011)
3650	Mg(OH) ₂ from HY	Free O-H vibration	(Choudhari et al., 1972, Lanas and Alvarez, 2004)
3700	Mg(OH) ₂	Antisymmetrical O-H stretching vibration of lattice hydroxide	(Choudhari et al., 1972, Frost and Klopogge, 1999)

There appears to be little or no difference between the FTIR spectra of the 30 % HY – 70 % MgO hydrated sample and the dry mixed 23 % HY – 77 % MgO sample, with every band corresponding to those seen in the pure HY spectrum apart from the 3700 cm⁻¹ band which is associated with O-H stretching vibration from brucite Mg(OH)₂. It is possible that there may be small bands in the region of 2350 cm⁻¹. However, the background noise is possibly too dominant and could overlay these signals. These bands at ~ 2350 cm⁻¹ s are more prominent

and numerous in the hydrated 30% HY – 70 % MgO sample than in the 23 % HY – 77 % MgO dry mix or the pure HY sample and they are also present in the hydrated MgO sample. A presence and absence of a peak at 2346 cm^{-1} (not marked in the spectra) was observed in a study of the dehydration and rehydration of HY respectively and authors assigned this to either a CO_2 inclusion or a terminal CO_2 , corresponding to the ν_3 fundamental of CO_2 (Schrader, 1989, Botha and Strydom, 2003). It is not known if this is significant and indicates the presence of a different material or if it is an artefact of dehydration that may have occurred as both the 100 % MgO and 30 % HY – 70 % MgO samples were dried before analysis.

Raman spectroscopy

Raman spectroscopy was also carried out to further investigate the vibrational modes of the hydrated MgO - HY system in order to help identify any new amorphous reaction products not ‘visible’ using FT-IR. Figure 5.15 shows the Raman spectra of HY powder, a hydrated 30 % HY – 70 % MgO sample, a hydrated 10 % HY – 90 % MgO sample and a hydrated 100% MgO sample. All hydrated samples had been cured for 28 days.

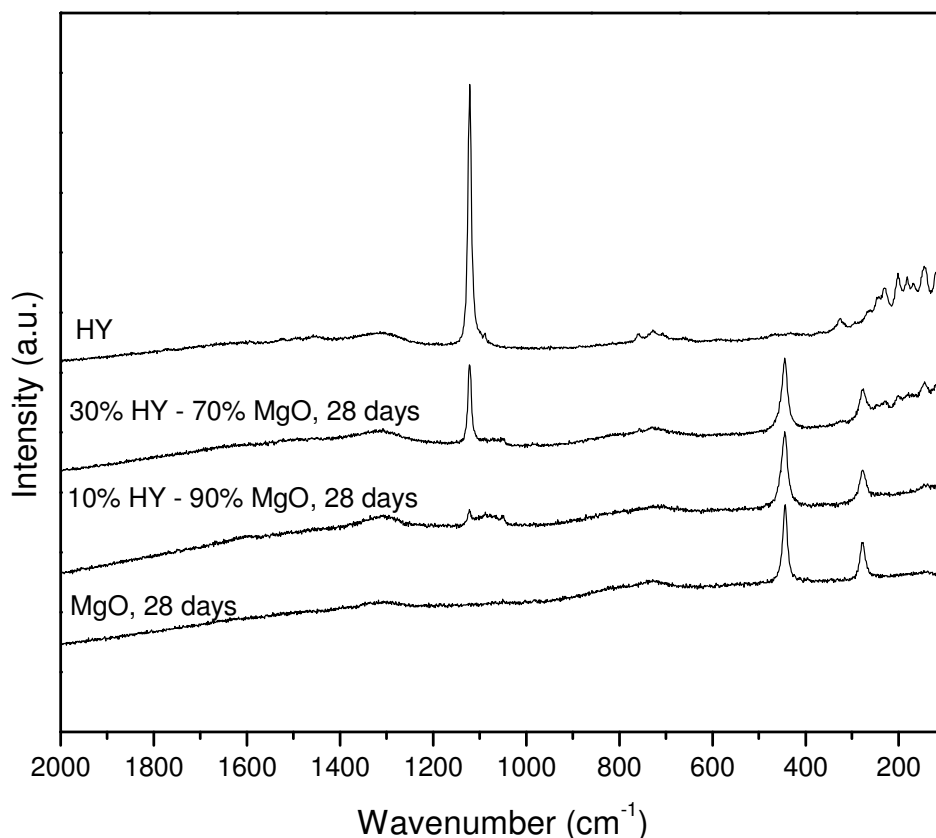


Figure 5.15: Raman spectra of HY raw material, 30 % HY – 70 % MgO hydrated 28 days, 10 % HY – 90 % MgO hydrated 28 days and MgO hydrated 28 days, from top to bottom.

The peaks at 280 cm^{-1} and 440 cm^{-1} observed in the hydrated MgO sample also appear in other spectra except for the spectrum of HY. These two peaks are therefore due to bonding in $\text{Mg}(\text{OH})_2$. Previous research into magnesium carbonates characterised bands in the $500 - 100\text{ cm}^{-1}$ region as arising from motions involving the entire lattice cell, whilst those between $1500 - 500\text{ cm}^{-1}$ are due to the internal motion of the molecular carbonate ion, in particular, the symmetrical stretching mode ν_1 of the CO_3^{2-} ion, between $1500 - 1000\text{ cm}^{-1}$ (Edwards et al., 2005, Scheetz and White, 1977). According to Edwards et al. (2005), the broad band at

around 1300 cm^{-1} is most likely due to the asymmetric stretching ν_3 band of CO_3^{2-} and the low intensity band at 700 cm^{-1} arises from the antisymmetric bending vibration ν_4 (Edwards et al., 2005, Hopkinson et al., 2008).

The work by Edwards studied the Raman spectral signatures of several calcium and magnesium carbonates (Edwards et al., 2005). They showed that the position of the main band, the stretching ν_1 , changes slightly between carbonates as seen in Figure 5.16.

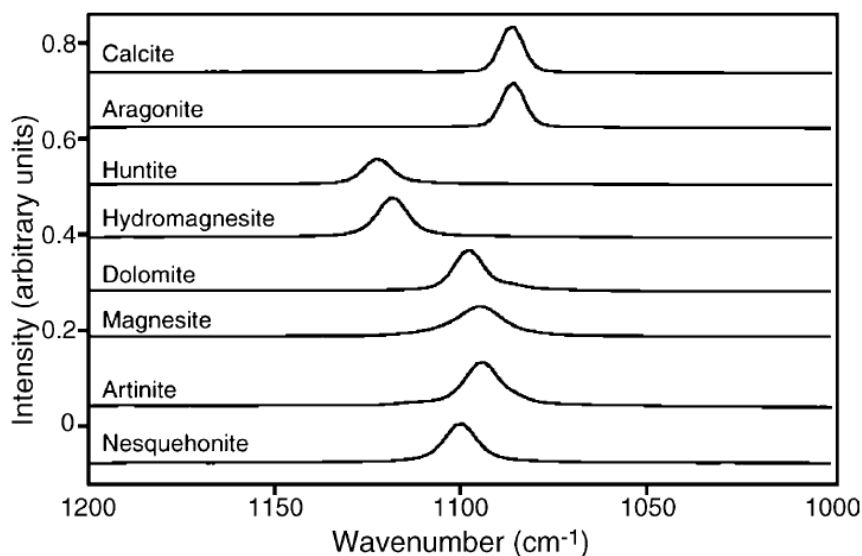


Figure 5.16: Magnified Raman spectra in the 1200 - 1000 cm^{-1} region for different types of hydrated magnesium and calcium carbonates (Edwards et al., 2005)

When examining at the spectra of all samples containing HY in Figure 5.15, it can be seen that the main stretching ν_1 band of HY is centred at 1120 cm^{-1} which agrees with the findings of Edwards et al., in Figure 5.16. However, for both the 10 % HY – 90 % MgO and 30 % HY – 70 % MgO hydrated samples, an additional low intensity broad band or shoulder is seen next to this HY peak between $1120 - 1050\text{ cm}^{-1}$. This peak is not seen in the hydrated MgO sample. The origin of this shoulder is not known, although perhaps it is due to the presence of a very small amount of other carbonate types that have their main stretching ν_1 peaks in a similar region, as shown in Figure 5.16. If so, this other carbonate type must arise from the hydration of the HY – MgO sample as it does not appear to be present in the 100 % HY sample analysed in this section.

Other researchers state that whilst this region can be used to differentiate between magnesium and calcium carbonates, differences are not large enough to identify specific members within

either group (Edwards et al., 2005). Therefore it is not possible to characterise the type of carbonate that causes the broad shoulder peak observed at $1120 - 1050 \text{ cm}^{-1}$. Considering the close proximity to the HY peak at $1120 - 1050 \text{ cm}^{-1}$ and the broadness and low intensity, it may not be due to another carbonate but perhaps to a different form or crystallinity of HY. This shifting and broadening of Raman peaks in various materials has been observed by other researchers (Taylor and Zograf, 1998, Puceat et al., 2004)

5.4.4 DISCUSSION

Results showed that the optimised 10 % HY – 90 % MgO sample made with the minimum water ratio possible starts to set at approximately 40 minutes and final set is achieved within the following 26 minutes.

The higher and earlier maximum heat output, measured by isothermal calorimetry, of 10 % HY – 90 % MgO paste compared to the 100 % MgO paste also confirms that the presence of HY increases hydration rate. This is in agreement with results of the hydration extent estimations made in 5.3. The fact that total heat output by the end of the calorimetry measurement is, as expected, higher for the 100 % MgO sample than for the 10 % HY – 90 % MgO sample, suggests that the hydration of $\text{Mg}(\text{OH})_2$ is the only reaction occurring. XRD of the optimised 10 % HY – 90 % MgO system over time supports this, showing that the only crystalline reaction product even in the oldest sample at 56 days is $\text{Mg}(\text{OH})_2$.

Observations of compressive strength development in the optimised 10 % HY – 90 % MgO system over time show that maximum strength of ~ 24 MPa is achieved by 28 days. XRD showed no changes over time other than an increase in $\text{Mg}(\text{OH})_2$ peak intensity and decrease in MgO peak intensity. This suggests that the increase in $\text{Mg}(\text{OH})_2$ content as remaining MgO continues to hydrate is responsible for strength development over time.

SEM images of optimised samples showed significantly larger interconnected platelets at 28 days than at 7 days. This shows that the platelets grow over time as MgO continues to hydrate, filling spaces previously occupied by water. This change in size is likely to be responsible for strength development associated with increased $\text{Mg}(\text{OH})_2$ content.

For the 100 % MgO sample, the pH lies between 11.5 and 12 depending on the time. It should be noted that this is higher than the expected value of 10.5 which is widely accepted as the pH of MgO, and is probably due to the small amount of alkaline CaO known to be present in the raw material B30 MgO (Shand, 2006). pH measurements over time also

showed that the presence of HY lowers the pH of MgO to just over pH 10. This is probably due to the acidic CO_3^{2-} and HCO_3^- ions released from the HY. FTIR results indicated that presence of both types of carbonate ions in MgO – HY and HY samples.

Results of FTIR suggested the possibility of the presence of another type of material in the reaction products. Raman studies showed the presence of a broad, low intensity shoulder next the major fingerprint peak, the ν_1 stretching band, of HY, in hydrated MgO – HY samples. This shoulder was not observed in the spectra of the HY or $\text{Mg}(\text{OH})_2$. It has been postulated that the shoulder indicates the presence of a small quantity of much less crystalline HY.

5.4.5 CONCLUSIONS

- The initial strength of the MgO – HY system is due to the cross-linked platelet microstructure formed which creates a denser, more connected network;
- The increase in strength of the system over time is probably due to growth of the platelets as MgO continues to hydrate and further $\text{Mg}(\text{OH})_2$ is formed, filling spaces and creating a better interface between particles, which requires the application of more force to achieve failure;
- In addition to the $\text{Mg}(\text{OH})_2$ formed, the possible presence of a type of very low crystallinity HY was detected;
- The highest strength achieved for the optimised 10 % HY – 90 % B30 system at lowest mouldable w/s ratio, was ~ 24 MPa achieved at 28 days;
- Once achieved, this strength remained constant over time;
- Setting time of the optimised system was fast with final setting completed within ~ 70 minutes.

5.5 PARTICLE SIZE EFFECTS

Particle size and distribution can have a huge effect on cement properties including water demand, particle packing, durability and strength (Lea, 1998, Kuhlmann et al., 1985). For example finer cement particles can result in higher early age strengths (Bentz et al., 1999, Celik, 2009, Binici et al., 2007). In this section, the effect of changing the average particle size on a MgO – HY has been investigated. This was investigated in order to determine whether the size of MgO particles or of the HY particles had more influence on the resulting compressive strength of samples and reaction product microstructure. Knowing this could allow further optimisation and the production of stronger samples.

5.5.1 MATERIALS

Magox MgO was used as it was available in large quantities and has similar purity to the B30 MgO used in previous sections. Equally important, it had a wide particle size distribution and could thus be ground to three different average particle sizes in order to allow the effect of MgO particle size to be investigated.

Hydromagnesite (IC HY) was used in this work. This is not a commercial HY but was produced in the lab from B30 MgO and Calmag HY to allow alteration of particle size distribution. The method by which the IC HY was synthesised along with the treatments used to produce the powders of different average particle size from the Magox MgO is described in the following 5.5.2.

Particle size distribution

The particle size distributions (PSDs) as measured according to 4.4.1, of the three powders of different average particle size for both the MgO and HY materials used are shown in Figure 5.17. The average particle sizes of each PSD are shown. It can be seen that for both materials, the milling or grinding treatment they underwent as described in 5.5.2, was effective, resulting in a shift in PSD towards lower particle sizes. The bimodal PSDs of the MgO (120 μm) changed into a more unimodal form after 5 minutes of milling. Milling of samples up to 40 minutes caused this unimodal PSD to shift towards lower particle sizes.

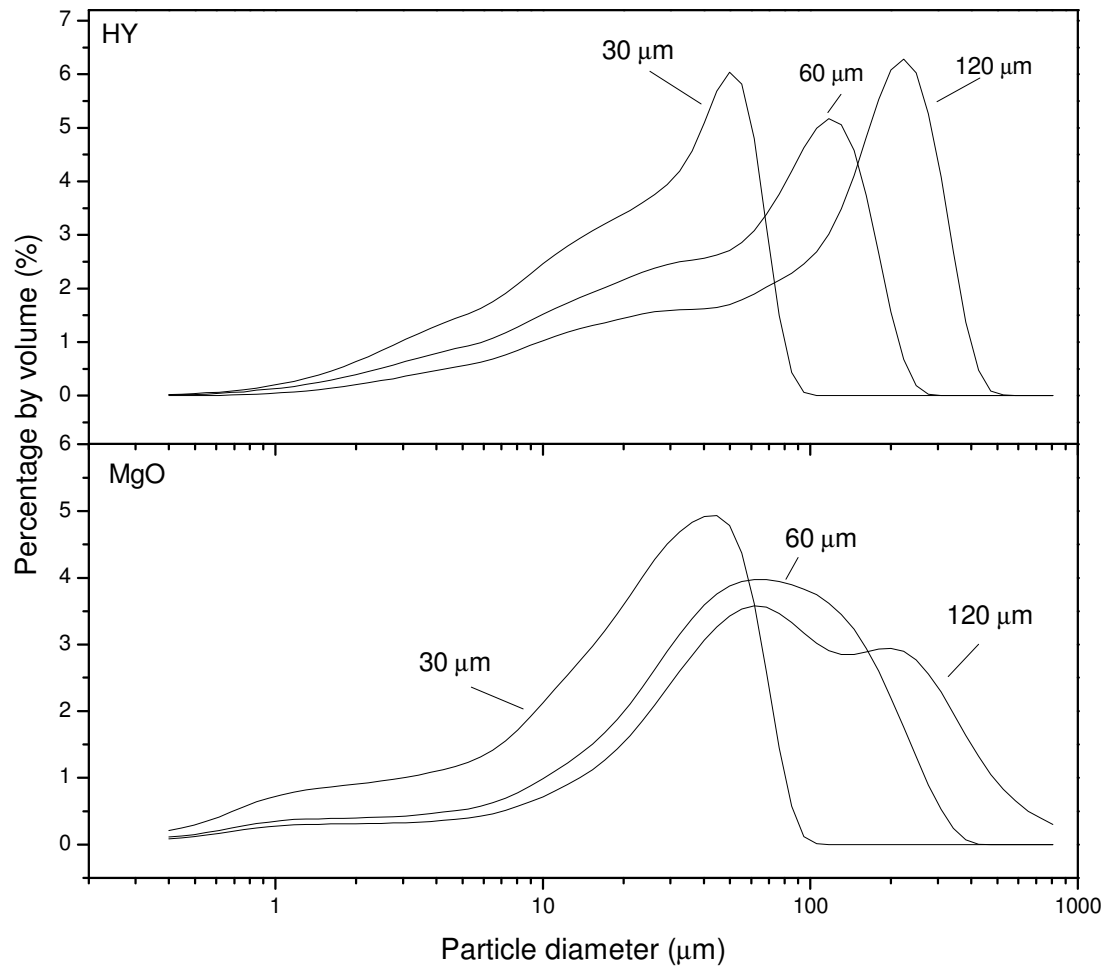


Figure 5.17: PSDs of the MgO and HY powders of different average particle size. Average particle size of each PSD is shown.

MgO reactivity

From Table 5-5 it can be seen that citric acid reactivity time, as measured according to 4.5.4 decreases with decreasing average MgO particle size. This is due to the increased surface area that higher numbers of smaller particles provide (Van der Merwe et al., 2004).

Table 5-5: Average reactivity times obtained from carrying out citric acid reactivity tests as described in section 4.4. for the three MgO powders of different average particle size used

Average MgO particle size (μm)	Average reactivity time (s)
30	67
60	115
120	165

5.5.2 METHODS

Production and milling of IC HY

The IC HY was synthesised using a two-step method. The first step involved producing a HY - $\text{Mg}(\text{OH})_2$ powder by hydration of commercially available MgO and HY. In this case, B30 and Calmag HY were used. The second step used the produced HY - $\text{Mg}(\text{OH})_2$ powders as starting materials for the production of HY using a CO_2 incubator. This first step is important in that it combines HY into the mix before carbonation. Preliminary tests showed that carbonation of $\text{Mg}(\text{OH})_2$ without HY under these conditions, fails to carbonate enough within 7 days to produce samples of pure HY, the product instead being a mix of carbonates and unreacted $\text{Mg}(\text{OH})_2$. It is believed that the presence of hydrated carbonates such as HY accelerates the carbonation of $\text{Mg}(\text{OH})_2$ (as discussed in 2.5.3).

Step 1: Preparation of material for carbonation

20 % HY and 80 % MgO were dry milled for 10 minutes in a 2 litre ceramic ball mill (Pascall Engineering) in order to homogenise the powders. Water was added to the ball mill to give a w/s ratio of 4. This was the lowest water addition that gave slurry sufficiently fluid for continuous mixing. Ball milling as opposed to using an automatic bottle shaker, magnetic stirrer and base, or carousel was the simplest and most effective method for hydrating $\text{Mg}(\text{OH})_2$ and allowed larger quantities of slurry to be mixed. The mill was then run at a medium-high speed for 24 hours.

After 24 hours of hydration, the ball mill was stopped and the milling balls removed out. The balls and inside of the mill were then rinsed repeatedly with de-ionised water in order to

recover as much hydrated solid as possible. The $\text{Mg}(\text{OH})_2$ – HY slurry was then dried at 60 °C to constant mass. The dried filter cake was then crushed to a powder using a pestle and mortar.

Step 2: Carbonation of material and milling

The synthesised and dried $\text{Mg}(\text{OH})_2$ – HY powder was distributed in Pyrex dishes in thin layers of approximately 20 mm depth. The dishes were then placed in a CO_2 incubator (Thermo Scientific Heracell 150) set at 30 °C, 5 % CO_2 concentration and > 95 % relative humidity (RH). Incubation was carried out for a total of 7 days after which a sample was crushed to a powder and analysed by XRD to confirm HY had been produced. The XRD spectrum of the sample is shown labelled in Figure 5.18, alongside that of the hydrated start material (formed in step 1) from which it was carbonated. It can be seen that by 7 days of incubation, none of the brucite, $\text{Mg}(\text{OH})_2$ peaks originally present in the sample upon incubation (at 0 days) remain. XRD software identified peaks as belonging to HY.

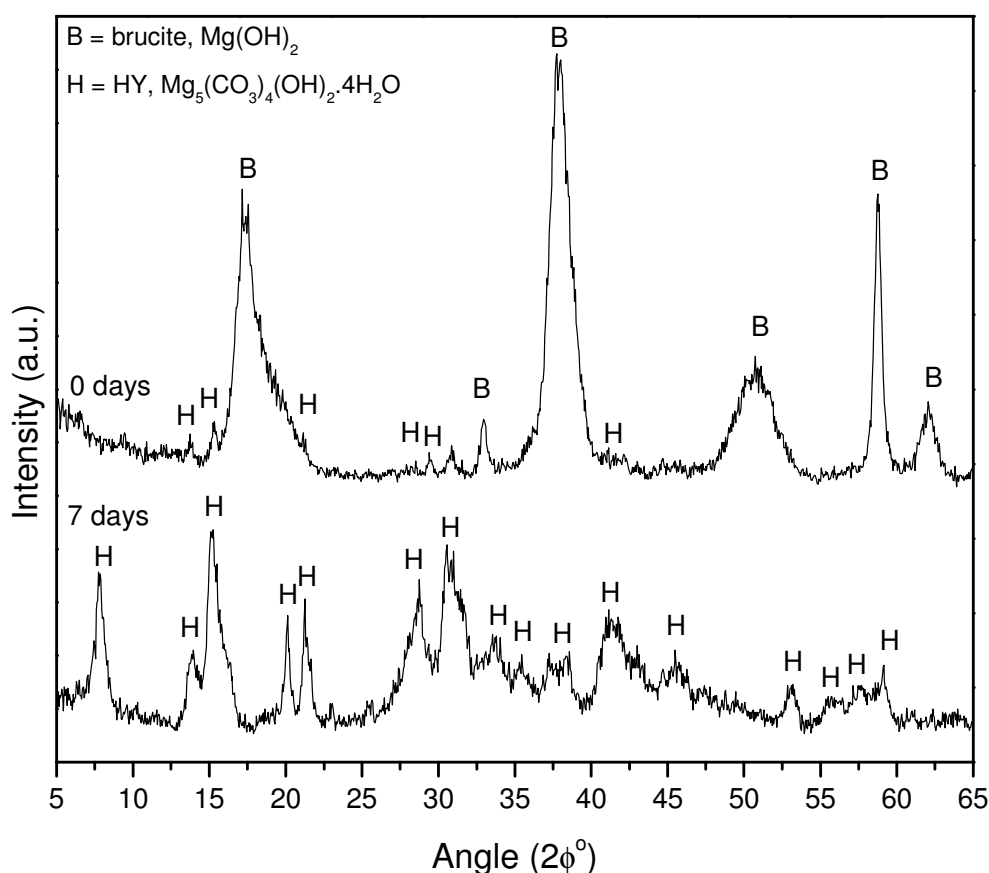


Figure 5.18: XRD spectra of the fully hydrated 20 % Calmag HY – 80 % B30 MgO sample made in step 1 labelled ‘0 days’ and of this sample carbonated for 7 days according to step 2, labelled ‘7 days’.

After checking the composition by XRD, the product, which forms in brittle, solid plates inside the dishes, was divided into three parts of equal mass. Each of the three parts was then milled using a pestle and mortar to pass through a particular sized sieve to form three IC HY powders of the same composition but with different particle size distributions. Preliminary tests had been undertaken to roughly determine the approximate average particle size of the resulting IC HY and Table 5-6 shows the sieve sizes used and desired average particle size. A ball mill or ring mill (Tema Ltd) could not be used to mill this IC HY as the heat generated by the milling results in the material agglomerating and sticking to the sides of the mill thus limiting any reduction in particle size.

Table 5-6: Table showing the sieve size that a chunk of solid IC HY has to be ground to fit through in order to roughly achieve the desired average particle size.

Average HY particle size (μm)	Size of sieve aperture (μm)
120	300
60	180
30	75

Milling of MgO

MgO was dry milled using a ball mill with 200 g of a mixture of small and large diameter alumina milling media. The mass of balls to powder ratio was 2. Preliminary tests had been performed in order to determine the milling times required to obtain particle size fraction of set average particle sizes. The times and resulting average particle size are shown in Table 5-7.

Table 5-7: Table of the ball milling times required to mill the Magox MgO to three different average particle sizes

Average MgO particle size (μm)	Milling time (minutes)
120	0
60	5
30	40

Sample production

Prismatic samples 10 x 10 x 60 mm³ made for compressive strength testing were prepared using the method described in 3.2. It should be noted that as the optimum ratios of 10 % HY – 90 % MgO, based on results from 5.3, were used for all samples.

The details of all samples made are given in

Table 5-8.

The minimum w/s possible was used for all nine samples. It was noted that whilst mixing samples in order to determine w/s ratio, that decreasing MgO and HY size, resulted in a less workable paste. However, for all samples, a w/s ratio of 0.62 was used.

Table 5-8: Summary of the samples made to investigate particle size effects.

HY and MgO content in dry mix (wt. %)		Average particle size (µm)		w/s ratio	Curing time (days)
HY	MgO	HY	MgO		
10	90	30	30	0.62	7, 28
			60		
			120		
		60	30		
			60		
			120		
		120	30		
			60		
			120		

Samples were tested for compressive strength after curing in water for 7 and 28 days with fractured test pieces treated with acetone to prevent further hydration and dried at 60 °C. Reaction product morphology on fracture surfaces was analysed using SEM. XRD was used

to analyse crystalline reaction products of dry samples after grinding to less than 250 μm . LOI test as described in 3.7.1 was used to approximate hydration rate of these powders.

5.5.3 RESULTS

Compressive strength

Figure 5.19 shows the relationship between average MgO particle size and average HY particle size (depicted by the different symbols) on compressive strength after 28 days curing. The results after 7 days curing are not shown as they are very similar to those tested after 28 days curing.

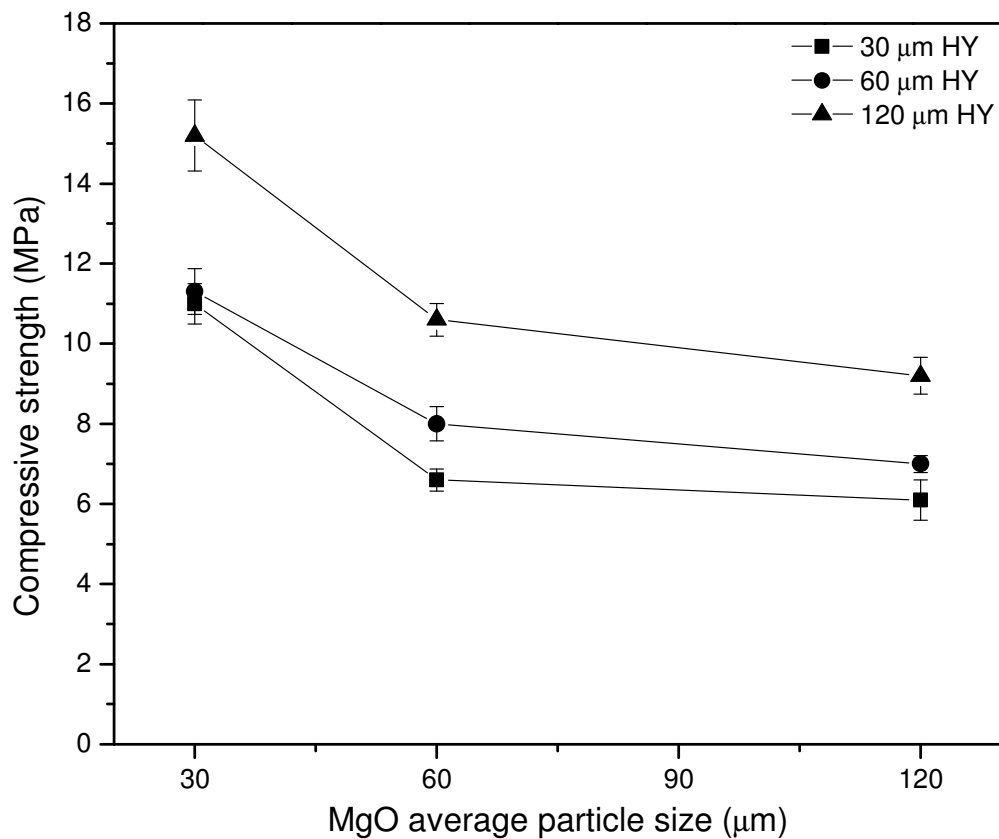


Figure 5.19: Graph showing the effect of MgO and HY average particle size on compressive strength of 10% HY – 90% MgO hydrated mixes made with different combination of particle sizes after 28 days curing.

From Figure 5.19, it can be seen that the samples which have the highest strengths are those made with the smallest average MgO particle size (30 μm) and the largest average HY particle size (120 μm). The strongest sample was that containing both HY with the largest

average particle size, 120 μm , and MgO with the smallest average particle size, 30 μm . This sample had a compressive strength of 16 MPa at 28 days compared to the weakest 28 day sample which only achieved approximately 8 MPa. The weakest sample contained the largest MgO size and the smallest HY size, in keeping with the observed trend. The relationship between MgO size and strength is not linear indicating that MgO average particle size makes more of a difference in the lower ranges, say 30 to 60 μm than in the higher size range 60 to 120 μm .

Figure 5.20 is a contour plot of the same 28 day compressive strength data shown in Figure 5.19 with labelled contour lines representing the compressive strength relationship between HY and MgO average particle size.

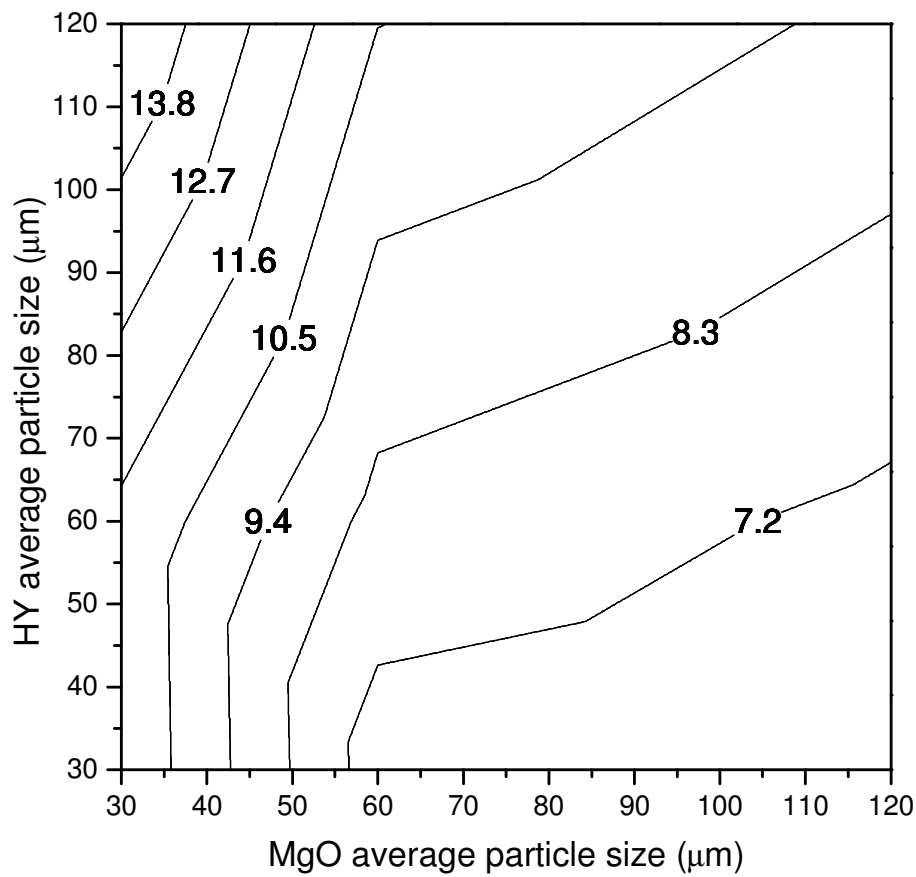


Figure 5.20: Contour plot showing the relationship between average MgO and HY particle size on 28 day compressive strength. Contour lines represent compressive strengths and are labelled.

Based on the closeness of the contour lines that meeting the x-axis, the MgO average particle size axis, compared to those of the y-axis, the HY average particle size axis, it appears that

MgO particle size has a more significant effect on compressive strength than HY average particle size, in particular in the 30 – 60 μm region. Whilst the plot suggests that HY average particle size may be a more significant factor in the higher particle size region, the 60 – 120 μm region, it is difficult to confirm this without making more samples containing HY powders of average particle size between these values. It also suggests that compressive strength is not linearly dependent upon HY and MgO particle size.

Analysis of crystalline reaction product

Figure 5.21 shows XRD spectra of six different samples after 28 days curing.

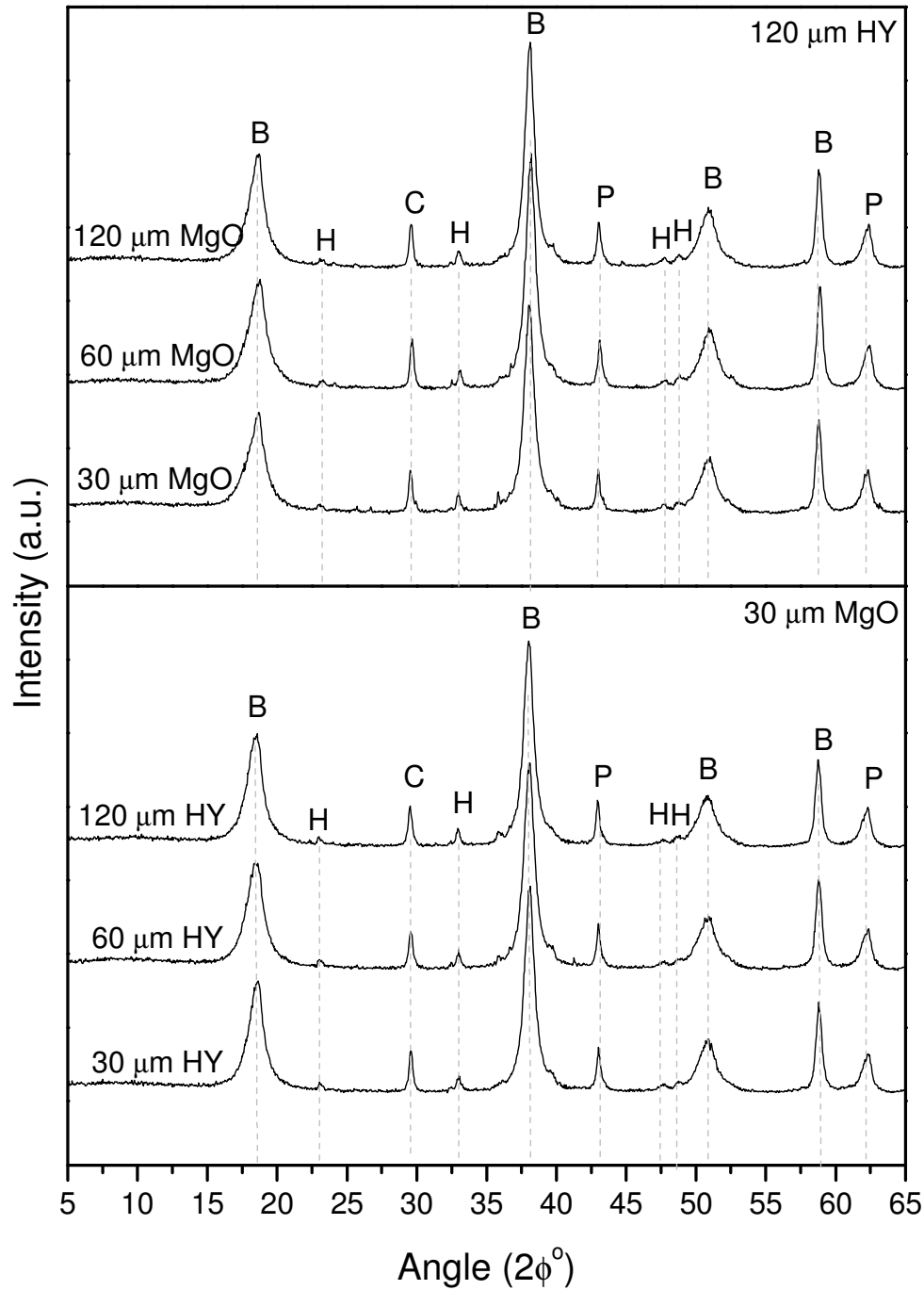


Figure 5.21: XRD spectra of 10 % HY – 90 % MgO after 28 days curing. Spectra in the upper graph are from samples made from 30 μm MgO and the three different HY particle sizes. Spectra in the lower graph are from samples made from 120 μm HY and the three different MgO particle sizes.

In the lower graph, samples were all made using the MgO of average particle size 30 μm but with average HY particle size of 30 μm , 60 μm and 120 μm . In the upper graph, samples were made using HY of average particle size 120 μm and average MgO particle sizes of 30

μm , 60 μm and 120 μm . XRD of samples made from 60 μm MgO were not included as the extremes i.e. the strongest and weakest samples are already represented in the other spectra.

The major peaks of all samples have been identified and labelled and any minor, unlabelled peaks have been identified as HY. In agreement with the previous results, it is observed that the crystalline reaction products consist of $\text{Mg}(\text{OH})_2$ only, with some unhydrated MgO remaining along with HY and calcite, which is most probably from the MgO. It was noted that the calcite peaks are more prominent than those observed in XRD spectra of samples made from 10 % Calmag HY – 90 % B30 MgO in Chapter 5. This is most likely because the raw material Magox MgO contains twice as much CaO as B30 MgO according to the chemical composition data seen in Table 4-1.

Within the upper and lower graphs, the three spectra are almost identical, indicating that the paste samples contain the same crystalline phases in similar amounts regardless of HY or MgO size. When comparing all the spectra, it can be seen that all six are more or less identical. Additionally, considering that the 28 day compressive strengths of the samples whose XRD spectra are shown in Figure 5.21 are not the same it is perhaps surprising that $\text{Mg}(\text{OH})_2$ peaks appear identical regardless of MgO particle size. It is known that smaller MgO particles generally hydrate faster than larger particles due to the higher reactivity as seen in Table 5-5, so it might be expected that there would be more $\text{Mg}(\text{OH})_2$ present (Van der Merwe et al., 2004). This would be observed as more intense $\text{Mg}(\text{OH})_2$ peaks in XRD of samples containing smaller MgO particles. However this was not observed.

It was also noted that for all the XRD spectra in Figure 5.21, there was no difference in the broadness of any of the $\text{Mg}(\text{OH})_2$ peaks indicating that the average particle size of HY and MgO does not affect $\text{Mg}(\text{OH})_2$ crystallite size.

Microstructural analysis

Figure 5.22 shows SEM images of two of the 10 % HY – 90 % MgO samples made to investigate particle size effects. The images shown are fracture surfaces of the strongest and the weakest sample based on compressive strength data. XRD spectra of all samples at 28 days were almost identical suggesting strength differences are due to microstructural effects so any differences should be apparent by SEM.

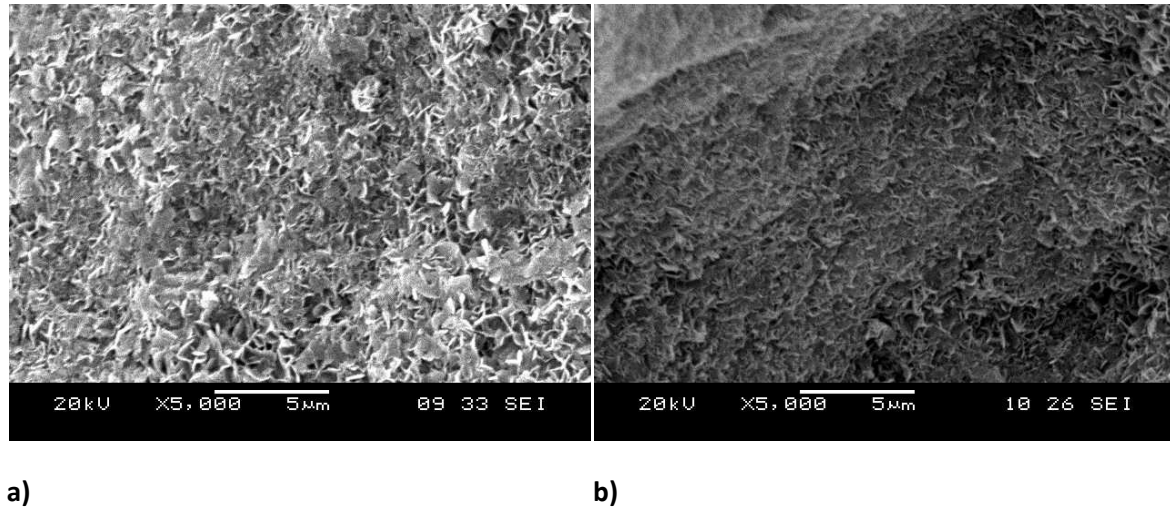


Figure 5.22: SEM images of two 28 day hydrated 10% HY – 90% MgO samples made to test particle size effects. Sample (a) is made from 30 μm HY and 120 μm MgO; (b) is made from 120 μm HY and 30 μm MgO. Samples (a) and (b) were the weakest and strongest samples respectively.

Both images reveal the type of prismatic interconnected microstructure similar to that reported in 5.3 and 5.4. for samples made from 10 % Calmag HY – 90 % B30 MgO. Images (a) and (b) suggest a similar microstructure although that in (b) appears to be denser. It should be noted that the size of the inter-linked platelets seen in these images are significantly smaller than those seen for the 10 % Calmag HY – 90 % B30 MgO sample also observed at 28 days.

5.5.4 DISCUSSION

It was found that within the three average particle size ranges tested for each material, samples with larger HY particles and smaller MgO particles produced the strongest samples. XRD spectra of all samples at 28 days are identical showing that the only crystalline reaction product formed is $\text{Mg}(\text{OH})_2$ and that some MgO and HY remain unreacted together with small amounts of calcite (CaCO_3). Comparison of XRD spectra for the strongest and weakest samples does not indicate significant differences with no apparent differences in $\text{Mg}(\text{OH})_2$ peak broadness observed. This suggests that particle size does not affect the crystallinity of the cement pastes produced or the amount of $\text{Mg}(\text{OH})_2$ formed or the size of the $\text{Mg}(\text{OH})_2$ crystallites. Therefore, the effect on strength must be due to the way in which the microstructure is arranged or the way in which particles are packed. It was also noted that the

size of the platelets in the sample was much smaller than those observed in 10 % Calmag HY – 90% B30 MgO samples at 28 days old. This could explain why Magox MgO/IC HY samples tested here achieved lower compressive strengths than B30 MgO/Calmag HY samples and indicates that the type of MgO and HY can make a significant difference to sample properties.

It appears from compressive strength results that smaller average MgO particles give stronger samples. This could be due to the larger number of particle contacts with HY that occur when smaller MgO particles are present (Nonat et al., 1997). This could allow for a closer transfer of $\text{Mg}(\text{OH})_2$ from MgO surfaces to HY surfaces and a denser microstructure. However, this does not explain why a large average HY particle size also produces stronger samples.

SEM showed that the prismatic cross-linked microstructure was present as seen in earlier work. No major differences were seen on comparison of SEM images of the strongest and weakest samples although a slightly denser microstructure was apparent in the strongest sample. This observation supports the findings from XRD and it is suggested that increased strength apparent in samples made from smaller MgO and larger HY particles, is due to improved particle packing.

5.5.5 CONCLUSIONS

- It was found that smaller MgO particles and larger HY particles result in higher strength samples;
- This is suggested that this could be due to the way the particles interact and pack in the microstructure, creating a more dense matrix;
- The size of the MgO particles appears to have a more significant effect on strength than HY size;
- Based on the XRD results, particle size, unlike HY content, does not affect the crystallinity of the resulting $\text{Mg}(\text{OH})_2$;
- Differences in $\text{Mg}(\text{OH})_2$ platelet size when compared to systems made from 10 % Calmag HY – 90 % B30 MgO were observed, indicating that the specific type of MgO and HY can make a significant difference to the MgO – HY binder properties.

5.6 DISCUSSION OF MECHANISM

It has been concluded that the formation of an inter-connected system of platelets, of $\text{Mg}(\text{OH})_2$, are responsible for the compressive strength gain of MgO – HY systems. SEM shows that these platelets grow on the surface of raw material particles. Calorimetry results revealed that the presence of HY increases the hydration rate as well as maximum heat of hydration, of MgO . It is believed that the precipitation and growth of $\text{Mg}(\text{OH})_2$ on the surface of HY particles is responsible for this increased hydration rate. This can be explained by considering an accepted mechanism of the hydration of MgO .

An accepted mechanism, as described in Chapter 2, of standard MgO hydration involves the precipitation of $\text{Mg}(\text{OH})_2$ on the surface of MgO particles, with hydration rate being retarded as MgO surfaces become increasingly covered in $\text{Mg}(\text{OH})_2$ (Feitknecht and Braun, 1967). However, in the presence of HY, SEM, hydration rate and calorimetry results from this work, suggest that HY acts as a nucleation site, providing additional surfaces on which $\text{Mg}(\text{OH})_2$ from the MgO surfaces can precipitate, thus allowing for less impeded MgO hydration. The presence of HY was also seen to lower pH. This would effectively accelerate MgO dissolution and $\text{Mg}(\text{OH})_2$ formation in comparison to 100 % MgO samples. As the hydration of MgO is exothermic, increasing hydration rate would increase the maximum heat of hydration, as observed in calorimetry.

Previous work has proposed that this increased heat further accelerates MgO dissolution, creating a high degree of supersaturation which in turn favours the nucleation of smaller crystallites (Vlasopoulos, 2007, Ginebra et al., 2004). It has been observed that smaller $\text{Mg}(\text{OH})_2$ crystallites are indeed formed in the presence of HY, indicated by XRD $\text{Mg}(\text{OH})_2$ peak broadening. The crystals which are grown from these crystallites are in the form of inter-connected platelets.

However, increasing the curing temperature of 100 % MgO samples, did not result in the formation of $\text{Mg}(\text{OH})_2$ crystallites of reduced size, although it did increase hydration rate. This indicates that the formation of the smaller $\text{Mg}(\text{OH})_2$ crystallites observed in hydrated MgO – HY samples is not just due increased heat of solution created by increased hydration rate. It is suggested that the formation of small $\text{Mg}(\text{OH})_2$ crystallites is also likely governed, by another factor. Also, only 10 % HY was used, which seems unlikely to provide enough surface for all $\text{Mg}(\text{OH})_2$ to precipitate on and results of 5.5 indicated that larger HY particles, which generally have lower surface area than smaller HY particles, gave stronger samples.

This also suggests that increased hydration rate and microstructure change are strongly governed by a chemical mechanism alongside a mechanical one.

Measurements of pH showed that the presence of acidic CO_3^{2-} and HCO_3^- released from the dissolution of HY decreases solution pH. Work by several researchers has concluded that pH and type of ion species can strongly influence the morphology of precipitated $\text{Mg}(\text{OH})_2$ crystals (Koh et al., 2011, Lu et al., 2004). The different morphology of $\text{Mg}(\text{OH})_2$ formed in the presence of HY may therefore be due to the pH of the solution. However, based on results here, a more specific reason for the shape of $\text{Mg}(\text{OH})_2$ crystals cannot credibly be given. Nonetheless, a possible reason based on pH to explain the existence of a HY of low crystallinity detected in Raman spectroscopy, as well as perhaps the small crystallite size of $\text{Mg}(\text{OH})_2$ has been suggested as follows.

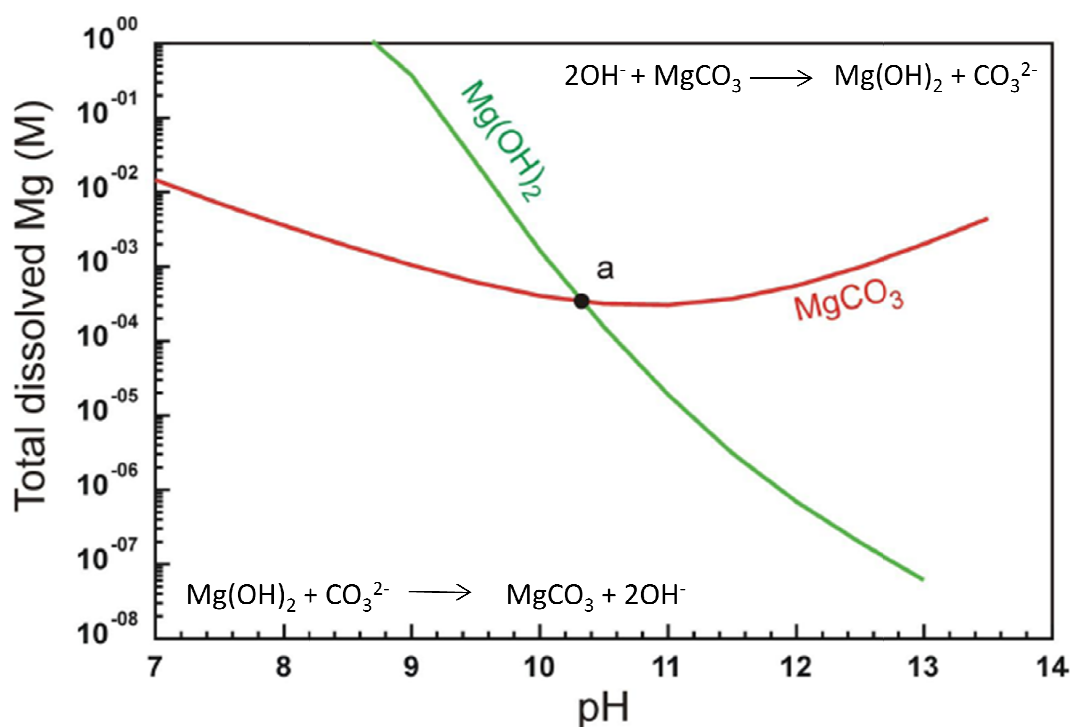


Figure 5.23: Graph showing dissolved Mg content against pH for $\text{Mg}(\text{OH})_2$ and MgCO_3 modelled using MINTEQA software (Zhang, 2012).

Figure 5.23 contains pH solubility data of MgCO_3 and $\text{Mg}(\text{OH})_2$ modelled by MINTEQA software (Zhang, 2012). It indicates the equilibrium composition of dilute aqueous solutions of these two compounds. If both MgCO_3 and $\text{Mg}(\text{OH})_2$ are present in the system and their

respective ions of CO_3^{2-} and OH^- are present, then at pH values lower than that at point 'a' (approximately 10.5 in this diagram), MgCO_3 is more likely to precipitate whilst at higher pH precipitation of $\text{Mg}(\text{OH})_2$ is more likely. If the system pH is equal to, or very close of the intersection at point 'a', an equilibrium could be achieved whereby precipitation of both species is likely and in order to fulfil both precipitations, both reactions occur so essentially an ion exchange reaction takes place.

The exact pH and range at which this could occur in the MgO – HY system is unknown as the data in Figure 5.23 was calculated based on different materials and depends on the specific materials used. Also, the data is for MgCO_3 whereas HY was used in this research, and is likely to have a slightly different solubility pH curve. Additionally, the pH was measured for slurry rather than a paste, so the recorded pH readings will vary from the pH of the actual systems used to make samples. Therefore the true pH of 'a' could be slightly higher or lower than pH 10.5.

It is proposed that the pH of the MgO - HY cement system is in the range such that CO_3^{2-} or HCO_3^- ions and OH^- ions dissolve and precipitate causing an ion exchange at the surface of the HY particles. This exchange could result in the reassembly and disruption of the surface of the HY, as $\text{Mg}(\text{OH})_2$ precipitates, lowering the crystallinity of the HY at the surface. This would explain the low crystallinity HY type material observed in Raman spectroscopy. Depending on the pH of the solution, it is possible that the $\text{Mg}(\text{OH})_2$ formed on the HY surface could dissolve and precipitate several times as Mg^{2+} ions are exchanged, which might explain why small crystallites exist, as they do not have time to grow. The pH or limited space in the region of the HY surface could influence the growth and shape of $\text{Mg}(\text{OH})_2$ platelets resulting in the observed $\text{Mg}(\text{OH})_2$ cross-linked microstructure. Extensive further work is required to test this tentatively proposed mechanism, particular in the area of HY dissolution and solubility.

A schematic of the proposed mechanism is shown in a schematic in Figure 5.24.

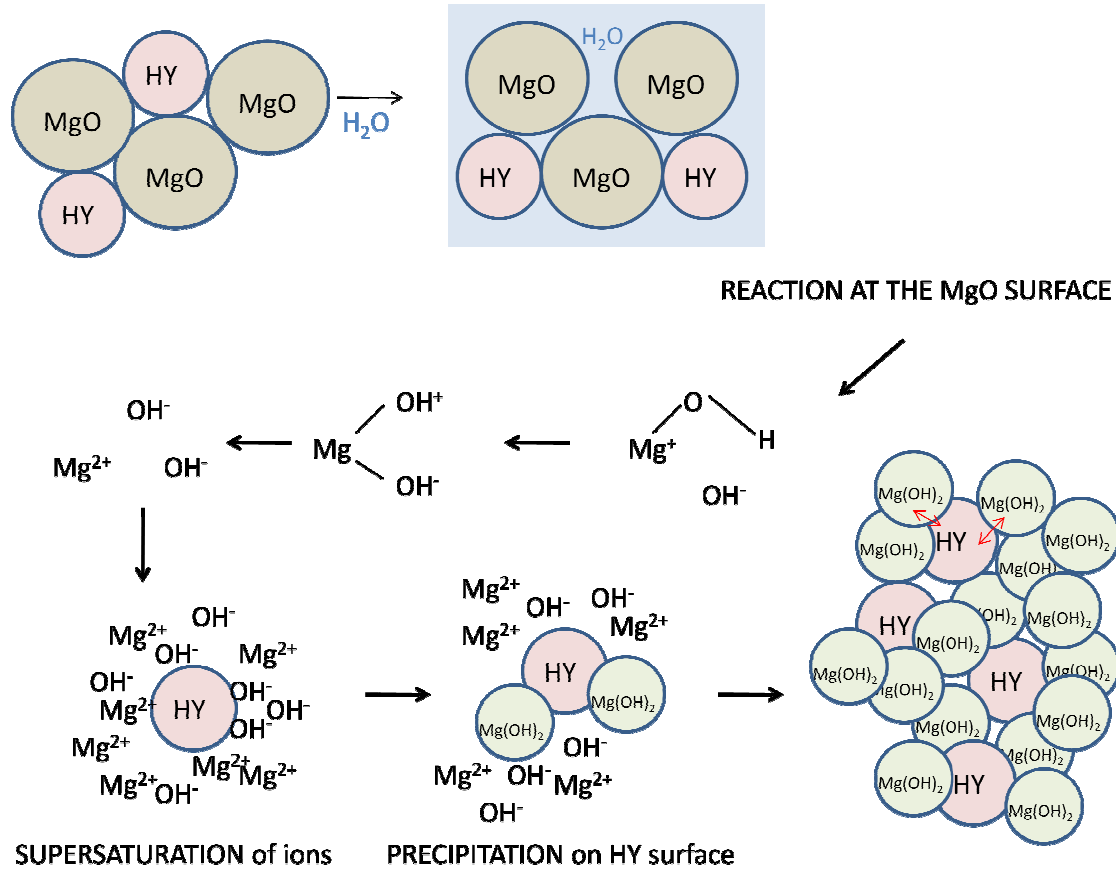


Figure 5.24: Proposed schematic of hydration of an HY-MgO system. The red double-headed arrows represent the ion of exchange between OH^- and CO_3^{2-} that occurs when the system pH is within the stated region.

5.7 OVERALL CHAPTER CONCLUSIONS

Chapter 5 has investigated the properties, reaction products and mechanism of the MgO – HY system. The main conclusions are summarised below:

- An altered mechanism of MgO – HY hydration has been suggested although further work is required to verify this. It is believed the pH of the system is the key to the types of $Mg(OH)_2$ crystal formed;
- SEM suggests that increasing HY content produces stronger samples but the high water requirements, particularly of the HY material, make it difficult to investigate the properties of samples of higher HY content;
- The optimised 10% HY – 90 % MgO sample achieved a maximum compressive strength of ~ 24 MPa at 28 days compared to ~ 120 MPa of a 100 % CEM I control sample. However, a significantly higher w/s ratio is required to achieve a mouldable

paste for the optimised sample. The use of plasticisers could effectively increase maximum compressive strength although their use has not been investigated.

- Samples do not exhibit loss of strength over time;
- Samples were cured in water so it is known that they are water resistant;
- The optimised system has good setting properties;
- Decreasing MgO particle size and increasing HY particle size, up to a certain extent which is currently unknown, whilst maintaining a relatively low w/s ratio could increase sample strength, widening the applications of the binder system;
- The MgO – HY system has displayed several promising properties which have highlighted its potential as an alternative binder to Portland cement. However, additional research is required to further optimise the system, particularly in terms of reducing water requirement and determining the properties of MgO – HY mortar and concrete systems.

6 STUDY OF THE MgO – SiO₂ SYSTEM

6.1 INTRODUCTION

In Chapter 5, a novel low CO₂ binder based on the MgO – HY system was been introduced which has the potential to be used for PC applications although further work is required. However, another proposed MgO - based potential binder is that of the MgO – SiO₂ system (Sandberg and Mosberg, 1988, Zhang et al., 2011). In this system, SiO₂ and MgO react to form magnesium silicate hydrate (M-S-H) gel thought to be analogous to calcium silicate hydrate (C-S-H) gel which is the main strength giving component of Portland cement (PC) (Gartner, 2004, Mehta and Monteiro, 2008, Chatterji, 1995).

The objective of the work reported in this section was to investigate the reaction products and properties of the MgO – SiO₂ system. This has been achieved by investigating the strengths of the system, finding the optimum MgO to SiO₂ ratio which was then used to determine the rate of production of reaction products and to gain fundamental understanding of the reaction mechanism behind the system. This chapter reports on the effect of SiO₂ content on MgO – SiO₂ compressive strength and reaction products, and the optimum ratio of SiO₂/MgO selected. This selected optimal ratio is then used to investigate the effect of using two different SiO₂ types on sample properties. Finally, a reaction mechanism, based on the observed results, is proposed.

6.2 OPTIMISATION OF THE MgO – SiO₂ RATIO

This section reports on experiments carried out to optimise the SiO₂ to MgO ratio in terms of achievable compressive strengths. The effect of SiO₂ content on the type and possible quantity of reaction product was also assessed.

6.2.1 MATERIALS

B30 MgO and 920d SiO₂ as characterised in 4.1, were used to produce samples. A synthesised M-S-H gel was also used for identification of M-S-H phases within the reaction products. This gel was synthesised using a precipitation method as described in 6.3.2 (Brew and Glasser, 2005b).

6.2.2 METHODS

M-S-H gel production

An M-S-H gel with a target Mg/Si ratio of 0.5 was produced via a precipitation method according to Brew and Glasser using solutions of sodium metasilicate pentahydrate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) and magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Brew and Glasser, 2005b). The silicate solution was stirred in a three-necked flask in an iced water bath in order to cool it to $\sim 0^\circ\text{C}$. The magnesium solution was then added dropwise with the mixture being continuously stirred to avoid inhomogeneous coprecipitation. The sample was then allowed to warm to ambient temperature and the precipitate to settle. After filtering, the precipitate was rinsed five times using approximately 1 litre of distilled water per rinse. This was followed by drying of the precipitate in a dessicator. XRD analysis was carried out on the dried precipitate and on comparison of peaks, or rather humps observed with those of the M-S-H gel observed in literature, was confirmed to be M-S-H gel. The XRD spectra can be found in the Appendix.

MgO – SiO₂ sample production

In order to determine whether the amount of SiO₂ effects sample strength and reaction product, a number of 10 x 10 x 60 mm³ samples were made differing in the MgO to SiO₂ ratio. It was found that increasing the amount of SiO₂ resulted in a slightly higher water demand, so the maximum percentage of SiO₂ in a dry mix was limited to 40 %. To avoid the effects of water content, the w/s ratio was set to 0.62 as this was the minimum water requirement that allowed all samples to be moulded regardless of the SiO₂ content.

The details of samples made are given in Table 6-1. All sample pastes were made from the 920d SiO₂ and B30 MgO according to the method described in section 4.3.1. As a control sample, a 100 % CEM I mix was also prepared with w/s ratio 0.3.

Table 6-1: Details of prepared MgO – SiO₂ paste samples.

w/s ratio	SiO ₂ and MgO content in dry mix (wt. %)	
	SiO ₂	MgO
0.62	10	90
	20	80
	30	70
	40	60

Compressive strength

Samples given in were tested for compressive strength after 7 and 28 days curing according to 4.3.2. Fragments were stored in acetone for 10 days to prevent further hydration and dried at 40 °C.

XRD analysis

XRD as described in 4.6.1 was used to analyse reaction product composition after the samples prepared for compressive strength tests were stored in acetone for 10 days, oven dried at 40 °C and ground to a fine powder.

TG analysis

TG analysis has been used to quantify the reaction products, including C-S-H and Ca(OH)₂, of Portland cement hydration (Cong and Kirkpatrick, 1995, Dweck et al., 2000, Kaminskas, 2008, Lilkov et al., 2012, Taylor, 1990). The TG analysis profiles of Mg(OH)₂, M-S-H gel and a hydrated and dried MgO – SiO₂ sample were characterised in order to determine the Mg(OH)₂ and the M-S-H gel quantities in hydrated MgO – SiO₂ samples.

A 28 day hydrated MgO paste sample (w/s ratio 0.6) which had been mixed according to the method in 4.3.1 was cured in a sealed bag to ensure a constant high humidity. It was then stored in acetone for 10 days to inhibit hydration, followed by drying at 40 °C to constant mass and grinding to a fine powder. TG analysis was then applied to this powder, a powdered M-S-H gel and the 28 day cured 40 % SiO₂ – 60 % MgO sample as shown in Table 6-1, which had also been stored in acetone to prevent further hydration and then dried and powdered. This sample was chosen in order to characterise reaction products by TG as it

contained the highest amount of SiO_2 and would therefore be likely to have the largest amount of M-S-H gel. The method and parameters described for TG analysis in 4.6.4 were used. Dried and powdered samples of all pastes given in Table 6-1 were also analysed by TG.

6.2.3 RESULTS

Compressive strength

Compressive strength results after 7 and 28 days are shown in Figure 6.1. Results of the CEM I control samples are also shown.

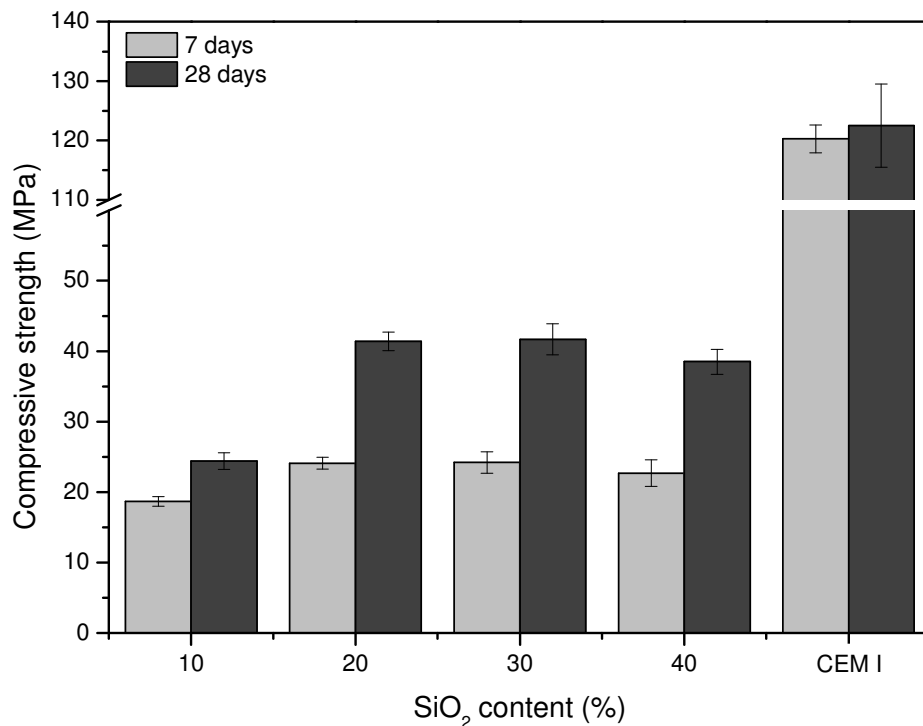


Figure 6.1: Graphs showing the relationship between SF content and average compressive strength of six bars after 7 days and 28 days for SiO_2 – MgO pastes.

After 7 days of curing, the compressive strength of all samples is approximately 20 MPa. However, after 28 days, there is a significant difference between the strengths of samples of 10 % SiO_2 and those containing higher SiO_2 contents. Between 10 % and 20 % SiO_2 samples, a difference of ~ 20 MPa can be seen. However, samples containing 20 % and 30 % SiO_2 appear to have similar strengths whilst strengths of 40 % SiO_2 samples were slightly lower. In comparison with the CEM I control samples strengths, even the highest MgO – SiO_2 compressive strength of ~ 42 MPa achieved by the 30 % SiO_2 – 70 % MgO sample at 28

days, is significantly lower. However, the w/s ratio of the MgO – SiO₂ samples is 0.62 compared to the 0.3 w/s ratio of the CEM I sample and lower water content is associated with higher strengths (Buj et al., 2009, Mehta and Monteiro, 2008, Taylor, 1990).

Crystalline analysis by XRD

The XRD spectra of samples after 7 and 28 days curing can be seen in Figure 6.2.

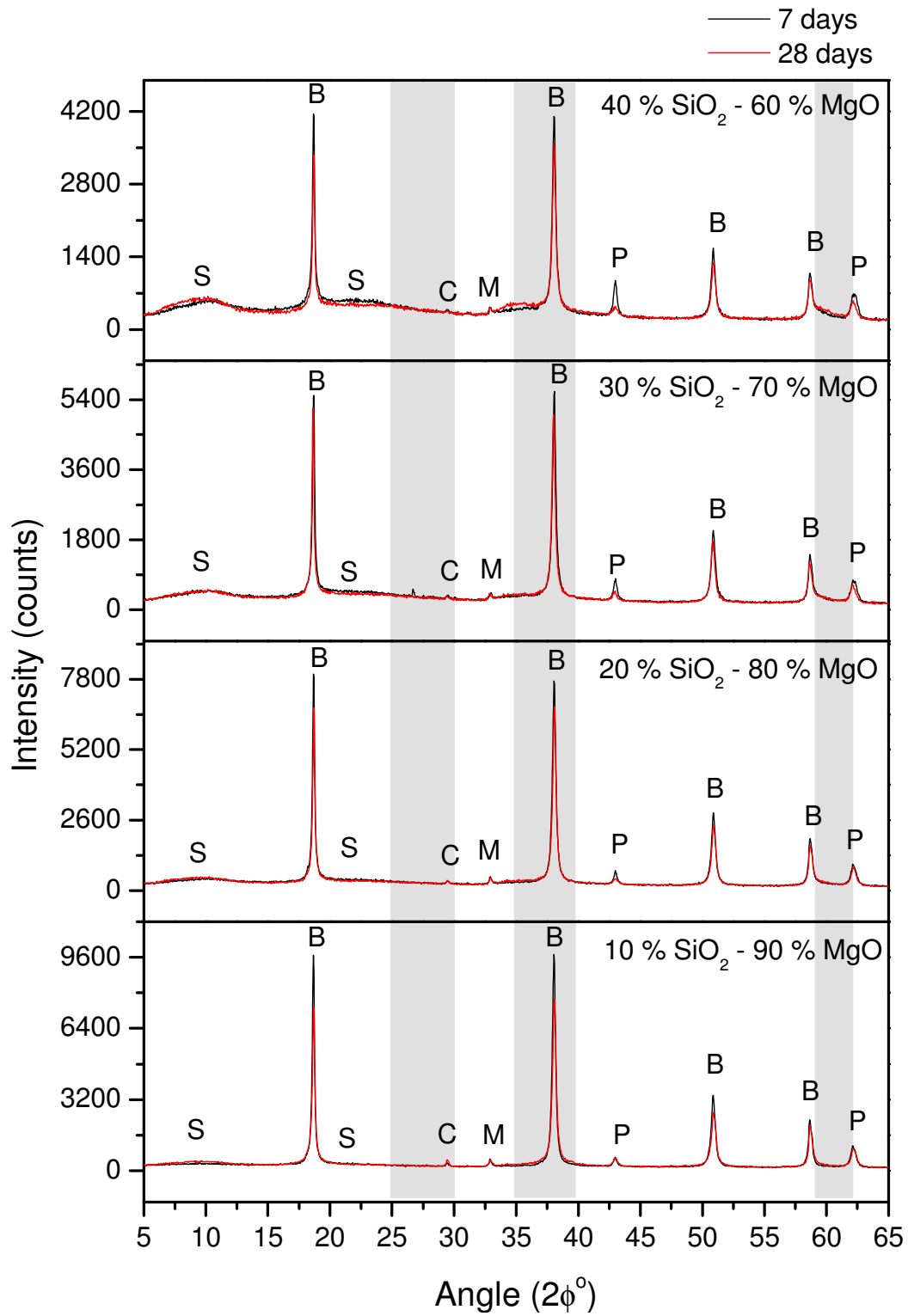


Figure 6.2: XRD spectra from top to bottom of hydrated samples of different SiO_2 contents after 7 days curing (black) and 28 days curing (red). B = brucite [$\text{Mg}(\text{OH})_2$], C = calcite [CaCO_3], M = magnesite [MgCO_3] and P = periclase [MgO]. The low intensity broad hump due to the presence of amorphous SiO_2 is indicated by the letter 'S'.

The major peaks have been identified with letters where B is brucite [$\text{Mg}(\text{OH})_2$], M is magnesite [MgCO_3], C is calcite [CaCO_3] and P is periclase [MgO]. S indicates the region in

which broad low intensity humps occur due to the amorphous SiO_2 present. The characteristic areas of M-S-H humps are $25 - 30$, $35 - 39$ and $59 - 62$ $2\theta^\circ$ and are highlighted grey.

Figure 6.2 shows that the major crystalline reaction product for all samples is $\text{Mg}(\text{OH})_2$ and that some MgO remains unreacted after 7 and 28 days. For analogous samples, both types of peaks decrease in intensity between these time periods suggesting that these materials are being consumed over time. It should be noted that due to the difference in composition, intensities of these peaks between samples of different SiO_2 content should not be compared. Low intensity peaks identified as calcite, CaCO_3 , and magnesite, MgCO_3 found in all samples are present and are believed to come from the B30 MgO material as given in the chemical composition data in Chapter 4.

Amorphous SiO_2 cannot be seen clearly from this figure as its broad humps are of too low a intensity in comparison with those of the crystalline phases. The same is true for any M-S-H peaks. However, by directly overlaying the spectra on top of the spectrum of a hydrated 100 % MgO sample and magnifying the areas in which characteristic M-S-H gel humps appear, based on synthesised M-S-H gels, the three amorphous humps can be identified. Figure 6.3 focuses on these amorphous humps showing the three regions of $25 - 30$, $33 - 38$ and $58 - 63$ $2\theta^\circ$.

Figure 6.3 shows six graphs, each with the four XRD spectra of the samples containing different percentages of HY, layered on top of each other and a baseline spectrum of hydrated 100 % MgO . Three of the graphs show the spectra of samples hydrated for 7 days, whilst the other three show the spectra of the samples hydrated for 28 days. For each time period, there are three graphs showing a magnified section of the spectra in which M-S-H humps would be expected. The areas in which Brew and Glasser stated as arising from M-S-H gel are $25 - 30$, $35 - 39$ and $59 - 62$ $2\theta^\circ$ (Brew and Glasser, 2005b). For $\text{MgO} - \text{SiO}_2$ samples made here, these regions were found to be in very similar and have been highlighted in grey. It is difficult to determine the start of the first M-S-H gel hump in the $25 - 30$ $2\theta^\circ$ area in images a and d due to its overlap with the amorphous SiO_2 hump.

In each of the graphs in Figure 6.3 it can be seen that M-S-H gel is a reaction product, and in general, the higher the percentage of SiO_2 , the more intense the XRD spectrum of the sample in the M-S-H region. This indicates that more M-S-H gel is present in samples made from higher SiO_2 contents. For the M-S-H regions in the $33 - 38$ and $58 - 63$ $2\theta^\circ$ regions, when comparing image b with e and c with f, there also appears to be a slight increase in M-S-H

hump intensity for analogous samples between 7 and 28 days. It is difficult to tell if this is true for the $25 - 30^\circ 2\theta^\circ$ M-S-H hump (images a and d) due to overlap with that of the amorphous SiO_2 hump.

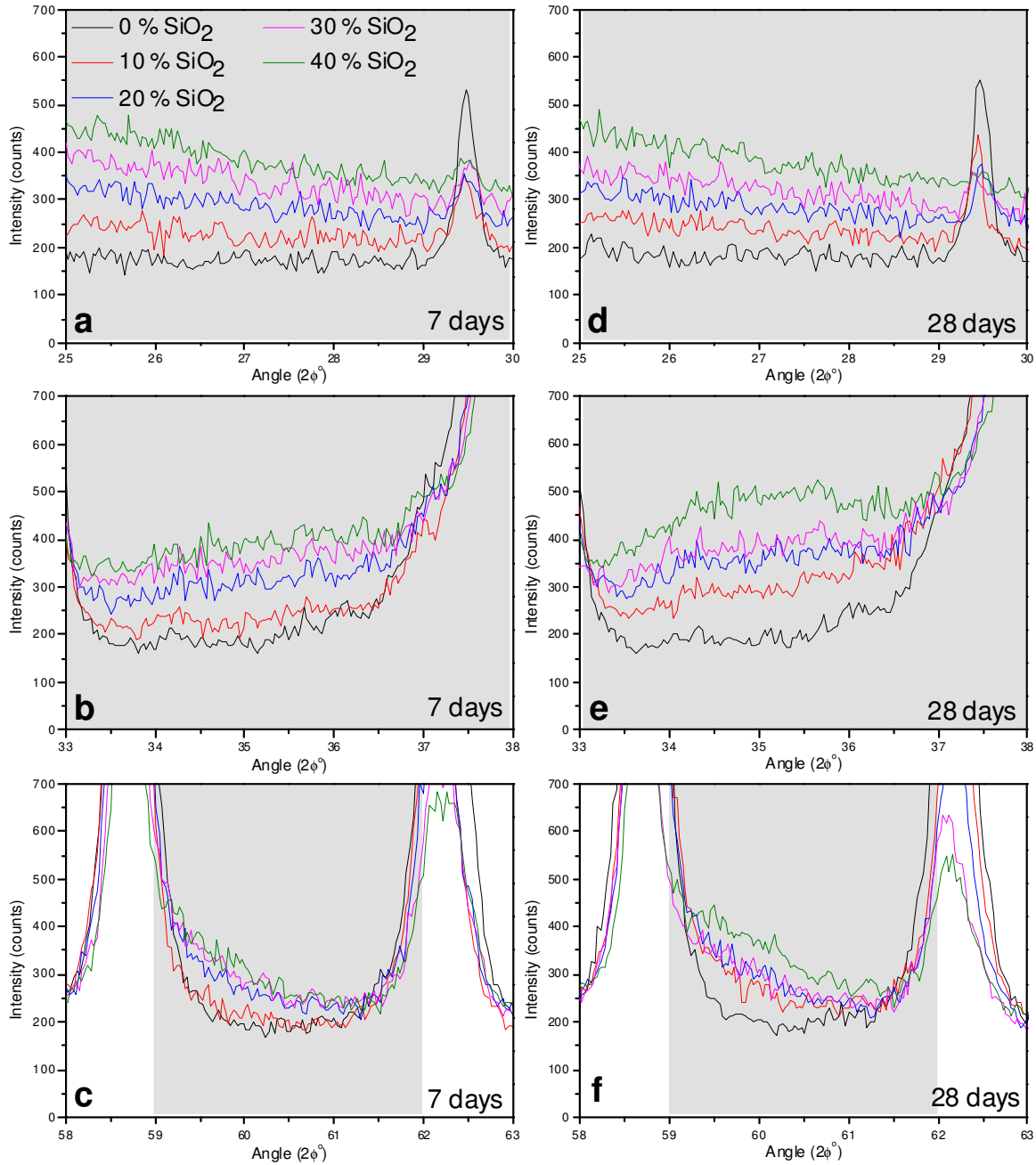


Figure 6.3: Magnified areas of the three characteristic M-S-H humps observed in the XRD spectra of hydrated 10%, 20%, 30% and 40% SiO_2 samples cured for 7 days (left) and 28 days (right). The 0% SiO_2 – 100% MgO sample is also included as a baseline. The areas of the M-S-H gel humps have been highlighted in grey.

TG analysis

Figure 6.4 shows the results of the TG analysis in the form of heatflow, DTA and TG mass loss curves for the two materials; 28 day hydrated MgO, 28 day hydrated 40 % SiO₂ – 60 % MgO sample, and the control M-S-H gel.

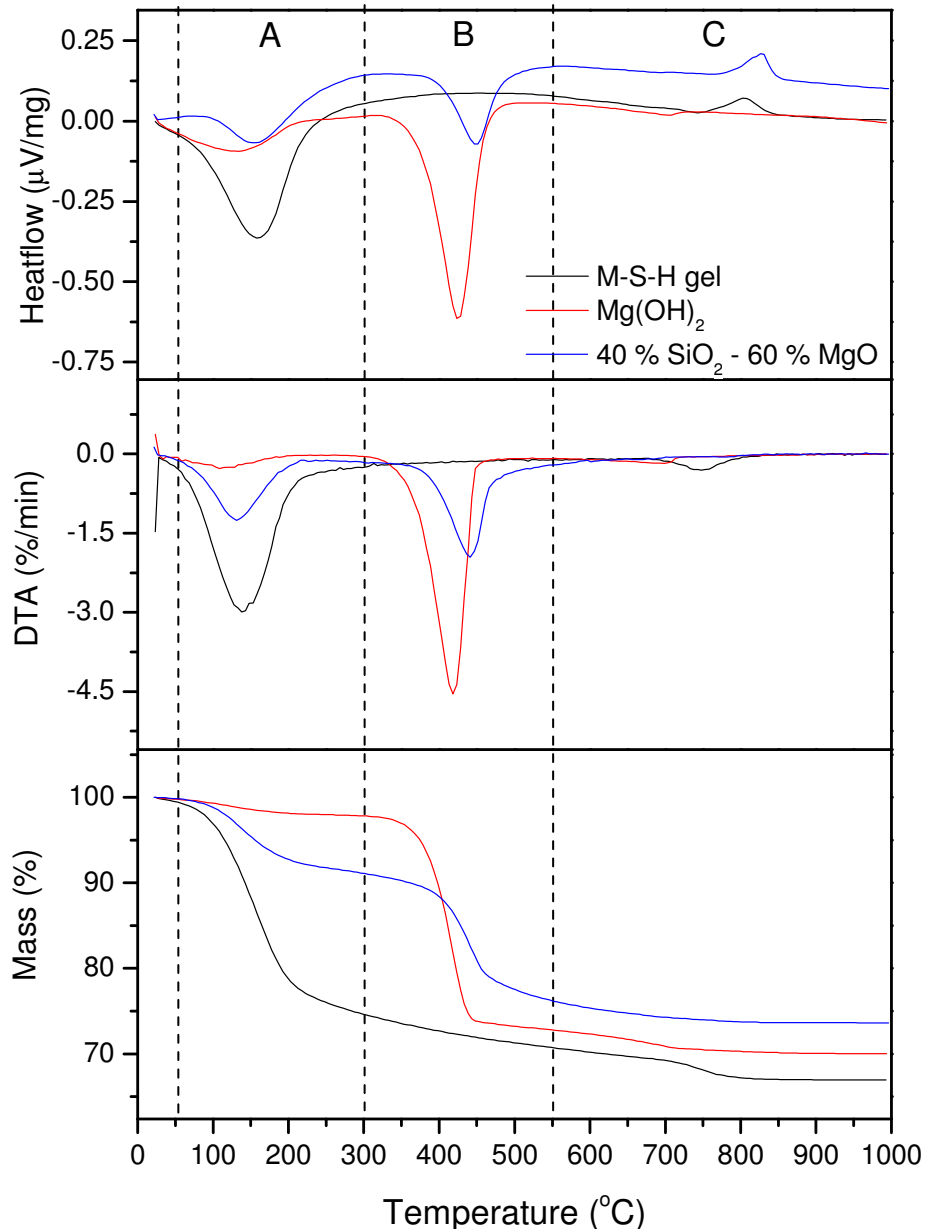


Figure 6.4: Heatflow, DTA and TG mass loss curves of 28 day hydrated MgO, a 28 day cured 40 % SiO₂ – 60 % MgO sample and the M-S-H gel synthesised by the Brew and Glasser method.

The MgO sample after 28 days hydration shows a 30 % mass loss that mainly occurs between 300 °C and 550 °C. This is due to the loss of water from the hydroxyl groups of Mg(OH)₂

(Shand, 2006, Anderson and Horlock, 1962). This can be seen as an endothermic peak in the heat-flow curve in the same temperature region. Two other regions of lesser mass loss for this hydrated MgO sample are seen at 50 – 200 °C and 650 – 700 °C in the TG and DTA. These are believed to due to the loss of weakly absorbed water and the decomposition of small amounts of MgCO_3 and CaCO_3 present in the raw material B30 MgO, detected previously by XRD. This has been reported to undergo decomposition in the ranges of 520 – 730 °C (Dweck et al., 2000). The mass due to weakly absorbed water, ~ 1.1 %, can be seen in the heat-flow curve and that due to carbonate decomposition is associated with a very weak endothermic peak.

The M-S-H gel underwent a mass loss of 33 % which, from looking at all three curves for this sample, mainly occurs at the lower temperatures of 50 – 300 °C, centred at ~ 150 °C although a small proportion of this occurs in the range of 670 – 800 °C.

Thermogravimetric studies of the hydration products of Portland cement hydration have reported that the mass loss of C-S-H occurs in the region of 100 – 320 °C as weakly bound water and OH^- groups in the ‘gel’ are lost (Cong and Kirkpatrick, 1995, Vedalakshmi et al., 2003, Lilkov et al., 2012). Brew and Glasser, in studies on the synthesis of M-S-H gels, concluded that the M-S-H gel they produced with a Mg/Si target ratio of 0.5, the same as that produced in 6.3.2 and has been TG analysed here, had a sepiolite like character (Brew and Glasser, 2005b). TG studies of sepiolite showed mass loss in the 250 °C region arising from loss of hygroscopic water and zeolite type water (Balci, 1999). The mass loss of the M-S-H gel observed in the 50 – 300 °C range has thus been assigned to the loss of this weakly adsorbed surface water and water bound to exchangeable cations in the gel.

Some mass loss, ~ 4.8 %, of the M-S-H gel occurred between 300 °C and 650 °C although loss was too gradual to be represented by a DTA peak. On comparison with sepiolite TG studies, this mass loss is due to loss of coordination water and hydroxyl groups (Frost and Ding, 2003, Balci, 1999).

TG analysis studies by other authors on the decomposition of the mineral sepiolite, $\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$, revealed amongst other mass losses, a mass loss in the 700 – 800 °C region, which was assigned to the loss of structural hydroxyl groups (Balci, 1999, Mora et al., 2010). It is therefore assumed that the mass loss in the 670 – 800 °C, is related to further and final decomposition of the M-S-H gel due to loss of further hydroxyl groups, which are more strongly bonded than those lost at the lower temperature region of 50 – 300 °C.

For the M-S-H gel, an exothermic peak between 750 – 850 °C is observed in the heat-flow curve but not in the DTA curve. TG studies on C-S-H revealed an exothermic peak at around 900 °C which is believed to be due to the formation of calcium silicates from C-S-H (Esteves, 2011, Vedalakshmi et al., 2003). A similar crystallisation of the dehydrated M-S-H gel to crystalline magnesium silicates could explain the exothermic ‘crystallisation’ heat-flow peak observed for the M-S-H gel, albeit at the slightly lower temperature, as well as explaining why no mass change is seen in the same temperature region. XRD analysis of the material after TG (i.e. after heating to 1000 °C) showed that the M-S-H gel had crystallised to crystalline magnesium silicate enstatite, MgSiO_3 confirming that crystallisation occurs. This was also observed in TG studies of the decomposition of sepiolite (Mora et al., 2010). The spectra can be seen in the Appendix.

Table 6-2: Summary of the mass losses observed and the proposed reasons for these mass losses for the 28 day hydrated MgO (i.e. essentially $\text{Mg}(\text{OH})_2$) and synthesised M-S-H gel.

Material	Temperature region (°C)	Reason for mass loss
$\text{Mg}(\text{OH})_2$	50 - 200	Loss of weakly bound water
	300 - 550	Loss of $\text{Mg}(\text{OH})_2$ hydroxyl groups
	650 - 700	Loss of CaCO_3 from raw MgO material
M-S-H gel	50 - 300	Loss of gel water and hygroscopic water
	300 - 650	Loss of coordination water and some hydroxyl units
	670 - 800	Loss of remaining hydroxyl groups

The regions of mass loss observed for the $\text{Mg}(\text{OH})_2$ and M-S-H gel samples along with the reason for the mass losses can be seen in Table 6-2. The hydrated 40 % SiO_2 – 60 % MgO sample shows mass losses, DTA and heat-flow peaks in the same regions as those observed in both the $\text{Mg}(\text{OH})_2$ and M-S-H gel, presumably as it contains both of these reaction products. There is a slight shift to higher temperature in the DTA and heat-flow peaks in region B in Figure 6.4, due to dehydration of $\text{Mg}(\text{OH})_2$.

TG analysis has shown that the major reaction products of the hydrated $\text{MgO} - \text{SiO}_2$ system, $\text{Mg}(\text{OH})_2$ and M-S-H, both lose mass in very similar temperature regions on heating to 1000 °C, as see in Figure 6.4. However, major mass losses of M-S-H gel overlap with minor mass losses of $\text{Mg}(\text{OH})_2$ and vice versa. For this reason, the minor mass losses will be assumed to be insignificant in comparison. Based on this assumptions, TG mass losses of hydrated $\text{MgO} - \text{SiO}_2$ samples can be assigned as either coming from $\text{Mg}(\text{OH})_2$ or M-S-H gel depending on temperature region in which they occurred. Table 6-3 below summarises which mass losses of a hydrated and dried $\text{MgO} - \text{SiO}_2$ mix will be assigned to which reaction product. The mass loss zones can be observed in Figure 6.4.

Table 6-3: Summary of how mass losses from TG analysis of hydrated and dried $\text{MgO} - \text{SiO}_2$ will be assigned as arising from either $\text{Mg}(\text{OH})_2$ or M-S-H depending on the temperature region in which they occur. The regions A, B and C can be seen depicted in Figure 6.4.

Mass loss zone	Temperature region (°C)	Reaction product
A	50 - 300	M-S-H gel
B	300 - 550	$\text{Mg}(\text{OH})_2$
C	550 - 1000	M-S-H gel

By summing the mass losses in the 50 – 300 °C region with those of the 550 – 1000 °C region, a total mass loss value roughly representing the M-S-H gel content can be calculated, whereas the mass loss over temperatures of 300 – 550 °C indicates the $\text{Mg}(\text{OH})_2$ content. Values presented reflect change in the quantity of these two materials either over time or between samples.

The TG mass losses of the 10 % - 40 % $\text{SiO}_2 - \text{MgO}$ hydrated samples are shown in Figure 6.5. The temperature regions (A, B, C) in which mass loss will be assigned to either M-S-H gel or $\text{Mg}(\text{OH})_2$ according to Table 6-3 are also shown.

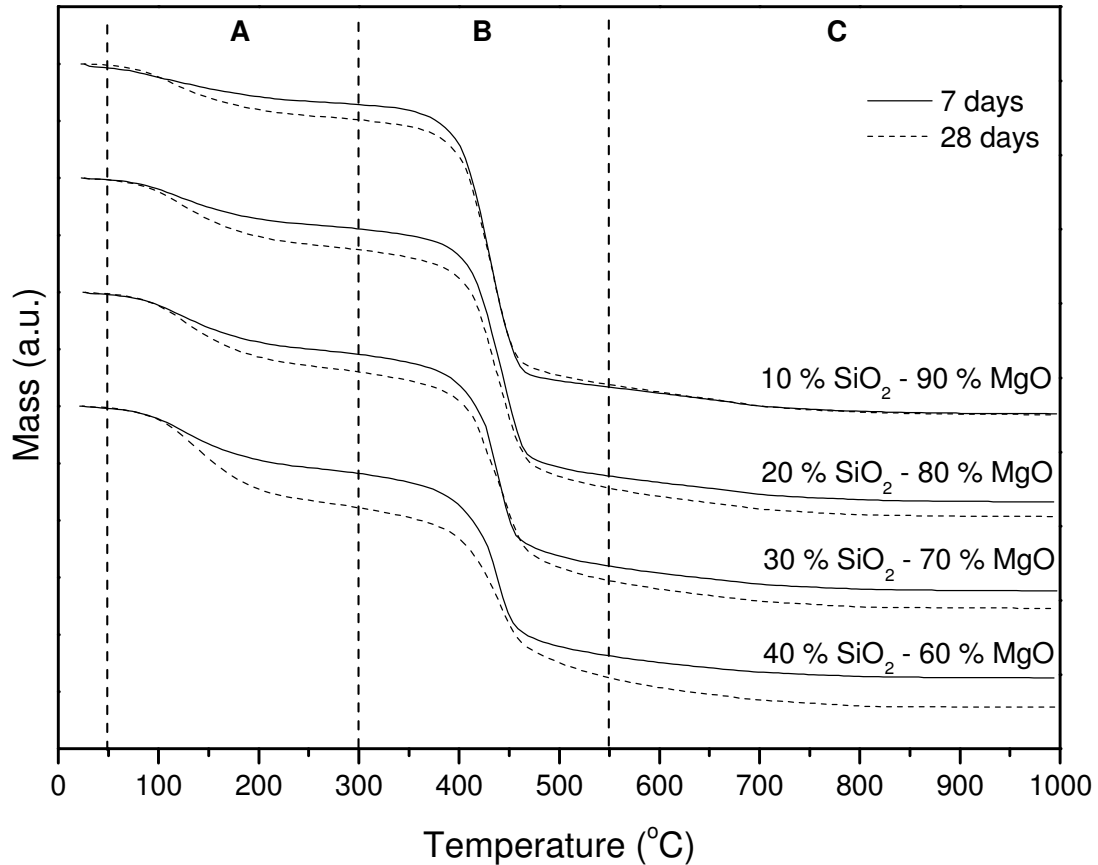


Figure 6.5: Graph of the mass loss curves obtained by TG analysis of the 10 %, 20 %, 30 % and 40 % SiO_2 samples after 7 and 28 days. The regions (A, B, C) have been labelled in which the mass loss value will be assigned to a specific reaction material according to Table 6-3.

Figure 6.5 shows that for each sample, mass loss increases between 7 and 28 days and that this increase is larger for samples containing higher percentages of SiO_2 . It can also be seen that in particular, mass losses are greater in region A than in B with increasing SiO_2 content. The specific values of the mass losses within each region are assigned to coming from one of the two reaction products, M-S-H gel or $\text{Mg}(\text{OH})_2$ according to Table 6-3 and have been plotted in Figure 6.6.

Figure 6.6 represents the difference in M-S-H gel and $\text{Mg}(\text{OH})_2$ content between samples containing different percentages of SiO_2 at 7 and 28 days. The $\text{Mg}(\text{OH})_2$ content has been adjusted to take into account the different percentages of MgO initially present in the samples and in knowledge that decomposition of $\text{Mg}(\text{OH})_2$ should show a 30.9 % mass loss. Therefore, the values shown for $\text{Mg}(\text{OH})_2$ represent the percentage of MgO that was originally present in the mix, that is now present as $\text{Mg}(\text{OH})_2$.

Figure 6.6 shows that with increasing SiO_2 content, M-S-H content increases. This is true at both 7 and 28 days. The higher M-S-H gel mass loss at 28 days also indicates that M-S-H gel content is increasing with time as further SiO_2 is consumed.

At 7 days, it is clear that the higher the SiO_2 content, the lower the $\text{Mg}(\text{OH})_2$ content of samples, presumably as more $\text{Mg}(\text{OH})_2$ has reacted with the higher SiO_2 contents to form further M-S-H gel. By 28 days, $\text{Mg}(\text{OH})_2$ content has reduced with all samples containing more similar $\text{Mg}(\text{OH})_2$ contents in the range of 83 – 84.5 %. This must be due to $\text{Mg}(\text{OH})_2$ reacting with SiO_2 to form more M-S-H gel, which is in agreement with M-S-H gel mass losses.

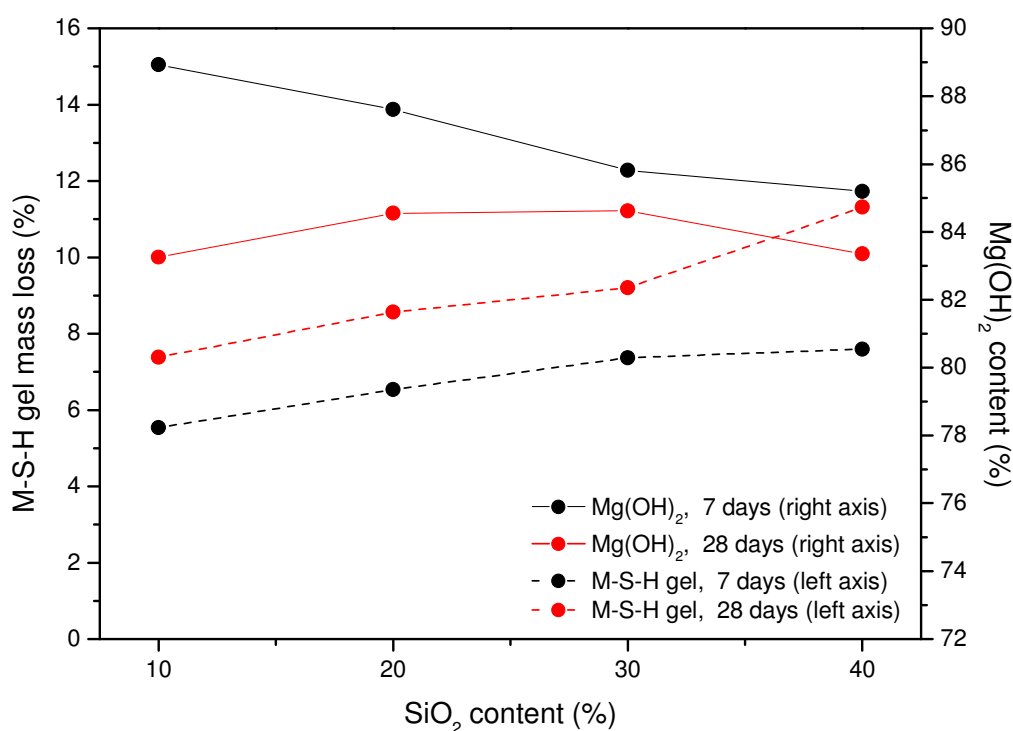


Figure 6.6: Graph showing the variation in M-S-H gel and $\text{Mg}(\text{OH})_2$ content with SiO_2 percentage and between 7 and 28 days.

As mentioned, Figure 6.6 shows the actual $\text{Mg}(\text{OH})_2$ content of samples based on TG mass losses. By knowing these values, it can be inferred that the maximum possible amount of M-S-H gel present in each sample the corresponding $\text{Mg}(\text{OH})_2$ content subtracted from 100 %. For example, for the 10 % SiO_2 sample at 7 days, $\text{Mg}(\text{OH})_2$ content is ~ 89 %. The remaining 11 % mass of the sample could be made up of M-S-H gel. However, without knowing the stoichiometry of the M-S-H gel formed it is not possible to say exactly what percentage of

this 11 % is M-S-H gel. Also, as seen in XRD results, an unquantifiable amount of unreacted MgO is present in the samples so less than 11 % of the sample is M-S-H gel.

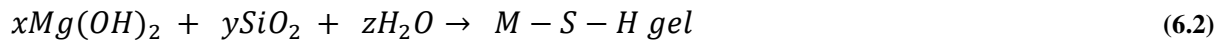
Based on this subtraction, it can be said, that even by 28 days, all samples contain a maximum M-S-H gel mass content of less than 17 % M-S-H gel. For the strongest sample, the 30 % SiO₂ – 70 % MgO sample, this value is less than 16 % M-S-H gel.

6.2.4 DISCUSSION

Compressive strength results show that the addition of amorphous SiO₂ to MgO, results in a significant increase in compressive strength upon hydration. These strengths are due to the formation of M-S-H which can be seen from the XRD spectra and TG results. Maximum strengths of 24 MPa and 42 MPa were measured after 7 days and 28 days hydration which was achieved in the 30 % SiO₂ – 70 % MgO.

XRD spectra of all samples made from amorphous SiO₂ and MgO show the presence of unreacted MgO, Mg(OH)₂, possibly SiO₂ as well as the three amorphous humps identified as M-S-H gel. These compounds were identified after both 7 and 28 days curing although a decrease in both Mg(OH)₂ and MgO peak intensity was observed between the two times showing that MgO hydrates to further Mg(OH)₂ which continues to react with SiO₂ to form additional M-S-H gel over this time. This is in agreement with the mass loss data. However, it was found that even at 28 days, for all samples, Mg(OH)₂ content by mass was still high, and no lower than 83 %.

Based on these results, a proposed reaction of formation of the hydration products observed are represented in two steps according to equations 6.1 and 6.2:



After the initial formation of the first Mg(OH)₂, these two reactions are believed to occur in tandem with freshly formed Mg(OH)₂ from the hydration of MgO then going on to react with SiO₂ to form M-S-H so that Mg(OH)₂ is constantly being formed and then consumed. This is in agreement with XRD and TG mass loss results which show that Mg(OH)₂ content decreases and M-S-H gel increases between 7 and 28 days. The exact rates at which they occur are unknown.

Equation 6.1 would be expected to continue until all MgO has been used up. Due to the relatively low percentages of SiO₂ used in this study, SiO₂ content will be a major limiting

factor in M-S-H gel formation so equation 6.2 will only apply until all soluble SiO_2 source has been consumed. It is proposed that not enough SiO_2 is available for all $\text{Mg}(\text{OH})_2$ to 'convert' into M-S-H gel for reasons discussed in the following paragraph.

The start Mg/Si ratios of the 10 %, 20 %, 30 % and 40 % SiO_2 containing samples are 11.6, 5.2, 3 and 1.9 respectively. Studies by Brew and Glasser tentatively concluded that for target Mg/Si ratios of higher than 1.5, a single reaction phase of M-S-H gel cannot exist (Brew and Glasser, 2005b). As all the target Mg/Si ratios were higher, this suggests that a single reaction product of only M-S-H gel will not exist even at later curing times, i.e. some unreacted $\text{Mg}(\text{OH})_2$ will always be present alongside the M-S-H gel.

The fact that the 30 % SiO_2 – 70 % MgO sample gave the highest strength results, despite containing lower M-S-H gel content than the 40 % SiO_2 – 60 % MgO sample according to both XRD and mass loss results, suggests that it is not merely the M-S-H content which determines the strength of the samples, but the ratio of materials in the hydrated mix. The exact reason as to how the ratio of $\text{Mg}(\text{OH})_2$ and M-S-H gel effects strength is unknown. A proposed reason is suggested below.

It has been proposed that M-S-H gels are phases of low crystallinity, having structures somewhere between those of true gels and of crystalline M-S-H minerals (Brew and Glasser, 2005a, Gollop and Taylor, 1992). For the high Mg/Si ratios use in this work, these M-S-H minerals are most likely to be serpentine [$3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$] or talc [$3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$] (Brew and Glasser, 2005b). For all these compositions, the ratios of H_2O to MgO are 0.67 and 0.33 respectively. In the hydration of MgO to $\text{Mg}(\text{OH})_2$, one mole of water is consumed for every mole of MgO hydrated so the ratio of H_2O to MgO is 1. Therefore, depending on the type and mix of M-S-H gel and its similarities to these crystalline M-S-H materials, the amount of water contained in M-S-H gels could be less than that 'fixed' by MgO hydration to $\text{Mg}(\text{OH})_2$.

Considering that all samples were made using the same w/s ratio, and the majority of water is probably consumed during MgO hydration as opposed to M-S-H gel formation, this means that samples made from higher SiO_2 content, and lower MgO content, mixes, will use up less water so will have more porosity. Up to a certain percentage of SiO_2 , this extra porosity could be counterbalanced by the formation of M-S-H gel which connects $\text{Mg}(\text{OH})_2$ particles and fills up void space. However, there must be a point at which M-S-H gel no longer counteracts the extra water. The optimum percentage of SiO_2 could be dependent upon finding the best

balance between M-S-H gel content and excess water. It appears that the 30 % SiO_2 – 70 % MgO system facilitates the optimum balance and thus produces the highest strengths.

However, this is just a hypothesis and based on the water contents of crystalline M-S-H phases as opposed to gels. Work into the investigation of the porosity and density, as well as shrinkage/expansions of samples of different MgO and SiO_2 contents would be required to test this hypothesis.

6.2.5 CONCLUSIONS

- The hydration of SiO_2 – MgO mixes containing 10 % to 40 % SiO_2 produces samples which achieve compressive strengths of up to 42 MPa after 28 days curing;
- M-S-H gel formed from the reaction of SiO_2 and MgO on hydration is believed to be the significant source of the compressive strengths although reaction to 100 % M-S-H gel was incomplete with Mg(OH)_2 present in all samples due to the relatively low SiO_2 contents with M-S-H gel content by weight estimated at being less than 16 %;
- M-S-H gel content was shown to increase between 7 and 28 days whilst Mg(OH)_2 content decreased, as Mg(OH)_2 is consumed in M-S-H gel formation;
- More M-S-H gel and less Mg(OH)_2 is formed in samples with higher SiO_2 content although the highest compressive strength, of 42 MPa at 28 days, was achieved by the 30 % SiO_2 – 70 % MgO system;
- It is thus proposed that compressive strength of hydrated MgO – SiO_2 samples is due not only to M-S-H gel content, but also to the quantity of Mg(OH)_2 present in the sample.

6.3 STUDY OF THE OPTIMISED 30 % SiO₂ – 70 % MgO SYSTEM

The low early age activity of silica fume with Ca(OH)₂ in cements to form C-S-H has been reported by several researchers (Larbi et al., 1990, Mitchell et al., 1998, Papadakis, 1999). Research on the comparison of the use of silica fume and nanosilica as a pozzolan to react with Ca(OH)₂ to form C-S-H in cement pastes concluded that nanosilica accelerates the cement hydration process increasing early age strength (Ye et al., 2007, Senff et al., 2010). For this reason, in order to attempt to improve strength development of the optimised MgO – SiO₂ system, a new SiO₂ source, in the form of the nanosilica powder, NY SiO₂, was also used to prepare samples.

This section studies the strength development and properties of the optimised sample over time. The 30 % SiO₂ – 70 % MgO was selected, made with two different SiO₂ sources, microsilica (silica fume) as used in the previous section, and a nanosilica.

6.3.1 MATERIALS

As in 6.3, 920d SiO₂ and B30 MgO were used. As observed in Table 4.1 in section 4.2, the NY SiO₂ has a much higher specific surface area of ~ 284 m²/g, than the 18.4 m²/g of the 920d SiO₂. This is due to the smaller average particle size of NY SiO₂ particles, which were measured as being ~ 3 µm as opposed to the average size of 920d SiO₂ agglomerates, of ~ 135 µm, despite being made up of individual SiO₂ particles of ~ 0.15 µm as shown in Table 4-1 in 4.2.

Another difference observed in Table 4-1 between the two SiO₂ types is the higher purity of the NY SiO₂ containing 99.7 wt. % SiO₂ as opposed to the 97.6 wt. % SiO₂ of the 920d SiO₂ powder, due to the presence of minor amounts of CaO and sulphate based compounds in this latter SiO₂.

XRD analysis of these SiO₂ powders is seen in Figure 6.7. For both SiO₂ types, a broad peak is seen centred at 22.5 2θ° which was identified as amorphous SiO₂. For the 920d SiO₂, the presence of quartz or crystalline SiO₂ was also identified as well as a small peak arising from silicon carbide. However, no other peaks were observed including those related to CaO or SO₃ based impurities.

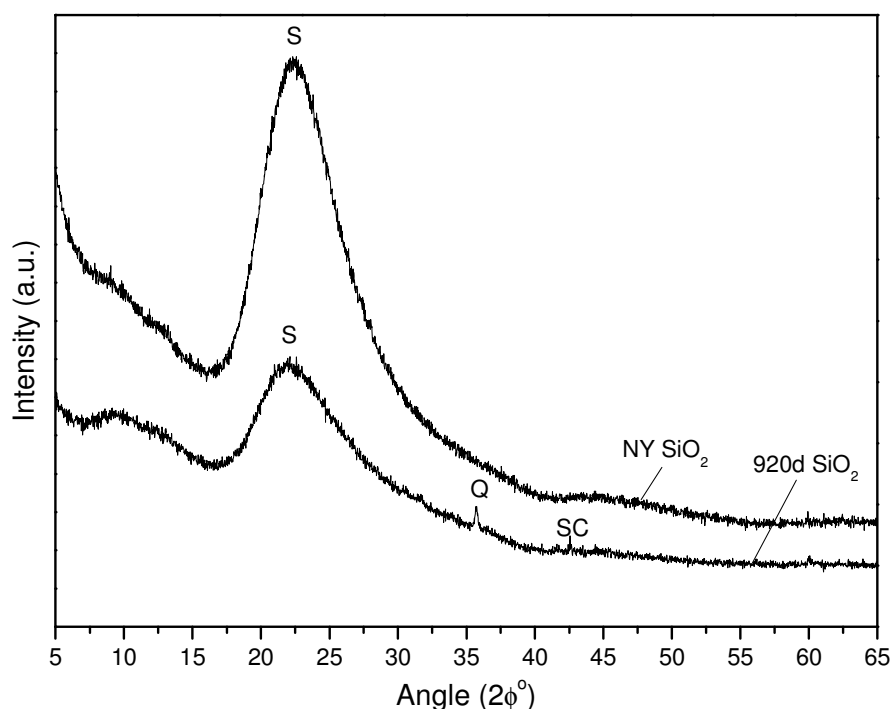


Figure 6.7: XRD spectra of the raw materials 920d SiO₂ and NY SiO₂. The letter S indicates amorphous SiO₂ whilst Q indicates crystalline SiO₂, i.e. quartz, and SC indicates silicon carbide.

6.3.2 METHODS

Measurement of system pH and SiO₂ dissolution rate

The pH of the 30 % SiO₂ – 70 % MgO system, for the two different SiO₂ types were measured along with the pH of the individual components of the system, the raw materials of 920d SiO₂, NY SiO₂ and MgO. Samples to be tested were prepared and measured according to the method in 4.5.1.

A major aim of this section was to determine whether the use of nanosilica increases strength development of the MgO –SiO₂. Therefore the rate of dissolution of both the 920d SiO₂ and NY SiO₂ was measured.

This involved creating sealed bottles containing a mix of 200 mg of SiO₂ powder and 25 ml of pH 11 buffer solution. The buffer chosen was pH 11 based on results of the pH tests. Bottles were stored in an automatic bottle shaker with a bottle for each SiO₂ type being removed periodically up to 7 days. Immediately after removal from the shaker, samples were filtered using a syringe filter through a filter paper of 0.45 µm in order to acquire the filtrate which was then measured using ICP-AES, via the method reported in 4.5.2.

Measurement of setting time

Paste samples at the same w/s ratios as in Table 6-4 were made (according to the method in 4.3.1) and their setting times measured using the Vicat needle method described in 4.4.3.

Compressive strength

In order to assess strength development over time, 30 % SiO₂ – 70 % MgO samples were made and tested for compressive strength after various curing periods. Samples were made with either 920d SiO₂ or NY SiO₂. Samples were made using the minimum w/s ratio possible in order to achieve a mouldable paste. Initial tests showed that due to high specific surface area, NY required the addition of more water in order to make mouldable samples. The samples made for compressive strength testing are summarised in Table 6-4. Samples were mixed and moulded according to the method in 4.3.1 and tested for compressive strength as in 4.4.4.

Table 6-4: Summary of the 30% SiO₂ – 70% MgO samples produced to assess compressive strength development over time for different types of silica.

SiO ₂ and MgO content in dry mix (wt. %)		SiO ₂ type	w/s ratio
SiO ₂	MgO		
30	70	920d	0.59
		NY	0.62

XRD analysis

Samples made were placed in acetone after various time periods. After storing in acetone for 10 days and oven drying to constant weight at 40 °C, they were ground to a fine powder. XRD analysis as described in 4.6.1 was carried out to analyse the crystalline reaction products of these powders.

Estimation of reaction product development

In order to observe the development of the reaction products Mg(OH)₂ and M-S-H gel over time as well, as the effects of the two different SiO₂ sources on the rate of development of these materials, pastes of 30 % SiO₂ – 70 % MgO were made according to 4.3.1 and stored in sealed plastic bags at high humidity. At various times, paste samples were removed from the

bags, crushed, rinsed, and filtered with acetone, after which they were oven dried at 40 °C to constant mass. These powder samples were then analysed by TG (see 4.6.4) and mass losses used to semi-quantify reaction products as described in 6.4. The times at which samples were cured for were: 2 hours, 4 hours, 8 hours, 16 hours, 24 hours, 48 hours, 96 hours (4 days), 7 days (168 hours), 14 days (336 hours), 28 days (672 hours) and 56 days (1344 hours).

6.3.3 RESULTS

pH development over time

Figure 6.8 shows the pH measurements over time for the two 30 % SiO₂ – 70 % MgO mixes, each made with the different SiO₂ types; 920d SiO₂ and NY SiO₂.

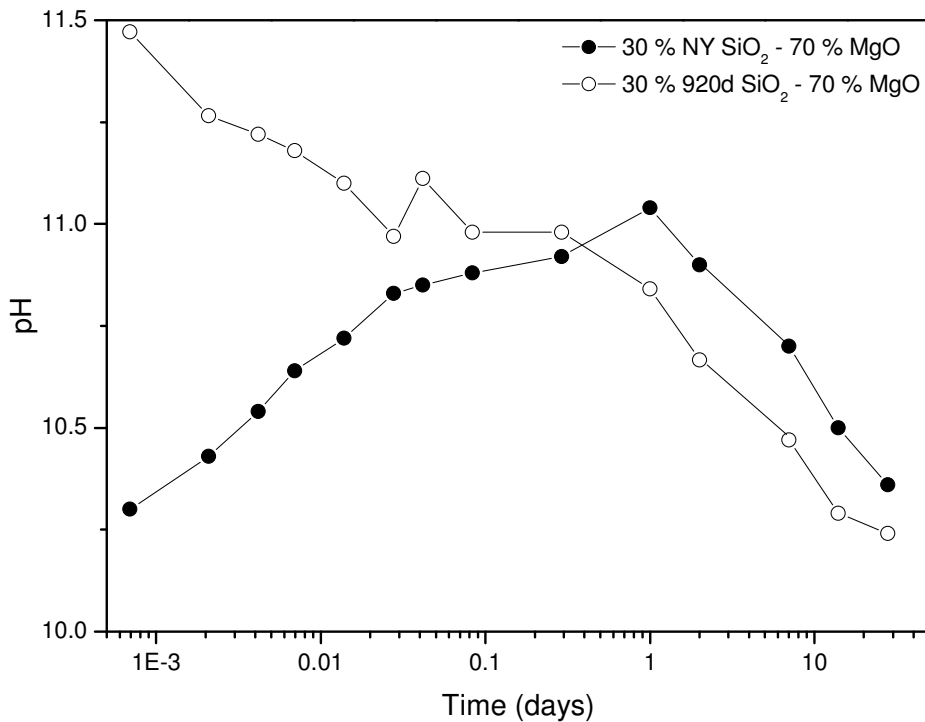


Figure 6.8: Graph of pH development over time of the two 30 % SiO₂ – 70 % MgO mixes made with 920d and NY SiO₂.

The pH of the mix containing 30 % 920d SiO₂ rises to ~11.5 at the start of pH measurement (1 minute) and then slowly decreases over time reaching a pH of ~ 10.8 within 1 day. The pH of the mix containing 30 % NY SiO₂ continues to increase gradually up to 1 day, to pH 11.2. The initial differences in pH are probably due to the lower pH of the NY SiO₂ raw material, of 5.5, compared to that of the 7.5 pH of the 920d SiO₂ as seen in 4.2 in Table 4-1.

After 1 day, the pH of both samples decrease with time at a similar rate although that pH of the 30 % 920d SiO_2 solution is lower, being 10.25 by 28 days compared to the ~ 10.35 of the 30 % NY SiO_2 solution.

The solubility of amorphous SiO_2 significantly increases with increasing pH with alkaline conditions proving preferential for SiO_2 dissolution (Bergna, 1994, Iler, 1979). The data in Figure 6.8 also shows that the pH values achieved are high enough so that SiO_2 should readily dissolve (Hiemstra and van Riemsdijk, 1990). Based on the pH measurement data, a pH 11 buffer was chosen to simulate the initial pH of the system as it represented the midway pH of the two solutions at the start of the measurement period. A pH 11 buffer was thus used as a solvent in which to measure the rate of dissolution of 920d and NY SiO_2 .

Rate of SiO_2 dissolution

The results of the rate of SiO_2 dissolution at pH 11 are shown in Figure 6.9. Curves of best fit have been applied to the data points.

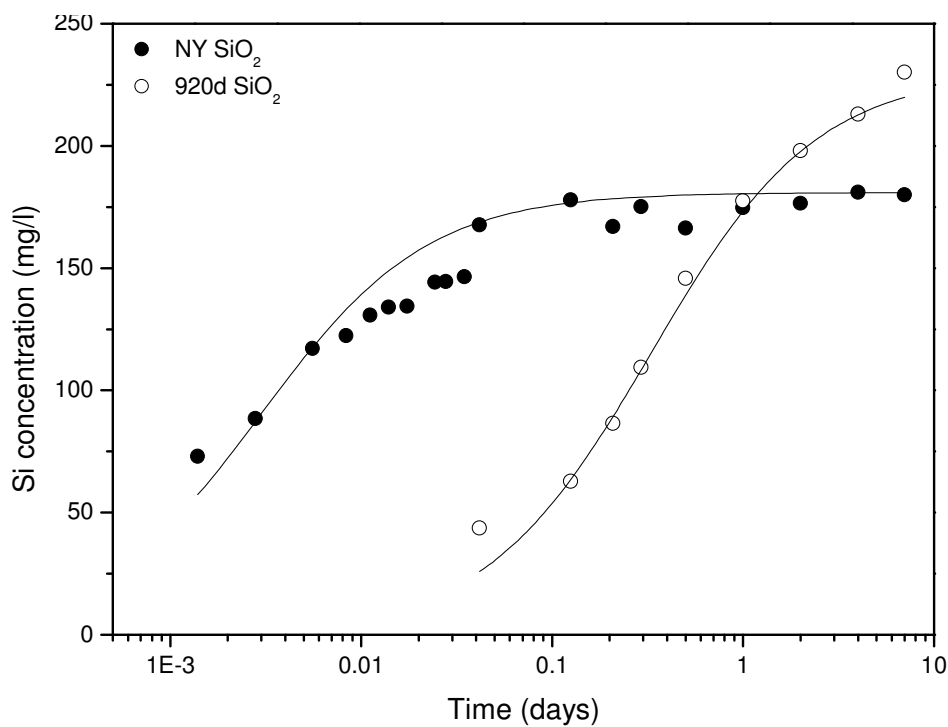


Figure 6.9: Graph showing the change in Si concentration over time of the 920d SiO_2 and NY SiO_2 at pH 11.

It appears from the graph in Figure 6.9 that Si concentration increases at a faster rate for NY SiO_2 than for 920d SiO_2 , levelling off at approximately 3 hours. The Si concentration of the solution containing 920d SiO_2 increases at a slower rate has equalled the maximum of the NY SiO_2 solution by 24 hours, and continues to slowly increase albeit at a slow rate from then

onwards, almost levelling off after 7 days. This data suggests that under pH 11 conditions, NY SiO₂ dissolves at a faster rate than the 920d SiO₂.

This is expected considering the difference in surface area of the two SiO₂ powders. As seen in Table 4-1 in 4.2, NY SiO₂ has a surface area of 284 m²/g, which is much larger than that of 920d SiO₂, which is ~ 18 m²/g, and higher surface areas have been linked to higher dissolution rates (Wilson and Batchelor, 1971, Rimstidt and Barnes, 1980, Berger et al., 1994, Gautier et al., 1994).

Setting time

Figure 6.10 depicts the development of set for the two optimised 30 % SiO₂ – 70 % MgO pastes made with 920d SiO₂ and with NY SiO₂.

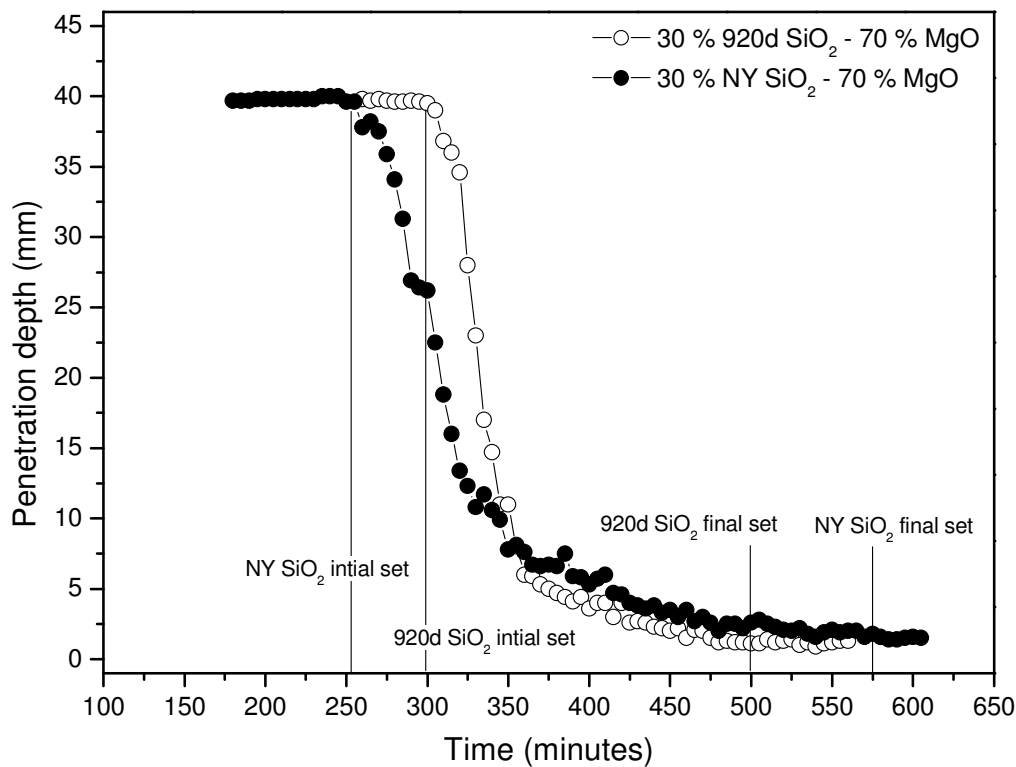


Figure 6.10: Graph depicting setting time of the two 30 % SiO₂ – 70 % MgO systems made with 920d SiO₂ and NY SiO₂.

For the sample made with 920d SiO₂, setting starts at ~ 300 ± 5 minutes, with final set occurring at 500 ± 5 minutes. For the sample containing nanosilica, the NY SiO₂, setting starts at an earlier time of 255 ± 5 minutes, with final setting taking place at 575 ± 5 minutes. From the start of mixing, this means that setting time of the NY SiO₂ containing sample took

585 ± 5 minutes to achieve final set and the 920d SiO₂ containing sample took 510 ± 5 minutes. These setting times are slightly longer than of those of standard Portland cement based sample stated in literature (Ylmen et al., 2009, Zhang, 2012).

Compressive strength

The development of compressive strength over time for samples made with both SiO₂ sources is shown in Figure 6.11.

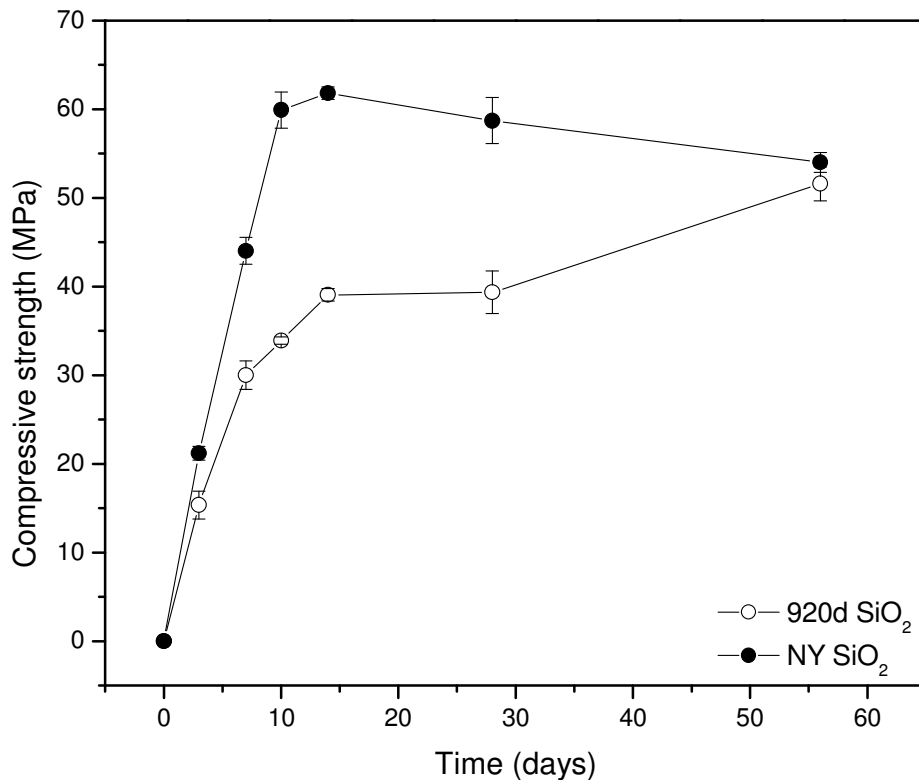


Figure 6.11: Graphs showing the development of compressive strength for hydrated 30% SiO₂ – 70% MgO samples made using the minimum w/s possible for each sample, with 920d SiO₂ and NY SiO₂.

It can be seen that the samples containing NY SiO₂ develop compressive strength faster than those containing 920d SiO₂, achieving a maximum strength of 62 MPa by 14 days. After this time, strength begins to decrease, although the error bars are quite large for samples measured at 28 and 56 days, with the final measurement at 56 days being ~ 54 MPa. On the contrary, the slower strength development of 920d SiO₂ samples means that only 39 MPa is achieved by 14 days. However, strength continues to increase up to 52 MPa by 56 days, the end of the measurement period.

Analysis of crystalline reaction products

Figure 6.12 contains the XRD spectra of hydrated samples of 30 % 920d SiO₂ – 70 % MgO (upper graph) and 30 % NY SiO₂ – 70 % MgO (lower graph) after various curing times. The major peaks have been identified with letters where B is brucite [Mg(OH)₂], M is magnesite [MgCO₃], C is calcite [CaCO₃] and P is periclase [MgO]. Spectra for 3 days and 10 days curing have not been included as they added little extra information. Areas in which M-S-H humps are expected to appear have been highlighted in grey.

As reported in 6.3, the major crystalline phases present in all samples are Mg(OH)₂ and unreacted MgO along with minor impurities, CaCO₃ and MgCO₃ present in the MgO. The most obvious difference between analogous samples over time is the decrease in intensity of the MgO peak at 42.5 2θ°, as it continues to hydrates to Mg(OH)₂ or reacts with SiO₂. On comparing samples made with different SiO₂, this peak appears to be lower in intensity for NY SiO₂ containing samples than for 920d SiO₂ samples, and at 56 days, is not present in NY SiO₂ samples.

The Mg(OH)₂ peaks of NY SiO₂ samples also seem to be slightly more intense than those of 920d SiO₂ samples at the same time periods although for the latter samples, the Mg(OH)₂ peaks appear to be slightly broader, so intensity cannot necessarily be related to Mg(OH)₂ content. It can be tentatively said that crystallite size is greater than 100 nm for the sharp peaks and slightly less than 100 nm for broadened peaks. However, the broadening is not sufficient enough to be able to calculate crystallite size without the application of stringent correction methods as the error of calculation will be large. For this reason, peak broadening will not be considered to be of issue here.

For both 920d SiO₂ and NY SiO₂ containing samples, Mg(OH)₂ peaks decrease slightly with time, indicating that it is being used up by reaction with SiO₂ to form M-S-H gel.

The characteristic M-S-H humps are not visible in Figure 6.12 so the relevant areas have been magnified and are shown in a different Figure 6.13.

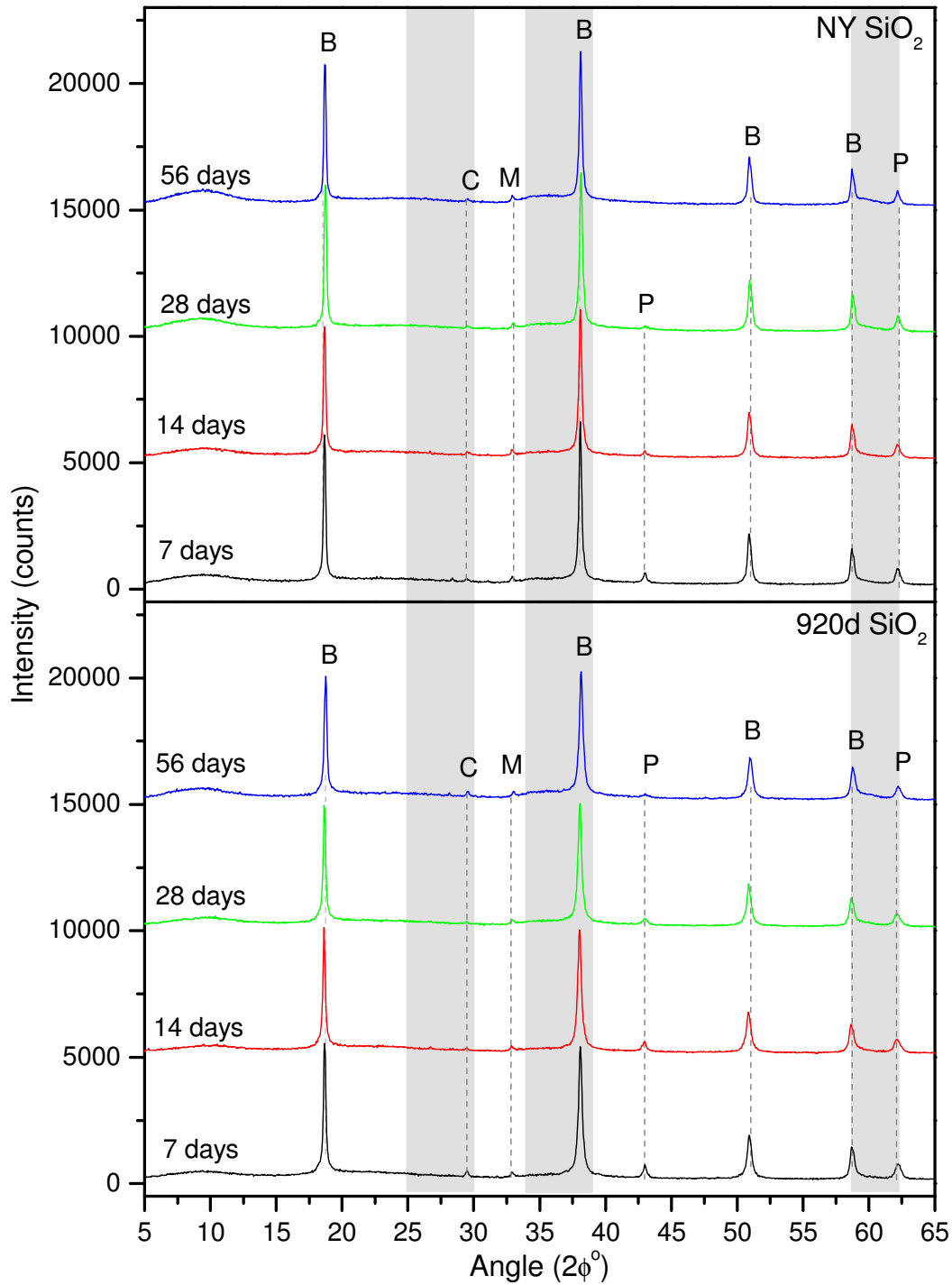


Figure 6.12: XRD spectra of samples of 30 % 920d SiO₂ - 70 % MgO (upper) and 30 % NY SiO₂ - 70 % MgO (lower) cured for various time periods. B = brucite, Mg(OH)₂, C = calcite [CaCO₃], M = magnesite [MgCO₃] and P = periclase [MgO].

Figure 6.13 shows the three magnified areas in which the characteristic humps of M-S-H gel would be expected to appear for 30 % SiO₂ – 70 % MgO samples containing 920d SiO₂ and

NY SiO₂. Within each section, the XRD spectra for each of the four time periods is shown. The angles in which M-S-H gel humps appear have been highlighted in grey.

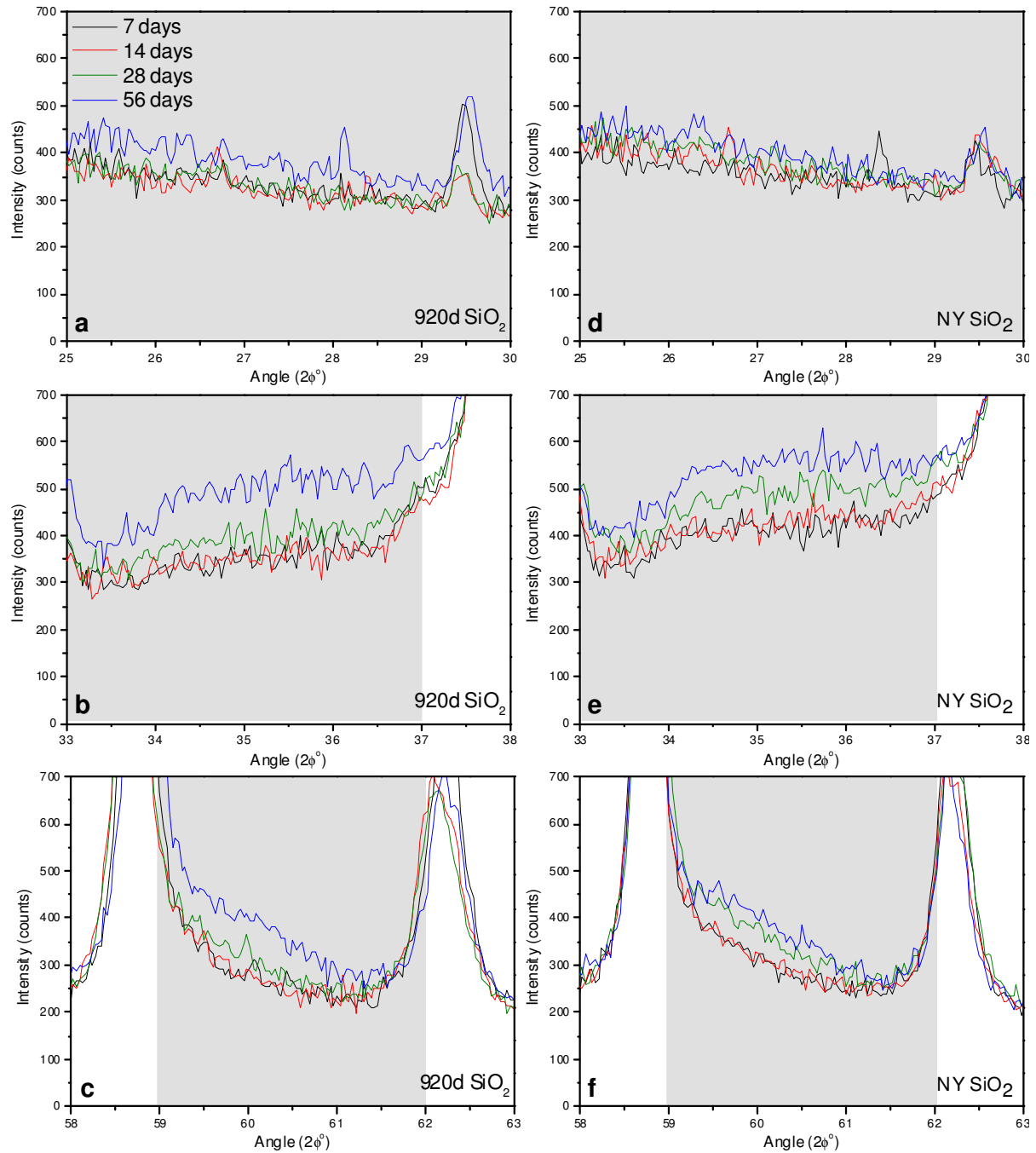


Figure 6.13: Magnified areas of the three characteristic M-S-H humps observed in the XRD spectra of hydrated 30% SiO₂ – 70% MgO samples containing either 920d SiO₂ (a, b, c) or NY SiO₂ (d, e, f). The areas of interest in which M-S-H gel is believed to be present have been highlighted in grey.

From Figure 6.13 it appears that in general, the intensity of the characteristic M-S-H humps increase with time suggesting that M-S-H content increases with time. For the 920d SiO₂

samples, the increase in intensity between 28 days and 56 days appears to be larger than that for the NY SiO₂ samples. On comparison of the two different sample types, it is possible that in general, M-S-H humps are slightly higher in intensity for samples made from NY SiO₂, particularly at 7 days.

Estimation of reaction products

From XRD results it is difficult to determine the development of reaction products. For this reason, TG analysis was used to estimate reaction product content. The results of TG analysis over time in the form of staggered mass loss curves can be seen in Figure 6.14. The mass changes for the 30 % 920d SiO₂ – 70 % MgO samples are shown in the lower graph whilst those of the 30 % NY SiO₂ – 70 % MgO samples are in the upper graph.

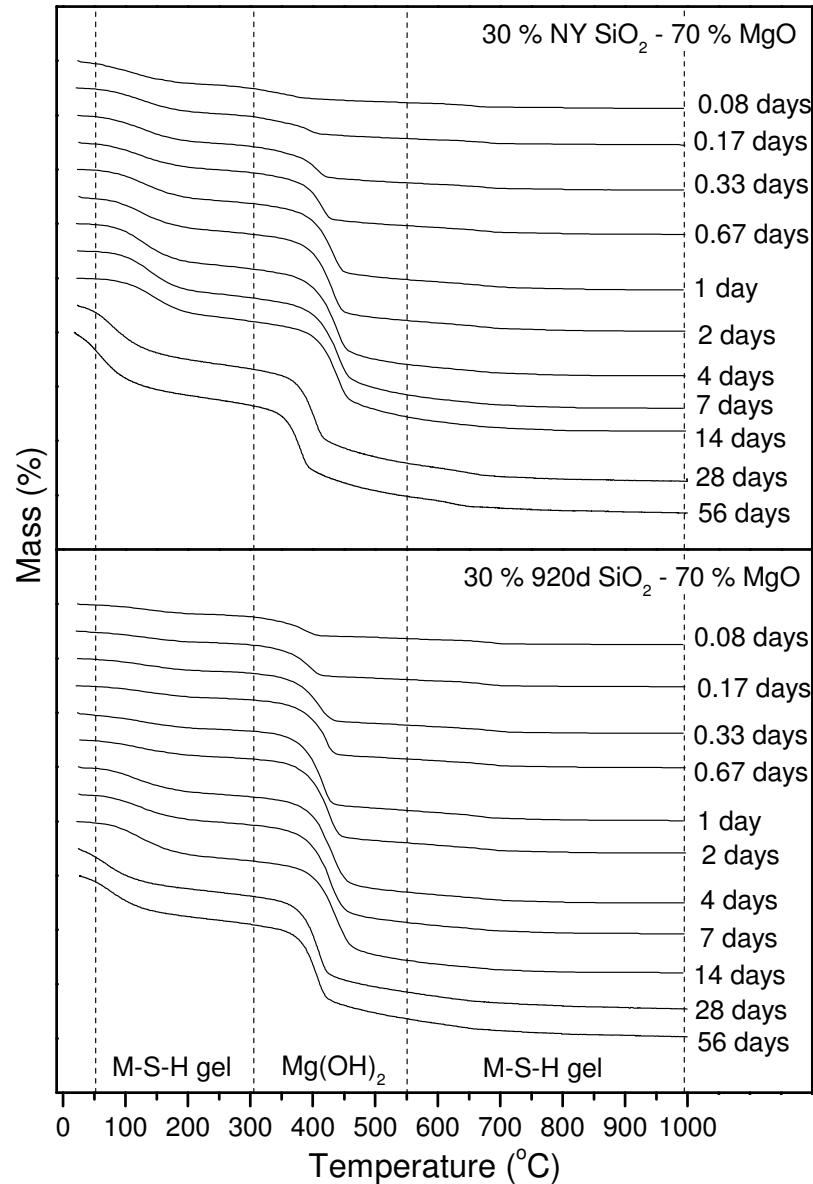


Figure 6.14: TG mass loss curves with temperature for both the 30 % 920d SiO₂ – 70 % MgO and the 30 % NY SiO₂ – 70 % MgO.

Ranges have been labelled with the reaction product whose decomposition is responsible for the mass loss observed within each range in order to approximate reaction product development by the method described in 6.3.

The mass loss data from Figure 6.14 is shown in Figure 6.15. Mass losses have been assigned to either Mg(OH)₂ or M-S-H gel depending upon the temperature region in which they occurred and values of Mg(OH)₂ content have been calculated based on the assumption that a sample of 100 % Mg(OH)₂ would lose 30.9 % mass on application of TG analysis.

Whilst Figure 6.15 shows the actual $\text{Mg}(\text{OH})_2$ content of the sample, the values of M-S-H gel in the samples are just mass losses associated with these reaction products. Actual M-S-H content could not be calculated due to the unknown stoichiometry of the M-S-H gel formed as well as unknown quantities of unreacted MgO and SiO_2 amounts but subtraction of $\text{Mg}(\text{OH})_2$ content from 100 can indicate the upper limit of M-S-H gel no MgO remains.

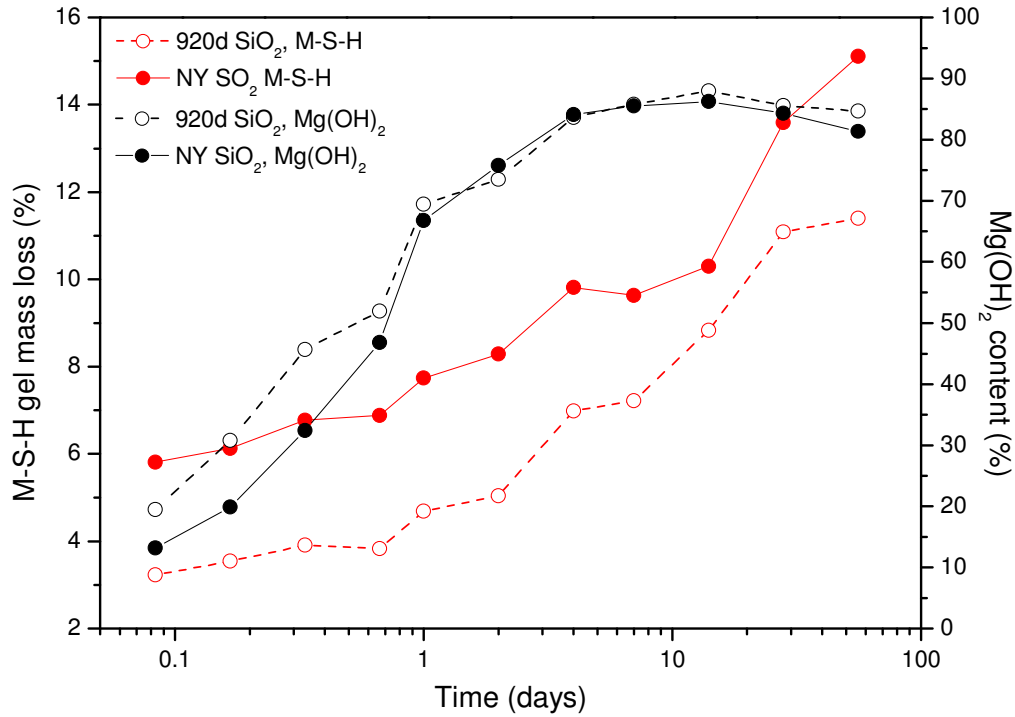


Figure 6.15: Graph showing the development of the reaction products $\text{Mg}(\text{OH})_2$ and M-S-H gel over time in 30 % SiO_2 – 70 % MgO paste samples made from different SiO_2 types; 920d SiO_2 and NY SiO_2 .

Figure 6.15 shows that mass losses due M-S-H gel increases up until 56 days, the end of the measurement period. In general, $\text{Mg}(\text{OH})_2$ content increases with time although it plateaus off at ~ 86 - 87 %, depending on SiO_2 type, before it starts to decrease from 14 days. This shows that both reaction products are forming simultaneously, although $\text{Mg}(\text{OH})_2$ content starts to decrease after 14 days, as its consumption in the formation of M-S-H gel starts to exceed MgO hydration, presumably as maximum available MgO has been hydrated.

On comparison of the pastes made with different SiO_2 types, 920d SiO_2 containing samples have higher $\text{Mg}(\text{OH})_2$ content than the NY SiO_2 containing pastes, in particular at early ages, up to 1 day. After 1 day, $\text{Mg}(\text{OH})_2$ content is almost equal for both types of paste, although the rate of decrease in $\text{Mg}(\text{OH})_2$ mass loss is slightly higher for NY SiO_2 containing samples

from 14 days onwards. This suggests that at early ages, $\text{Mg}(\text{OH})_2$ in 920d SiO_2 samples is consumed at a lower rate than NY SiO_2 samples to produce M-S-H gel.

Throughout the whole testing period, mass losses due to M-S-H gel are higher for NY SiO_2 samples than for 920d SiO_2 samples. This suggests that M-S-H gel forms faster in the presence of NY SiO_2 as NY SiO_2 reacts faster with $\text{Mg}(\text{OH})_2$ than 920d SiO_2 due to the higher surface area and dissolution rate of NY SiO_2 as observed in Figure 6.9. It also indicates that by 56 days, samples made from NY SiO_2 contain a higher percentage of M-S-H gel than those made from 920d SiO_2 . This is in agreement with the slightly lower $\text{Mg}(\text{OH})_2$ content of NY SiO_2 samples indicating that maximum M-S-H content could be up to 19 % as opposed to 15 % calculated from $\text{Mg}(\text{OH})_2$ content of 920d SiO_2 samples at 56 days.

6.3.4 DISCUSSION

M-S-H and $\text{Mg}(\text{OH})_2$ formation over time

Both XRD and TG data showed that the reaction products formed were $\text{Mg}(\text{OH})_2$ and M-S-H gel. Both products were seen to increase with time although a decrease in $\text{Mg}(\text{OH})_2$ content was observed from 14 days onwards. It was also noted that $\text{Mg}(\text{OH})_2$ content was always much higher than M-S-H gel content. These results indicate that $\text{Mg}(\text{OH})_2$ is formed more rapidly by the hydration of MgO , than it is consumed by the reaction with SiO_2 to form M-S-H gel, so a build up of $\text{Mg}(\text{OH})_2$ occurs. However, at later time periods, from 14 days, the rate of MgO hydration slows so that the rate of $\text{Mg}(\text{OH})_2$ consumption is more rapid than its production. This could be because lower amounts of MgO are available to convert to $\text{Mg}(\text{OH})_2$. Unreacted MgO was seen to decrease with time, which supports this.

Dissolution rates of the two SiO_2 types and relation to observed properties

Measurements of pH showed that in general, a pH of ~ 11 represented the 30 % SiO_2 – 70 % MgO system for both types of SiO_2 . As mentioned, this high pH is required by the system in order to facilitate the ready dissolution of SiO_2 (Bergna, 1994, Iler, 1979). Due to its much larger surface area, NY SiO_2 was seen to dissolve at a higher rate than 920d SiO_2 .

This suggests that M-S-H gel is likely to be formed quicker in MgO – SiO_2 samples made with NY SiO_2 as SiO_2 becomes available for pozzolanic reaction faster. Faster M-S-H gel formation could also explain the earlier initial setting time of NY SiO_2 samples although does not help explain why final set occurs slightly later for these samples.

On comparison of the different SiO_2 types, $\text{Mg}(\text{OH})_2$ content is higher in 920d SiO_2 samples than NY SiO_2 up to 1 day and that M-S-H gel content of NY SiO_2 samples was continuously higher than that of 920d SiO_2 samples.

This is linked to the fact that NY SiO_2 dissolves faster than 920d SiO_2 . In the presence of NY SiO_2 , more dissolved SiO_2 is available so the reaction with $\text{Mg}(\text{OH})_2$ is faster than with 920d SiO_2 , explaining the lower $\text{Mg}(\text{OH})_2$ content and the higher M-S-H gel contents of NY SiO_2 samples, in comparison to 920d samples.

The faster rate of M-S-H gel development observed in NY SiO_2 samples explains why samples of NY SiO_2 experienced higher rates of strength development, than those of 920d SiO_2 , achieving maximum strengths of ~ 62 MPa at, whilst compressive strengths of 920d SiO_2 samples continued to increase up 52 MPa at 56 days, the end of the testing period. The smaller size of the nanosilica, NY, could also contribute more to strength than the large 920d SiO_2 microsilica, via the filler effect where the fine SiO_2 particles help to fill the spaces between cement grains thus reducing porosity, increasing density, thus resulting in an improvement of physical properties such as strength and durability (Kontoleon et al., 2012, Kadri et al., 2009, Detwiler, 1989).

Strength decrease of NY SiO_2 containing samples

Despite achieving maximum strength earlier, NY SiO_2 samples showed signs of strength decrease from 14 days onwards, although this needs further investigation. Both NY SiO_2 and 920d SiO_2 samples had achieved comparable $\text{Mg}(\text{OH})_2$ contents by 14 days, which then decreased by similar amounts to 56 days. However, mass losses due to M-S-H gel were significantly higher for the NY SiO_2 sample, which continued to increase from ~ 10.5 % to ~ 15 % from 14 days to 56 days, which is when the strength decrease was observed. For the 920d SiO_2 sample, M-S-H gel mass losses increase from ~ 9 % to 10.5 % over the same time period. Unlike the NY SiO_2 sample though, the 920d SiO_2 sample increased in strength to 56 days, achieving maximum strength of 52 MPa.

This indicates that maximum achievable strength depends on the ratio of the quantity of reaction products in the sample and suggests that too high a proportion of M-S-H gel starts to have a negative effect on compressive strength. One idea is, similar to that discussed in 6.2.4, that $\text{Mg}(\text{OH})_2$ ‘locks up’ more water than the M-S-H gel. For lower levels of M-S-H gel content, the strength provided by the M-S-H gel can balance the excess water and hence porosity it creates. However, as M-S-H gel formation starts to use up more $\text{Mg}(\text{OH})_2$,

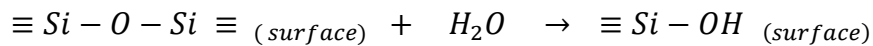
creating more porosity, there comes a point when its strength can no longer negate the weakness the extra porosity has created, weakening samples. This is just a proposal and studies into sample porosity are required to support or invalidate this suggestion. The different densities of the reaction products and shrinkage/expansion over time should also be investigated to help determine the source of this strength decrease.

Possible reaction mechanism

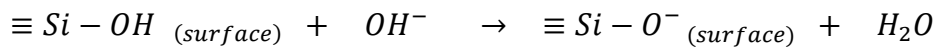
Several researchers studying the formation of C-S-H gel by the reaction of $\text{Ca}(\text{OH})_2$ with a SiO_2 pozzolan have concluded that the pozzolanic reaction is heterogeneous (solid-solution) and based on the absorption of ions and precipitation of reaction products on surfaces of the pozzolan (Chagas Cordeiro et al., 2009, Nair et al., 2008, Yu et al., 1999, James and Rao, 1986) Therefore the particle size or surface area of the pozzolan strongly influences the rate at which C-S-H is formed, further explaining the difference the rate M-S-H formation and related properties, in samples made with the NY SiO_2 , as there its larger surface area will not only increase dissolution but increase availability of activated SiO_2 surfaces on which M-S-H gel can nucleate.

Assuming that the reaction of SiO_2 with $\text{Mg}(\text{OH})_2$ is analogous to the pozzolanic reactions that form C-S-H, the following mechanism of M-S-H gel formation is suggested.

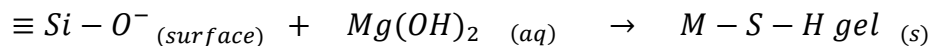
The siloxane bonds on the surface of SiO_2 react on contact with water producing $\equiv \text{Si} - \text{OH}$ at the surface (Bulteel et al., 2002, Iler, 1979). The reaction with water also creates silicic acid, H_4SiO_4 , which was measured by ICP-OES to assess the solubility of the SiO_2 types (Bai et al., 2009).



In basic solutions, the following reaction at the surface occurs (Dove and Crerar, 1990):



$\text{Mg}(\text{OH})_2$ in solution then reacts with these new surfaces, so M-S-H gel nucleates on the SiO_2 surface (Ye et al., 2007).



Summary

Results have shown that $\text{Mg}(\text{OH})_2$ and M-S-H gel formation occurs simultaneously. $\text{Mg}(\text{OH})_2$ and M-S-H gel formation depends on their solubility and nucleation rates, which in

turn depends on the relative concentration of their ions in solution and the availability of nucleation sites on solid surfaces, which has shown to vary depending on SiO₂ type used. NY SiO₂, which has a larger surface areas, reacts with Mg(OH)₂ faster than 920d SiO₂ thus forming M-S-H gel faster, resulting in the faster strength development of samples. However, although maximum strength is achieved earlier, strength decrease is believed to be related to quantities of reaction products Mg(OH)₂ and M-S-H gel was observed for these samples. Further research needs to be carried out to determine the exact reason for this strength decrease and if it also occurs at later time periods for 920d samples. Understanding this will allow the further optimisation and improvement of MgO – SiO₂ sample properties.

6.3.5 CONCLUSIONS

- Properties of samples made from the optimised 30 % SiO₂ – 70 % MgO system can display different properties depending on whether nanosilica or microsilica silica fume is used;
- Regardless of the SiO₂ type, promising strengths can be achieved although the rate at which this compressive strength is developed depends on the SiO₂ type;
- The sample which gave the highest compressive strength overall and showed the best strength development was the 30 % NY SiO₂ – 70 % MgO sample, which achieved 62 MPa at 14 days;
- Due to larger specific surface area, leading to higher pozzolanic activity the reaction of NY SiO₂ with MgO is much faster than that of 920d SiO₂, leading to higher M-S-H contents;
- The rate of strength gain is believed to be related to the rate at which M-S-H gel forms, with faster formation leading to higher earlier strengths. It is proposed that the ratio of Mg(OH)₂ to M-S-H gel content, and not just final M-S-H gel content, plays an important role in determining the maximum achievable strength;
- The samples which gave the highest strength, the 30 % NY SiO₂ sample decreases in strength after reaching maximum compressive strength. Longer curing times (> 56 days) are required to validate the extent of this decrease as well as seeing if this is also a problem at later timer periods for 30 % 920d SiO₂ samples;
- Setting times of ~ 8 to 10 hours depending on SiO₂ type used, are longer than reported for Portland cements.

6.4 OVERALL CHAPTER CONCLUSIONS

- Based on compressive strength data and taking into consideration the noted decrease in workability that the addition of SiO_2 to MgO produces, a 30 % SiO_2 – 70 % MgO mix has been selected as the optimum MgO – SiO_2 binder. This corresponds to a Mg/Si ratio is 3;
- Due to the high Mg/Si ratio, the reaction products are a mixture of M-S-H gel and Mg(OH)_2 ;
- The mixture of M-S-H gel and Mg(OH)_2 create samples with promising compressive strengths although strength development with 920d SiO_2 is slow;
- The use of a nanosilica as opposed to microsilica was found to accelerate strength development due to faster M-S-H gel formation;
- It is proposed that the ratio of Mg(OH)_2 to M-S-H gel content is a key parameter in creating strong and stable samples;
- TG studies showed that the overlap of mass loss of M-S-H gel and Mg(OH)_2 , as well as the unknown stoichiometry of the M-S-H gel make it difficult to quantify sample composition;
- It has been possible to compare the development of Mg(OH)_2 and M-S-H gel of samples made with the same MgO/SiO_2 ratio using mass loss data derived from TG analysis. Results appear to be in agreement with XRD results. This method can provide some data on the compositional data of MgO – SiO_2 binders;
- Setting times are longer than those stated for standard cement samples but MgO – SiO_2 sample could have potential in applications where fast set is not required;
- Extensive further work is required to investigate this optimised system.

7 STUDY OF THE MgO – HY – SiO₂ SYSTEM

7.1 INTRODUCTION

Chapter 5 investigated the strengths and reaction products of the MgO – HY binder. This binder is one example of an MgO – hydrated magnesium carbonate system that, as discussed in 2.5, is the focus of research being undertaken by Novacem to manufacture commercial low carbon MgO based cements.

As described in 2.5.2, Novacem produce both MgO and hydrated magnesium carbonates for the Novacem binder from magnesium silicate. This involves CO₂ recovery in order to reduce the emissions associated with raw materials processing. According to the original Novacem patent, SiO₂ is present in the resulting Novacem product together with MgO and hydrated magnesium carbonates (Vlasopoulos and Simons, 2012). For this reason, it is necessary to understand the effects of SiO₂ on the MgO – hydrated magnesium carbonate binder system.

Previous chapters have reported on investigations into the MgO – HY and the MgO – SiO₂ systems. This chapter investigates the properties of the three-component MgO – HY – SiO₂ system which is believed to be analogous to materials resulting from the Novacem manufacturing process

7.2 MATERIALS

The raw materials used were B30 MgO, Calmag HY, 920d SiO₂ and NY SiO₂. Deionised water was used.

7.3 METHODS

It was decided to investigate only samples with 70 % MgO content and vary the proportion of HY and SiO₂. This was because, of the two systems, the one which contained the highest proportion of MgO, the MgO – SiO₂ system, consisted of 30 % SiO₂ – 70 % MgO, which was the optimum MgO – SiO₂ system selected in Chapter 6. All sample pastes were made according to the method in 4.3.1

Future references to the samples will be written in an abbreviated fashion, of the form X/Y, where X indicates the percentage of HY and Y indicates the percentage of SiO₂. If referring to a specific type of SiO₂, the name of the SiO₂ will follow. If no name follows, then the

notation applies to both SiO₂ type. For example, a 5/25 NY sample is referring to a sample made from 5 % HY and 25 % NY SiO₂.

Compressive strength

Samples made for compressive strength testing are summarised in Table 7-1. The abbreviated names of samples are also included.

Table 7-1: Summary of MgO - HY - SiO₂ samples made for compressive strength testing.

Abbreviated sample name	MgO/HY/SiO ₂ content in dry mix (wt. %)			SiO ₂ source	w/s ratio	Curing time (days)
	MgO	HY	SiO ₂			
30/0		30	0		0.66	56
25/5 920d		25	5		0.65	2, 7, 28, 56
20/10 920d		20	10		0.64	56
15/15 920d	70	15	15	920d	0.63	56
10/20 920d		10	20		0.62	56
5/25 920d		5	25		0.61	2, 7, 28, 56
0/30 920d		0	30		0.6	56
30/0		30	0		0.66	56
25/5 NY		25	5		0.66	2, 7, 28, 56
20/10 NY		20	10		0.65	56
15/15 NY	70	15	15	NY	0.65	56
10/20 NY		10	20		0.64	56
5/25 NY		5	25		0.64	2, 7, 28, 56
0/30 NY		0	30		0.64	56

The lowest w/s ratio possible was used to make each sample. It was observed that the HY, being made of many small particles and void spaces as seen in Chapter 5, required the

addition of a larger percentage of water in order to achieve a mouldable paste, than either of the two SiO_2 powders so in general, increasing HY content resulted in the use of higher w/s ratios. Due to its larger surface area in comparison to the 920d SiO_2 , as observed in 4.6.1, the NY SiO_2 had a high water demand more similar to that of the HY. Therefore, samples made from HY and 920d SiO_2 were made using a wider w/s ratio range than those made from HY and NY SiO_2 , which should be noted when analysing compressive strength results. These high water demands were another reason why MgO content of these MgO – HY – SiO_2 compositions was kept at a relatively high value of 70 %.

All samples were tested for compressive strength at 56 days but some, representing the upper and lower ratios of HY/ SiO_2 of the MgO – HY – SiO_2 samples were tested for compressive strength more frequently in order to observe the general strength development over time. Compressive strength tests were carried out as described in 4.4.4.

XRD analysis

XRD as described in 4.6.1 was used to analyse reaction product composition after the samples prepared for compressive strength tests were stored in acetone for 10 days, oven dried at 40 °C and ground to a fine powder.

TG analysis

TG analysis of the dried and powdered reaction products $\text{Mg}(\text{OH})_2$, formed by 28 day hydration of MgO, and M-S-H gel made according to 6.2.2, alongside the raw material HY, was carried out in accordance with the method stated in 4.6.4. It was done in order to determine the mass loss regions of products expected to be present in hydrated MgO – HY – SiO_2 samples.

SEM analysis

Cured pastes were stored in acetone for 10 days and then oven dried to constant mass at 40 °C. Fragments from selected samples were analysed using SEM (4.6.2).

7.4 RESULTS

Compressive strength

Compressive strength results for all samples tested at 56 days, are shown in **Error! Reference source not found.** along with curves of best fit.

From Figure 7.1 it can be seen that for both SiO_2 types, whilst increasing SiO_2 content from 0 to 15 % and reducing HY content from 30 % to 15 %, results in no significant difference in strength, further increases in SiO_2 content to 20 % or over, increases strength. This increase in strength is not linear and increasing SiO_2 content from 25 % to 30 %, completely removing HY from the samples, results in the largest strength increase.

The highest strengths of 56 MPa and 52 MPa are achieved for the 0/30 NY SiO_2 sample and the 0/30 920d sample, respectively. Also, for samples containing at least 20 % SiO_2 , the type of SiO_2 makes a difference to strength, whilst for samples lower amounts of SiO_2 and higher amounts of HY, analogous NY SiO_2 and 920d SiO_2 samples produce similar strengths.

It should also be noted that the initial addition of SiO_2 to a 30/0 NY sample, effectively producing a 25/5 NY sample, produces a slightly weaker sample than that of the 30 % HY, although a further SiO_2 increase to a 20/10 mix results in samples of equal strength to the 30/0 sample. This is only seen for NY SiO_2 containing samples and it is not clear from the figure if this is a significant observation or related to sampling error.

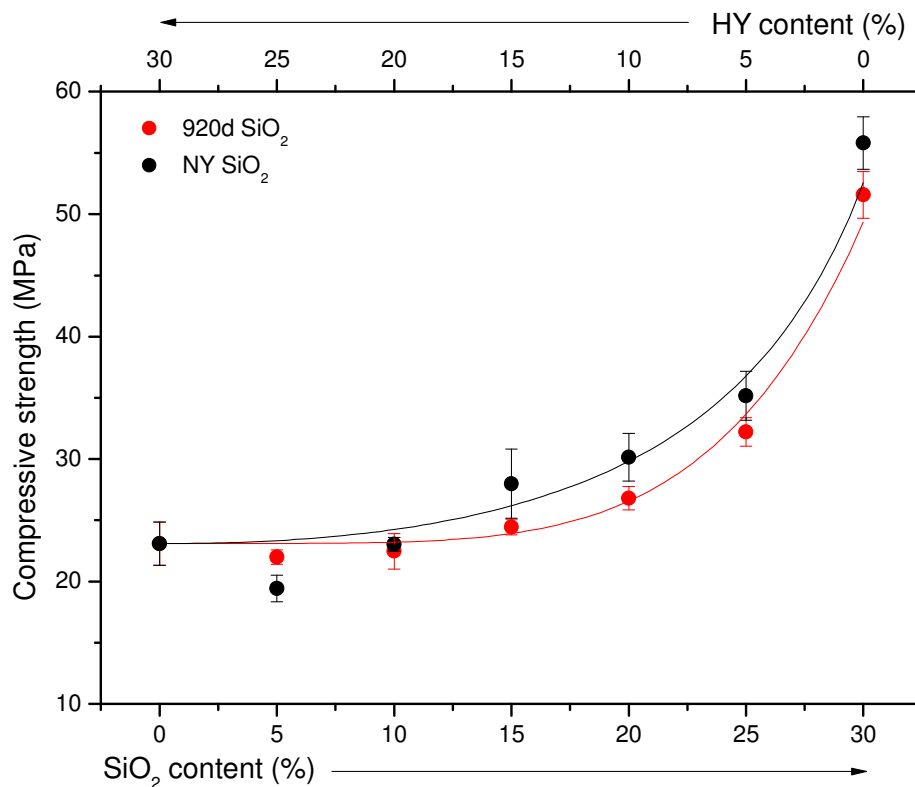


Figure 7.1: Graphs showing the relationship between the SiO_2 and HY content for the MgO - HY - SiO_2 system and 56 day compressive strength.

As seen in Table 7-1 the 30/0 samples requiring the highest w/s ratio of 0.66, with w/s ratio reducing with increased SiO_2 substitution, which could influence compressive strength results. For the 920d SiO_2 samples, this decrease of w/s ratio with increasing SiO_2 was almost linear, but the change in compressive strength with increasing SiO_2 content is not. Also, NY SiO_2 samples were made using a narrower w/s ratio range of 0.66 to 0.64 and showed a similar trend in change of compressive strength with SiO_2 value, even achieving higher maximum strengths at high SiO_2 contents than 920d SiO_2 samples made with lower w/s ratios. Together, these observations indicate that the differing w/s ratio had a much lower, if any, effect than SiO_2 content on strength. For this reason, the different w/s ratios of samples will not be considered to be of issue for the purposes of this work.

Figure 7.2 shows the compressive strength development over time of samples representing the upper and lower limits of the MgO – HY – SiO_2 system investigated. These samples are of 5/25 and 25/5 samples. Results from both the NY SiO_2 (upper graph) and the 920d SiO_2 (lower graph) containing samples are shown.

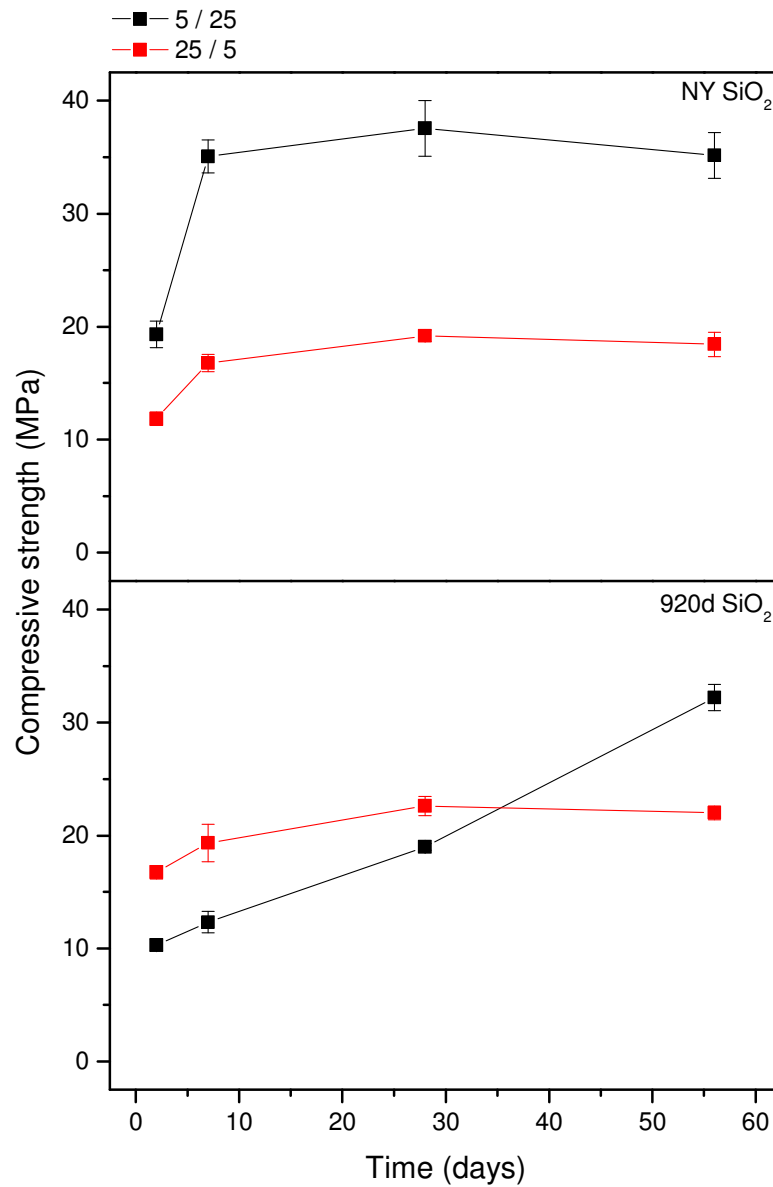


Figure 7.2: Graphs showing compressive strength development over time for three component systems of HY 5/25 and 25/5 made with NY SiO₂ (top graph) or 920d SiO₂ (bottom graph).

For the 5/25 NY and 25/5 NY samples, strength increases rapidly up to 7 days, by which time, close to the maximum strengths are achieved and by 28 days, both samples have reached maximum strength. For the 5/25 NY sample, a strength of 37 MPa reported whilst a lower maximum strength of 18 MPa is achieved in the 25/5 NY system. However, the stronger sample, the 5/25 NY sample experiences a slight mass loss between 28 and 56 days whilst the strength of the weaker 25/5 NY sample, remains constant.

Results of the 920d SiO₂ containing samples show quite different strength developments. The strength of the 25/5 920d sample increases in a similar manner to the 25/5 NY sample in the

upper graph although achieves a higher maximum strength of 23 MPa. Also similar to the 25/5 NY sample, no strength decrease is seen. The 5/25 920d SiO₂ sample increases in strength rapidly to ~ 10 MPa within 2 days, after which strength increases in a linear fashion up to 32 MPa by 56 days. It appears that strength development has not completed by the end of the testing period, 56 days.

Analysis of crystalline reaction products

Figure 7.3 contains the XRD spectra of the samples made at varying HY/SiO₂ ratios after 56 days curing. The upper graph is for samples made with 920d SiO₂ whilst the lower is for samples made with NY SiO₂. Regions in which M-S-H gel is reported to occur have been highlighted in grey (Brew and Glasser, 2005b).

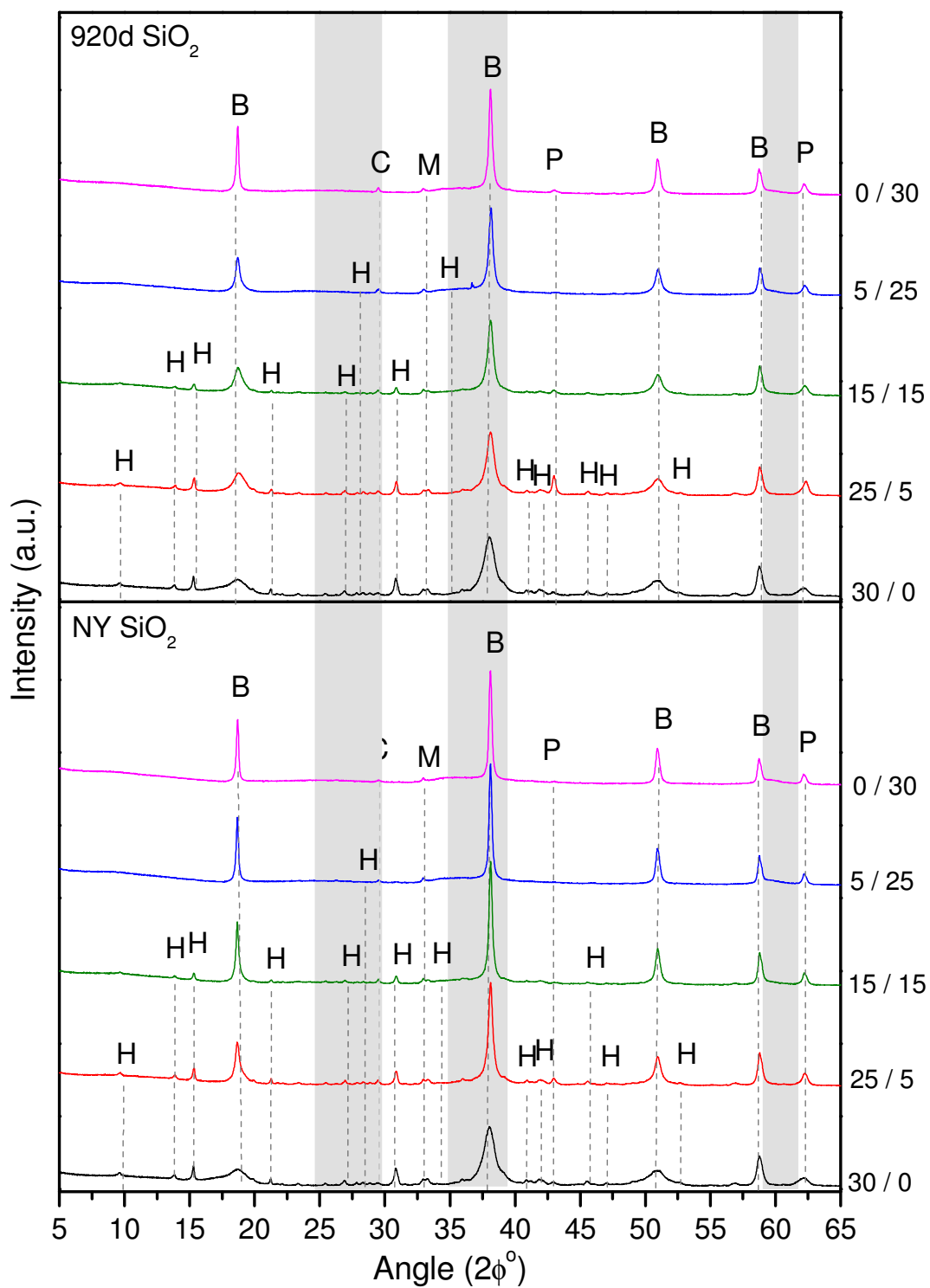


Figure 7.3: XRD spectra of the range of samples made with varying ratios of HY/SiO₂ after 56 days curing. Key: B = brucite [Mg(OH)₂], C = calcite [CaCO₃], H = hydromagnesite [Mg₅(CO₃)₄(OH)₂·4H₂O], M = magnesite [MgCO₃] and P = periclase [MgO].

Peaks have been identified and labelled B = brucite [$\text{Mg}(\text{OH})_2$], C = calcite [CaCO_3], H = hydromagnesite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$], M = magnesite [MgCO_3] and P = periclase [MgO]. Very low intensity peaks observed in samples containing HY were identified but not all have been labelled due to the high number and low intensity.

Regardless of SiO_2 type, the major crystalline materials present are $\text{Mg}(\text{OH})_2$ and MgO although HY is present in all samples except those of 0/30. As with all samples made with B30 MgO in previous chapters, minor MgCO_3 and CaCO_3 peaks are present from the raw material. MgO peaks are seen in most samples although these decrease in intensity with increasing SiO_2 /decreasing HY content. However, these MgO peaks are of slightly higher intensity in the 25/5 samples than in the 30/0 samples. This suggests that somehow, that the initial addition of SiO_2 to a MgO – HY system, somehow limits MgO hydration.

With increasing SiO_2 content, $\text{Mg}(\text{OH})_2$ peak intensities increase. More $\text{Mg}(\text{OH})_2$ peak broadening is observed as SiO_2 content decreases and HY content increases regardless of SiO_2 type.

Due to the amorphous state, M-S-H gel humps are not clearly visible in Figure 7.3. Figure 7.4 contains magnified areas of the XRD spectra shown in Figure 7.3. The angles in which M-S-H gel humps are expected to occur have been highlighted in grey.

From Figure 7.4 it can be seen that M-S-H hump intensity increases as SiO_2 content increases and HY content decreases although the increase in intensity varies depending on the specific M-S-H XRD region and varies slightly depending on whether NY or 920d SiO_2 was used. This shows that M-S-H gel is formed in MgO – HY – SiO_2 systems.

M-S-H humps from NY SiO_2 containing samples appear to have slightly higher intensities than those of analogous 920d SiO_2 containing samples for samples containing at least 15 % SiO_2 indicating that these MgO – HY – SiO_2 samples contain more M-S-H gel than analogous samples made using 920d SiO_2 . There does not appear to be further significant differences between samples made with different SiO_2 type visible from the spectra in this figure.

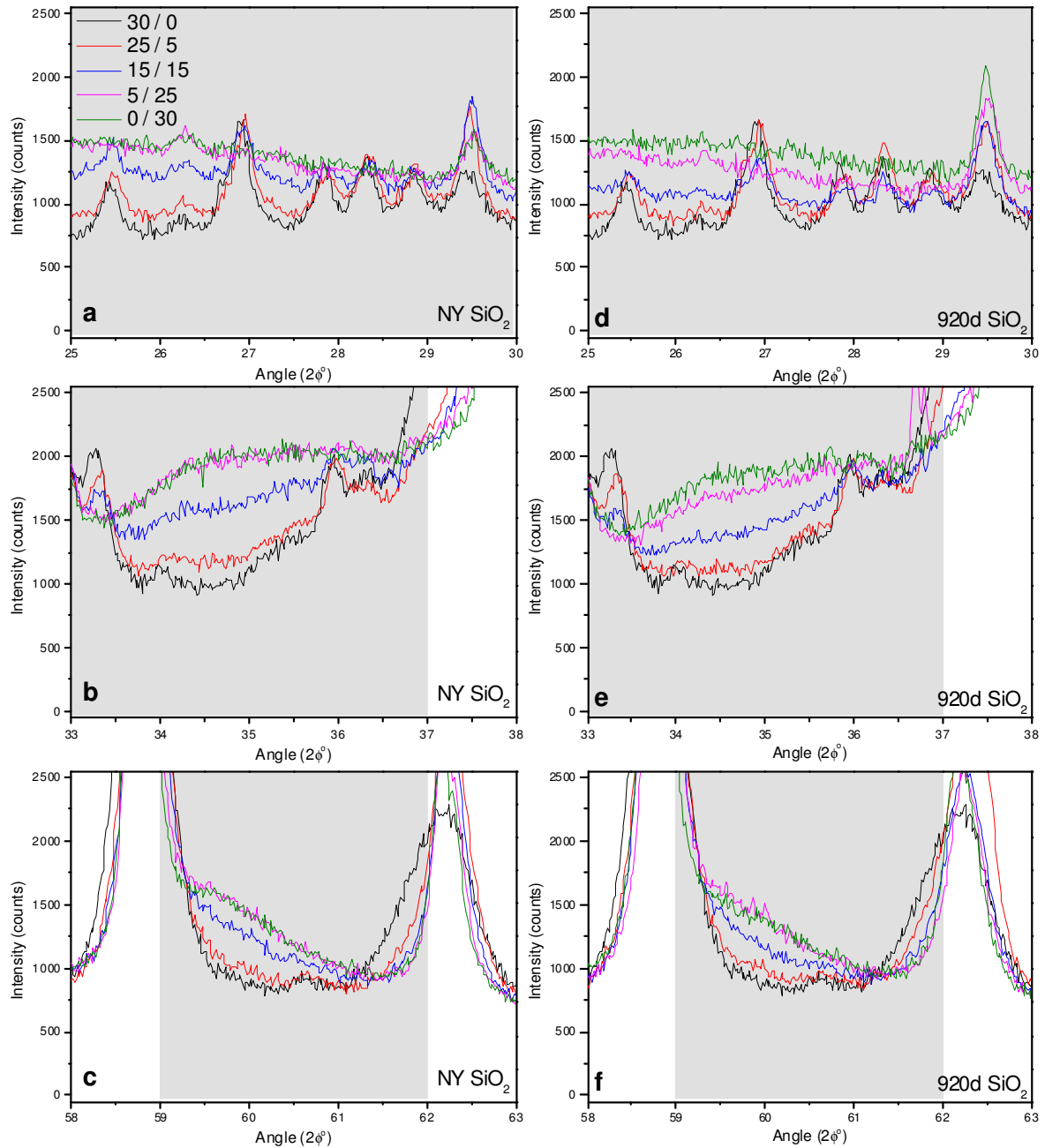


Figure 7.4: Magnified areas of the three characteristic M-S-H humps observed in the XRD spectra of hydrated 30/0, 25/5, 15/15, 5/25 and 30/0 samples made from NY SiO₂ (a, b, c) and 920d SiO₂ (d, e, f) after 56 days curing. The areas of interest in which M-S-H gel humps occur have been highlighted in grey.

TG analysis

Figure 7.5 shows the results of the TG analysis in the form of heatflow, DTA and TG mass loss curves for the 28 day hydrated MgO, control M-S-H gel and raw material HY. The temperature zones previously determined in Chapter 6 in order to assign mass loss to a particular material present in the hydrated MgO – HY – SiO₂ samples are also shown.

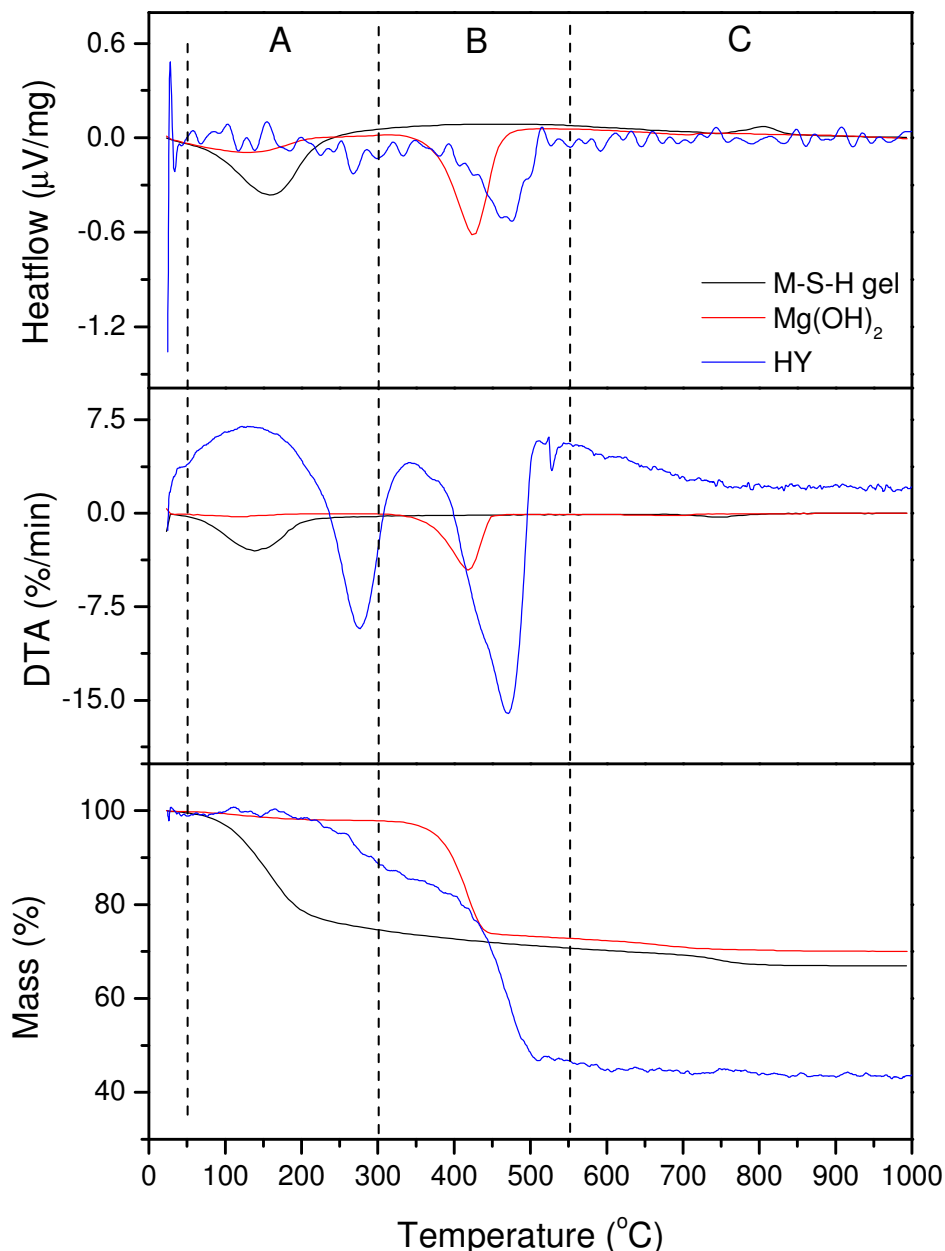
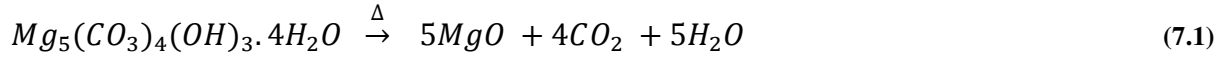


Figure 7.5: Heat-flow, DTA and TG mass loss curves of 28 day hydrated MgO , M-S-H gel synthesised by the Brew and Glasser method and of HY. The temperature zones previously determined in Chapter 6 in order to assign mass loss to a particular material are also shown.

The mass losses of the $\text{Mg}(\text{OH})_2$ and M-S-H gel are, as discussed in 6.2.3, due to the loss of hydroxyl groups, and of bound water and different types of hydroxyl groups, respectively. Also described in 6.2.3, the major $\text{Mg}(\text{OH})_2$ mass loss occurs in the 300 – 550 °C region (B) whilst the M-S-H mass losses have been designated as occurring in the temperature regions of 50 – 300 °C and 550 - 1000 °C.

HY is known to decompose to MgO by the release of CO₂ and H₂O according to equation 7.1 (Hollingbery and Hull, 2012, Hollingbery and Hull, 2010, Haurie et al., 2006)

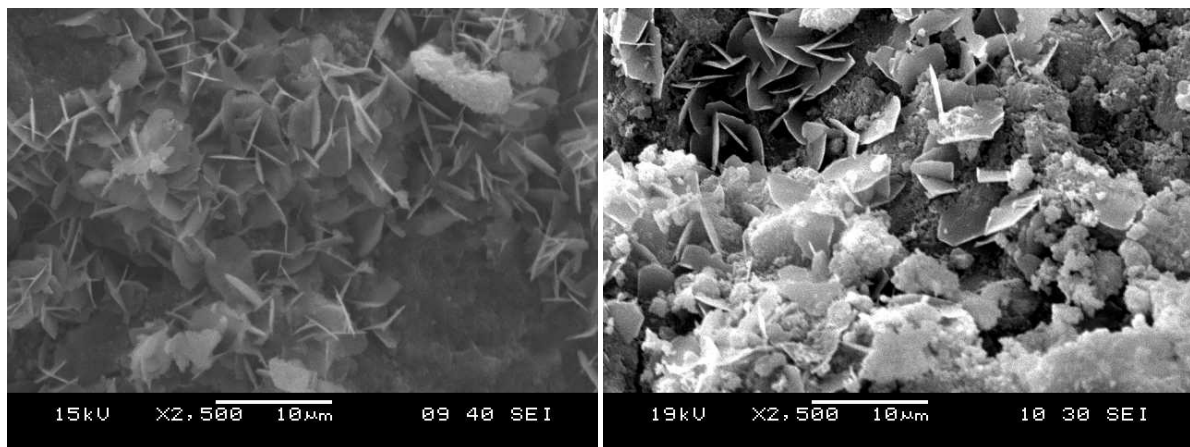


From Figure 7.5 two major mass loss regions are observed centred at ~ 275 °C and 475 °C of approximately 14 % and 50 % respectively, which is in agreement with literature, and are due to the loss of the four water of crystallisation molecules, and at higher temperatures, the loss of water from the hydroxide ions and of CO₂ from the carbonate (Hollingbery and Hull, 2012, Hollingbery and Hull, 2010, Sawada et al., 1978). These peaks overlap slightly with each other, also in agreement with the literature.

As these mass losses overlap, with those of the Mg(OH)₂ and M-S-H gel, in particular, that of the Mg(OH)₂, it is much more complicated to estimate reaction product development as in Chapter 6 and this method will not be used here.

SEM analysis

Figure 7.6 shows the SEM images of the 15/15 920d SiO₂ and the 15/15 NY SiO₂ samples cured for 56 days. Some of the larger interconnected platelet Mg(OH)₂ crystals characteristic of MgO hydrated in the presence of HY, as observed in Chapter 5 can clearly be seen in both samples. Patches of a more globular material are observed on some parts of these Mg(OH)₂ crystals. This could be M-S-H gel, unreacted SiO₂ or some of it could be Mg(OH)₂ of different morphology. It appears that the components in the images are inhomogeneously dispersed.



a)

b)

Figure 7.6: SEM images of (a) 15/15 920d and (b) 15/15 NY samples after 56 days curing.

7.5 DISCUSSION

Owing to different water demands of the individual components of the MgO – HY – SiO₂ system, as observed in **Error! Reference source not found.**, a range of w/s ratios were used depending on HY/SiO₂ ratio, with higher ratios requiring higher w/s ratios. These differences in w/s ratio requirements of the raw materials, as previously discussed in Chapters 5 and 6, are likely due to the void space in HY particles and the differences in surface area of the two SiO₂ powders. For cements, it is known that increasing water content generally results in higher porosity and thus samples of lower durability and strength (Mehta and Monteiro, 2008, Kalinski and Hippley, 2005, Lea, 1998, Taylor, 1990). However, as mentioned in the compressive strength results of 7.4, due to the lack of linear strength increase with increasing SiO₂ content, and to the similarity of strength differences with SiO₂ content between the different SiO₂ types, it has been concluded that the variation in w/s ratio is not of issue in this work. It will not be mentioned further.

Increases in 56 day compressive strength were only observed by increasing SiO₂ content of samples containing 20 % SiO₂ or more, i.e. for 20/10 samples or samples with higher SiO₂ content. For lower SiO₂ contents, little difference in compressive strength was observed between samples. It was also seen that the type of SiO₂ only appears to make a difference to strength for samples of 20 % SiO₂ or higher, with NY SiO₂ samples exhibiting higher strengths than 920d SiO₂ samples.

The 25/5 samples were found to be the weakest out of all samples tested. Based on peak intensity, XRD analysis indicates that the 25/5 samples, the weakest samples, contain the highest amounts of unreacted MgO. This suggests that unreacted MgO content is related to sample strength and that higher amounts of MgO result in weaker samples although little other evidence is currently available to create a strong argument.

When considering strength development, 25/5 samples, both SiO₂ types show very similar strength development curves, achieving the majority of strength in 7 days, with maximum compressive strengths achieved by 28 days, which is a similar strength development pattern to that of the MgO – HY system of 5.5. For 5/25 samples, the rate of strength development appeared more similar to those of the two component optimised MgO – SiO₂ systems seen in 6.6, with the 5/25 NY sample exhibiting high strengths at early ages but a decrease in strength after 28 days. Conversely, the 5/25 920d sample displayed a much more gradual strength increase that continued until the end of the testing period, at 56 days, which is more

similar to the strength development of the 30 % 920d SiO_2 – 70 % MgO sample seen previously in 6.6.

From Chapter 5, it was concluded that the strength of MgO – HY systems essentially comes from the formation of an interconnected $\text{Mg}(\text{OH})_2$ platelet system, whilst Chapter 6 concluded that strength of the MgO – SiO_2 system is based on the formation of M-S-H gel, which binds SiO_2 and $\text{Mg}(\text{OH})_2$ components together. SEM and XRD showed that both of these reaction products were present in all of the hydrated MgO – HY – SiO_2 samples. XRD results also indicated that samples made from higher SiO_2 contents contain larger amounts of M-S-H gel. Also, only in samples of higher SiO_2 content is a difference in M-S-H gel between samples made with different SiO_2 type observed, with more M-S-H gel apparent in NY SiO_2 samples than in 920d SiO_2 samples.

Compressive strength results and reaction product analysis all indicate that SiO_2 and HY ratio of the MgO – HY – SiO_2 system determines the extent to which of the two strength giving reaction products are formed which thus influences the strength properties of the system and their similarity to either the MgO – HY or MgO – SiO_2 system. It is proposed that for samples containing less than 20 % SiO_2 and more than 10 % HY, the major reaction product is the interconnected $\text{Mg}(\text{OH})_2$ platelet and so strength properties more strongly mimic those of the MgO – HY system. However, for samples of composition 20 % SiO_2 and over, and 10 % or less HY, M-S-H gel is the dominating strength giving reaction product and thus has more influence on resulting strength properties. Therefore, maximum strength and strength development, as well as the impact of SiO_2 type on these properties, will be more similar to that of the binary MgO – SiO_2 system than the MgO – HY system.

It was also observed that the 30 % HY system is much lower in strength than the 30 % SiO_2 system, which suggests that M-S-H gel provides more strength to the system than the cross-linked $\text{Mg}(\text{OH})_2$ platelets. Further tests such as the effect of composition on density and quantification the amount of the types of material formed is required.

Overall, results suggest that the inclusion of a small amount of SiO_2 into the MgO – HY would have no disadvantageous effects on sample strength properties but substitution of SiO_2 with HY, could be detrimental to maximum achievable strength. However, substitution of SiO_2 with HY could possibly be used to influence strength development and the stabilisation of the maximum compressive strength of the MgO – SiO_2 system, although at cost to this maximum strength. The effects of composition on other properties would also be of interest.

7.6 CONCLUSIONS

- In terms of maximum achievable compressive strength, the 30 % SiO_2 – 70 % MgO system, made with NY is the best system. Substituting SiO_2 for HY results in a significant decrease in strength;
- There is no benefit in substituting SiO_2 with HY in the MgO based system in terms of maximum compressive strength;
- The formation of M-S-H gel appears to provide more strength to samples than the formation of the interconnected $\text{Mg}(\text{OH})_2$ platelet microstructure;
- The MgO – SiO_2 system is the controlling factor on strength properties for samples containing over 20 % SiO_2 whilst the MgO – HY system has more influence over strength properties for systems containing less SiO_2 ;
- Therefore, in terms of the produced raw materials of Novacem, the presence of low amounts of SiO_2 is not detrimental to the properties of the MgO – HY system;
- Altering the MgO – HY – SiO_2 composition in terms of HY/ SiO_2 ratio has potential in controlling strength development although, this is likely to compromise to maximum compressive strength.

8 THESIS CONCLUSIONS

The aim of this research was to develop an understanding of the strength giving reaction products and mechanism that occur in MgO - based binder systems. The two systems investigated were MgO – HY, a specific mix of MgO and a hydrated magnesium carbonate and the MgO – SiO₂ system. The strength properties of the three component system MgO – HY – SiO₂ have also been investigated.

8.1 MgO – HY SYSTEM

MgO hydrated in the presence of HY results in the development of samples with compressive strength. For a set w/s ratio, increasing the HY content from 10 % to 30 % did not increase the compressive strength and increasing HY content reduced the paste workability. For these reasons, the 10 % HY – 90 % MgO system was selected as the optimum binder ratio. 28 day strengths of up to 24 MPa at were obtained for these samples. The strongest MgO - HY binder required a w/s ratio of 0.62. The MgO - HY binder system could have potential if this high water demand could be significantly reduced.

The strength of MgO - HY cements results from the morphology of Mg(OH)₂ crystals formed when HY is present as under these conditions smaller Mg(OH)₂ crystallites are formed. When MgO hydrates to Mg(OH)₂ in the absence of HY, poorly formed globular particles of Mg(OH)₂ develop which appear to clump together. Hydrated MgO samples do not exhibit any significant compressive strength. When MgO hydrates in the presence of HY, Mg(OH)₂ crystals form in a much more highly cross-linked formation. This change to an interconnected microstructure is responsible for strength formation in hydrated MgO - HY cements.

The increased hydration rate of MgO - HY samples results from HY providing surfaces on which Mg(OH)₂ can form, freeing up MgO surfaces thus allowing further MgO hydration to occur. The pH of the system is the main attributing factor to the formation of the smaller Mg(OH)₂ crystallites which grow to form Mg(OH)₂ crystals of crosslinked platelet morphology, responsible for the system's strength

8.2 MgO – SiO₂ SYSTEM

Based on compressive strength results for MgO – SiO₂ pastes made with varying weight ratios of MgO to SiO₂ a 30 % SiO₂ – 70 % MgO ratio was selected as the optimum composition.

It was found that MgO – SiO₂ pastes made with nanosilica achieved compressive strengths of up to 64 MPa whilst those with microsilica achieved 54 MPa. However the high w/s ratios required by the MgO – SiO₂ system limits the maximum achievable strengths.

When silica fume, a microsilica, is used, strength development was very slow, with sample strengths continuing to increase up to the end of the test period. The use of nanosilica significantly increased the rate of strength development, allowing maximum strength to be achieved by 14 days. However, the results for nanosilica containing samples exhibit a loss in strength at ages after 14 days.

Analysis by XRD and TG concluded that strength development was due to the formation of semi-amorphous M-S-H gel which forms from the hydration reactions between MgO and SiO₂. Unreacted Mg(OH)₂ was detected in all samples. It is proposed that maximum achievable strength is dependent upon the ratio of M-S-H and Mg(OH)₂ content and that excessive M-S-H could be responsible for the observed loss of strength. Further work is required to investigate the exact reason for this loss.

8.3 MgO – HY – SiO₂ SYSTEM

The composition of the three component system consisted of 70 % MgO, with the remaining 30 % composed of different ratios of HY to SiO₂.

The addition of HY to the MgO – SiO₂ systems did not have any beneficial effects with substitution of SiO₂ by HY resulting in paste samples with reduced compressive strengths.

Evidence of the interconnected Mg(OH)₂ platelet system and M-S-H gel was present in all hydrated MgO – HY – SiO₂ samples. Maximum strength and strength development depends on whether the SiO₂ content is lower or higher than 15 %. The HY/SiO₂ content could be used to tailor strength and possibly other properties towards those of either the MgO – HY or MgO – SiO₂, depending on application, although significant further work is required to understand the characteristics of this three component system.

8.4 OVERALL CONCLUSIONS

The results of this research has shown that MgO – HY, MgO – SiO₂ and MgO – HY – SiO₂ systems have potential to be used as alternatives to Portland cement. However, extensive work to further is required to understand the science of these systems. Further characterisation and optimisation of the properties of mortar and concretes made from these binders is also required.

Based on the knowledge derived from this research, the following conclusions about the systems studied in this work have been made:

1. The most promising binder was the MgO – SiO₂ system made with nanosilica;
2. Compressive strengths of all three systems studied were significantly lower than those of the control CEM I sample. The most promising binder system exhibited some loss of strength over time. Based on the results obtained none of the binder systems as formulated in this research are viable alternatives to PC;
3. The water contents required by all these systems to give reasonable flow properties are high and this is a major limitation to achieving high compressive strengths and other physical properties comparable to those of PC;
4. If these systems could achieve comparable properties to PC, the relatively high cost of the raw materials, would be a considerable commercial constraint.

Chapter 9 outlines the main recommendations for further work that would be required to optimise these MgO based binder systems and to determine their feasibility as commercial binders.

9 RECOMMENDATIONS FOR FURTHER WORK

The previous chapter concluded that based on the work reported in this thesis, none of the three systems investigated are currently realistic or viable alternatives to PC. This chapter outlines recommendations for additional work that would be required to further optimise these systems. It also highlights key issues that would need to be addressed in order to make more informed conclusions on the potential of MgO based systems as low carbon binders.

1. Only the MgO – HY system was studied in this work. Investigations are therefore necessary on other MgO – hydrated magnesium carbonate systems such as MgO – nesquehonite [$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$] and MgO – dypingite [$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$];
2. Previous research proposed that MgO – hydrated magnesium carbonate systems can gain additional strength due to accelerated fixation of CO_2 . Further work should be completed to investigate the effect of atmospheric and accelerated carbonation on MgO – hydrated magnesium carbonate samples, in particular the effects on compressive strength;
3. Silica fume and particularly nanosilica are expensive materials. Therefore cheaper alternative sources of SiO_2 , such as rice husk ash should be used in the MgO – SiO_2 system with the aim at making the system more economically viable;
4. High water demand was a major issue for all of the three systems studied in this research. Lowering this water demand is vital to improve the strength and durability of these systems. Therefore the use of super-plasticisers, as well as determining optimum particle packing by varying the particle size distributions of the components should be investigated;
5. This research has been limited to working with paste systems. Mortar and concrete samples using various compositions of the MgO – HY and the MgO – SiO_2 systems as binders should be prepared and a wider range of properties need to be characterised. Of particular importance would be the investigation of the durability of mortar and concrete made with selected optimised MgO based binders;
6. The effect of different curing conditions used in the precast concrete products industry on MgO – HY and MgO – SiO_2 concrete sample properties needs to be investigated;
7. Long term durability studies of MgO based concretes would be essential. Accelerated curing methods such as high temperature steam curing could initially be used to indicate the properties over long time periods;

8. The underlying driver for the development of MgO based cements is the high CO₂ emissions associated with the manufacture of PC. Therefore the total CO₂ emissions involved in the transport and manufacture of MgO – HY and MgO – SiO₂ systems need to accurately quantified to assess the overall carbon and embodied energy in these binder systems;
9. In addition to embodied carbon, other environmental issues associated with these binder systems would need to be assessed. This includes factors such as how and where the raw materials would be sourced and the effects this would have on the local environment. The overall sustainability of the new binders would need to be accurately assessed;
10. The global and localised availability and the long term sustainability of MgO, HY and SiO₂ sources should also be determined;
11. Finally the overall economic viability of using new MgO based binder systems in construction would need to be carefully assessed.

APPENDIX

DERIVATION OF CALCULATIONS OF HYDRATION EXTENT

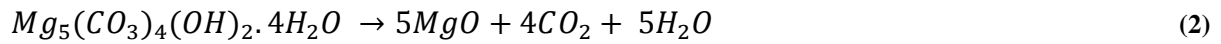
The following work-up shows how the calculations of hydration extent (stated in 4.6.5) for the MgO – HY system can be derived based on the percentage mass loss after application of LOI to dried hydrated powders prepared according to the method in 4.3.2. This derivation is based on the mass losses that occur on decomposition of Mg(OH)₂ and HY.

Mg(OH)₂ and HY decompose to leave the solid of MgO on application of the LOI test.

Mg(OH)₂ decomposes on application of heat via LOI tests via equation 1 :



The total decomposition of HY can be represented by equation 10.4:



Using the molecular masses listed in Table I and equations 1 and 2 above, the mass losses for the decomposition of Mg(OH)₂ and HY were calculated as 30.9 % and 56.9 % respectively.

Table I: List of formula of the main compounds and their molecular masses that are used in the derivation of hydration extent equations.

Compound	Formula	Molecular mass
Magnesium hydroxide	Mg(OH) ₂	58.32
Hydromagnesite, HY	Mg ₅ (CO ₃) ₄ (OH) ₂ ·4H ₂ O	467.64
Magnesium oxide	MgO	40.3

The hydration of MgO in the presence of H₂O is represented in equation 3:



However, if 100 % hydration does not occur, unreacted MgO remains. For example, for 30 % hydration, i.e. 30 % of the MgO is converted to Mg(OH)₂, the mass of solid MgO and Mg(OH)₂ that exists after hydration can be calculated using the molecular mass and assuming initial MgO present is 10 g mass. Therefore, total solid mass before and after can be calculated as seen in equations 4 to 6.

$$10 \text{ g } MgO \rightarrow (0.7 * 10) \text{ g } MgO + \left(\frac{0.3*10}{(40.3)} * 58.32 \right) \text{ g } Mg(OH)_2 \quad (4)$$

$$10 \text{ g } MgO \rightarrow 0.7 \text{ g } MgO + 4.34 \text{ g } Mg(OH)_2 \quad (5)$$

$$10 \text{ g solid} \rightarrow 11.34 \text{ g solid} \quad (6)$$

As mentioned, decomposition of $Mg(OH)_2$ results in a 30.9 % mass loss but MgO will show no significant mass loss on application of LOI. Therefore, for the above 100 % MgO sample that has hydrated by 30 %, using the values calculated from equations 4 to 6, mass loss on application of the LOI test is:

$$0.309 * 4.34 \text{ g} = 1.34 \text{ g} \quad (7)$$

In terms of percentage mass loss, this is:

$$\left(\frac{1.34 \text{ g}}{11.34 \text{ g}} \right) * 100 = 11.83 \% \quad (8)$$

The same method as above was used to calculate percentage mass losses of 100 % MgO samples hydrated to different extents. The calculated mass losses are shown later in Table II.

For a $MgO - HY$ system, it is known that HY and thus its mass remains unchanged on hydration. Thus for a 10 % $HY - 90 \% MgO$ system, that undergoes 30 % hydration (30 % of the MgO hydrates), using molecular masses stated in Table I and a similar method as used above for the 100 % MgO sample, assuming total solid mass at the start is 10 g, both the mass of $Mg(OH)_2$ formed and thus total solid mass after hydration can be calculated as follows:

$$9 \text{ g } MgO + 1 \text{ g } HY \rightarrow (0.7 * 9) \text{ g } MgO + \left(\frac{0.3*9}{(40.3)} * 58.32 \right) \text{ g } Mg(OH)_2 + 1 \text{ g } HY \quad (9)$$

$$10 \text{ g solid} \rightarrow 6.3 \text{ g } MgO + 3.91 \text{ g } Mg(OH)_2 + 1 \text{ g } HY \quad (10)$$

$$10 \text{ g solid} \rightarrow 11.20 \text{ g solid} \quad (11)$$

Considering the mass losses of $Mg(OH)_2$ and HY on decomposition are 30.9 % and 56.9 % respectively, and assuming MgO has no mass loss, the percentage mass loss of the 10 % $HY - 90 \% MgO$ sample after 30 % hydration on application of the LOI test is:

$$0.309 * 3.91 \text{ g} + 0.569 * 1 \text{ g} = 1.78 \text{ g} \quad (12)$$

$$\left(\frac{1.78 \text{ g}}{11.20 \text{ g}} \right) * 100 = 15.85 \% \quad (13)$$

The same method as above (equations 9 to 13) was used to calculate percentage mass losses of 20 % HY – 80 % MgO and 30 % HY – 70 % MgO samples, hydrated to different extents. The calculated mass losses are shown in Table II.

Table II: Summary of the calculated mass losses for the 0 % HY – 100 % MgO, 10 % HY – 90 % MgO, 20 % HY – 80 % MgO and 30 % HY – 70 % MgO samples based on different MgO hydration extents.

Hydration extent (%)	Calculated mass loss (%)			
	0 % HY	10 % HY	20 % HY	30 % HY
0	0	5.69	11.38	17.07
10	4.28	9.34	14.44	19.59
20	8.21	12.72	17.3	21.96
30	11.83	15.85	19.97	24.19
40	15.17	18.76	22.47	26.3
50	18.27	21.49	24.83	28.29
60	21.15	24.03	27.04	30.59
70	23.84	26.42	29.13	31.98
80	26.35	28.66	31.1	33.68
90	28.7	30.77	32.96	35.3
100	30.9	32.75	34.73	36.84

The data shown in Table II was then used to plot a graph of percentage hydration (on the x-axis) against calculated mass loss (on the y-axis). Polynomial 2nd order curves of best fit was then applied to the data points using Excel which gave the equation of each of the curves. Figure I shows the data points plotted, the curves fitted and the equations of each curve.

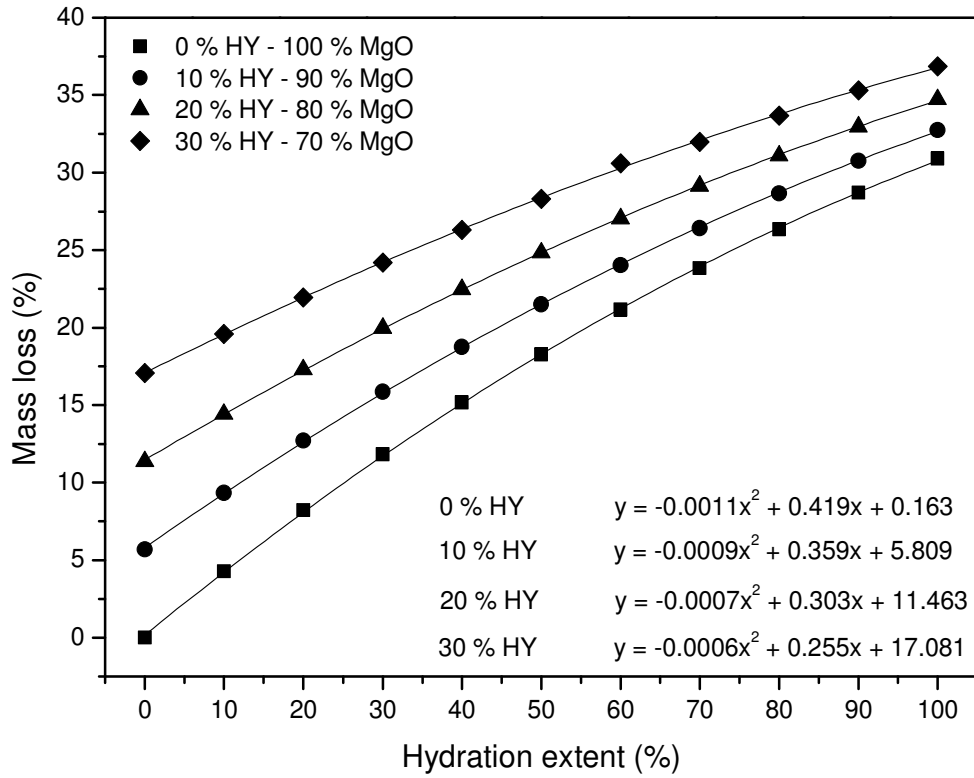


Figure I: Graph showing the calculated mass loss data against hydration extent for hydrated 0 % HY - 100 % MgO, 10 % HY - 90 % MgO, 20 % HY - 80 % MgO, 30 % HY - 70 % MgO and 40 % HY - 60 % MgO samples. Curves have been fitted to the data points and equations of these curves are shown.

These four equations, representing mixes of 0% HY – 100 % MgO, 10 % HY – 90 % MgO, 20 % HY – 80 % MgO and 30 % HY – 70 % MgO, have been rearranged to the form of equation 14 shown below as equation 15, equation 16, equation 17 and equation 18, respectively.

$$ax^2 + bx + c = 0 \quad (14)$$

$$-0.0011x^2 + 0.419x + (0.163 - y) = 0 \quad (15)$$

$$-0.0009x^2 + 0.359x + (5.809 - y) = 0 \quad (16)$$

$$-0.0007x^2 + 0.303x + (11.463 - y) = 0 \quad (17)$$

$$-0.0006x^2 + 0.255x + (17.081 - y) = 0 \quad (18)$$

By knowing the mass loss as a percentage (y), on application of LOI of a hydrated and dried MgO – HY sample, equations 15 to 18 can be solved for x , MgO hydration degree, by substituting the values of a , b and c into equation 19 below:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (19)$$

9.1 CONFIRMATION OF M-S-H GEL PRODUCTION

Figure II shows the XRD spectrum of the end product of the M-S-H gel synthesis. It can clearly be seen that no crystalline phases are present and only three humps centred around $25 - 30^\circ$, $35 - 39^\circ$ and $58 - 62^\circ$ are observed. This is in agreement with the M-S-H XRD spectrum of several other researchers, thus showing that the reaction product is indeed M-S-H gel (Brew and Glasser, 2005b, Sandberg and Mosberg, 1988).

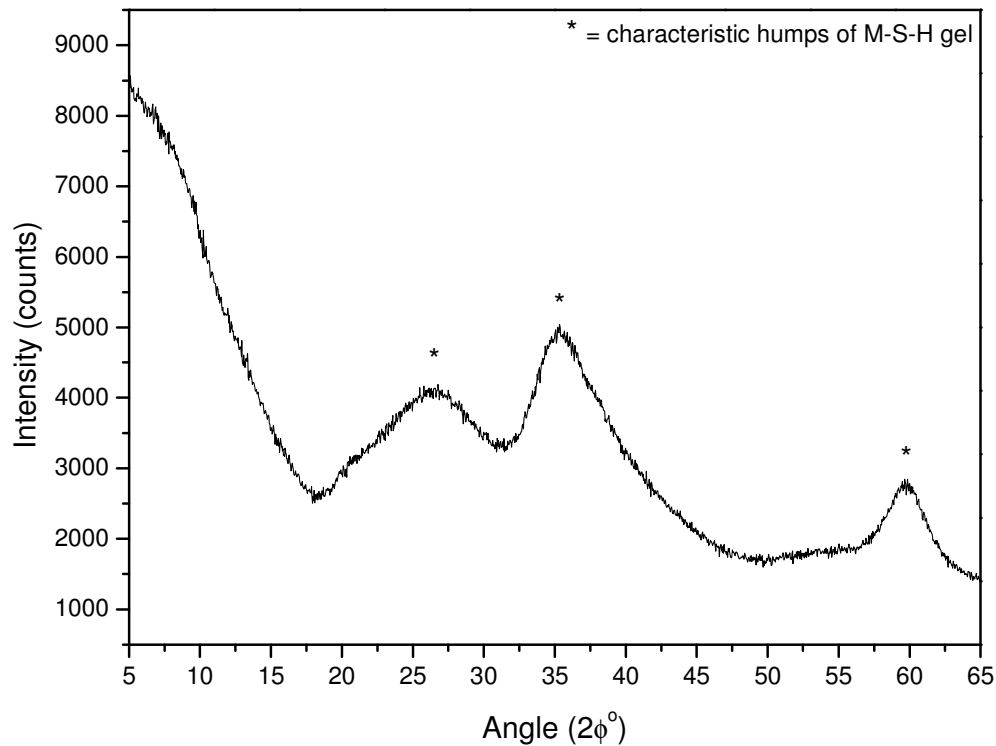


Figure II: XRD spectra of the product of the Glass and Brewer method for M-S-H gel synthesis. The characteristic peaks of M-S-H gel have been labelled with *.

9.2 XRD OF M-S-H GEL BEFORE AND AFTER HEATING TO 1000 °C

Figure III shows the XRD spectra of the synthesised M-S-H gel before and after heating to 1000 °C.

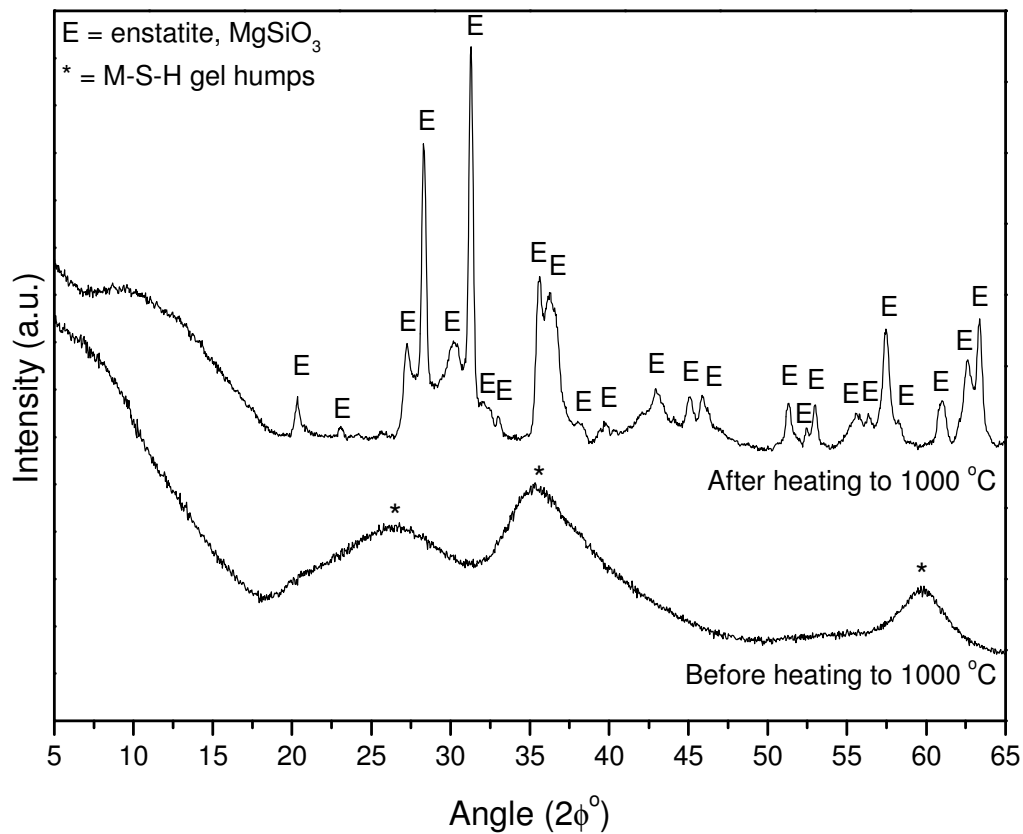


Figure III: XRD spectra of synthesised M-S-H gel before and after heating to 1000 °C.

REFERENCES

- AL-TABBAA, A. & IYENGAR, S. R. 2007. Developmental study of a low-pH magnesium phosphate cement for environmental applications. *Environmental Technology*, 28, 1387 - 1401.
- ANDERSON, P. J. & HORLOCK, R. F. 1962. Thermal decomposition of magnesium hydroxide. *Trans. Faraday Soc.*, 58, 1993 - 2004.
- BAI, S., URABE, S., OKAUE, Y. & YOKOYAMA, T. 2009. Acceleration effect of sulfate ion on the dissolution of amorphous silica. *Journal of Colloid and Interface Science*, 331, 551 - 554.
- BALCI, S. 1999. Effect of heating and acid pre-treatment on pore size distribution of sepiolite. *Clay Minerals*, 34, 647 - 655.
- BEAUDOIN, J. J. & RAMACHANDRAN, V. S. 1975. Strength development in magnesium oxysulfate cement. *Cement and Concrete Research*, 8, 103 - 112.
- BENTUR, A., KOVLER, J. & GOLDMAN, A. 1994. Gypsum of improved performance using blends with portland cement and silica fume. *Advanced Cement Research* 6, 109 - 116.
- BENTZ, D. P., GARBOCZI, E. J., HAECKER, C. J. & JENSEN, O. M. 1999. Effects of cement particle size distribution on performance properties of Portland cement-based materials. *Cement and Concrete Research* 29, 1663 - 1671.
- BERETKA, J., DE VITO, B., SANTORO, L., SHERMAN, N. & VALENTI, G. L. 1993. Hydraulic behaviour of calcium sulfoaluminate-based cements derived from industrial process wastes. *Cement and Concrete Research*, 23, 1205 - 1214.
- BERGER, G., CARDORE, E., SCHOTTE, J. & DOVE, P. M. 1994. Dissolution rate of quartz in lead and sodium electrolyte solutions between 23 and 300 °C. Effect of the nature of surface complexes and reaction affinity. *Geochimica et Cosmochimica Acta*, 58, 541 - 551.
- BERGNA, H. E. 1994. The colloid chemistry of silica. *200th American Chemical Society national meeting*. Washington DC, USA: American Chemical Society.
- BHATTI, A. S., DOLLIMORE, D. & DYER, A. 1984. Magnesium from seawater: a review. *Clay Minerals*, 19, 865 - 875.
- BINICI, H., AKSOGAN, O., CAGATAY, I. H., TOKYAY, M. & EMSEN, E. 2007. The effect of particle size distribution on the properties of blended cements incorporating GGBFS and natural pozzolan (NP). *Powder Technology*, 177.
- BIRCHAL, V. S., ROCHA, S. D. F., MANSUR, M. B. & CIMINELLI, V. S. T. 2001. A simplified mechanistic analysis of the hydration of magnesia. *The Canadian Journal of Chemical Engineering*, 79, 507 - 511.
- BJORNSTROM, J., MARTINELLI, A., MATIC, A., BORJESSON, L. & PANAS, I. 2004. Accelerating effects of colloidal nano-silica for beneficial calcium-silicate-hydrated formation incement. *Chemical Physics Letters*, 392, 242 - 248.
- BOTHA, A. & STRYDOM, C. A. 2003. DTA and FT-IR analysis of the rehydration of basic magnesium carbonate. *Journal of Thermal Analysis and Calorimetry*, 71, 987-995.
- BREW, D. R. M. & GLASSER, F. P. 2005a. The magnesia - silica gel phase in slage cements: alkali (K, Cs) sorption potential of synthetic gels. *Cement and Concrete Research*, 35, 77 - 83.
- BREW, D. R. M. & GLASSER, F. P. 2005b. Synthesis and characterisation of magnesium silicate hydrate gels. *Cement and Concrete*, 35, 85 - 98.
- BRUNI, S., CARIATI, F., FERMO, P., POZZI, A. & TONIOLO, L. 1998. Characterization of ancient magnesian mortars coming from northern Italy. *Thermochimica Acta*, 321, 161 - 165.
- BSI 2005. Methods of testing cement. *Part 1: Determination of strength*.
- BUJ, I., TORRAS, J., CASELLAS, D., ROVIRA, M. & DE PABLO, J. 2009. Effect of heavy metals and water content on the strength of magnesium phosphate cements. *Journal of Hazardous Materials*, 170, 345 - 350.
- BULTEEL, D., GARCIA-DIAZ, E., VERNET, C. & ZANNI, H. 2002. Alkali-silica reaction: A method to quantify the reaction degree. *Cement and Concrete Research*, 3, 1199 - 1206.

- CANTERFORD, J. H. & MOORREES, C. 1985. Magnesia from magnesite by calcination/carbonic leaching: precipitation from solution and final product recovery. *Bulletin and Proceedings - Australian Institute of Mining and Metallurgy*, 290, 67 - 70.
- CELIK, I. B. 2009. The effect of particle size distribution and surface area upon cement strength development. *Powder Technology*, 188, 272 - 276.
- CHAGAS CORDEIRO, G., FILHO, R. D. T., TAVARES, L. M. & DE MORAES REGO FAIRBAIRN, E. 2009. Ultrafine grinding of sugar cane bagasse ash for application as pozzolanic admixture in concrete. *Cement and Concrete Research*, 39, 110 - 115.
- CHATTERJI, S. 1995. Concrete durability and CaO/SiO₂ mole ratio of C-S-H. *Cement and Concrete Research*, 25, 929 - 932.
- CHAU, C. K. & LI, Z. 2008. Microstructures of magnesium oxychloride Sorel Cements. *Nature*, 21, 64 - 66.
- CHOUDHARI, B. P., VAIDYA, M. C. & DATAR, D. S. 1972. Physico-chemical studies on basic magnesium carbonates. *Indian Journal of Chemistry*, 10, 731 - 733.
- COLAK, A. 2002. The long-term durability performance of gypsum - Portland cement - natural pozzolan blends. *Cement and Concrete Research*, 32, 109 - 115.
- CONG, X. & KIRKPATRICK, R. J. 1995. Effects of the temperature and relative humidity on the structure of C-S-H gel. *Cement and Concrete Research*, 25, 1237 - 1245.
- DAMTOFT, J. S., LUKASIK, J., HERFORT, D., SORRENTINO, D. & GARTNER, E. M. 2007. Sustainable development and climate change initiatives. *Cement and Concrete Research*, 38, 115 - 127.
- DAVIDOVITS, J. 1991. Geopolymers: inorganic polymeric new materials. *Journal of Thermal Analysis*, 37, 1633 - 1656.
- DENG, D. 2003. The mechanism of soluble phosphates to improve the water resistance of magnesium oxychloride cement. *Cement and Concrete Research*, 33, 1311 - 1317.
- DETWILER, R. J. M., P. K. 1989. Chemical and physical effects of silica fume on the mechanical behavior of concrete. *ACI Materials Journal*, 86, 609 - 614.
- DHEILLY, R. M., SEBAIBI, Y., TUDO, J. & QUENEUEDEC, M. 1998. Importance de la présence de magnésie dans le stockage de la chaux : carbonatation de l'oxyde et de l'hydroxyde de magnésium. *Canadian Journal of Chemistry*, 76, 1188 - 1196.
- DOVE, P. M. & CRERAR, D. A. 1990. Kinetics of quartz dissolution in electrolyte solutions using a hydrothermal mixed flow reactor. *Geochimica et Cosmochimica Acta*, 54, 955 - 969.
- DUXSON, P., PROVIS, J. L., LUKEY, G. C. & VAN DEVENTER, J. S. J. 2007. The role of the inorganic polymer technology in the development of green concrete. *Cement and Concrete Research*, 37, 1587 - 1590.
- DWECK, J., BUCHLER, P. M., COELHO, A. C. V. & CARTLEDGE, F. K. 2000. Hydration of a Portland cement blended with calcium carbonate. *Thermochimica Acta*, 346, 105 - 113.
- EDWARDS, H. G. M., JORGE VILLAR, S. E., JEHLICKA, J. & MUNSHI, T. 2005. FT-Raman spectroscopic study of calcium-rich and magnesium-rich carbonate materials. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 61, 2273-2280.
- ESTEVEZ, L. P. 2011. On the hydration of water-entrained cement-silica systems: Combined SEM, XRD and thermal analysis in cement pastes. *Thermochimica Acta*, 518, 27 - 35.
- FEITKNECHT, W. & BRAUN, H. 1967. Der mechanismus der hydratation von magnesiumoxid mit wasserdampf. *Helvetica Chimica Acta*, 50.
- FERNANDEZ, A., CHIMENOS, J. M., SEGARRA, M., FERNANDEZ, M. A. & ESPIELL, F. 1999. Kinetic study of carbonation of MgO slurries. *Hydrometallurgy*, 53, 155 - 167.
- FLATT, R. J., ROUSSEL, N. & CHEESEMAN, C. R. 2012. Concrete: an eco material that needs to be improved. *Journal of European Ceramic Society*, 32, 2787 - 2798.
- FROST, R. L. & DING, Z. 2003. Controlled rate thermal analysis and differential scanning calorimetry of sepiolites and palygorskites. *Thermochimica Acta*, 397, 119 - 128.
- FROST, R. L. & KLOPPROGGE, J. T. 1999. Infrared emission spectroscopic study of brucite. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 55, 2195 - 2205.

- GARCIA-MATE, M., SANTACRUZ, I., DE LA TORRE, A. G., LEON-REINA, L. & ARANDA, M. A. G. 2012. Rheological and hydration characterisation of calcium sulfoaluminate cement pastes. *Cement and Concrete Composites*, 34, 684 - 691.
- GARTNER, E. 2004. Industrially interesting approaches to "low-CO₂" cements. *Cement and Concrete Research*, 34, 1489 - 1498.
- GARTNER, E. Year. Improvements in cement sustainability *In*: 31st Cement and Concrete Science Conference, 2011 Imperial College London, UK.
- GARTNER, E. & QUILLIN, K. Year. Low - CO₂ cements based on calcium sulfoaluminates. *In*: Proceedings of International Conference on Sustainability in the Cement and Concrete Industry, 2007 Lillehammer, Norway. 95 - 105.
- GAUTIER, J. M., OELKERS, E. H. & SCHOTTE, J. 1994. Experimental study of K-feldspar dissolution rates as a function of chemical affinity at 150 °C and pH 9. *Geochimica et Cosmochimica Acta*, 58, 4549 - 4560.
- GINEBRA, M. P., DRIESSENS, F. C. M. & PLANELL, J. A. 2004. Effect of the particle size on the micro and nanostructural features of a calcium phosphate cement: a kinetic analysis. *Biomaterials*, 25, 3453 - 3462.
- GLASSER, F. P. & ZHANG, L. 2001. High - performance cement matrices based on calcium sulfoaluminate - belite compositions. *Cement and Concrete Research*, 31, 1881 - 1886.
- GLASSON, D. R. 1963. Reactivity of lime and related oxides (Part VII) - Production of activated lime and magnesia. *Journal of Applied Chemistry*, 13, 111 - 118.
- GOLDSTEIN, J., NEWBURY, D., JOY, D., LYMAN, C., ECHLIN, P., LIFSHIN, E., SAWYER, L. & MICHAEL, J. (eds.) 2007. *Scanning electron microscopy and x-ray microanalysis*: Springer.
- GOLLOP, R. S. & TAYLOR, H. F. W. 1992. Microstructural and microanalytical studies of sulfate attack: 1. Ordinary Portland cement paste. *Cement and Concrete Research*, 22, 1027 - 1038.
- HAN, H., HU, S., FENG, J. & GAO, H. 2011. Effect of stearic acid, zinc stearate coating on the properties of synthetic hydromagnesite. *Applied Surface Science*, 257, 2677 - 2682.
- HARRISON, J. 2001. *Reactive magnesium oxide cements*.
- HARRISON, J. Year. New cements based on the addition of reactive magnesia to portland cement with or without added pozzolan. *In*: CIA, ed. CIA conference: Concrete of the Third Millennium, 2003 Brisbane, Australia.
- HARRISON, J. 2005. TecEco Eco-Cement Masonry Product Update - Carbonation = Sequestration. *10th Canadian Masonry Conference*. Banff, Alberta, Canada.
- HAURIE, L., FERNANDEZ, A. I., VELASCO, J. I., CHIMENOS, J. M., LOPEZ-CUESTA, J. M. & ESPIELL, F. 2006. Effects of milling on the thermal stability of synthetic hydromagnesite. *Materials Research Bulletin*, 42, 1010 - 1018.
- HENRIST, C., MATHIEU, J. P., VOGELS, C., RULMONT, A. & CLOOTS, R. 2003. Morphological study of magnesium hydroxide nanoparticles precipitated in dilute aqueous solution. *Journal of Crystal Growth*, 249, 321 - 330.
- HIEMSTRA, T. & VAN RIEMSDIJK, W. H. 1990. Multiple activated complex dissolution of metal (hydr)oxides: A thermodynamic approach applied to quartz. *Journal of Colloid and Interface Science*, 136.
- HOLLINGBERY, L. A. & HULL, T. R. 2010. The thermal decomposition of huntite and hydromagnesite - A review. *Thermochimica Acta*, 509, 1 - 11.
- HOLLINGBERY, L. A. & HULL, T. R. 2012. The thermal decomposition of natural mixtures of huntite and hydromagnesite. *Thermochimica Acta*, 528, 45 - 52.
- HOPKINSON, L., RUTT, K. & CRESSEY, G. 2008. The transformation of nesquehonite to hydromagnesite in the system CaO-MgO-H₂O-CO₂ : an experimental spectroscopic study. *The Journal of Geology*, 116, 387-400.
- ILER, R. K. 1979. *The Chemistry of Silica*, New York, Wiley.
- INSTITUTION, B. S. 2005. Methods of testing cement. *Part 3: Determination of setting times and soundness*. London.

- JAMES, J. & RAO, M. S. 1986. Reactivity of rice husk ash. *Cement and Concrete Research*, 16, 296 - 302.
- JIANG, S. P., MUTIN, J. C. & NONAT, A. Year. Effect of fillers on the kinetics of cement hydration. *In: 3rd International Symposium on Cement and Concrete*, 1993 Beijing. 126 - 131.
- JOST, H., BRAUN, M. & CARIOUS, C. 1997. The role of reactivity in syntheses and the properties of magnesium oxide. *Solid State Ionics*, 101 - 103, 221 - 228.
- KADRI, E. H., DUVAL, R., AGGOUN, S. & KENAI, S. 2009. Silica fume effect on hydration heat and compressive strength of high-performance concrete. *ACI Materials Journal*, 106, 107 - 113.
- KALINSKI, M. E. & HIPPLEY, B. T. 2005. The effect of water content and cement content on the strength of portland cement-stabilized compacted fly ash. *Fuel* 84, 1812 - 1819.
- KAMINSKAS, R. 2008. The effect of pozzolana on the properties of the finest fraction of separated Portland cement. Part II. *Ceramics - Sillicaty*, 52, 183 - 189.
- KITAMURA, A., ONIDUKA, K. & TANAKA, K. 1966. Hydration characteristics of magnesia. *The Technical Association of Relectories, Japan*, 48, 112 - 122.
- KLUG, H. P. & ALEXANDER, L. E. 1974. *X-ray Diffraction Procedures: For Polycrystalline and Amorphous Materials*, Wiley - Blackwell.
- KOH, P. Y., YAN, J. & TEJA, A. 2011. Precipitation and growth of magnesium hydroxide nanopetals on zeolite 4A surface. *Journal of Crystal Growth*, 331, 56 - 63.
- KONTOLEONTOS, F., TSAKIRIDIS, P. E., MARINOS, A., KALOIDAS, V. & KATSIOTI, M. 2012. Influence of colloidal nanosilica on ultrafine cement hydration: Physicochemical and microstructural characterization. *Construction and Building Materials*, 35, 347 - 360.
- KRAMER, D. A. 2001. Magnesium; its alloys and compounds. *US Geological Survey Open-File Report 01-341*.
- KUHLMANN, K., ELLERBROCK, H. G. & SPRUNG, S. 1985. Particle size distribution and properties of cement. Part 1: Strength of Portland cement. *Zement - Kalk - Gips*, 38, 169 - 178.
- LAGMUIR, D. 1965. Stability of carbonates in system MgO - CO₂ - H₂O. *Journal of Geology*, 73, 730 - 754.
- LANAS, J. & ALVAREZ, J. I. 2004. Dolomitic lime: thermal decomposition of nesquehonite. *Thermochimica Acta*, 421, 123 - 132.
- LANGFORD, J. I. & LOUER, J. 1996. Powder Diffraction. *Rep. Prog. Phys.*, 59, 131 - 234.
- LARBI, J. J., FRAAY, A. L. A. & BIJENN, J. M. 1990. The chemistry of the pore fluid of silica fume - blended cement systems. *Cement and Concrete Research*, 20, 506.
- LEA 1998. *Lea's Chemistry of Cement and Concrete*, Oxford, Elsevier.
- LEE, W. K. W. & VAN DEVENTER, J. S. 2002. The effect of ionic contaminants on the early -stage properties of alkali - activated fly ash based cements. *Cement and Concrete Research*, 32, 577 - 584.
- LI, G., LI, J. & YU, Y. 2008. The influence of compound additive on magnesium oxychloride cement/urban refuse floor tile. *Construction and Building Materials*, 22, 521 - 525.
- LILKOV, V., PETROV, O., TZVETANOVA, Y. & SAVOV, P. 2012. Mossbauer, DTA and XRD study of Portland cement blended with fly ash and silica fume. *Construction and Building Materials*, 29, 33 - 41.
- LU, J., QIU, L. & QU, B. 2004. Controlled growth of three morphological structures of magnesium hydroxide nanoparticles by wet precipitation method. *Journal of Crystal Growth*, 267, 676 - 684.
- MAROTO-VALER, M. M., FAUTH, D. J., KUCHTA, M. E., ZHANG, Y. & ANDERSEN, J. M. 2005. Activation of magnesium rich minerals as carbonation feedstock materials for CO₂ sequestration. *Fuel Processing Technology*, 88, 1627 - 1645.
- MARYŠKA, M. & BLAHA, J. 1997. Hydration kinetics of magnesium oxide: Part 3 hydration rate of MgO in terms of temperature and time of its firing. *Ceramics - Sillicaty*, 41, 121 - 123.

- MATABOLA, K. P., VAN DER MERWE, E. M., STRYDOM, C. & LABUSCHAGNE, F. J. W. 2010. The influence of hydrating agents on the hydration of industrial magnesium oxide. *J Chem Technol Biotechnol*, 85, 1569 - 1574.
- MATHUR, R. & MISRA, A. K. 2007. Magnesium oxychloride cement concrete. *Bulletin of Material Science*, 30, 239 - 246.
- MEHTA, P. & MONTEIRO, P. 2008. *Concrete: Microstructures, properties and materials*.
- MEYER, C. 2004. Concrete materials and sustainable development in the USA. *Structural Engineering International*, 14, 203 - 207.
- MITCHELL, D. R. G., HINCZAK, I. & DAY, R. A. 1998. Interaction of silica fume with calcium hydroxide solutions and hydrated cement pastes. *Cement and Concrete Research*, 28, 1571 - 1584.
- MO, L. & PANESAR, D. K. 2012. Effects of accelerated carbonation on the microstructure of Portland cement pastes containing reactive MgO. *Cement and Concrete Research*, 42, 769 - 777.
- MORA, M., LOPEZ, M. I., CARMONA, M. A., JIMENEZ - SANCHIDRIAN, C. & RUIZ, J. R. 2010. Study of the thermal decomposition of a sepiolite by mid- and near-infrared spectroscopies. *Polyhedron*, 29, 3046 - 3051.
- NAIR, D. G., FRAAIJ, A., KLAASSEN, A. A. K. & KENTGENS, A. P. M. 2008. A structural investigation relating to the pozzolanic activity of rice husk ashes. *Cement and Concrete Research*, 38, 861 - 869.
- NAVARRO, C. R., HANSEN, F. E. & GINNELL, W. S. 1998. Calcium hydroxide crystal evolution upon ageing of lime putty. *Journal of American Ceramic Society*, 81, 3032-3034.
- NEHDI, M. 2000. Why some carbonate fillers cause rapid increases of viscosity in dispersed cement-based materials. *Cement and Concrete*, 30, 1663 - 1669.
- NONAT, A., MUTIN, J. C., LECOQ, X. & JIANG, S. P. 1997. Physico-chemical parameters determining hydration and particle interactions during the setting of silicate cements. *Solid State Ionics*, 101 - 103, 923 - 930.
- O'ROURKE, B., MCNALLY, C. & RICHARDSON, M. G. 2009. Development of calcium sulfate - ggbs - Portland cement binders. *Construction and Building Materials*, 23, 340 - 346.
- PADE, C. & GUIMARAES, M. 2007. The CO₂ uptake of concrete in a 100 year perspective. *Cement and Concrete Research*, 37, 1348 - 1356.
- PAPADAKIS, V. G. 1999. Experimental investigation and theoretical modeling of silica fume activity in concrete. *Cement and Concrete Research*, 29, 79 - 86.
- PESSIKI, S. P. & CARINO, N. J. 1988. Setting time and strength of concrete using the impact-echo method. *ACI Materials Journal*, 85, 389 - 399.
- POPPE, A. M. & DE SCHUTTER, G. 2005. Cement hydration in the presence of high filler contents. *Cement and Concrete Research*, 35, 2290 - 2299.
- PUCEAT, E., REYNARD, B. & LECUYER, C. 2004. Can crystallinity be used to determine the degree of chemical alteration of biogenic apatites? *Chemical Geology*, 205, 83 - 97.
- QUADRELLI, R. & PETERSON, S. 2007. The energy-climate challenge: Recent trends in CO₂ emissions from fuel combustion. *Energy Policy*, 35, 5938 - 5952.
- QUILLIN, K. 2001. Performance of belite-sulfoaluminate cements. *Cement and Concrete Research*, 31, 1341 - 1349.
- QUOI, F., LIN, W., CHAU, C. K. & LI, Z. J. 2008. Property assessment of magnesium phosphate cement. *Advances in Concrete and Structures*, 400, 115 - 120.
- RAADE, G. 1970. Dypingite, a new hydrous basic carbonate of magnesium, from Norway. *The American Mineralogist*, 55, 1457.
- RIMSTIDT, J. D. & BARNES, H. L. 1980. The kinetics of silica-water reactions. *Geochimica et Cosmochimica Acta*, 44, 1683 - 1699.
- ROCHA, S. D. F., MANSUR, M. B. & CIMINELLI, V. S. T. 2004. Kinetics and mechanistic analysis of caustic magnesia hydration. *Journal of Chemical Technology and Biotechnology*, 79, 816 - 821.

- ROY, D. M. 1999. Alkali - activated cements: opportunities and challenges. *Cement and Concrete Research*, 29, 249 - 254.
- SAHU, S. 1994. Developments in low energy clinkers. *Ceramics - Sillicaty*, 38, 191 - 200.
- SANDBERG, B. & MOSBERG, T. 1988. Use of microsilica in binder systems for ultra-low cement castables. *Advances in Refractories Technology*, 4, 245 - 258.
- SAWADA, Y., UEMATSU, K., MIZUTANI, N. & KATO, M. 1978. Thermal decomposition of hydromagnesite $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. *Journal of Inorganic and Nuclear Chemistry*, 40.
- SAWADA, Y., YAMAGUCHI, J., SAKURAI, O., UEMATSU, K., MIZUTANI, N. & KATO, M. 1979. Thermal decomposition of basic magnesium carbonates under high-pressure gas atmospheres. *Thermochimica Acta*, 32, 277-291.
- SCHEETZ, B. E. & WHITE, W. B. 1977. Vibrational spectra of the alkaline earth double carbonates. *American Mineralogist*, 62, 36 - 50.
- SCHNEIDER, M., ROMER, M., TSCHUDIN, M. T. & BOLIO, H. 2011. Sustainable cement production - present and future. *Cement and Concrete Research*, 41, 642 - 650.
- SCHRADER, B. 1989. *Infrared and Raman spectroscopy: methods and applications*, London, Wiley.
- SENFF, L., HOTZA, D., REPETTE, W. L., FERREIRA, V. M. & LABRINCHA, J. A. 2010. Mortars with nano- SiO_2 and micro- SiO_2 investigated by experimental design. *Construction and Building Materials*, 24, 1432 - 1437.
- SHAND, M. A. 2006. *The Chemistry and Technology of Magnesia*, New Jersey, USA, Wiley and Sons.
- SHRIVER, D. F. & ATKINS, P. W. 1999. *Inorganic Chemistry. Chapter 4 - Molecular symmetry*. Oxford: Oxford University Press.
- SLEIMAN, H., PERRO, A. & AMZIANE, S. 2010. A new look at the measurement of cementitious paste setting by Vicat test. *Cement and Concrete Research*, 40, 681 - 686.
- SMITHSON, G. L. & BAKHSHI, N. N. 1969. The kinetics and mechanism of the hydration of magnesium oxide in a batch reactor. *The Canadian Journal of Chemical Engineering*, 47, 508 - 513.
- STRYDOM, C. A., VAN DER MERWE, E. M. & APHANE, M. E. 2005. The effect of calcining conditions on the rehydration of dead burnt magnesium oxide using magnesium acetate as a hydrating agent. *Journal of Thermal Analysis and Calorimetry*, 80, 659 - 662.
- TAYLOR, H. F. W. 1990. *Cement Chemistry*, London, UK, Academic Press.
- TAYLOR, L. S. & ZOGRAFI, G. 1998. The quantitative analysis of crystallinity using FT-Raman spectroscopy. *Pharmaceutical Research*, 15, 755 - 761.
- THYGESEN, L. G., LOKKE, M. M., MICKLANDER, E. & ENGELSEN, S. B. 2003. Vibrational microspectroscopy of food. Raman vs. FT-IR. *Trends in Food Science and Technology*, 14, 50 - 57.
- VAN DER MERWE, E. M., STRYDOM, C. & BOTHA, A. 2004. Hydration of medium reactive industrial magnesium oxide with magnesium acetate. *Journal of Thermal Analysis and Calorimetry*, 77, 49-56.
- VANDEPERRE, L. J., LISKA, M. & AL-TABBAA, A. 2008. Microstructures of reactive magnesia cement blends. *Cement and Concrete Composites*, 30, 706 - 714.
- VANDEPERRE, L. J., LISKA, M. & AL TABBAA, A. 2007. Hydration and mechanical properties of magnesia, pulverized fuel ash and Portland cement blends. *Journal of Materials in Civil Engineering*, 20, 375 - 383.
- VEDALAKSHMI, R. S., SUNDARA RAJ, A., SRINIVASAN, S. & GANESH BABU, K. 2003. Quantification of hydrated cement products of blended cements in low and medium strength concrete using TG and DTA technique. *Thermochimica Acta*, 407, 49 - 60.
- VLASOPOULOS, N. 2007. *Waste minimisation through sustainable magnesium oxide cement products*. PhD, Imperial College London.
- VLASOPOULOS, N. & CHEESEMAN, C. 2009. *Binder Composition*. PCT/GB2009/001610.
- VLASOPOULOS, N. & SIMONS, H. 2012. *Integrated process for producing compositions containing magnesium*. UK patent application PCT/EP2011/063627.
- WENDLANDT, W. W. (ed.) 1974. *Thermal methods of analysis*, New York: Wiley-Interscience.

- WHITE, W. B. 1971. Infrared characterization of water and hydroxyl ion in the basic magnesium carbonate minerals. *American Mineralogist*, 56, 46 - 53.
- WILSON, A. D. & BATCHELOR, R. F. 1971. Initial solubility and disintegration of dental silicate cements; a test with miniature specimens. *British Dental Journal*, 130, 143 - 146.
- WORRELL, E., BERNSTEIN, L., ROY, J., PRICE, L. & HARNISCH, J. 2009. Industrial energy efficiency and climate change mitigation. *Energy Efficiency*, 2, 109 - 123.
- YE, Q., ZHANG, Z., KONG, D. & CHEN, R. 2007. Influence of nano-SiO₂ addition on properties of hardened cement paste as compared with silica fume. *Construction and Building Materials*, 21, 539 - 545.
- YLMEN, R., JAGLID, U., STEENARI, B. & PANAS, I. 2009. Early hydration and setting of Portland cement monitored by IR, SEM and Vicat techniques. *Cement and Concrete Research*, 39, 433 - 439.
- YU, Q., SAWAYAMA, K., SUGITA, S., SHOYA, M. & ISOJIMA, Y. 1999. The reaction between rice husk ash and Ca(OH)₂ solution and the nature of its product. *Cement and Concrete Research*, 29, 37 - 43.
- ZHANG, T. 2012. *Development of novel low pH magnesium silicate hydrate (M-S-H) cement systems for encapsulation of problematic nuclear wastes*. PhD, Imperial College London.
- ZHANG, T., CHEESEMAN, C. & VANDEPERRE, L. J. 2011. Development of low pH cement systems forming magnesium silicate hydrate (M-S-H). *Cement and Concrete Research*, 41, 439 - 442.
- ZHENG, J., ZHANG, J. & SCHERER, G. W. 2012. Prediction of the degree of hydration at initial setting time of cement paste with particle agglomeration. *Cement and Concrete Research*, 42, 1280 - 1285.